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A neutron diffraction study of the crystal of benzoic acid from 6 to 293 K and a macroscopic-scale quantum theory of the lattice of hydrogen-bonded dimers

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Abstract

Measurements via different techniques of the crystal of benzoic acid have led to conflicting conceptions of tautomerism: statistical disorder for diffraction; semi-classical jumps for relaxometry; quantum states for vibrational spectroscopy. We argue that these conflicts follow from the prejudice that nuclear positions and eigenstates are pre-existing to measurements, what is at variance with the principle of complementarity. We propose a self-contained quantum theory. First of all, new single-crystal neutron-diffraction data accord with long-range correlation for proton-site occupancies. Then we introduce a macroscopic-scale quantum-state emerging from phonon condensation, for which nuclear positions and eigenstates are indefinite. As to quantum-measurements, an incoming wave (neutron or photon) entangled with the condensate realizes a transitory state, either in the space of static nuclear-coordinates (diffraction), or in that of the symmetry coordinates (spectroscopy and relaxometry). We derive temperature-laws for proton-site occupancies and for the relaxation rate, which compare favorably with measurements.

Keywords: Benzoic acid, Neutron diffraction, Hydrogen bonding, Tautomerism, tunneling, Quantum mechanics.

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1. Introduction

The crystal of benzoic acid (C_6H_5COOH) is a showcase for proton transfer across hydrogen bonds and tautomerism, which are both of importance in many fields across physics, chemistry and biology [1–22]. Diffraction reveals bistable centrosymmetric cyclic-dimers $(C_6H_5COOH)_2$ linked through hydrogen bonds. The lattice is comprised of tautomers, say L_1L_2 (preferred) and R_1R_2 (less favoured), exclusive of the symmetry-breaking configurations L_1R_2 and R_1L_2 (Fig. 1). The ratio $R_1R_2 : L_1L_2$ increases smoothly and reversibly with temperature. Experimental and theoretical investigations enlighten the behavior of hydrogen bonds in a complex environment, with particular emphasis on proton tunneling that is a beacon for the emergence of classical from quantum.

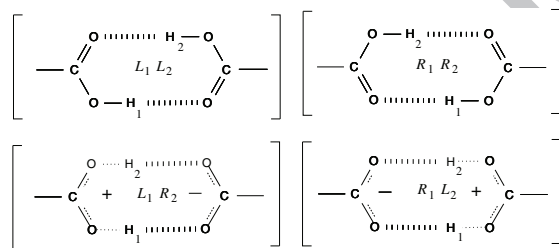


Figure 1: Schematic lattice configurations for a crystal of benzoic acid.

At this point in time, there is no widespread agreement on the representation of proton transfer and tautomerism. (i) The coexistence of tautomers evidenced by diffraction is thought of as a random distribution of uncorrelated dimers L_1L_2 and R_1R_2 [4]. (ii) The proton relaxation-rate measured through solid-state-NMR or quasi-elastic neutron scattering (QENS) is represented by semiclassical stochastic jumps of rigid proton-pairs [7–20]. (iii) Vibrational spectra reveal the quantum nature of the crystal, as well as the nonlocal character of proton-states [21, 22]. (iv) Computational models for the crystal of benzoic acid [23–26], or for isolated dimers of formic acid [27–46], are based on Born-Oppenheimer separation of quantum electrons, on the one hand, and classical nuclei at fixed positions, on the other. Dynamical interconversion of tautomers

is represented by two mechanisms as concerted proton transfer in quasi 1-D at low temperature or/and stepwise single-proton transfer in quasi 2-D more likely at elevated temperature.

Here, we seek a self-contained theory bound to unquestionable facts. (i) The observed symmetry-related selection rules (u -infrared versus g -Raman) are those anticipated for centrosymmetric Bloch-states. (ii) There is no visible $u - g$ splitting of the proton stretching-states to suggest any significant intradimer coupling term. (iii) For similar centrosymmetric dimers in the crystal of potassium hydrogen carbonate (KHCO_3), the effective oscillator-mass of the proton states measured via inelastic neutron-scattering is practically 1 amu [47]. (iv) The observed energy-levels are consistent with double-well operators virtually identical for $\nu_g\text{OH}$ and $\nu_u\text{OH}$ (Table 1). The existing models are in conflict with these observations: (i) excludes interconversion via single-proton transfer; (ii) rules out concerted pairwise interconversion; (iii) excludes coupling terms with heavy atoms. The desired theory should be quantum in nature, what excludes definite trajectories for dimensionless nuclei [48].

A serious hurdle on the way toward a consistent theory is the diffraction work by Wilson et al. [4] reporting a significant amount of the less favored tautomer at low temperature ($\approx 13\%$ at 20 K). This was attributed to a difference in tautomer entropy, that does not make any contact with solid-state NMR [15] and Fig. 1. In order to check this point, we have conducted new diffraction measurements and the data analysis reported in Sec. 2 argues against entropy. As to the theory, conflicts of representation appear when vibrational states and nuclei are thought of as elements of an objective reality attached to the crystal, irrespective of whether they are observed or not. In this present paper, this standpoint is referred to as “microrealism”, by analogy with the notion of macrorealism introduced by Leggett and Garg [49]. Within the framework of quantum mechanics, conflicts can be ruled out because outcomes of measurements depend on the measuring apparatus. They are context-dependent and, according to the principle of complementarity [50], there is no deterministic relationship between positions and energies. Outcomes should be interpreted either

in the time-dependent wave-like representation, for spectroscopy and relaxometry, or in the static particle-like representation, for diffraction, knowing that these measurements are mutually exclusive and their representations pertain to orthogonal spaces. We elaborate on a crystal-state pre-existing to measurements, that is consistent with both representations. To this end, we introduce in Sec. 3 the notion of “quantum condensation”, in line with our previous report on potassium dihydrogen phosphate (KH_2PO_4 or KDP) [51].

2. Neutron diffraction

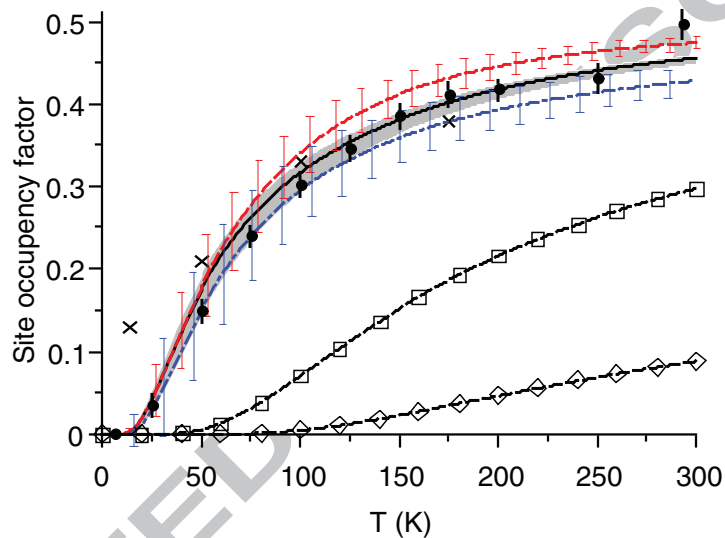


Figure 2: (Color on line) Temperature laws for the occupancy factor of the less favored proton sites. \bullet with error bars: experimental points (this work). \times : experimental points after [4]. Blue dot dashed with bars: eq. (7). Solid plus grey zone: eq. (8). Red dashed with bars: eq. (6). The grey zone and the bars represent dispersions of the theoretical curves due to uncertainties for the parameters. $h\nu_l = (54 \pm 6) \text{ cm}^{-1}$ and $h\nu_{01} = (172 \pm 4) \text{ cm}^{-1}$ are deduced from vibrational spectra. \square and \diamond : (6) and (8), respectively, for $p_l = 0$.

Needle-shaped single-crystals ($3 \times 3 \times 10 \text{ mm}^3$) were grown by slowly cooling an ethanol-hexane solution. A specimen wrapped in aluminum was loaded in a

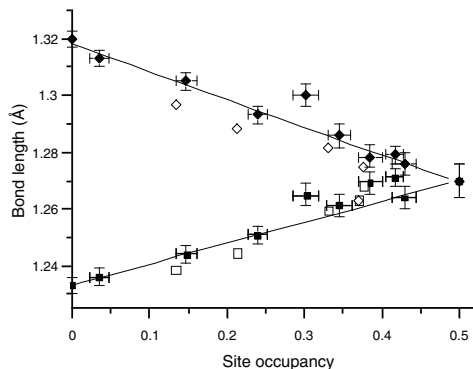


Figure 3: CO bond lengths as a function of the occupancy of the less favored proton sites. ■ and ◆ with error bars: experimental points (this work). □ and ◇: after Ref. [[4]]. The straight lines are guides for the eyes.

closed-cycle-refrigerator. The temperature was controlled to within ± 1 K. Data were collected with the four-circle diffractometer, 5C2, based at the Orphée reactor of the Laboratoire Léon Brillouin [52].

Inspection of intensities for absent reflections confirms the $P2_1/c$ (C_{2h}^5) space-group assignment at every temperature [53]. The best structural parameters gathered in Table 2 were refined with CRYSTALS [54]. All parameters and probability densities at split proton-sites (ρ_L , ρ_R) were refined from Bragg-peak intensities, without further constraint. Temperature effects on the unit-cell parameters, the O \cdots O lengths of C_i -dimers, the distances between proton sites along O \cdots O bonds ($d_{LR} \approx 0.70$ Å), as well as the aromatic-ring geometry, are rather modest and do not demonstrate any obvious trend.

The S -shaped $\rho_R(T)$ (Fig. 2) as well as the best least squares fit to van't Hoff's law

$$\begin{aligned} \ln \frac{\rho_R}{\rho_L} &= \Delta S_\rho + \Delta H_\rho/T \\ &= -(0.07 \pm 0.03) + (86.8 \pm 1.7)/T \end{aligned} \quad (1)$$

are consistent with a two-level system with negligible or even zero entropy. The enthalpy $\Delta H_\rho = (86.8 \pm 1.7)$ K compares with previous estimates based on neutron diffraction, (80 ± 7) K [4], solid-state NMR, (86.5 ± 1.5) K [15], or

Raman, $(54 \pm 6) \text{ cm}^{-1} = (81 \pm 9) \text{ K}$ [21, 22].

Fig. 3 suggests a linear correlation between CO-bond lengths and ρ_L, ρ_R :

$$\begin{aligned} R_{\text{C}_1\text{O}_1}(T) &= \rho_L(T)R_{\text{C}=\text{O}} + \rho_R(T)R_{\text{C}-\text{O}}; \\ R_{\text{C}_1\text{O}_2}(T) &= \rho_L(T)R_{\text{C}-\text{O}} + \rho_R(T)R_{\text{C}=\text{O}}; \end{aligned} \quad (2)$$

$R_{\text{C}=\text{O}} = 1.233 \text{ \AA}$, $R_{\text{C}-\text{O}} = 1.320 \text{ \AA}$, $\rho_L(T) = (1 + \beta)^{-1}$, $\rho_R(T) = \rho_L(T)\beta$, $\beta = e^{-\Delta H_\rho/T}$. This suggests distinct sublattices with fixed bond-lengths, in line with temperature-independent vibrational frequencies of the CO-modes [21, 22].

The total probability density at proton-sites is a constant: $\rho = \rho_L(T) + \rho_R(T) \equiv 1.00(1)$ [55]. This should be confronted with the cross-section anticipated for a static random distribution of uncorrelated occupied and empty sites with coherent scattering lengths b_{H} and 0, respectively. According to Nield and Keen [56], we can split the scattering length at each site into two parts. The first part is the average scattering length $b_{\text{H}}^{av} = [b_{\text{H}} + 0]/2$ and the second is the deviation $b_{\text{H}}^d = \pm r b_{\text{H}}$, where $0 \leq r \leq 1/2$ is the occupancy of the less favored site. Then, the coherent differential cross-section is comprised of two non vanishing terms. Firstly, Bragg scattering proportional to $(1 - r)^2 b_{\text{H}}^2$. Secondly, a constant background of elastic diffuse scattering proportional to $\overline{(b_{\text{H}}^d)^2} = r^2 b_{\text{H}}^2$, hidden by the huge incoherent signal. Consequently, the total occupancy, that is a constant equal to 1, should be different from the total probability density ρ deduced from Bragg peak intensities effectively measured, that is expected to decrease from 1 at a very low temperature to 1/4 for $r = 1/2$ at room temperature. Our data suggest that ρ is independent of r , so $\rho_L = (1 - r)$ and $\rho_R = r$. It transpires that probability densities at proton sites are strongly correlated and strict periodicity throughout the lattice yields Bragg scattering exclusively. Protons should be represented by extended density-waves, such that one and the same scatterer with coherent scattering length b_{H} is simultaneously at every site with probability ρ_L and ρ_R , respectively. Then, Fig. 3 and (1) accord with a system of two tautomer-sublattice states at thermal equilibrium. Similar representations have been reported for various hydrogen bonded crystals [51, 57–61].

On the one hand, our $\rho_R(T)$ -values are practically identical to those derived from solid-state NMR [15]. On the other hand, they are significantly different from those reported by Wilson et al. below 100 K [4] (X in Fig. 2), although their R -factors suggest data of reasonably good quality. Since hysteresis was excluded [4], temperatures claimed to be 50 K and 20 K by these authors were likely not the actual temperatures of the crystal.

Wilson et al. compared two structural models. On the one hand, they refined the mean position of protons (Fig. 2 in [4]). As the temperature increases, positions shift toward the bond center and thermal functions elongate dramatically along O \cdots O. This model is incompatible with the lack of frequency-shift for ν OH modes. On the other hand, Wilson et al. considered protons split over two sites, as presented above. They set the total “occupancy”, in fact the total probability density, to be a constant equal to 1 and they constrained the isotropic temperature factors to be equal (Fig. 3 in [4]). These two constraints amount to suppose strong correlations between proton-site occupancies and to exclude any random distribution. This model was found to be satisfactory, in accordance with our own data analysis. However, this work was not self-consistent, inasmuch as constrained probability densities and temperature factors were in conflict with the misleading entropy value of (0.27 ± 0.08) cal.mol. $^{-1}$ K $^{-1}$ implying existence of more than two distinguishable tautomers. By contrast, our data show that $\rho \equiv 1$ and $\Delta S_\rho \approx 0$ are model-free.

3. Quantum theory

A crystal is commonly represented by an ensemble of nuclear oscillators for which quantum correlations are destroyed by mechanisms extrinsic to the quantum theory [48], such as environment-induced decoherence [62–65]. In the harmonic approximation the molar Helmholtz energy for N degrees of freedom

per unit cell is

$$\left. \begin{aligned} A_i &= K + V - TS, \\ &= \sum_{n=1}^N \left[\mathcal{N}_0 \frac{h\nu_n}{2} + \mathcal{R}T \ln \left(1 - \exp -\frac{h\nu_n}{kT} \right) \right], \end{aligned} \right\} \quad (3)$$

where K , V , S , \mathcal{N}_0 are the kinetic energy, the potential energy, the entropy and Avogadro's constant, respectively.

The decoherence scheme does not account for correlated occupancies at proton sites revealed by neutron diffraction (Sec. 2). In fact, for each degree of freedom of an isolated crystal, a superposition of phonons, say $\propto \exp i(\mathbf{k} \cdot \mathbf{u} - \omega(\mathbf{k})t + \phi)$, with continuous distribution of arbitrary phases ϕ yields a pure state, say $|\Phi\rangle$, that complies with the space-group symmetry operators of the crystal. The complexity of the statistical representation is hidden and new properties emerge. The wavefunction $\Phi \equiv 0$ has continuous space-time-translation symmetry [51, 66]. Wavevectors, nuclear positions and time are indefinite. The potential energy and the entropy vanish. The eigenenergy for $N\mathcal{N}_0$ free degrees-of-freedom at thermal equilibrium is $N\mathcal{R}T/2$. It is single valued. Such a condensate is stable, as compared with the incoherent regime, if $N\mathcal{R}T/2 < A_i$. Since this condition is satisfied as $TS \rightarrow 0$ and not satisfied as $TS \rightarrow \infty$, there is a dividing temperature for each mode. We suppose equipartition excludes coexistence in the same crystal of a coherent condensate for some degrees of freedom and incoherent phonons for other degrees of freedom, so the transition temperature of the crystal, say T_{ci} , should depend on the mean oscillator-energy $h\bar{\nu}$.

The isolated condensate has no definite property at the microscopic level. Our knowledge follows from statistics of contextual outcomes of complementary measurements, which are mutually exclusive. An incoming plane-wave (photon or neutron) entangled with the condensate breaks the continuous translation-symmetry and realizes a transitory Bloch-state at T , in-phase with the wave, that is not an eigenstate of the isolated crystal. Every single realization can be projected onto the eigenstates of a context-dependent operator distinctive of the quantum event in question. Bragg diffraction, namely coherent elas-

tic momentum-transfer breaking the continuous space-translation symmetry, realizes a static lattice-state in the momentum representation. Data acquisition reveals a pattern that can be transformed into positional parameters for nuclear-densities in direct space. Disorder is pointless. Coherent elastic diffuse scattering realizes a static non-periodic state. Incoherent elastic scattering realizes the static distribution of positional parameters. In every case, time remains indefinite, since there is no energy transfer, and temporal averaging is meaningless. Alternatively, energy transfer breaking the time-translation symmetry at a definite time t_0 realizes either an eigenstate of the potential operator through resonance (Sec. 3.1), or a superposition through off resonance (Sec. 3.3), while nuclear positions remain indefinite. Bragg-diffraction, diffuse-coherent or incoherent elastic scattering, as well as quasi-elastic or inelastic events occur at random and are mutually exclusive, inasmuch as the outgoing wave is always detected as a single final state (wavefunction collapse). Individual quantum events are unpredictable. Only statistics are repeatable. Consequently, there is no deterministic relationship between contextual outcomes. Mutual exclusivity and lack of determinism still hold if one and the same instrument, such as a diffractometer, collects indiscriminately all events, coherent or incoherent, elastic or inelastic. Then, statistical outcomes of incompatible quantum events should be treated separately, within their respective representations, for a comprehensive account of the crystal.

On the molar-scale, the condensate as a whole is virtually unaffected by a single realization induced by a measuring instrument, or by the environment, and spontaneous decay of the induced state (Sect. 3.3) destroys quantum correlations with the outgoing wavefunction. The crystal is immune to decoherence. In addition, the probability for a wave to entangle a state previously realized is insignificant, so the outcome is independent of previous events.

Equation (3) yields $T_{ci} > 300$ K if $h\nu > 350$ cm⁻¹, what is likely for benzoic acid. We infer that a monodomain crystal at thermal equilibrium can be tentatively represented by a condensate that determines which microstate can be effectively realized and what outcome can be anticipated in the specific context

of a measuring apparatus. Diffraction data (Sec. 2) show that Bragg diffraction realizes a superposition of static sublattice-states and the outcome is a linear combination of nuclear-densities for disorder-free sublattices L_1L_2 and R_1R_2 . There is no evidence of coherent diffuse scattering due to a non-periodic distribution of static positions. Alternatively, vibrational spectroscopy reveals a two-level system, say $l = 0$ or 1 , with energy gap $h\nu_l$, and eigenstates amenable to double-well operators [21, 22], which are rationalized in Sec. 3.1. Finally, relaxometry reveals a superposition state realized through off-resonance energy transfer (Sec. 3.3).

3.1. Vibrational spectroscopy

It is commonly accepted that vibrational states can be deduced from a scalar potential function of the nuclear coordinates in direct space. However, this deterministic representation is in contradiction with two principles of quantum mechanics. Firstly, Heisenberg's uncertainty principle applied to nuclei at fixed positions means that kinetic momenta and the energy of the system are undetermined. Secondly, Bohr's complementarity principle [50]: because of the randomness of quantum events, there is no deterministic relationship between positions and energies, which are realized at random via mutually exclusive and unpredictable elastic or inelastic events, respectively. It is, therefore, necessary to consider distinct representations for nuclear positions and energy levels.

An introduction to our line of argument is the textbook case of two harmonic oscillators, say particles 1 and 2, represented by positional coordinates X_1, X_2 , coupled via $2K(X_1 - X_2)$. In classical mechanics, the normal coordinates X_u, X_g , diagonalizing the Hamiltonian $H(X_1, X_2) = H_u(X_u) + H_g(X_g)$, are linear combinations of X_1 and X_2 . The particles oscillate in the plane $\{X_1; X_2\} \equiv \{X_u; X_g\}$ with definite positions and momenta at any time. In quantum mechanics, deterministic trajectories are meaningless. The symmetry coordinates Ξ_u, Ξ_g , for the Hamiltonian operator $\mathcal{H}_u(\Xi_u) + \mathcal{H}_g(\Xi_g)$ are not linear combinations of X_1, X_2 . The classical representation in one and the same plane is replaced by a dichotomous representation in orthogonal planes:

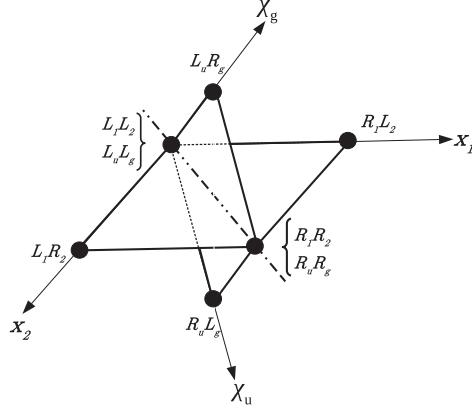


Figure 4: Schematic of the proton static coordinates in the plane (x_1, x_2) perpendicular to that of the symmetry coordinates (χ_u, χ_g) for eigenstates. Bullets are distinctive positions discussed in the text. Sticks between bullets are guides for the eye.

$\{\Xi_u; \Xi_g\}$ for eigenfunctions on the one hand, $\{X_1; X_2\}$ for static positions on the other. There is neither energy-scale nor time-scale for $\{X_1; X_2\}$, whereas positions are indefinite for $\{\Xi_u; \Xi_g\}$. There is no correspondence between the potential operator $\nabla_u(\Xi_u) + \nabla_g(\Xi_g)$ associated with the vibrational state vectors and the scalar potential $V(X_1, X_2)$ for classical particles. The operator is, therefore, outside the bounds of the Born-Oppenheimer separation. It can be deduced from outcomes of measurements exclusively.

For the crystal of benzoic acid, we introduce nonlocal coordinates for particles or waves, beyond the bounds of the harmonic approximation. The static positional-parameters along $O \cdots O$ bonds of particle-like protons 1_i and 2_i in the periodic lattice of dimers indexed i , $1 \leq i \leq \mathcal{N}_0$, are represented by orthonormal coordinates $x_1 = x_{1i}$, $x_2 = x_{2i} \forall i$, in the plane $\{x_1; x_2\}$ (Fig. 4). The symmetry coordinates for the degrees-of-freedom indexed m , $1 \leq m \leq \mathcal{N}_0$, are represented by orthogonal coordinates $\chi_u = \chi_{um}$, $\chi_g = \chi_{gm} \forall m$, in the plane $\{\chi_u; \chi_g\} \perp \{x_1; x_2\}$. $\{x_1; x_2\}$ is specific to static representations of outcomes of elastic events, while $\{\chi_u; \chi_g\}$ holds for energy levels realized via inelastic events. This plane compares with the coordinates traditionally referred to as

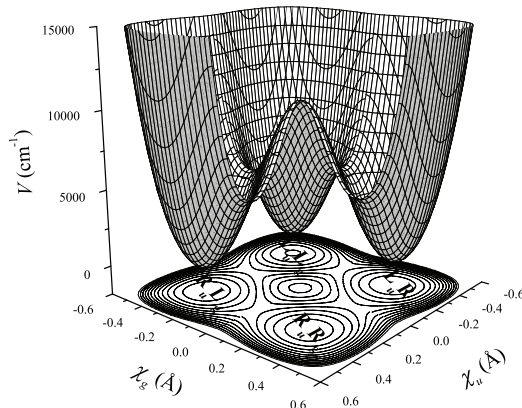


Figure 5: Perspective view of the measurement-induced potential operator for the hydrogen bonding protons in the crystal of benzoic acid in the state $l = 0$. χ_u and χ_g are the symmetry coordinates of the “stretching” degrees of freedom.

“stretching”, or νOH , in the classical harmonic approximation. This terminology remains convenient in quantum mechanics, but it does not refer any more to displacements.

The intersection line (dot-dashed in Fig. 4) is the locus for centrosymmetric configurations in x -space. Apart from this locus, configurations breaking C_i -symmetry, eg R_1L_2 or L_1R_2 , are forbidden by space-group symmetry. The C_i -symmetry is preserved throughout the χ -plane, by construction. The eigenstates of the potential operators in 1-D, say $\mathbb{V}_\xi(\chi_\xi)$, $\xi = “u”$ or “ g ”, are $|\psi_{\xi n}(\chi_\xi)\rangle$. The vibrational spectra [21, 22] are consistent with asymmetric double-wells for bare proton-waves, virtually identical for u and g species (Table 1), which are temperature-independent.

Vibrational spectra and neutron diffraction accord with realization of a combination of state vectors with energy-gap $h\nu_l$:

$$|\phi\rangle = [|\mathcal{L}\rangle + p_l|\mathcal{R}\rangle](1 + p_l)^{-1}; \quad (4)$$

where $p_l = \exp(-h\nu_l/kT)$ is a deterministic temperature factor. These states are either separable (aka disentangled) for spectroscopy or non-separable (aka entangled) for diffraction or relaxometry. $\mathbb{V}_{\mathcal{L}} = \mathbb{V}_0(\chi_u) + \mathbb{V}_0(\chi_g)$ is the operator

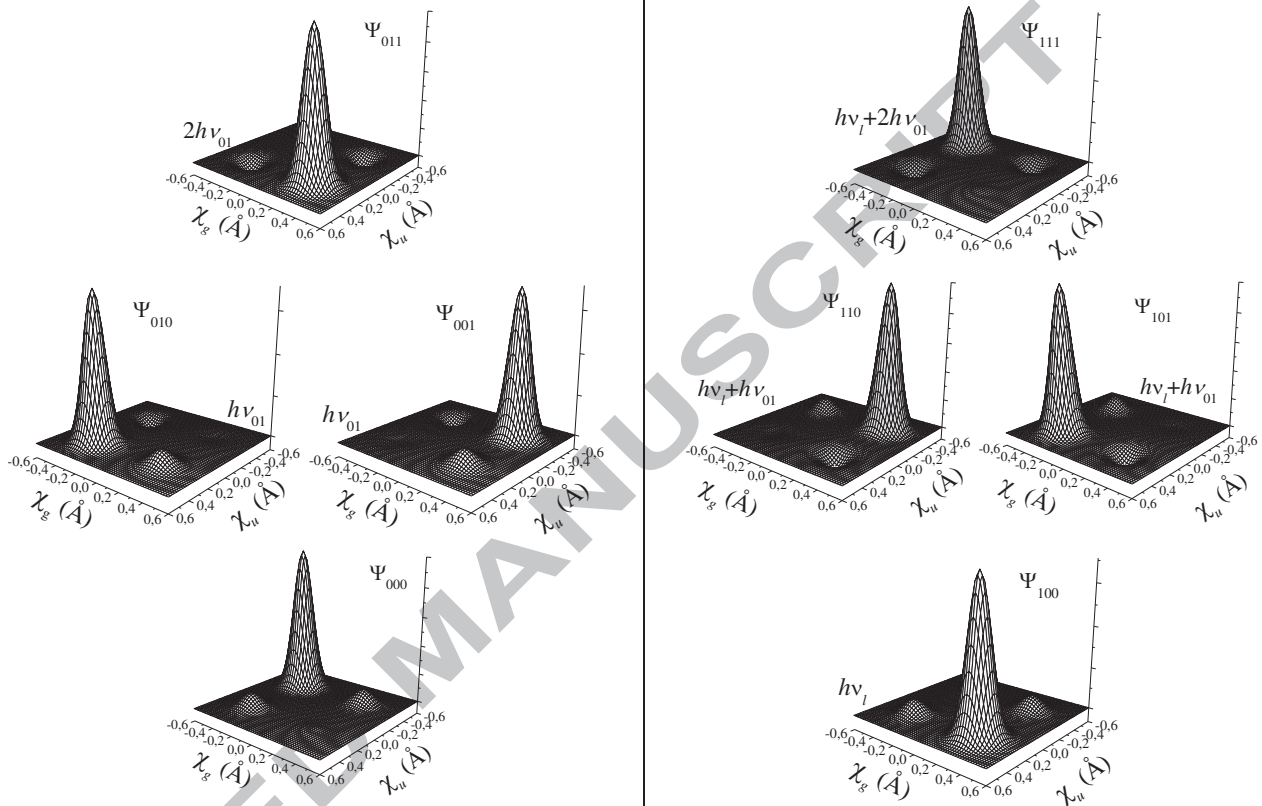


Figure 6: Schematic view of the wavefunctions of the measurement-induced “stretching” states. χ_u and χ_g are the symmetry coordinates. The weak component of the wave function in one-dimension is enhanced by a factor of 5. The quantum numbers are l, n_u, n_g , respectively.

for $l = 0$, $\mathbb{V}_{\mathcal{R}} = \mathbb{V}_1(\chi_u) + \mathbb{V}_1(\chi_g) + h\nu_l$ for $l = 1$, $|ln_u n_g\rangle = |ln_u\rangle|ln_g\rangle$ are the eigenstates. By convention, the minimum at L_ξ is lower than that at R_ξ for $l = 0$ and the energy difference between $|01_\xi\rangle$ and $|00_\xi\rangle$ is $E_{01_\xi} - E_{00_\xi} = h\nu_{01}$ (Table 1). A l -flip ($0 \longleftrightarrow 1$) toggles the sign of the double-well asymmetry, so R_ξ is lower than L_ξ and $E_{11_\xi} - E_{10_\xi} = h\nu_{01}$. The eigenstates of interest read:

$$\left. \begin{aligned} |00_\xi\rangle &= \cos\theta|\psi_{L\xi}\rangle + \sin\theta|\psi_{R\xi}\rangle; |10_\xi\rangle = \sin\theta|\psi_{L\xi}\rangle + \cos\theta|\psi_{R\xi}\rangle; \\ |01_\xi\rangle &= -\sin\theta|\psi_{L\xi}\rangle + \cos\theta|\psi_{R\xi}\rangle; |11_\xi\rangle = \cos\theta|\psi_{L\xi}\rangle - \sin\theta|\psi_{R\xi}\rangle. \end{aligned} \right\} \quad (5)$$

$\psi_{L\xi}$ and $\psi_{R\xi}$ are eigenfunctions for polynomial expansions of the double-wells around L_ξ and R_ξ , respectively. $2\theta = \arctan[\nu_{0\pm}/(\nu_{01} - \nu_{0\pm})]$, where $h\nu_{0\pm} = (6 \pm 1) \text{ cm}^{-1}$ would be the ground-state splitting if $h\nu_{01} = 0$. Hence $\cos\theta \approx 1$ and $\sin\theta = \varepsilon = (1.8 \pm 0.3)10^{-2}$. $\langle 00_\xi|\chi_\xi|00_\xi\rangle$ and $\langle 11_\xi|\chi_\xi|11_\xi\rangle$ are localized to order ε^2 at $\langle L_\xi\rangle$, whereas $\langle 10_\xi|\chi_\xi|10_\xi\rangle$ and $\langle 01_\xi|\chi_\xi|01_\xi\rangle$ are localized at $\langle R_\xi\rangle$.

The potential operator in 2×1 -D and the eigenfunctions $\Psi_{ln_u n_g}(\chi_u, \chi_g)$ are sketched in Figs 5 and 6, respectively. In previous works [21, 22], the separation of x -space and χ -space was overlooked, so the potential operator was represented as a scalar potential in direct space that is meaningless in quantum mechanics. Similarly, eigenfunctions represented in x -space were meaningless. In Fig. 5 the central barrier of $\mathbb{V}_{\mathcal{L}}$ ($\approx 10^4 \text{ cm}^{-1}$) is surrounded by four minima and we set the origin of the energy-scale to the lowermost state $|000\rangle$. Superposition of $\mathbb{V}_{\mathcal{L}}$ and $\mathbb{V}_{\mathcal{R}}$ yields 8 distinct minima. In Fig. 6, Ψ_{000} at zero and Ψ_{111} at $h\nu_l + 2h\nu_{01}$ are localized to order ε around $\langle L_u L_g\rangle$, centred at $(-\Delta\chi_u/2, -\Delta\chi_g/2)$. $|\Psi_{000}|^2$ and $|\Psi_{111}|^2$ are probability densities in $\{x_1; x_2\}$ around the preferred configuration $L_1 L_2$ at $(-d_{LR}/2, -d_{LR}/2)$ (Fig. 4). Ψ_{100} at $h\nu_l$ and Ψ_{011} at $2h\nu_{01}$ are localized around $\langle R_u R_g\rangle$ centred at $(\Delta\chi_u/2, \Delta\chi_g/2)$. $|\Psi_{100}|^2$ and $|\Psi_{011}|^2$ are probability densities around the less favoured configuration $R_1 R_2$ at $(d_{LR}/2, d_{LR}/2)$. A dramatic consequence of the separation of x -plane and χ -plane, as compared with classical mechanics, is that the states $|ln_u \neq n_g\rangle$ at $lh\nu_l + h\nu_{01}$ are localized outside the x -plane, around $\langle R_u L_g\rangle$, $(\Delta\chi_u/2, -\Delta\chi_g/2)$, or $\langle L_u R_g\rangle$, $(-\Delta\chi_u/2, \Delta\chi_g/2)$. The $|\Psi_{ln_u \neq n_g}|^2$'s are probability densities for proton-waves exclusively. They do not correspond to any static configuration.

This is a graphic illustration of the complementarity principle.

3.2. Proton site occupancies

From the energy levels presented in fig. 6, we deduce the different temperature laws shown in fig. 2. Firstly, within the framework of microrealism, the R -site occupancy is

$$\rho_1 = \frac{p'_l}{(1+p'_l)(1+p'_{01})^2} + \frac{p'_{01}}{(1+p'_{01})^2} + \frac{p'^2_{01}}{(1+p'_l)(1+p'_{01})^2}, \quad (6)$$

where $p'_l = p_l$ and $p'_{01} = \exp(-h\nu_{01}/kT)$ are statistical population factors (see red dash in Fig. 2). Secondly, from condensate viewpoint, measurement-induced lattice configurations depend on the deterministic temperature factors p_l and $p_{01} = p'_{01}$. In Fig. 2 we display two options. (i) The blue dot-dash for the two-level system:

$$\rho_2 = \frac{p_l}{1+p_l}. \quad (7)$$

(ii) The black solid if the states $|l10\rangle$ and $|l01\rangle$ are not realized via diffraction:

$$\rho_3 = \frac{p_l + p^2_{01}}{(1+p_l)(1+p^2_{01})}. \quad (8)$$

This is the best option. Although there is no energy scale in x -space, temperature factors transpire from χ -space through probability densities around the contact points $L_u L_g - L_1 L_2$ and $R_u R_g - R_1 R_2$, while probability densities around $R_u L_g$ or $L_u R_g$ have no counterpart in x -space. Consequently, it is impossible to deduce the complete set of eigenstates of the potential operator from nuclear densities and, conversely, the complete energy level scheme is not representative of the probability density effectively measured via diffraction. Eigenstates and probability densities must be determined separately, via complementary measurements.

The site-occupancies are comprised of two terms: $\rho_L = a(|\Psi_{000}|^2 + p_l p^2_{01} |\Psi_{111}|^2)$; $\rho_R = a(p_l |\Psi_{100}|^2 + p^2_{01} |\Psi_{011}|^2)$; $a = [(1+p_l)(1+p^2_{01})]^{-1}$. According to the classical words of chemistry, the states $|000\rangle$ and $|100\rangle$ would correspond to COO-configurations $L_1 L_2$ and $R_1 R_2$ (Fig. 1), respectively, while the states $|011\rangle$ and $|111\rangle$ would correspond to transposition of proton pairs from C–O-sites to

C=O-sites at a rather modest energy cost. Then, the thermal laws for the mean CO-bond lengths should be different from (2). Alternatively, from condensate viewpoint, the COO-groupings are indefinite in the χ -representation. The linear correlation (2) (Fig. 3) suggests that CO-bond lengths realized via diffraction match the proton-site occupancies determined via the contact points, so as to avoid the less favored structures.

From (8), we obtain $\ln \frac{\rho_R}{\rho_L} = \ln(p_l + p_{01}^2)$ that is slightly different from (1). This could explain the residual entropy and the small difference, close to within data statistics, between ΔH_p and $h\nu_l$. On the other hand, we anticipate that NMR should realize a linear combination of every eigenstates (see below sec. 3.3) and yield $\ln \frac{\rho_R}{\rho_L} = \ln(\frac{p_l}{1-p_l})$. In practice, (6), (7) or (8) cannot be distinguished conclusively on the ln-scale of van't Hoff plots.

3.3. Relaxometry

Off-resonance energy-transfer realizes at the time $t = 0$ of the event a transitory state at T :

$$|S\rangle = \sum_{l, n_u, n_g} a_l b_{n_u n_g} |ln_u n_g\rangle; \quad (9)$$

$a_0^2 = (1+p_l)^{-1}$; $a_1^2 = p_l a_0^2$; $b_{0,0}^2 = (1+p_{01})^{-2}$; $b_{1,0}^2 = b_{0,1}^2 = p_{01} b_{0,0}^2$; $b_{1,1}^2 = p_{01}^2 b_{0,0}^2$. Because $S \equiv 0$, each event realizes the same state and the relaxation statistics for a large number of events is predictable. The critical rate in 2×1 -D is twice the ground-state splitting in 1-D ($\nu_{0\pm} = 2\varepsilon\nu_{01}$) scaled by the amplitude of that part of the wavefunction equally delocalized over the four wells. Inspection of Fig. 6 allows us to distinguish three channels:

$$\tau^{-1} = 4\varepsilon\nu_{01} \left[2\varepsilon^2 + \varepsilon p_{01}^{1/2} + 2p_{01}^{3/2} \right]. \quad (10)$$

The first term accounts for decay of $\sum_{n_u, n_g} (a_0 b_{n_u n_g} |0n_u n_g\rangle + a_1 b_{n_u n_g} |1n_u n_g\rangle)$ through the 1-quantum channel $1-h\nu_l$, scaled by $4\varepsilon^2$. The second term is the $1-h\nu_{01}$ channel for $a_l b_{n_u n_g} |ln_u n_g\rangle + a_l b_{n'_u n'_g} |ln'_u n'_g\rangle$, $l = 0$ or 1 , $n'_u + n'_g - (n_u + n_g) = 1$. The scaling amplitude is 2ε . The last term is the $2-h\nu_{01}$ channel for $\sum_{n_u, n_g} a_l b_{n_u n_g} |ln_u n_g\rangle$, $l = 0$ or 1 , scaled by a factor of 4. Further n -quantum channels are negligible. It turns out that τ^{-1} is independent of p_l . The rate

is distinctive of quantum interferences, via probability amplitudes $\varepsilon, p_{01}^{1/2}, p_{01}^{3/2}$, while positional coordinates remain indefinite. The notion of particle-like protons tunneling back and forth across a barrier is meaningless.

As opposed to (10), Neumann et al. [15] have fitted NMR and QENS data with six phenomenological parameters inspired by the statistical model of Skinner and Trommsdorff [9]:

$$\begin{aligned} \tau_{exp}^{-1} &= (1.72 \pm 0.02)10^8 \coth[(43 \pm 1)/kT] \\ &+ 10^{10} \exp(-120/kT) + 6.3 \times 10^{11} \exp(-400/kT). \end{aligned} \quad (11)$$

Here the rate follows from spontaneous fluctuations of nuclear positions and the measurement is a very weak process mirroring the unperturbed system. The first term represents “phonon-assisted” interconversion through “incoherent-tunneling” of rigid pairs. The other terms model classical jumps above potential barriers for distinct reaction-paths. This scheme accords with the existence of three relaxation channels, but rigid-pairs, low barriers and “phonon-assisted-tunneling” are excluded by spectroscopy.

In Fig. 7, (10) and (11) are similar, but their merits are quite different: two fixed parameters for the former as compared to six tuned parameters, which cannot be measured independently, for the latter. More fundamental, relaxometry is not amenable to microrealism because a snapshot of a stochastic ensemble of pre-existing particles, or wave packets, taken via a non-perturbing wave, is necessarily space-time averaged and should not demonstrate any rate. Alternatively, synchronization of the probe and the instability is intrinsic to quantum measurements of a pre-existing condensate.

In Fig. 7, there is no visible increase of the measured rate (11), as compared to (10), to suggest incoherent decay and/or emergence of the classical regime at elevated temperatures. In contrast with [7–20], relaxometry confirms that the bulk of the crystal is immune to decoherence.

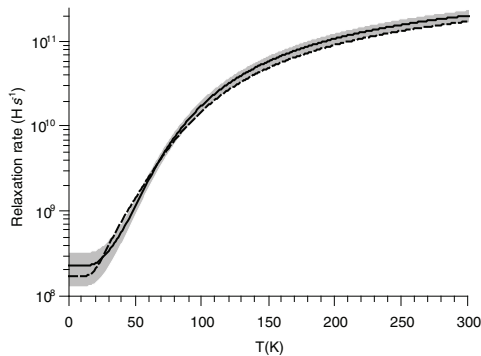


Figure 7: Comparison of the empirical temperature law of benzoic acid (11) (solid line for unknown data statistics) with the quantum theory (10) (dot-dashed): $\nu_{01} = 5.16 \times 10^{12} \text{ s}^{-1}$, $\varepsilon = 0.018$, $\tau^{-1} = (2.3 \pm 1)10^8 + (6.77 \pm 1.15)10^9 \exp[-(128 \pm 13)/T] + (7.2 \pm 1.2)10^{11} \exp[-(385 \pm 9)/T]$, in proton per second units. The grey zone features the uncertainty of the theoretical curve.

4. Discussion

The crystal of benzoic acid is an open system amenable to the framework of quantum mechanics without any bias. The condensate follows from the linear formalism of quantum mechanics. The free energy determines thermal stability. The measurement-induced vibrational states are fully characterized by $h\nu_l$, $h\nu_{01}$ and ε , effectively measured. The level-scheme in χ -space is model-free, inasmuch as the potential operator supporting the assignment scheme is of no physical importance. Positional parameters and proton-site occupancies in x -space are also model-free. The theory is self-contained.

The temperature laws (8) and (10) oppose to microrealism for which different statistics revealed by diffraction or spectroscopy should correspond to different physical systems. Alternatively, they accord with contextual outcomes of incompatible measurements. The relaxation rate of the delocalized proton-wave is not representative of nuclear-displacements and the notion of dynamical interconversion through proton transfer is meaningless. In contrast with the

locally causal relationship between positions and energy in classical mechanics, well-established empirical correlations between structures in x -space and eigenstates in χ -space are not amenable to local interactions. They emerge from statistics of unpredictable events building up either a diffraction pattern or a vibrational spectrum out from a condensate for which nuclear positions and energy levels are indefinite. The origin of such correlations could be in the quantum interplay between electrons and nuclei, that is beyond the bounds of the Born-Oppenheimer separation of quantum electrons and classical-like nuclei.

The framework can be applied to various hydrogen-bonded crystals [51]. In particular, the monoclinic crystal of KHCO_3 demonstrates quantum correlations up to 340 K [59, 67–69]. With hindsight, such correlations follow logically from a pre-existing condensate. The analogy with benzoic acid is straightforward since KHCO_3 is comprised of centrosymmetric dimers linked through hydrogen-bonds amenable to double-well operators: $h\nu_{01} \approx 216 \text{ cm}^{-1}$ and $\varepsilon \approx 5 \times 10^{-2}$ [70, 71]. The main difference is that the eigenstates of KHCO_3 at room temperature and below correspond to the left-hand-side column in Fig. 6, for a single four-well operator ($p_l = 0$). Only $|\Psi_{000}\rangle^2$ and $|\Psi_{011}\rangle^2$ are relevant to diffraction. The difference between (6) and (8) is enhanced (Fig. 2, \square and \diamond , respectively) and diffraction accords with the latter, in line with contextuality. In addition, the relaxation rate (10) turns into

$$\tau^{-1} = 4\varepsilon\nu_{01} \left[\varepsilon p_{01}^{1/2} + 2p_{01}^{3/2} \right] \quad (12)$$

that vanishes as $T \rightarrow 0$, as effectively observed [72].

The framework can be also applied to isolated dimers of carboxylic-acids as follows. (i) Superposition of vibrational states yields a molecular condensate. (ii) Realization of non-separable isoenergetic $|\mathcal{L}\rangle$ and $|\mathcal{R}\rangle$ states yields a D_{2h} -state [73]. (iii) The scheme for bare proton-waves is that depicted in Fig. 6 with $h\nu_l = 0$. (iv) The ground-state splitting is $2h\tau^{-1}$ (10). The value $2h\tau^{-1} = (1.6 \pm 0.4) \times 10^{-2} \text{ cm}^{-1}$ for the crystal of benzoic acid at $T = 0$ compares favourably with those reported for various dimers in supersonic jet-expansions: $\approx 4.6 \times 10^{-2} \text{ cm}^{-1}$ for benzoic acid [74]; $\approx 1.8 \times 10^{-2} \text{ cm}^{-1}$ for benzoic-formic

acid heterodimers [75]; $\approx 1.9 \times 10^{-2} \text{ cm}^{-1}$ for 3-fluoro-benzoic acid [76]; $0.3 \times 10^{-2} - 1.6 \times 10^{-2} \text{ cm}^{-1}$ for $(\text{HCCOH})_2$ or $(\text{DCOOH})_2$ [77–79]; $\approx 0.8 \times 10^{-2} \text{ cm}^{-1}$ for formic-acetic acid [80]; $\approx 10^{-2} \text{ cm}^{-1}$ for formic-propionic acid [81] etc. A superposition of four-well operators with opposite symmetries in $2 \times 1\text{-D}$ could be thus a common feature for dimers of carboxylic acids and the mean observed splitting of $\approx 1.76 \times 10^{-2} \text{ cm}^{-1}$ suggests that $h\nu_1$ and ε are marginally affected by temperature and/or chemical substitution from crystals to isolated dimers.

Within the framework of classical mechanics, the dot-dash ($x_1 = x_2$) in Fig. 4 is the mean reaction-path for C_i proton-transfer. The configurations R_1L_2 and L_1R_2 at high energy being of no importance in supersonic jets, interconversion occurs in quasi 1-D. The distance between L_1L_2 and R_1R_2 is $\sqrt{2}d_{LR}$. The mass of the collective variable is 2 amu, or even more if it is correlated with displacements of heavy nuclei. The scalar double-well along the C_i locus should compare with cuts of $\mathbb{V}_{\mathcal{L}}$ or $\mathbb{V}_{\mathcal{R}}$ along the intersection line ($\chi_u = \chi_g$), through the central barrier of $\approx 10^4 \text{ cm}^{-1}$ ($\approx 30 \text{ Kcal.mol}^{-1}$), that is twice that in 1-D (Table 1). This is much greater than 3–12 Kcal.mol^{-1} computed with quantum chemistry methods for the dimer of formic acid (see Table 2 in [46]). This difference is no wonder since the operator holds for bare proton-waves in χ -space while quantum chemistry focuses on adiabatic transfer involving many degrees of freedom in x -space. In fact the condensate framework and quantum chemistry methods account for different systems, although with identical names. They are not comparable. It may happen that the lower adiabatic barrier counterbalances the longer inter-well distance and the greater collective mass, so as to yield, accidentally, a plausible value of the semiclassical tunneling-rate. Nevertheless, the classical view based on the Born-Oppenheimer separation is untenable since the barrier height, the inter-well distance and the collective mass are not in line with spectroscopy. As a matter of fact, the zero-point energy of a νOH transition observed at $\approx 3000 \text{ cm}^{-1}$ yields a lower bound of $\approx 4500 \text{ cm}^{-1}$ ($\approx 13.5 \text{ Kcal.mol}^{-1}$) for the barrier height in 1-D.

More fundamentally, beyond the great variety of computational models, an energy landscape in x -space is relevant for classical nuclei exclusively [30]. For

quantum nuclei, x -space is specific to elastic scattering events. There is neither energy-scale, nor potential function, nor spontaneous oscillations, nor locally causal relationship between positions and vibrational states. The dot-dashed locus in Fig. 4 is not a trajectory for the time evolution of a dimer. In contrast with previous works, eg [27, 33, 35, 42], the measurement-induced vibrational states cannot be deduced from a scalar landscape decorated with a quantized Hamiltonian. Minimum energy-paths [27, 28, 36], averaged trajectories [29, 34, 46], instanton rates [32, 33, 37] and collective variables do not capture any quantum phenomenon.

In addition to spectroscopic studies of cold molecules in supersonic jets, matter wave interferometry of C_{60} [82], C_{70} [83] and perfluoroalkylated molecules [84] sublimated at $\approx 10^3$ K under high vacuum ($\sim 10^{-11}$ bar) suggest that quantum condensation could be relevant for non hydrogenous molecules at elevated temperature. Interference fringes support the view that each molecule interferes with itself only. However, such interferences should not be visible if every single molecule could be represented by an incoherent mixture of internal vibrational states, since the spatial expansion of the vibrational wavefunctions should be similar to the de Broglie wavelength $\lambda_{dB} \approx 0.025$ Å for C_{60} , or even greater than λ_{dB} for perfluoroalkylated derivatives. Translational and vibrational waves should not be separate through diffraction and each vibrational state should give its own pattern depending on the symmetry-related dephasing between neighboring slits. As a matter of fact, superposition of complementary fringes for symmetric or anti-symmetric states should smooth out the diffraction pattern. By contrast, the reported decoupling of the internal and external degrees of freedom under high vacuum accords with quantum condensation of the internal states, while the suppression of quantum interference as a function of the gas pressure in the vacuum chamber [85] accords with collision-induced breakdown of the continuous space-time translation symmetry.

5. Conclusion

The crystal of benzoic acid at thermal equilibrium behaves as a condensate that is energetically favored, as compared to an incoherent mixture of phonons. Energy levels and nuclear positions (eg chemical bonds or tautomers) are indefinite. This framework can be applied to isolated dimers as well.

Outcomes of incompatible quantum measurements (diffraction versus spectroscopy) pertain to mutually exclusive representations, either in the space of static positional parameters, or in the orthogonal space of the symmetry coordinates for time-dependent eigenfunctions. Experimental studies of these complementary representations are necessary for a comprehensive account of the crystal.

Temperature effects are rationalized within a self-contained framework as follows: (i) measurement-induced realization of a temperature-dependent superposition of the state vectors of a two-level system; (ii) to each level is associated a four-well operator for bare proton-waves in 2×1 -D that is comprised of identical asymmetric double-wells for each symmetry coordinate; (iii) the double-wells have opposite asymmetries for either state. Then, the temperature laws for proton-site occupancies, revealed by diffraction, or for the relaxation-rate of proton-waves, measured through solid-state NMR or quasi-elastic neutron scattering, and the energy-level scheme, revealed by spectroscopy, witness to the contextuality of outcomes of incompatible measurements. All observations accord with the quantum regime from cryogenic to room temperature.

In classical mechanics, tautomers are thought of as objective entities undergoing dynamical interconversion via nuclear trajectories, reaction paths and transition states. Archetypal mechanisms are concerted proton transfer in quasi 1-D at low temperature or/and stepwise single-proton transfer in quasi 2-D, more likely at elevated temperature. This intuitive scheme does not capture the quantum nature of the dimer of benzoic acid attested by spectroscopy. In the quantum regime, dynamical interconversion is meaningless. On the one hand, nuclear-site occupancies mirror the static tautomerization degree. On the other

hand, C_i -symmetry coordinates account for delocalization of proton waves in 2×1 -D. There is no causal relationship due to local interactions between these representations. It turns out that for those systems whose quantum nature is attested by any technique, among which vibrational spectroscopy is the most straightforward, computational chemistry, nuclear trajectories, proton-transfer mechanisms, reaction paths along collective variables, transition states, etc, are pointless.

- [1] S. Hayashi, J. Umemura, Disappearances of COOH infrared bands of benzoic acid, *J. Chem. Phys.* 60 (7) (1974) 2630–2633.
- [2] S. Hayashi, J. Umemura, Infrared spectroscopic evidence for the coexistence of two molecular conformations in crystalline fatty acids, *J. Chem. Phys.* 63 (5) (1975) 1732–1740.
- [3] S. Hayashi, M. Oobatake, R. Nakamura, K. Machida, Interpretation for the anomaly of the C=O stretching band in benzoic acid crystal, *J. Chem. Phys.* 94 (6) (1991) 4446–4452.
- [4] C. C. Wilson, N. Shankland, A. J. Florence, Direct determination of the temperature dependence of proton transfer in the benzoic acid dimer by single crystal neutron diffraction, *Chem. Phys. Letters* 253 (1996) 103–107.
- [5] C. C. Wilson, N. Shankland, A. J. Florence, A single-crystal neutron diffraction study of the temperature dependence of hydrogen-atom disorder in benzoic acid dimers, *J. Chem. Soc., Faraday Trans.* 92 (1996) 5051–57.
- [6] C. C. Wilson, X. Xu, A. J. Florence, N. Shankland, Temperature dependence of proton transfer in 4-chlorobenzoic acid, *New J. Chem.* 30 (2006) 979–981.
- [7] B. H. Meier, F. Graf, R. R. Ernst, Structure and dynamics of intramolecular hydrogen bonds in carboxylic acid dimers: A solid state NMR study, *J. Chem. Phys.* 76 (2) (1982) 767–774.

- [8] R. Meyer, R. R. Ernst, Hydrogen transfer in double minimum potential: Kinetic properties derived from quantum dynamics, *J. Chem. Phys.* 86 (2) (1987) 784–801.
- [9] J. L. Skinner, H. P. Trommsdorff, Proton transfer in benzoic acid crystals: A chemical spin-boson problem. Theoretical analysis of nuclear magnetic resonance, neutron scattering, and optical experiments, *J. Chem. Phys.* 89 (2) (1988) 897–907.
- [10] A. Stöckli, B. H. Meier, R. Meyer, R. R. Ernst, Hydrogen bond dynamics in isotopically substituted benzoic acid dimers, *J. Chem. Phys.* 93 (3) (1990) 1502–1520.
- [11] R. Meyer, R. R. Ernst, Transitions induced in a double minimum system by interaction with a quantum mechanical heat bath, *J. Chem. Phys.* 93 (8) (1990) 5518–5532.
- [12] A. Heuer, U. Haeberlen, The dynamics of hydrogens in double well potentials: The transition of the jump rate from the low temperature quantum-mechanical to the high temperature activated regime, *J. Chem. Phys.* 95 (1991) 4201–4214.
- [13] V. P. Sakun, M. V. Vener, N. D. Sokolov, Proton tunneling assisted by the intermolecular vibration excitation. Temperature dependence of the proton spin-lattice relaxation time in benzoic acid powder, *J. Chem. Phys.* 105 (2) (1996) 379–387.
- [14] D. F. Brougham, A. J. Horsewill, R. I. Jenkinson, Proton transfer dynamics in the hydrogen bond: a direct measurement of the incoherent tunneling rate by NMR and the quantum-to-classical transition, *Chem. Phys. Letters* 272 (1997) 69–74.
- [15] M. Neumann, D. F. Brougham, C. J. McGloin, M. R. Johnson, A. J. Horsewill, H. P. Trommsdorff, Proton tunneling in benzoic acid crystals

at intermediate temperatures: Nuclear magnetic resonance and neutron scattering studies, *J. Chem. Phys.* 109 (17) (1998) 7300–7311.

- [16] L. Latanowicz, E. C. Reynhardt, Quantum mechanical and classical dynamics of double proton transfer in the hydrogen bond, *Chem. Phys. Letters* 341 (2001) 561–567.
- [17] S. Takeda, A. Tsuzuminati, An indication of slowing down of hydrogen atom transfer in isotopically mixed hydrogen bonds of benzoic acid crystals, *Magn. Reson. Chem.* 39 (2001) S44–S49.
- [18] L. Latanowicz, E. C. Reynhardt, J. Boguszyńska, Complex dynamics of proton and deuteron transfer in double hydrogen bond of benzoic acid isotopes, *J. Molec. Struct. (Theochem)* 710 (2004) 111–117.
- [19] Q. Xue, A. J. Horsewill, M. R. Johnson, H. P. Trommsdorff, Isotope effects associated with tunneling and double proton transfer in the hydrogen bonds of benzoic acid, *J. Chem. Phys.* 120 (23) (2004) 11107–11119.
- [20] W. Wu, D. L. Noble, A. J. Horsewill, The correspondence between quantum and classical mechanics: an experimental demonstration of the smooth transition between the two regimes, *Chem. Phys. Letters* 402 (2005) 519–523.
- [21] F. Fillaux, M.-H. Limage, F. Romain, Quantum proton transfer and interconversion in the benzoic acid crystal: vibrational spectra, mechanism and theory, *Chem. Phys.* 276 (2002) 181–210.
- [22] F. Fillaux, F. Romain, M.-H. Limage, N. Leygue, Extended tunneling states in the benzoic acid crystal: Infrared and raman spectra of the OH and OD stretching modes, *Phys. Chem. Chem. Phys.* 8 (2006) 4327 – 4336.
- [23] M. Plazanet, N. Fukushima, M. R. Johnson, A. J. Horsewill, H. P. Trommsdorff, The vibrational spectrum of crystalline benzoic acid: Inelastic neutron scattering and density functional theory calculations, *J. Chem. Phys.* 115 (7) (2001) 3241–3248.

- [24] M. R. Johnson, H. P. Trommsdorff, Dispersion of vibrational modes in benzoic acid crystals, *Chem. Phys. Letters* 364 (2002) 34–38.
- [25] M. Takahashi, Y. Kawazoe, Y. Ishikawa, H. Ito, Interpretation of temperature-dependent low frequency vibrational spectrum of solid-state benzoic acid dimer, *Chem. Phys. Letters* 479 (2009) 211–217.
- [26] R. Li, J. A. Zeitler, D. Tomerini, E. P. J. Parrott, L. F. Gladden, G. M. Day, A study into the effect of subtle structural details and disorder on the terahertz spectrum of crystalline benzoic acid, *Phys. Chem. Chem. Phys.* 12 (2010) 5329–5340.
- [27] N. Shida, P. F. Barbara, J. Almlöf, A reaction surface hamiltonian treatment of the double proton transfer of formic acid dimer, *J. Chem. Phys.* 94 (5) (1991) 3633–3643.
- [28] Y. Kim, Direct dynamics calculation for the double proton transfer in formic acid dimer, *J. Am. Chem. Soc.* 118 (1996) 1522–1528.
- [29] S. Miura, M. E. Tuckerman, M. L. Klein, An ab initio path integral molecular dynamics study of double proton transfer in the formic acid dimer, *J. Chem. Phys.* 109 (1998) 5290–5299.
- [30] H. Ushiyama, K. Takatsuka, Successive mechanism of double-proton transfer in formic acid dimers: a classical study, *J. Chem. Phys.* 115 (13) (2001) 5903–5912.
- [31] Z. Smedarchina, A. Fernandez-Ramos, W. Siebrand, Calculation of the tunneling splitting in the zero-point level and CO-stretch fundamental of the formic acid dimer, *Chem. Phys. Letters* 395 (2004) 339–345.
- [32] Z. Smedarchina, A. Fernandez-Ramos, W. Siebrand, Tunneling dynamics of double proton transfer in formic acid and benzoic acid dimers, *J. Chem. Phys.* 122 (2005) 134309–12.

- [33] G. V. Mil'nikov, O. Kühn, H. Nakamura, Ground-state and vibrationally assisted tunneling in the formic acid dimer, *J. Chem. Phys.* 123 (2005) 074308–9.
- [34] P. R. L. Markwick, N. L. Doltsinis, D. Marx, Targeted Car-Parinello molecular dynamics: Elucidating double proton transfer in formic acid dimer, *J. Chem. Phys.* 122 (2005) 054112–8.
- [35] D. Luckhaus, Concerted hydrogen exchange tunneling in formic acid dimer, *J. Phys. Chem. A* 110 (2006) 3151–3158.
- [36] I. Matanović, N. Došlić, O. Kühn, Ground and asymmetric CO-stretch excited state tunneling splittings in the formic acid dimer, *J. Chem. Phys.* 127 (2007) 014309–7.
- [37] Z. Smedarchina, W. Siebrand, A. Fernández-Ramos, Correlated double-proton transfer. I. Theory, *J. Chem. Phys.* 127 (2007) 174513.
- [38] G. L. Barnes, E. L. Sibert III, The effects of asymmetric motions on the tunneling splittings in formic acid dimer, *J. Chem. Phys.* 129 (2008) 164317–9.
- [39] G. L. Barnes, S. M. Squires, E. L. Sibert III, Symmetric double proton tunneling in formic acid dimer: A diabatic basis approach, *J. Phys. Chem. B* 112 (2008) 595–603.
- [40] I. Matanović, N. Došlić, B. R. Johnson, Generalized approximation to the reaction path: The formic acid dimer case, *J. Chem. Phys.* 128 (2008) 084103–10.
- [41] W. Siebrand, Z. Smedarchina, A. Fernández-Ramos, Tunneling splitting and level ordering in a CO-stretch fundamental of the formic acid dimer, *Chem. Phys. Letters* 459 (2008) 22–26.
- [42] D. Luckhaus, Hydrogen exchange in formic acid dimer: tunneling above the barrier, *Phys. Chem. Chem. Phys.* 12 (2010) 8357–8361.

- [43] B. Saritha, M. Durga Prasad, An electronic structure perspective of the promoter modes in proton transfer reactions, *J. Phys. Chem. A* 115 (2011) 2802–2810.
- [44] A. Jain, E. L. Sibert III, Tunneling splittings in formic acid dimer: An adiabatic approximation to the Herring formula, *J Chem Phys* 142 (2015) 084115.
- [45] G. A. Pitsevich, A. E. Malevich, E. N. Kozlovskaya, I. Y. Doroshenko, V. Sablinskas, V. E. Pogorelov, D. Dovgal, V. Balevicius, Anharmonic analysis of C–H and O–H stretching vibrations of the formic acid dimer, *Vibrational Spectroscopy* 79 (2015) 67–75.
- [46] S. D. Ivanov, I. M. Grant, D. Marx, Quantum free energy landscapes from ab initio path integral metadynamics: Double proton transfer in the formic acid dimer is concerted but not correlated, *J. Chem. Phys.* 143 (2015) 124304.
- [47] S. Ikeda, S. Kashida, H. Sugimoto, Y. Yamada, S. M. Bennington, F. Fillaux, Inelastic neutron scattering study of the localized dynamics of protons in KHCO_3 single crystals, *Phys. Rev. B* 66 (2002) 184302.
- [48] A. J. Leggett, Testing the limits of quantum mechanics: motivation, state of play, prospects, *J. Phys.: Condens. Matter* 14 (2002) R415–R451.
- [49] A. J. Leggett, A. Garg, Quantum mechanics versus macroscopic realism: Is the flux there when nobody looks?, *Phys. Rev. Letters* 54 (9) (1985) 857–860.
- [50] A. Plotnitsky, What is complementarity?: Niels Bohr and the architecture of quantum theory, *Phys. Scr. T163* (2014) 01402 (20pp).
- [51] F. Fillaux, A. Cousson, Quantum interferences revealed by neutron diffraction accord with a macroscopic-scale quantum-theory of ferroelectrics $\text{KH}_{2(1-\rho)}\text{D}_{2\rho}\text{PO}_4$, *Eur. Phys. J. B* 89 (2016) 72–13.

- [52] <http://www-llb.cea.fr>.
- [53] See supplementary material at [] for crystallographic information files.
- [54] <http://www.xtl.ox.ac.uk/crystals.html>.
- [55] See supplementary material Tables at [] for the refined structural parameters.
- [56] V. M. Nield, D. A. Keen, Diffuse neutron scattering from crystalline materials, Vol. 14 of Oxford series on neutron scattering in condensed matter, Clarendon Press, Oxford, 2001.
- [57] R. J. Nelmes, On the structural evidence for a direct proton tunnelling effect in the KH_2PO_4 -type transition, *J. Phys. C:Solid State Phys.* 21 (1988) L881–L886.
- [58] F. Fillaux, A. Cousson, M. J. Gutmann, Proton transfer across hydrogen bonds: From reaction path to Schrödinger's cat, *Pure Appl. Chem.* 79 (6) (2007) 1023–1039.
- [59] F. Fillaux, A. Cousson, Nonlocal protons and deuterons opposed to disorder: a single-crystal neutron diffraction study of $\text{KH}_{0.76}\text{D}_{0.24}\text{CO}_3$ and a theoretical framework, *J. Phys.: Condens. Matter* 20 (2008) 252202.
- [60] F. Fillaux, A. Cousson, M. J. Gutmann, Evidence of macroscopically entangled protons in a mixed crystal of $\text{KH}_p\text{D}_{1-p}\text{CO}_3$, *J. Phys.: Cond. Matter* 22 (2010) 045402.
- [61] F. Fillaux, A. Cousson, Neutron scattering studies of $\text{K}_3\text{H}(\text{SO}_4)_2$ and $\text{K}_3\text{D}(\text{SO}_4)_2$: The particle-in-a box model for the quantum phase transition, *J. Chem. Phys.* 137 (2012) 074504–10.
- [62] E. Joos, H. D. Zeh, The emergence of classical properties through interaction with the environment, *Z. Phys. B-Cond. Matter* 59 (1985) 223–243.

- [63] W. H. Zurek, Decoherence and the transition from quantum to classical, *Phys. Today* 44 (1991) 36–44.
- [64] W. H. Zurek, Decoherence, einselection and the quantum origin of the classical, *Rev. Modern Phys.* 75 (3) (2003) 715–775.
- [65] W. H. Zurek, Quantum darwinism, classical reality, and the randomness of quantum jumps, *Phys. Today* 67 (2014) 44–50.
- [66] P. Coleman, Time crystals, *Nature* 493 (2013) 166–167.
- [67] S. Ikeda, F. Fillaux, Incoherent-elastic-neutron scattering study of the vibrational dynamics and spin-related symmetry of protons in the KHCO_3 crystal, *Phys. Rev. B* 59 (1999) 4134–4145.
- [68] F. Fillaux, A. Cousson, M. J. Gutmann, Macroscopic quantum entanglement and “super-rigidity” of protons in the KHCO_3 crystal from 30 to 300 K, *J. Phys.: Cond. Matter* 18 (2006) 3229–3249.
- [69] F. Fillaux, A. Cousson, M. J. Gutmann, A neutron diffraction study of macroscopically entangled proton states in the high temperature phase of the KHCO_3 crystal at 340 K, *J. Phys.: Cond. Matter* 20 (2008) 015225.
- [70] F. Fillaux, Calculation of infrared and raman band profiles of strong hydrogen bonds. OH stretching band and proton dynamics in crystalline potassium hydrogen carbonate, *Chem. Phys.* 74 (1983) 405–412.
- [71] F. Fillaux, J. Tomkinson, J. Penfold, Proton dynamics in the hydrogen bond. The inelastic neutron scattering spectrum of potassium hydrogen carbonate at 5 K, *Chem. Phys.* 124 (3) (1988) 425–437.
- [72] G. Eckold, H. Grimm, M. Stein-Arsic, Proton disorder and phase transition in KHCO_3 , *Physica B* 180-181 (1992) 336–338.
- [73] F. Fillaux, Quantum entanglement and nonlocal proton transfer dynamics in dimers of formic acid and analogues, *Chem. Phys. Letters* 408 (2005) 302–306.

- [74] I. Kalkman, C. Vu, M. Schmitt, W. L. Meerts, Tunneling splittings in the S_0 and S_1 states of the benzoic acid dimer determined by high-resolution UV spectroscopy, *Chemphyschem* 9 (2008) 1788–1797.
- [75] L. Evangelisti, P. Écija, E. J. Cocinero, F. C. o, A. Lesarri, W. C. R. Meyer, Proton tunneling in heterodimers of carboxylic acids: A rotational study of the benzoic acidformic acid bimolecule, *J. Phys. Chem Letters* 3 (2012) 3770–3775.
- [76] A. M. Daly, S. J. Carey, A. M. Pejlovas, K. Li, L. Kang, S. G. Kukolich, Gas phase measurements of mono-fluoro-benzoic acids and the dimer of 3-fluoro-benzoic acid, *J. Chem. Phys.* 142 (2015) 144303.
- [77] F. Madeja, M. Havenith, High resolution spectroscopy of carboxylic acid in the gas phase: Observation of proton transfer in $(\text{DCOOH})_2$, *J. Chem. Phys.* 117 (15) (2002) 7162–7168.
- [78] M. Ortlieb, M. Havenith, Proton transfer in $(\text{HCOOH})_2$: An IR high-resolution spectroscopy study of the antisymmetric C–O stretch, *J. Phys. Chem. A* 111 (2007) 7355–7363.
- [79] A. Gutberlet, G. W. Schwaab, M. Havenith, High resolution IR spectroscopy of the carbonyl stretch of $(\text{DCOOD})_2$, *Chem. Phys.* 343 (2008) 158–167.
- [80] M. C. D. Tayler, B. Ouyang, B. J. Howard, Unraveling the spectroscopy of coupled intramolecular tunneling modes: A study of double proton transfer in the formic-acetic acid complex, *J. Chem. Phys.* 134 (2011) 054316–9.
- [81] A. M. Daly, K. O. Douglass, L. C. Sarkozy, J. L. Neill, M. T. Muckle, D. P. Zaleski, B. H. Pate, S. G. Kukolich, Microwave measurements of proton tunneling and structural parameters for the propiolic acid-formic acid dimer, *J. Chem. Phys.* 135 (2011) 154304–12.

- [82] M. Arndt, O. Nairz, J. Vos-Andreae, C. Keller, G. van der Zouw, A. Zeilinger, Waveparticle duality of c_{60} molecules, *Nature* 401 (1999) 680–682.
- [83] B. Brezger, L. Hackermüller, S. Uttenthaler, J. Petschinka, M. Arndt, A. Zeilinger, Matter-wave interferometer for large molecules, *Phys. Rev. Letters* 88 (2002) 100404.
- [84] S. Gerlich, S. Eibenberger, M. Tomandl, S. Nimmrichter, K. Hornberger, P. J. Fagan, J. Tüxen, M. Mayor, M. Arndt, Quantum interference of large organic molecules, *Nature communications* 2 (2011) 263.
- [85] K. Hornberger, S. Uttenthaler, B. Brezger, L. Hackermüller, M. Arndt, A. Zeilinger, Collisional decoherence observed in matter wave interferometry, *Phys. Rev. Letters* 90 (2003) 160401.

Table 1: Double-well operators, distances between minima ($\Delta\chi_\xi$), barrier heights (H_ξ), and energy levels, for the crystal of Benzoic acid. χ_ξ are the symmetry species infrared- (χ_u) or Raman-active (χ_g). The oscillator mass is $\mu_u = \mu_g = 1$ amu. *: observed via inelastic neutron scattering after Ref. [[23]].

	$\mathbb{V}_{L\xi}(\chi_\xi)$ (cm^{-1})	$\Delta\chi_0$ (\AA)	H_ξ (cm^{-1})	$h\nu_{01\xi}$ (cm^{-1})	$h\nu_{02\xi}$ (cm^{-1})	$h\nu_{03\xi}$ (cm^{-1})
Infrared [21]	$265\chi_u + 0.2860 \times 10^6\chi_u^2$ $+171480 \exp(-2.17\chi_u^2)$	0.70	5005	$(172 \pm 4)^*$	2570 ± 20	2840 ± 20
Raman [22]	$270\chi_g + 0.2829 \times 10^6\chi_g^2$ $+171120 \exp(-2.15\chi_g^2)$	0.69	5006	171 ± 4	2602 ± 4	2853 ± 4

Table 2: Neutron single crystal diffraction data and structure refinement of benzoic acid. $\lambda = 0.8305$ Å. Space group $P2_1/c$. $\sigma(I)$ limit: 3.00.Refinement on F. The occupation numbers for the proton sites are ρ_L and ρ_R . The variance for the last digit is given in parentheses.

Crystal data	6 K	25 K	50 K	75 K	100 K	125 K	150 K	175 K	200 K	250 K
a (Å)	5.401(1)	5.401(1)	5.415(1)	5.415(1)	5.500(1)	5.427(1)	5.456(1)	5.456(1)	5.500(1)	5.500(1)
b (Å)	5.004(1)	5.004(1)	5.016(1)	5.016(1)	5.100(1)	5.112(1)	5.074(1)	5.074(1)	5.100(1)	5.100(1)
c (Å)	21.879(1)	21.879(1)	21.826(1)	21.826(1)	22.020(1)	21.810(1)	21.875(1)	21.875(1)	22.020(1)	22.020(1)
β	98.47(1)°	98.47(1)°	98.44(1)°	98.44(1)°	97.90(1)°	98.26(1)°	98.12(1)°	98.12(1)°	97.90(1)°	97.90(1)°
Volume (Å ³)	584.8(2)	584.8(2)	586.4(2)	586.4(2)	611.8(2)	598.8(2)	599.4(2)	599.4(2)	611.8(2)	611.8(2)
Reflections measured	2950	3594	2797	3364	3067	3092	2778	3607	3502	3828
Independent reflections	2589	2637	1946	2645	2724	2283	2297	2300	2714	2748
Reflections used	1649	1679	1382	1472	1363	1122	1018	951	1031	755
R-factor	0.093	0.079	0.058	0.090	0.051	0.048	0.047	0.041	0.069	0.049
Weighted R-factor	0.114	0.097	0.068	0.051	0.053	0.048	0.049	0.037	0.045	0.032
Number of parameters	132	137	137	137	137	137	137	137	137	137
Goodness of fit	1.148	1.117	1.113	1.026	1.085	1.124	1.134	1.101	1.033	1.113
Occupation ρ_L	1.00	0.966(13)	0.852(13)	0.761(13)	0.69(1)	0.65(1)	0.61(1)	0.59(1)	0.583(12)	0.57(2)
Occupation ρ_R	0.00	0.034(13)	0.148(13)	0.239(13)	0.31(1)	0.34(1)	0.38(1)	0.41(1)	0.417(12)	0.43(2)
d_{LR} (Å)	—	—	0.68(1)	0.71(1)	0.69(1)	0.69(1)	0.67(1)	0.72(1)	0.70(1)	0.69(2)
R_{OO} (Å)	2.623(5)	2.621(5)	2.619(5)	2.614(5)	2.646 (5)	2.628(5)	2.621(5)	2.610 (5)	2.624(5)	2.623(5)
Bond length C1O1 (Å)	1.233(3)	1.236(3)	1.244(3)	1.251(3)	1.268(2)	1.261(3)	1.269(3)	1.263(2)	1.271(3)	1.264(3)
Bond length C1O2 (Å)	1.320(3)	1.313(3)	1.305(3)	1.293(3)	1.302(1)	1.286(3)	1.279(3)	1.280(3)	1.279(3)	1.276(4)

Supplementary files:

Single-crystal neutron diffraction data of benzoic acid

6 K

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_audit_creation_date 10-07-01

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'-x,-y,-z'

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'x,-y+1/2,z+1/2'

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_atom_type_scatter_Cromer_Mann_a3
_atom_type_scatter_Cromer_Mann_b3
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# Found Formula = C7 H6 O2
# Dc =      1.39 F000 =      148.00 Mu =      1.02 M =      122.12

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# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2635

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_refine_ls_weighting_details

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Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)

[weight] = 1.0/[A⁰*T⁰(x)+A¹*T¹(x) ... +Aⁿ⁻¹*Tⁿ⁻¹(x)]

where Aⁱ are the Chebychev coefficients listed below and x= Fcalc/Fmax

Method = Robust Weighting (Prince, 1982)

W = [weight] * [1-(deltaF/6*sigmaF)²]²

Aⁱ are:

0.741 0.554 0.247

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;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,

Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,

Munksgaard, Copenhagen, 291-294.

Prince, E.

Mathematical Techniques in Crystallography
and Materials Science

Springer-Verlag, New York, 1982.

Watkin D.J. (1994).

Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

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Uequiv = arithmetic mean of U_i i.e. U_{equiv} = (U₁+U₂+U₃)/3

Replace last . with number of unfound hydrogen atoms attached to an atom.

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. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or Uij restraint (rigid bond) P partial occupancy constraint

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C5 C 0.3252(4) 0.8872(4) 0.19183(10) 0.0074 1.0000 Uani
C6 C 0.1167(4) 0.7290(4) 0.19765(10) 0.0073 1.0000 Uani
C7 C 0.0404(4) 0.5320(5) 0.15356(10) 0.0064 1.0000 Uani
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H5 H 0.3854(10) 1.0409(11) 0.2261(2) 0.0218 1.0000 Uani
H6 H 0.0131(10) 0.7578(12) 0.2362(2) 0.0224 1.0000 Uani
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H10 H 0.1420(8) -0.0014(10) -0.0342(2) 0.0179(8) 1.0000 Uiso
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O2 0.0078(8) 0.0098(10) 0.0062(8) -0.0002(8) 0.0029(6) -0.0013(7)
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H4 0.0193(17) 0.023(2) 0.027(2) -0.0084(18) 0.0084(15) -0.0086(16)
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H6 0.027(2) 0.029(2) 0.0139(17) -0.0065(16) 0.0117(15) -0.0031(18)
H7 0.0211(17) 0.022(2) 0.0198(19) -0.0032(16) 0.0070(14) -0.0092(16)

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02 . C1 . 1.320(3)   yes
C1 . C2 . 1.487(3)   yes
C2 . C3 . 1.398(3)   yes
C2 . C7 . 1.399(3)   yes
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C3 . H3 . 1.091(6)   no
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C5 . H5 . 1.091(5)   no
C6 . C7 . 1.398(3)   yes
C6 . H6 . 1.089(6)   no
C7 . H7 . 1.088(5)   no
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  _geom_angle_site_symmetry_1
  _geom_angle_atom_site_label_2
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_geom_angle
_geom_angle_publ_flag

H10	2_555	O2	.	C1	.	109.9(4)	no
O2	.	C1	.	O1	.	123.6(2)	yes
O2	.	C1	.	C2	.	114.1(2)	yes
O1	.	C1	.	C2	.	122.3(2)	yes
C1	.	C2	.	C3	.	118.98(19)	yes
C1	.	C2	.	C7	.	120.48(18)	yes
C3	.	C2	.	C7	.	120.54(19)	yes
C2	.	C3	.	C4	.	119.39(19)	yes
C2	.	C3	.	H3	.	119.6(3)	no
C4	.	C3	.	H3	.	121.0(3)	no
C3	.	C4	.	C5	.	120.26(19)	yes
C3	.	C4	.	H4	.	119.8(3)	no
C5	.	C4	.	H4	.	120.0(3)	no
C4	.	C5	.	C6	.	120.2(2)	yes
C4	.	C5	.	H5	.	119.9(3)	no
C6	.	C5	.	H5	.	120.0(4)	no
C5	.	C6	.	C7	.	119.7(2)	yes
C5	.	C6	.	H6	.	120.6(4)	no
C7	.	C6	.	H6	.	119.7(4)	no
C2	.	C7	.	C6	.	119.88(19)	yes
C2	.	C7	.	H7	.	119.6(3)	no
C6	.	C7	.	H7	.	120.5(3)	no

25 K

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_audit_creation_method    CRYSTALS_ver_12.84

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_chemical_melting_point          ?

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_cell_length_b                 5.0037(10)
_cell_length_c                 21.8787(10)
_cell_angle_alpha              90
_cell_angle_beta               98.475(10)
_cell_angle_gamma              90
_cell_volume                   584.78(16)

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_symmetry_space_group_name_Hall  '??'
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  '-x,-y,-z'
  '-x,y+1/2,-z+1/2'
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loop_
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_atom_type_scat_Cromer_Mann_b1
_atom_type_scat_Cromer_Mann_a2
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_atom_type_scat_Cromer_Mann_a3
_atom_type_scat_Cromer_Mann_b3
_atom_type_scat_Cromer_Mann_a4
_atom_type_scat_Cromer_Mann_b4
_atom_type_scat_Cromer_Mann_c
_atom_type_scat_source
D      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  6.6710 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
N      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  9.3600 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

_cell_formula_units_Z          4

# Given Formula = C1.75 H1.75 O0.50
# Dc =      0.35 Fooo =      148.00 Mu =      0.26 M =      30.78
# Found Formula = C7 H6 O2
# Dc =      1.39 F000 =      148.00 Mu =      1.02 M =      122.12

_chemical_formula_sum          'C7 H6 O2'

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_exptl_crystal_size_max      '10mm'  
  
_exptl_crystal_density_diffn  1.387  
_exptl_crystal_density_meas  
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# Sheldrick geometric approximat 1.00 1.00  
_exptl_absorpt_correction_type none  
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_diffn_radiation_type         ' neutrons '  
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_diffn_measurement_method     \w
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# and date from subsequent references.

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_computing_structure_refinement 'CRYSTALS (Betteridge et al., 2003)'
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_computing_molecular_graphics  'CAMERON (Watkin et al., 1996)'

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_diffn_standards_decay_%       0

_diffn_ambient_temperature     25
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# Number of reflections with Friedels Law is 2637
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2659

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_diffn_measured_fraction_theta_max 0.995

_diffn_reflns_theta_full       42.766
_diffn_measured_fraction_theta_full 0.995
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_diffn_reflms_limit_l_min     -35
_diffn_reflms_limit_l_max      35
_reflms_limit_h_min           -8
_reflms_limit_h_max           8
_reflms_limit_k_min           0
_reflms_limit_k_max           8
_reflms_limit_l_min           0
_reflms_limit_l_max           35

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_oxford_diffn_Wilson_scale     0.00

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# _atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

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_refine_ls_number_restraints   1
_refine_ls_number_parameters   137

#_refine_ls_R_factor_ref 0.0791
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_refine_ls_goodness_of_fit_ref    1.1173

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_refine_ls_R_factor_all           0.1198
_refine_ls_wR_factor_all          0.1904

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
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_refine_ls_R_factor_gt            0.0791
_refine_ls_wR_factor_gt           0.0973

_refine_ls_shift/su_max           8.271246

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     mixed      # none, undef, noref, refall,
                                           # refxyz, refU, constr or mixed
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details

;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-1~(x)]

```

where A_i are the Chebychev coefficients listed below and $x = F_{\text{calc}}/F_{\text{max}}$

Method = Robust Weighting (Prince, 1982)

$W = [\text{weight}] * [1 - (\Delta F / 6 * \sigma F)^2]^{-2}$

A_i are:

0.562 0.432 0.111

;

_publ_section_references

;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,

Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,

Munksgaard, Copenhagen, 291-294.

Prince, E.

Mathematical Techniques in Crystallography
and Materials Science

Springer-Verlag, New York, 1982.

Watkin D.J. (1994).

Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{\text{equiv}} = (U_1 + U_2 + U_3) / 3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or Uij restraint (rigid bond) P partial occupancy constraint

loop_

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_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

_atom_site_refinement_flags_posn

_atom_site_refinement_flags_adp

_atom_site_refinement_flags_occupancy

_atom_site_disorder_assembly

_atom_site_disorder_group

_atom_site_attached_hydrogens

O1 O 0.2096(4) 0.2431(4) 0.01300(10) 0.0087 1.0000 Uani

O2 O -0.1036(4) 0.1474(4) 0.06641(9) 0.0091 1.0000 Uani

C1 C 0.0952(3) 0.2835(4) 0.05705(8) 0.0063 1.0000 Uani

C2 C 0.1734(3) 0.4938(4) 0.10378(8) 0.0063 1.0000 Uani

C3 C 0.3823(3) 0.6516(4) 0.09795(8) 0.0077 1.0000 Uani

C4 C 0.4573(3) 0.8486(4) 0.14206(8) 0.0084 1.0000 Uani

C5 C 0.3251(3) 0.8872(4) 0.19179(8) 0.0082 1.0000 Uani
C6 C 0.1166(3) 0.7291(4) 0.19762(8) 0.0081 1.0000 Uani
C7 C 0.0404(3) 0.5319(4) 0.15358(8) 0.0073 1.0000 Uani
H3 H 0.4832(8) 0.6194(10) 0.0590(2) 0.0235 1.0000 Uani
H4 H 0.6197(8) 0.9739(10) 0.1374(2) 0.0242 1.0000 Uani
H5 H 0.3853(8) 1.0409(10) 0.2262(2) 0.0229 1.0000 Uani
H6 H 0.0128(9) 0.7585(10) 0.2360(2) 0.0232 1.0000 Uani
H7 H -0.1234(8) 0.4110(10) 0.1571(2) 0.0238 1.0000 Uani
H10 H 0.1423(8) -0.0011(9) -0.03414(19) 0.0191(8) 0.966(13) Uiso . . P . . .
H11 H 0.18(2) 0.14(3) -0.008(6) 0.0191(8) 0.034(13) Uiso . . P . . .
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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0092(7) 0.0107(8) 0.0067(7) -0.0014(7) 0.0025(6) -0.0018(6)
O2 0.0086(7) 0.0100(8) 0.0089(7) -0.0017(6) 0.0022(6) -0.0016(6)
C1 0.0066(6) 0.0068(7) 0.0051(6) -0.0010(5) 0.0003(5) -0.0003(5)
C2 0.0065(7) 0.0067(7) 0.0056(7) -0.0003(5) 0.0004(5) -0.0001(5)
C3 0.0071(6) 0.0084(7) 0.0078(6) -0.0013(6) 0.0021(5) -0.0013(5)
C4 0.0079(6) 0.0086(7) 0.0087(6) -0.0017(5) 0.0012(5) -0.0014(5)
C5 0.0083(6) 0.0091(7) 0.0069(6) -0.0012(5) 0.0005(5) -0.0010(5)
C6 0.0088(6) 0.0088(7) 0.0066(6) -0.0018(5) 0.0013(5) -0.0011(5)
C7 0.0079(6) 0.0083(7) 0.0061(6) -0.0014(5) 0.0020(5) -0.0011(5)
H3 0.0227(16) 0.030(2) 0.0204(15) -0.0059(15) 0.0119(13) -0.0064(16)
H4 0.0217(16) 0.025(2) 0.0271(18) -0.0087(16) 0.0085(14) -0.0089(15)
H5 0.0253(17) 0.0208(18) 0.0224(16) -0.0084(15) 0.0023(14) -0.0068(14)
H6 0.0263(18) 0.028(2) 0.0180(16) -0.0086(14) 0.0131(13) -0.0037(16)

H7 0.0223(16) 0.026(2) 0.0245(17) -0.0064(15) 0.0090(14) -0.0108(15)

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_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1678(13)

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_geom_bond_site_symmetry_2

_geom_bond_distance

_geom_bond_publ_flag

O1 . C1 . 1.236(3) yes

O1 . H11 . 0.70(14) no

O2 . H10 2_555 1.017(5) no

O2 . C1 . 1.313(3) yes

C1 . C2 . 1.485(3) yes

C2 . C3 . 1.399(3) yes

C2 . C7 . 1.403(3) yes

C3 . C4 . 1.397(3) yes

C3 . H3 . 1.089(4) no

C4 . C5 . 1.400(3) yes

C4 . H4 . 1.095(5) no

C5 . C6 . 1.397(3) yes

C5 . H5 . 1.091(4) no

C6 . C7 . 1.398(3) yes

C6 . H6 . 1.086(5) no

C7 . H7 . 1.084(4) no

loop_

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_geom_angle_atom_site_label_2
_geom_angle_site_symmetry_2
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_geom_angle_site_symmetry_3
_geom_angle
_geom_angle_publ_flag
C1 . O1 . H11 . 120(10) no
H10 2_555 O2 . C1 . 110.7(3) no
O2 . C1 . O1 . 123.46(19) yes
O2 . C1 . C2 . 114.62(17) yes
O1 . C1 . C2 . 121.92(18) yes
C1 . C2 . C3 . 119.27(16) yes
C1 . C2 . C7 . 120.31(16) yes
C3 . C2 . C7 . 120.41(16) yes
C2 . C3 . C4 . 119.41(16) yes
C2 . C3 . H3 . 119.4(3) no
C4 . C3 . H3 . 121.2(3) no
C3 . C4 . C5 . 120.33(16) yes
C3 . C4 . H4 . 119.6(3) no
C5 . C4 . H4 . 120.1(3) no
C4 . C5 . C6 . 120.20(17) yes
C4 . C5 . H5 . 119.9(3) no
C6 . C5 . H5 . 119.9(3) no
C5 . C6 . C7 . 119.72(17) yes
C5 . C6 . H6 . 120.6(3) no
C7 . C6 . H6 . 119.7(3) no
C2 . C7 . C6 . 119.92(17) yes
C2 . C7 . H7 . 119.7(3) no
C6 . C7 . H7 . 120.3(3) no

50 K

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_audit_creation_method CRYSTALS_ver_12.84

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_chemical_name_systematic ?

_chemical_melting_point ?

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_cell_length_b 5.0160(10)

_cell_length_c 21.8260(10)

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_cell_angle_beta 98.442(10)

_cell_angle_gamma 90

_cell_volume 586.41(16)

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'-x,-y,-z'

'-x,y+1/2,-z+1/2'

'x,-y+1/2,z+1/2'

loop_

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C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
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N      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
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O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

_cell_formula_units_Z      4

# Given Formula = C1.75 H1.75 O0.50
# Dc =      0.35 F000 =      148.00 Mu =      0.26 M =      30.78
# Found Formula = C7 H6 O2
# Dc =      1.38 F000 =      148.00 Mu =      1.02 M =      122.12

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_exptl_crystal_size_mid       '3mm'  
_exptl_crystal_size_max       '10mm'  
  
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# Non-dispersive F(000):  
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# Sheldrick geometric approximat 1.00 1.00  
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_exptl_absorpt_correction_T_max 1.0000  
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_diffrn_measurement_method        \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.

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_computing_cell_refinement        'USER DEFINED CELL REFINEMENT'
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# Number of reflections with Friedels Law is 1946
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2663

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_diffn_refl_limit_k_min      0
_diffn_refl_limit_k_max      8
_diffn_refl_limit_l_min     -35
_diffn_refl_limit_l_max      34
_refl_limit_h_min           -8
_refl_limit_h_max            8
_refl_limit_k_min            0
_refl_limit_k_max            8
_refl_limit_l_min            0
_refl_limit_l_max            35

_oxford_diffn_Wilson_B_factor 0.00
_oxford_diffn_Wilson_scale    0.00

_atom_sites_solution_primary  direct #heavy,direct,difmap,geom
# _atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min     -0.53
_refine_diff_density_max      0.62

_refine_ls_number_reflns     1382
_refine_ls_number_restraints  1
_refine_ls_number_parameters  137
```

```
#_refine_ls_R_factor_ref 0.0582
_refine_ls_wR_factor_ref      0.0683
_refine_ls_goodness_of_fit_ref 1.1131

#_reflns_number_all 1796
_refine_ls_R_factor_all      0.0927
_refine_ls_wR_factor_all     0.1393

# The I/u(I) cutoff below was used for refinement as
# well as the  $\sigma$  R-factors:
_reflns_threshold_expression  I>3.0\sigma(I)
_reflns_number_gt            1382
_refine_ls_R_factor_gt       0.0582
_refine_ls_wR_factor_gt      0.0683

_refine_ls_shift/su_max      6.843274

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     mixed      # none, undef, noref, reffall,
                                           # refxyz, refU, constr or mixed
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details

;
```

Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)

$$[\text{weight}] = 1.0/[A_0^*T_0(x)+A_1^*T_1(x) \dots +A_{n-1}^*T_{n-1}(x)]$$
 where $A_i^$ are the Chebychev coefficients listed below and $x= F_{\text{calc}}/F_{\text{max}}$
 Method = Robust Weighting (Prince, 1982)

$$W = [\text{weight}] * [1-(\text{delta}F/6*\text{sigma}F)^2]^{2^}$$
 $A_i^$ are:
 0.403 0.242 0.793E-01
 ;

_publ_section_references

;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
 Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
 Munksgaard, Copenhagen, 291-294.

Prince, E.
 Mathematical Techniques in Crystallography
 and Materials Science
 Springer-Verlag, New York, 1982.

Watkin D.J. (1994).
 Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
 Crystallography Laboratory, Oxford, UK.

;


```

# Uequiv = arithmetic mean of Ui i.e. Uequiv = (U1+U2+U3)/3

# Replace last . with number of unfound hydrogen atoms attached to an atom.

# ...refinement_flags...
# . no refinement constraints          S special position constraint on site
# G rigid group refinement of site    R riding atom
# D distance or angle restraint on site T thermal displacement constraints
# U Uiso or Uij restraint (rigid bond) P partial occupancy constraint

loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_U_iso_or_equiv
  _atom_site_occupancy
  _atom_site_adp_type
  _atom_site_refinement_flags_posn
  _atom_site_refinement_flags_adp
  _atom_site_refinement_flags_occupancy
  _atom_site_disorder_assembly
  _atom_site_disorder_group
  _atom_site_attached_hydrogens
O1 O 0.2122(3) 0.2439(5) 0.01305(9) 0.0117 1.0000 Uani . . . . .
O2 O -0.1013(3) 0.1457(5) 0.06612(9) 0.0114 1.0000 Uani . . . . .
C1 C 0.0950(3) 0.2828(3) 0.05717(8) 0.0077 1.0000 Uani . . . . .
C2 C 0.1744(3) 0.4931(4) 0.10381(7) 0.0077 1.0000 Uani . . . . .

```

C3 C 0.3830(3) 0.6498(4) 0.09787(8) 0.0092 1.0000 Uani
C4 C 0.4580(3) 0.8471(4) 0.14203(8) 0.0102 1.0000 Uani
C5 C 0.3253(3) 0.8861(4) 0.19165(7) 0.0103 1.0000 Uani
C6 C 0.1171(3) 0.7278(4) 0.19744(8) 0.0099 1.0000 Uani
C7 C 0.0411(3) 0.5318(4) 0.15349(7) 0.0091 1.0000 Uani
H3 H 0.4841(7) 0.6189(10) 0.0589(2) 0.0268 1.0000 Uani
H4 H 0.6204(8) 0.9702(10) 0.1373(2) 0.0285 1.0000 Uani
H5 H 0.3858(8) 1.0391(10) 0.2263(2) 0.0275 1.0000 Uani
H6 H 0.0133(8) 0.7601(11) 0.2360(2) 0.0280 1.0000 Uani
H7 H -0.1222(7) 0.4090(10) 0.1572(2) 0.0249 1.0000 Uani
H10 H 0.1421(8) -0.0004(11) -0.0339(2) 0.0215(9) 0.852(13) Uiso . . P
H11 H 0.168(5) 0.105(7) -0.0139(13) 0.0215(9) 0.148(13) Uiso . . P
loop_
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_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0121(6) 0.0139(8) 0.0097(7) -0.0022(7) 0.0041(5) -0.0019(6)
O2 0.0106(6) 0.0138(9) 0.0101(7) -0.0015(7) 0.0020(5) -0.0028(6)
C1 0.0080(5) 0.0084(8) 0.0068(6) -0.0005(5) 0.0018(4) -0.0002(5)
C2 0.0082(5) 0.0086(7) 0.0063(6) -0.0003(5) 0.0015(4) -0.0008(5)
C3 0.0086(5) 0.0097(7) 0.0097(6) -0.0007(6) 0.0029(4) -0.0022(5)
C4 0.0090(5) 0.0102(7) 0.0114(6) -0.0006(5) 0.0014(4) -0.0016(5)
C5 0.0107(5) 0.0104(7) 0.0096(6) -0.0014(5) 0.0003(4) -0.0009(5)
C6 0.0111(5) 0.0098(7) 0.0091(6) -0.0011(5) 0.0026(4) -0.0010(5)
C7 0.0091(5) 0.0099(7) 0.0083(6) -0.0009(5) 0.0022(4) -0.0012(5)
H3 0.0231(14) 0.035(2) 0.0255(17) -0.0109(17) 0.0147(13) -0.0072(15)
H4 0.0240(15) 0.030(2) 0.034(2) -0.0083(18) 0.0107(14) -0.0132(15)

H5 0.0297(16) 0.027(2) 0.0250(18) -0.0100(17) 0.0021(14) -0.0066(15)
H6 0.0329(17) 0.031(2) 0.0230(17) -0.0068(17) 0.0153(14) -0.0055(17)
H7 0.0226(13) 0.029(2) 0.0256(17) -0.0043(15) 0.0116(12) -0.0115(14)

_refine_ls_extinction_coef 4.8(6)
_refine_ls_extinction_method
'Larson (1970), Equation 22'
_oxford_refine_ls_scale 0.1626(10)

loop_

_geom_bond_atom_site_label_1
_geom_bond_site_symmetry_1
_geom_bond_atom_site_label_2
_geom_bond_site_symmetry_2
_geom_bond_distance
_geom_bond_publ_flag

01 . C1 . 1.244(3) yes
01 . H11 . 0.92(3) no
02 . H10 2_555 1.015(6) no
02 . C1 . 1.305(2) yes
C1 . C2 . 1.485(2) yes
C2 . C3 . 1.398(2) yes
C2 . C7 . 1.402(2) yes
C3 . C4 . 1.399(3) yes
C3 . H3 . 1.088(4) no
C4 . C5 . 1.399(2) yes
C4 . H4 . 1.091(4) no
C5 . C6 . 1.400(2) yes
C5 . H5 . 1.093(5) no
C6 . C7 . 1.392(2) yes
C6 . H6 . 1.090(4) no
C7 . H7 . 1.090(4) no

H10 . H11 . 0.68(3) no
loop_
_geom_angle_atom_site_label_1
_geom_angle_site_symmetry_1
_geom_angle_atom_site_label_2
_geom_angle_site_symmetry_2
_geom_angle_atom_site_label_3
_geom_angle_site_symmetry_3
_geom_angle
_geom_angle_publ_flag
C1 . O1 . H11 . 120.1(17) no
H10 2_555 O2 . C1 . 112.0(3) no
O2 . C1 . O1 . 123.53(19) yes
O2 . C1 . C2 . 115.60(16) yes
O1 . C1 . C2 . 120.87(16) yes
C1 . C2 . C3 . 119.50(14) yes
C1 . C2 . C7 . 119.93(14) yes
C3 . C2 . C7 . 120.57(15) yes
C2 . C3 . C4 . 119.39(15) yes
C2 . C3 . H3 . 119.9(3) no
C4 . C3 . H3 . 120.7(3) no
C3 . C4 . C5 . 120.13(15) yes
C3 . C4 . H4 . 119.5(3) no
C5 . C4 . H4 . 120.4(3) no
C4 . C5 . C6 . 120.19(16) yes
C4 . C5 . H5 . 119.8(3) no
C6 . C5 . H5 . 120.0(3) no
C5 . C6 . C7 . 119.90(15) yes
C5 . C6 . H6 . 119.9(3) no
C7 . C6 . H6 . 120.2(3) no
C2 . C7 . C6 . 119.82(14) yes

C2 . C7 . H7 . 119.6(3) no
C6 . C7 . H7 . 120.6(3) no
O2 2_555 H10 . H11 . 176(2) no
H10 . H11 . O1 . 177(4) no

75 K

data_CRYSTALS_cif

_audit_creation_date 10-07-01

_audit_creation_method CRYSTALS_ver_12.84

_oxford_structure_analysis_title 'benzoic acid 75K 5C2'

_chemical_name_systematic ?

_chemical_melting_point ?

_cell_length_a 5.4150(10)

_cell_length_b 5.0160(10)

_cell_length_c 21.8260(10)

_cell_angle_alpha 90

_cell_angle_beta 98.442(10)

_cell_angle_gamma 90

_cell_volume 586.41(16)

_symmetry_cell_setting 'Monoclinic'

_symmetry_space_group_name_H-M 'P 1 21/c 1 '

_symmetry_space_group_name_Hall '??'

loop_

_symmetry_equiv_pos_as_xyz

'x,y,z'

'-x,-y,-z'

'-x,y+1/2,-z+1/2'

'x,-y+1/2,z+1/2'

loop_

_atom_type_symbol

_atom_type_scatter_dispersion_real

_atom_type_scatter_dispersion_imag

_atom_type_scatter_Cromer_Mann_a1

_atom_type_scatter_Cromer_Mann_b1

_atom_type_scatter_Cromer_Mann_a2

_atom_type_scatter_Cromer_Mann_b2

_atom_type_scatter_Cromer_Mann_a3

_atom_type_scatter_Cromer_Mann_b3

_atom_type_scatter_Cromer_Mann_a4

_atom_type_scatter_Cromer_Mann_b4

_atom_type_scatter_Cromer_Mann_c

_atom_type_scatter_source

D	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	6.6710	'International Tables Vol C 4.2.6.8 and 6.1.1.4'					
C	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	6.6460	'International Tables Vol C 4.2.6.8 and 6.1.1.4'					
H	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	-3.7390	'International Tables Vol C 4.2.6.8 and 6.1.1.4'					
N	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	9.3600	'International Tables Vol C 4.2.6.8 and 6.1.1.4'					
O	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	5.8030	'International Tables Vol C 4.2.6.8 and 6.1.1.4'					

_cell_formula_units_Z

4

```
# Given Formula = C1.75 H1.75 O0.50
# Dc =          0.35 F000 =          148.00 Mu =          0.26 M =          30.78
# Found Formula = C7 H6.00 O2
# Dc =          1.38 F000 =          148.00 Mu =          1.02 M =          122.12

_chemical_formula_sum          'C7 H6.00 O2'
_chemical_formula_moiety      'C7 H6.00 O2'
_chemical_compound_source     'commercial'
_chemical_formula_weight      122.12

_cell_measurement_reflns_used      0
_cell_measurement_theta_min        0
_cell_measurement_theta_max        0
_cell_measurement_temperature      75

_exptl_crystal_description       'needle'
_exptl_crystal_colour            'white'
_exptl_crystal_size_min          '3mm'
_exptl_crystal_size_mid          '3mm'
_exptl_crystal_size_max          '10mm'

_exptl_crystal_density_diffn     1.383
_exptl_crystal_density_meas

# Non-dispersive F(000):
_exptl_crystal_F_000            148
_exptl_absorpt_coefficient_mu    0.102

# Sheldrick geometric approximat 1.00 1.00
_exptl_absorpt_correction_type    none
_exptl_absorpt_correction_T_min   1.0000
```

```
_exptl_absorpt_correction_T_max 1.0000
_diffrn_measurement_device_type 'Unknown'
_diffrn_radiation_monochromator 'copper 220'
_diffrn_radiation_type ' neutrons '
_diffrn_radiation_wavelength 0.83200
_diffrn_measurement_method \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection 'USER DEFINED DATA COLLECTION'
_computing_cell_refinement 'USER DEFINED CELL REFINEMENT'
_computing_data_reduction 'USER DEFINED DATA REDUCTION'
_computing_structure_solution 'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement 'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material 'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics 'CAMERON (Watkin et al., 1996)'

_diffrn_standards_interval_time 0
_diffrn_standards_interval_count 0
_diffrn_standards_number 0
_diffrn_standards_decay_% 0

_diffrn_ambient_temperature 75
_diffrn_reflns_number 3364
_reflns_number_total 2645
_diffrn_reflns_av_R_equivalents 0.164
# Number of reflections with Friedels Law is 2645
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2667
```


_diffn_reflns_theta_min 2.209
_diffn_reflns_theta_max 42.811
_diffn_measured_fraction_theta_max 0.991

_diffn_reflns_theta_full 41.955
_diffn_measured_fraction_theta_full 0.999

_diffn_reflns_limit_h_min -8
_diffn_reflns_limit_h_max 1
_diffn_reflns_limit_k_min 0
_diffn_reflns_limit_k_max 8
_diffn_reflns_limit_l_min -35
_diffn_reflns_limit_l_max 35
_reflns_limit_h_min -8
_reflns_limit_h_max 8
_reflns_limit_k_min 0
_reflns_limit_k_max 8
_reflns_limit_l_min 0
_reflns_limit_l_max 35

_oxford_diffn_wilson_B_factor 0.00
_oxford_diffn_wilson_scale 0.00

_atom_sites_solution_primary direct #heavy,direct,difmap,geom
#_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min -0.53
_refine_diff_density_max 0.62

```
_refine_ls_number_reflns          1472
_refine_ls_number_restraints      1
_refine_ls_number_parameters      137

#_refine_ls_R_factor_ref 0.0902
_refine_ls_wR_factor_ref          0.0506
_refine_ls_goodness_of_fit_ref    1.0256

#_reflns_number_all 2579
_refine_ls_R_factor_all           0.1621
_refine_ls_wR_factor_all          0.0573

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
_reflns_threshold_expression      I>3.0\s(I)
_reflns_number_gt                 1472
_refine_ls_R_factor_gt            0.0902
_refine_ls_wR_factor_gt           0.0506

_refine_ls_shift/su_max           8.229464

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     mixed      # none, undef, noref, reffall,
```

refxyz, refU, constr or mixed

```
_refine_ls_weighting_scheme      calc
```

```
_refine_ls_weighting_details
```

```
;
```

```
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
```

```
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~*T~n-1~(x)]
```

```
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
```

```
Method = Robust Weighting (Prince, 1982)
```

```
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
```

```
A~i~ are:
```

```
0.641 -1.47 0.282 -0.595
```

```
;
```

```
_publ_section_references
```

```
;
```

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,

Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,

Munksgaard, Copenhagen, 291-294.

Prince, E.

Mathematical Techniques in Crystallography

and Materials Science

Springer-Verlag, New York, 1982.

Watkin D.J. (1994).

Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical

Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

_atom_site_refinement_flags_posn

_atom_site_refinement_flags_adp

_atom_site_refinement_flags_occupancy

_atom_site_disorder_assembly

_atom_site_disorder_group

_atom_site_attached_hydrogens

01 O 0.2139(4) 0.2447(5) 0.01297(9) 0.0149 1.0000 Uani

02 O -0.0988(4) 0.1442(5) 0.06581(10) 0.0155 1.0000 Uani

C1 C 0.0952(3) 0.2817(4) 0.05725(8) 0.0106 1.0000 Uani
 C2 C 0.1751(3) 0.4917(4) 0.10374(8) 0.0101 1.0000 Uani
 C3 C 0.3835(3) 0.6488(4) 0.09791(8) 0.0127 1.0000 Uani
 C4 C 0.4583(3) 0.8455(4) 0.14199(9) 0.0143 1.0000 Uani
 C5 C 0.3259(3) 0.8850(4) 0.19167(8) 0.0135 1.0000 Uani
 C6 C 0.1182(4) 0.7272(4) 0.19739(8) 0.0143 1.0000 Uani
 C7 C 0.0425(3) 0.5314(4) 0.15360(8) 0.0122 1.0000 Uani
 H3 H 0.4843(9) 0.6142(12) 0.0591(2) 0.0320 1.0000 Uani
 H4 H 0.6199(9) 0.9679(12) 0.1369(3) 0.0334 1.0000 Uani
 H5 H 0.3867(10) 1.0390(11) 0.2260(2) 0.0324 1.0000 Uani
 H6 H 0.0118(10) 0.7578(12) 0.2358(2) 0.0314 1.0000 Uani
 H7 H -0.1206(9) 0.4090(11) 0.1566(2) 0.0305 1.0000 Uani
 H10 H 0.1419(10) -0.0045(13) -0.0344(3) 0.0244(10) 0.761(13) Uiso . . P
 H11 H 0.168(3) 0.112(4) -0.0159(9) 0.0244(10) 0.239(13) Uiso . . P
 loop_
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 _atom_site_aniso_U_11
 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
 O1 0.0189(8) 0.0151(9) 0.0117(7) -0.0021(8) 0.0060(6) -0.0013(8)
 O2 0.0169(9) 0.0143(9) 0.0155(8) -0.0021(7) 0.0031(7) -0.0024(7)
 C1 0.0129(7) 0.0102(8) 0.0090(6) -0.0009(5) 0.0027(5) -0.0008(5)
 C2 0.0110(6) 0.0099(7) 0.0096(6) 0.0001(5) 0.0018(5) 0.0004(5)
 C3 0.0124(6) 0.0124(8) 0.0138(7) -0.0023(6) 0.0033(5) -0.0022(6)
 C4 0.0127(6) 0.0147(8) 0.0155(7) -0.0030(6) 0.0025(5) -0.0024(6)
 C5 0.0158(7) 0.0105(8) 0.0139(7) -0.0019(6) 0.0007(5) -0.0006(6)
 C6 0.0177(7) 0.0135(8) 0.0120(6) -0.0025(6) 0.0031(5) 0.0003(6)
 C7 0.0152(7) 0.0117(8) 0.0102(7) 0.0004(5) 0.0039(5) -0.0017(6)

H3 0.0278(18) 0.041(3) 0.031(2) -0.011(2) 0.0158(16) -0.0064(19)
H4 0.0269(18) 0.034(3) 0.042(2) -0.012(2) 0.0147(17) -0.0155(18)
H5 0.036(2) 0.028(2) 0.032(2) -0.0119(18) 0.0026(17) -0.0095(19)
H6 0.044(2) 0.029(2) 0.0259(18) -0.0110(18) 0.0207(17) -0.009(2)
H7 0.0285(18) 0.037(3) 0.0296(19) -0.0062(18) 0.0148(16) -0.0145(18)

_refine_ls_extinction_coef 5.2(4)

_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1625(8)

loop_

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_geom_bond_atom_site_label_2

_geom_bond_site_symmetry_2

_geom_bond_distance

_geom_bond_publ_flag

O1 . C1 . 1.251(3) yes
O1 . H11 . 0.92(2) no
O2 . H10 2_555 0.984(7) no
O2 . C1 . 1.293(3) yes
C1 . C2 . 1.482(3) yes
C2 . C3 . 1.398(3) yes
C2 . C7 . 1.403(2) yes
C3 . C4 . 1.396(3) yes
C3 . H3 . 1.086(5) no
C4 . C5 . 1.399(3) yes
C4 . H4 . 1.088(5) no
C5 . C6 . 1.396(3) yes
C5 . H5 . 1.093(5) no
C6 . C7 . 1.390(3) yes

C6 . H6 . 1.096(5) no
C7 . H7 . 1.085(5) no
H10 . H11 . 0.71(2) no
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_geom_angle_atom_site_label_3
_geom_angle_site_symmetry_3
_geom_angle
_geom_angle_publ_flag
C1 . O1 . H11 . 121.1(12) no
H10 2_555 O2 . C1 . 113.2(4) no
O2 . C1 . O1 . 123.6(2) yes
O2 . C1 . C2 . 116.21(17) yes
O1 . C1 . C2 . 120.21(19) yes
C1 . C2 . C3 . 119.78(15) yes
C1 . C2 . C7 . 120.05(16) yes
C3 . C2 . C7 . 120.18(16) yes
C2 . C3 . C4 . 119.48(16) yes
C2 . C3 . H3 . 119.0(3) no
C4 . C3 . H3 . 121.5(3) no
C3 . C4 . C5 . 120.29(17) yes
C3 . C4 . H4 . 119.0(3) no
C5 . C4 . H4 . 120.7(3) no
C4 . C5 . C6 . 120.03(18) yes
C4 . C5 . H5 . 119.7(3) no
C6 . C5 . H5 . 120.3(3) no
C5 . C6 . C7 . 119.97(18) yes
C5 . C6 . H6 . 120.7(3) no

C7 . C6 . H6 . 119.4(3) no
C2 . C7 . C6 . 120.05(17) yes
C2 . C7 . H7 . 118.7(3) no
C6 . C7 . H7 . 121.2(3) no
O2 2_555 H10 . H11 . 170.2(17) no
H10 . H11 . O1 . 171(3) no

100 K

data_CRYSTALS_cif

_audit_creation_date 10-07-01

_audit_creation_method CRYSTALS_ver_12.84

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_chemical_melting_point ?

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_cell_length_b 5.1000(10)

_cell_length_c 22.0200(10)

_cell_angle_alpha 90

_cell_angle_beta 97.900(10)

_cell_angle_gamma 90

_cell_volume 611.80(17)

_symmetry_cell_setting 'Monoclinic'

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_symmetry_space_group_name_Hall '??'

loop_

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'-x,y+1/2,-z+1/2'
'x,-y+1/2,z+1/2'
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loop_
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_atom_type_scatter_dispersion_real
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_atom_type_scatter_dispersion_imag
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_atom_type_scatter_Cromer_Mann_a2
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_atom_type_scatter_Cromer_Mann_b2
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C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
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N      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
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O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
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# Given Formula = C1.75 H1.75 O0.50
# Dc =      0.33 Ffoo =    148.00 Mu =      0.24 M =    30.78
# Found Formula = C7 H6.00 O2
# Dc =      1.33 F000 =    148.00 Mu =      0.98 M =   122.12

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_chemical_formula_moiety       'C7 H6.00 O2'
_chemical_compound_source      'commercial'
_chemical_formula_weight       122.12

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_cell_measurement_theta_min     0
_cell_measurement_theta_max     0
_cell_measurement_temperature   100

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_exptl_crystal_colour          'white'
_exptl_crystal_size_min        '3mm'
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_exptl_crystal_size_max        '10mm'

_exptl_crystal_density_diffn   1.326
_exptl_crystal_density_meas

# Non-dispersive F(000):
_exptl_crystal_F_000           148.000
_exptl_absorpt_coefficient_mu  0.098

# Sheldrick geometric approximat 1.00 1.00
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_diffraction_radiation_wavelength   0.83200
_diffraction_measurement_method      \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.

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_computing_data_reduction           'USER DEFINED DATA REDUCTION'
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_computing_publication_material     'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics      'CAMERON (Watkin et al., 1996)'

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_diffraction_standards_decay_percent 0

_diffraction_ambient_temperature     100
_diffraction_reflections_number      3067
_reflections_number_total             2724
_diffraction_reflections_av_R_equivalents 0.052

# Number of reflections with Friedels Law is 2724
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2724
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_diffnrn_measured_fraction_theta_max 0.991

_diffnrn_reflms_theta_full 41.678
_diffnrn_measured_fraction_theta_full 0.999

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_diffnrn_reflms_limit_h_max 8
_diffnrn_reflms_limit_k_min 0
_diffnrn_reflms_limit_k_max 8
_diffnrn_reflms_limit_l_min 0
_diffnrn_reflms_limit_l_max 35
_reflms_limit_h_min -8
_reflms_limit_h_max 8
_reflms_limit_k_min 0
_reflms_limit_k_max 8
_reflms_limit_l_min 0
_reflms_limit_l_max 35

_oxford_diffnrn_Wilson_B_factor 0.00
_oxford_diffnrn_Wilson_scale 0.00

_atom_sites_solution_primary direct #heavy,direct,difmap,geom
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min -1.38

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_refine_ls_number_restraints      1
_refine_ls_number_parameters      137

#_refine_ls_R_factor_ref 0.0507
_refine_ls_wR_factor_ref          0.0531
_refine_ls_goodness_of_fit_ref    1.0846

#_reflns_number_all 2638
_refine_ls_R_factor_all           0.1454
_refine_ls_wR_factor_all          0.1280

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
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_reflns_number_gt                 1363
_refine_ls_R_factor_gt            0.0507
_refine_ls_wR_factor_gt           0.0531

_refine_ls_shift/su_max           0.001550

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
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                                         # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme    calc
_refine_ls_weighting_details
;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
A~i~ are:
0.284 0.190E-01 0.551E-01
;

_publ_section_references
;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

```

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

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_atom_site_fract_x

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_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

_atom_site_refinement_flags_posn

_atom_site_refinement_flags_adp

_atom_site_refinement_flags_occupancy

_atom_site_disorder_assembly

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_atom_site_attached_hydrogens
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O2 O -0.0970(3) 0.1442(4) 0.06542(8) 0.0194 1.0000 Uani . . . . .
C1 C 0.0963(3) 0.2803(3) 0.05746(6) 0.0135 1.0000 Uani . . . . .
C2 C 0.1761(3) 0.4893(3) 0.10386(6) 0.0133 1.0000 Uani . . . . .
C3 C 0.3843(3) 0.6459(4) 0.09788(7) 0.0172 1.0000 Uani . . . . .
C4 C 0.4585(3) 0.8424(4) 0.14174(7) 0.0195 1.0000 Uani . . . . .
C5 C 0.3267(3) 0.8815(3) 0.19141(7) 0.0180 1.0000 Uani . . . . .
C6 C 0.1196(3) 0.7253(4) 0.19728(7) 0.0190 1.0000 Uani . . . . .
C7 C 0.0430(3) 0.5294(3) 0.15339(6) 0.0159 1.0000 Uani . . . . .
H3 H 0.4842(8) 0.6146(10) 0.05877(19) 0.0394 1.0000 Uani . . . . .
H4 H 0.6202(8) 0.9649(10) 0.1370(2) 0.0412 1.0000 Uani . . . . .
H5 H 0.3868(8) 1.0333(9) 0.22579(19) 0.0380 1.0000 Uani . . . . .
H6 H 0.0147(9) 0.7578(11) 0.23559(18) 0.0414 1.0000 Uani . . . . .
H7 H -0.1206(8) 0.4068(9) 0.15662(19) 0.0350 1.0000 Uani . . . . .
H10 H 0.1414(10) -0.0032(13) -0.0343(3) 0.0296(10) 0.692(10) Uiso . . P . . .
H11 H 0.166(2) 0.104(3) -0.0150(6) 0.0296(10) 0.308(10) Uiso . . P . . .
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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0262(8) 0.0192(8) 0.0154(6) -0.0041(6) 0.0089(5) -0.0039(7)
O2 0.0202(7) 0.0200(8) 0.0183(6) -0.0050(6) 0.0031(5) -0.0072(7)
C1 0.0154(5) 0.0143(7) 0.0109(5) -0.0004(5) 0.0025(4) -0.0010(5)
C2 0.0139(5) 0.0157(6) 0.0104(5) 0.0011(5) 0.0015(4) -0.0007(5)
C3 0.0156(5) 0.0181(7) 0.0186(5) -0.0023(5) 0.0045(5) -0.0035(5)
```


C4 0.0185(6) 0.0168(7) 0.0228(6) -0.0041(6) 0.0016(5) -0.0037(6)
C5 0.0208(6) 0.0160(7) 0.0164(5) -0.0029(5) -0.0002(5) -0.0006(5)
C6 0.0234(7) 0.0191(8) 0.0152(5) -0.0045(5) 0.0046(5) -0.0025(6)
C7 0.0191(6) 0.0153(7) 0.0141(5) -0.0022(5) 0.0048(5) -0.0018(5)
H3 0.0377(18) 0.048(2) 0.0362(18) -0.0092(18) 0.0186(16) -0.0115(18)
H4 0.0325(16) 0.042(2) 0.051(2) -0.017(2) 0.0116(17) -0.0181(17)
H5 0.045(2) 0.035(2) 0.0328(17) -0.0160(16) 0.0027(15) -0.0087(18)
H6 0.055(2) 0.043(2) 0.0313(16) -0.0163(17) 0.0240(16) -0.011(2)
H7 0.0345(16) 0.038(2) 0.0357(16) -0.0063(15) 0.0145(14) -0.0151(16)

_refine_ls_extinction_coef 3.6(4)

_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1433(6)

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_geom_bond_site_symmetry_2

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O1 . H11 . 0.955(15) no
O2 . H10 2_555 1.001(7) no
O2 . C1 . 1.302(2) yes
C1 . C2 . 1.500(2) yes
C2 . C3 . 1.417(2) yes
C2 . C7 . 1.4095(18) yes
C3 . C4 . 1.412(2) yes
C3 . H3 . 1.095(4) no
C4 . C5 . 1.407(2) yes

C4 . H4 . 1.104(4) no
C5 . C6 . 1.411(2) yes
C5 . H5 . 1.101(4) no
C6 . C7 . 1.413(2) yes
C6 . H6 . 1.098(4) no
C7 . H7 . 1.106(4) no
H10 . H11 . 0.695(13) no
loop_
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_geom_angle_site_symmetry_3
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_geom_angle_publ_flag
C1 . O1 . H11 . 118.3(7) no
H10 2_555 O2 . C1 . 114.7(3) no
O2 . C1 . O1 . 123.06(17) yes
O2 . C1 . C2 . 117.08(13) yes
O1 . C1 . C2 . 119.86(15) yes
C1 . C2 . C3 . 120.11(12) yes
C1 . C2 . C7 . 119.73(12) yes
C3 . C2 . C7 . 120.16(13) yes
C2 . C3 . C4 . 119.82(13) yes
C2 . C3 . H3 . 119.4(3) no
C4 . C3 . H3 . 120.8(3) no
C3 . C4 . C5 . 120.07(14) yes
C3 . C4 . H4 . 119.9(3) no
C5 . C4 . H4 . 120.0(3) no
C4 . C5 . C6 . 120.01(14) yes

C4 . C5 . H5 . 119.7(3) no
 C6 . C5 . H5 . 120.2(3) no
 C5 . C6 . C7 . 120.33(13) yes
 C5 . C6 . H6 . 120.1(3) no
 C7 . C6 . H6 . 119.6(3) no
 C2 . C7 . C6 . 119.61(13) yes
 C2 . C7 . H7 . 118.8(2) no
 C6 . C7 . H7 . 121.6(2) no
 O2 2_555 H10 . H11 . 173.6(13) no
 H10 . H11 . O1 . 173.7(19) no

125 K

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 _audit_creation_method CRYSTALS_ver_12.84

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 _chemical_melting_point ?

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 _cell_length_b 5.1118(10)
 _cell_length_c 21.8100(10)
 _cell_angle_alpha 90
 _cell_angle_beta 98.260(10)
 _cell_angle_gamma 90
 _cell_volume 598.83(16)

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    '-x,-y,-z'
    '-x,y+1/2,-z+1/2'
    'x,-y+1/2,z+1/2'

loop_
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  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
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  _atom_type_scatter_Cromer_Mann_b1
  _atom_type_scatter_Cromer_Mann_a2
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  _atom_type_scatter_Cromer_Mann_b3
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  _atom_type_scatter_Cromer_Mann_b4
  _atom_type_scatter_Cromer_Mann_c
  _atom_type_scatter_source
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      0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

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_cell_formula_units_Z          4

# Given Formula = C1.75 H1.50 O0.50
# Dc =      0.34 Ffoo =    148.00 Mu =      0.25 M =    30.53
# Found Formula = C7 H6.00 O2
# Dc =      1.35 F000 =    148.00 Mu =      1.00 M =   122.12

_chemical_formula_sum          'C7 H6.00 O2'
_chemical_formula_moiety       'C7 H6.00 O2'
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_chemical_formula_weight       122.12

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_cell_measurement_theta_min    0
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_cell_measurement_temperature  125

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_exptl_crystal_size_mid        '3mm'
_exptl_crystal_size_max        '10mm'

_exptl_crystal_density_diffn   1.355
_exptl_crystal_density_meas

# Non-dispersive F(000):
_exptl_crystal_F_000           148.000
_exptl_absorpt_coefficient_mu  0.100

# Sheldrick geometric approximat 1.00 1.00
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_exptl_absorpt_correction_T_max   1.0000
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_diffrn_radiation_monochromator    'copper 220'
_diffrn_radiation_type             ' neutrons '
_diffrn_radiation_wavelength       0.83200
_diffrn_measurement_method         \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.

_computing_data_collection         'USER DEFINED DATA COLLECTION'
_computing_cell_refinement         'USER DEFINED CELL REFINEMENT'
_computing_data_reduction          'USER DEFINED DATA REDUCTION'
_computing_structure_solution      'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement    'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material    'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics      'CAMERON (Watkin et al., 1996)'

_diffrn_standards_interval_time    0
_diffrn_standards_interval_count   0
_diffrn_standards_number           0
_diffrn_standards_decay_%          0

_diffrn_ambient_temperature        125
_diffrn_reflns_number              3092
_reflns_number_total                2283
_diffrn_reflns_av_R_equivalents    0.065

# Number of reflections with Friedels Law is 2283
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2281
```

_diffnrn_reflms_theta_min 2.204
_diffnrn_reflms_theta_max 39.661
_diffnrn_measured_fraction_theta_max 0.997

_diffnrn_reflms_theta_full 39.661
_diffnrn_measured_fraction_theta_full 0.997

_diffnrn_reflms_limit_h_min -8
_diffnrn_reflms_limit_h_max 8
_diffnrn_reflms_limit_k_min -7
_diffnrn_reflms_limit_k_max 2
_diffnrn_reflms_limit_l_min -33
_diffnrn_reflms_limit_l_max 3
_reflms_limit_h_min -8
_reflms_limit_h_max 8
_reflms_limit_k_min 0
_reflms_limit_k_max 7
_reflms_limit_l_min 0
_reflms_limit_l_max 33

_oxford_diffnrn_Wilson_B_factor 0.00
_oxford_diffnrn_Wilson_scale 0.00

_atom_sites_solution_primary direct #heavy,direct,difmap,geom
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min -0.87

```
_refine_diff_density_max          0.84

_refine_ls_number_reflns          1122
_refine_ls_number_restraints      1
_refine_ls_number_parameters      137

#_refine_ls_R_factor_ref 0.0479
_refine_ls_wR_factor_ref          0.0479
_refine_ls_goodness_of_fit_ref    1.1245

#_reflns_number_all 2240
_refine_ls_R_factor_all           0.1365
_refine_ls_wR_factor_all          0.1443

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
_reflns_threshold_expression      I>3.0\s(I)
_reflns_number_gt                 1122
_refine_ls_R_factor_gt            0.0479
_refine_ls_wR_factor_gt           0.0479

_refine_ls_shift/su_max           0.000087

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
```



```

_refine_ls_matrix_type          full
_refine_ls_hydrogen_treatment  mixed      # none, undef, noref, refall,
                                         # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme    calc
_refine_ls_weighting_details
;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
A~i~ are:
0.214 -0.127E-01 0.206E-01
;

_publ_section_references
;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

```

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

_atom_site_refinement_flags_posn

_atom_site_refinement_flags_adp

_atom_site_refinement_flags_occupancy

_atom_site_disorder_assembly

```
_atom_site_disorder_group
_atom_site_attached_hydrogens
O1 O 0.2169(4) 0.2431(5) 0.01298(9) 0.0240 1.0000 Uani . . . . .
O2 O -0.0964(4) 0.1428(5) 0.06521(10) 0.0241 1.0000 Uani . . . . .
C1 C 0.0961(3) 0.2790(4) 0.05755(7) 0.0162 1.0000 Uani . . . . .
C2 C 0.1766(3) 0.4881(4) 0.10389(7) 0.0148 1.0000 Uani . . . . .
C3 C 0.3838(3) 0.6449(4) 0.09773(8) 0.0205 1.0000 Uani . . . . .
C4 C 0.4587(3) 0.8409(4) 0.14166(9) 0.0231 1.0000 Uani . . . . .
C5 C 0.3268(3) 0.8793(4) 0.19123(8) 0.0222 1.0000 Uani . . . . .
C6 C 0.1200(3) 0.7231(4) 0.19715(8) 0.0225 1.0000 Uani . . . . .
C7 C 0.0444(3) 0.5287(4) 0.15338(7) 0.0192 1.0000 Uani . . . . .
H3 H 0.4838(8) 0.6142(11) 0.0589(2) 0.0408 1.0000 Uani . . . . .
H4 H 0.6200(9) 0.9635(12) 0.1368(3) 0.0461 1.0000 Uani . . . . .
H5 H 0.3869(9) 1.0308(11) 0.2256(2) 0.0440 1.0000 Uani . . . . .
H6 H 0.0159(10) 0.7535(12) 0.2356(2) 0.0452 1.0000 Uani . . . . .
H7 H -0.1184(9) 0.4071(10) 0.1571(2) 0.0391 1.0000 Uani . . . . .
H1 H 0.1408(11) 0.0009(15) -0.0344(3) 0.0309(11) 0.655(11) Uiso . . P . . .
H2 H 0.173(2) 0.103(3) -0.0144(6) 0.0309(11) 0.345(11) Uiso . . P . . .
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_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0296(9) 0.0260(10) 0.0187(8) -0.0045(9) 0.0113(7) -0.0051(9)
O2 0.0254(9) 0.0257(11) 0.0225(8) -0.0012(8) 0.0077(7) -0.0086(8)
C1 0.0176(6) 0.0174(8) 0.0142(6) -0.0007(6) 0.0047(5) -0.0015(6)
C2 0.0167(6) 0.0145(7) 0.0139(6) 0.0004(5) 0.0041(5) -0.0011(6)
C3 0.0182(7) 0.0226(9) 0.0216(7) -0.0027(7) 0.0063(5) -0.0047(7)
```

C4 0.0197(7) 0.0223(9) 0.0276(8) -0.0052(7) 0.0042(6) -0.0041(7)
C5 0.0230(7) 0.0212(9) 0.0218(7) -0.0062(6) 0.0014(6) -0.0016(7)
C6 0.0282(8) 0.0234(9) 0.0169(6) -0.0037(6) 0.0067(6) -0.0019(7)
C7 0.0214(7) 0.0205(8) 0.0172(7) -0.0004(6) 0.0078(6) -0.0014(6)
H3 0.039(2) 0.045(3) 0.043(2) -0.008(2) 0.0226(18) -0.007(2)
H4 0.0361(19) 0.047(3) 0.058(3) -0.016(2) 0.0140(19) -0.020(2)
H5 0.047(2) 0.045(3) 0.039(2) -0.022(2) 0.0034(18) -0.009(2)
H6 0.059(3) 0.045(3) 0.037(2) -0.012(2) 0.0241(19) -0.009(2)
H7 0.0391(19) 0.042(2) 0.0407(19) -0.0078(18) 0.0198(16) -0.0179(19)

_refine_ls_extinction_coef 2.5(3)

_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1291(5)

loop_

_geom_bond_atom_site_label_1

_geom_bond_site_symmetry_1

_geom_bond_atom_site_label_2

_geom_bond_site_symmetry_2

_geom_bond_distance

_geom_bond_publ_flag

O1 . C1 . 1.261(2) yes
O1 . H2 . 0.940(15) no
O2 . H1 2_555 1.002(8) no
O2 . C1 . 1.286(3) yes
C1 . C2 . 1.493(2) yes
C2 . C3 . 1.403(2) yes
C2 . C7 . 1.395(2) yes
C3 . C4 . 1.405(3) yes
C3 . H3 . 1.081(4) no
C4 . C5 . 1.394(3) yes

C4 . H4 . 1.094(5) no
C5 . C6 . 1.398(3) yes
C5 . H5 . 1.095(5) no
C6 . C7 . 1.398(3) yes
C6 . H6 . 1.087(4) no
C7 . H7 . 1.093(4) no
H1 . H2 . 0.687(13) no

loop_
_geom_angle_atom_site_label_1
_geom_angle_site_symmetry_1
_geom_angle_atom_site_label_2
_geom_angle_site_symmetry_2
_geom_angle_atom_site_label_3
_geom_angle_site_symmetry_3
_geom_angle
_geom_angle_publ_flag

C1 . O1 . H2 . 119.2(7) no
H1 2_555 O2 . C1 . 115.6(4) no
O2 . C1 . O1 . 122.9(2) yes
O2 . C1 . C2 . 117.63(16) yes
O1 . C1 . C2 . 119.47(17) yes
C1 . C2 . C3 . 120.32(14) yes
C1 . C2 . C7 . 119.84(14) yes
C3 . C2 . C7 . 119.84(15) yes
C2 . C3 . C4 . 119.95(15) yes
C2 . C3 . H3 . 119.4(3) no
C4 . C3 . H3 . 120.6(3) no
C3 . C4 . C5 . 119.92(17) yes
C3 . C4 . H4 . 119.9(3) no
C5 . C4 . H4 . 120.1(3) no
C4 . C5 . C6 . 119.98(17) yes

C4 . C5 . H5 . 119.7(3) no
C6 . C5 . H5 . 120.3(3) no
C5 . C6 . C7 . 120.24(16) yes
C5 . C6 . H6 . 120.1(3) no
C7 . C6 . H6 . 119.6(3) no
C6 . C7 . C2 . 120.07(15) yes
C6 . C7 . H7 . 121.0(3) no
C2 . C7 . H7 . 119.0(3) no
O2 2_555 H1 . H2 . 177.1(13) no
H1 . H2 . O1 . 179.9(18) no

150 K

data_CRYSTALS_cif
_audit_creation_date 10-07-01
_audit_creation_method CRYSTALS_ver_12.84

_oxford_structure_analysis_title 'benzoic acid 150K'
_chemical_name_systematic ?
_chemical_melting_point ?

_cell_length_a 5.4555(10)
_cell_length_b 5.0738(10)
_cell_length_c 21.8745(10)
_cell_angle_alpha 90
_cell_angle_beta 98.116(10)
_cell_angle_gamma 90
_cell_volume 599.42(16)

_symmetry_cell_setting 'Monoclinic'

```

_symmetry_space_group_name_H-M    'P 1 21/c 1 '
_symmetry_space_group_name_Hall    '?'
loop_
  _symmetry_equiv_pos_as_xyz
    'x,y,z'
    '-x,-y,-z'
    '-x,y+1/2,-z+1/2'
    'x,-y+1/2,z+1/2'

loop_
  _atom_type_symbol
  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
  _atom_type_scatter_Cromer_Mann_a1
  _atom_type_scatter_Cromer_Mann_b1
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  _atom_type_scatter_Cromer_Mann_b2
  _atom_type_scatter_Cromer_Mann_a3
  _atom_type_scatter_Cromer_Mann_b3
  _atom_type_scatter_Cromer_Mann_a4
  _atom_type_scatter_Cromer_Mann_b4
  _atom_type_scatter_Cromer_Mann_c
  _atom_type_scatter_source
C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
      0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

```

```
_cell_formula_units_Z          4

# Given Formula = C1.75 H1.50 O0.50
# Dc =      0.34 Ffoo =    148.00 Mu =      0.25 M =    30.53
# Found Formula = C7 H6.00 O2
# Dc =      1.35 F000 =    148.00 Mu =      1.00 M =   122.12

_chemical_formula_sum          'C7 H6.00 O2'
_chemical_formula_moiety       'C7 H6.00 O2'
_chemical_compound_source      'commercial'
_chemical_formula_weight       122.12

_cell_measurement_reflns_used   0
_cell_measurement_theta_min     0
_cell_measurement_theta_max     0
_cell_measurement_temperature   150

_exptl_crystal_description     'needle'
_exptl_crystal_colour          'white'
_exptl_crystal_size_min        '3mm'
_exptl_crystal_size_mid        '3mm'
_exptl_crystal_size_max        '10mm'

_exptl_crystal_density_diffn   1.353
_exptl_crystal_density_meas

# Non-dispersive F(000):
_exptl_crystal_F_000           148.000
_exptl_absorpt_coefficient_mu  0.100

# Sheldrick geometric approximat 1.00 1.00
```



```
_exptl_absorpt_correction_type      none
_exptl_absorpt_correction_T_min    1.0000
_exptl_absorpt_correction_T_max    1.0000
_diffrn_measurement_device_type     'Unknown'
_diffrn_radiation_monochromator     'copper 220'
_diffrn_radiation_type              ' neutrons '
_diffrn_radiation_wavelength        0.83200
_diffrn_measurement_method          \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.

_computing_data_collection          'USER DEFINED DATA COLLECTION'
_computing_cell_refinement          'USER DEFINED CELL REFINEMENT'
_computing_data_reduction           'USER DEFINED DATA REDUCTION'
_computing_structure_solution       'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement     'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material     'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics       'CAMERON (Watkin et al., 1996)'

_diffrn_standards_interval_time     0
_diffrn_standards_interval_count    0
_diffrn_standards_number            0
_diffrn_standards_decay_%           0

_diffrn_ambient_temperature         150
_diffrn_reflns_number               2778
_reflns_number_total                 2297
_diffrn_reflns_av_R_equivalents     0.099

# Number of reflections with Friedels Law is 2297
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2303
```

_diffnrn_reflms_theta_min 2.197
_diffnrn_reflms_theta_max 39.816
_diffnrn_measured_fraction_theta_max 0.993

_diffnrn_reflms_theta_full 39.020
_diffnrn_measured_fraction_theta_full 1.000

_diffnrn_reflms_limit_h_min -8
_diffnrn_reflms_limit_h_max 8
_diffnrn_reflms_limit_k_min -7
_diffnrn_reflms_limit_k_max 1
_diffnrn_reflms_limit_l_min -33
_diffnrn_reflms_limit_l_max 0
_reflms_limit_h_min -8
_reflms_limit_h_max 8
_reflms_limit_k_min 0
_reflms_limit_k_max 7
_reflms_limit_l_min 0
_reflms_limit_l_max 33

_oxford_diffnrn_Wilson_B_factor 0.00
_oxford_diffnrn_Wilson_scale 0.00

_atom_sites_solution_primary direct #heavy,direct,difmap,geom
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min -0.72

```
_refine_diff_density_max          0.96

_refine_ls_number_reflns          1018
_refine_ls_number_restraints      1
_refine_ls_number_parameters      137

#_refine_ls_R_factor_ref 0.0470
_refine_ls_wR_factor_ref          0.0491
_refine_ls_goodness_of_fit_ref    1.1337

#_reflns_number_all 2252
_refine_ls_R_factor_all           0.1560
_refine_ls_wR_factor_all          0.1662

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
_reflns_threshold_expression      I>3.0\s(I)
_reflns_number_gt                 1018
_refine_ls_R_factor_gt            0.0470
_refine_ls_wR_factor_gt           0.0491

_refine_ls_shift/su_max           0.000064

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
```

```

_refine_ls_matrix_type          full
_refine_ls_hydrogen_treatment  mixed      # none, undef, noref, refall,
                                         # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme    calc
_refine_ls_weighting_details
;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
A~i~ are:
0.190 -0.136E-02 -0.409E-02 -0.160E-01
;

_publ_section_references
;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

```

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

_atom_site_refinement_flags_posn

_atom_site_refinement_flags_adp

_atom_site_refinement_flags_occupancy

_atom_site_disorder_assembly

```
_atom_site_disorder_group
_atom_site_attached_hydrogens
O1 O 0.2189(5) 0.2419(5) 0.01309(10) 0.0281 1.0000 Uani . . . . .
O2 O -0.0946(5) 0.1427(6) 0.06514(10) 0.0279 1.0000 Uani . . . . .
C1 C 0.0960(3) 0.2786(4) 0.05750(7) 0.0193 1.0000 Uani . . . . .
C2 C 0.1772(3) 0.4867(4) 0.10378(7) 0.0165 1.0000 Uani . . . . .
C3 C 0.3853(4) 0.6423(5) 0.09771(9) 0.0249 1.0000 Uani . . . . .
C4 C 0.4591(4) 0.8365(5) 0.14141(9) 0.0264 1.0000 Uani . . . . .
C5 C 0.3277(4) 0.8763(4) 0.19123(9) 0.0255 1.0000 Uani . . . . .
C6 C 0.1209(4) 0.7209(5) 0.19693(8) 0.0261 1.0000 Uani . . . . .
C7 C 0.0458(3) 0.5270(4) 0.15344(8) 0.0212 1.0000 Uani . . . . .
H3 H 0.4837(10) 0.6099(13) 0.0588(2) 0.0493 1.0000 Uani . . . . .
H4 H 0.6189(10) 0.9610(13) 0.1367(3) 0.0524 1.0000 Uani . . . . .
H5 H 0.3879(10) 1.0275(12) 0.2259(2) 0.0494 1.0000 Uani . . . . .
H6 H 0.0198(11) 0.7515(13) 0.2358(2) 0.0515 1.0000 Uani . . . . .
H7 H -0.1159(9) 0.4055(11) 0.1567(2) 0.0435 1.0000 Uani . . . . .
H1 H 0.1370(15) 0.0003(19) -0.0346(4) 0.0381(14) 0.615(13) Uiso . . P . . .
H2 H 0.174(2) 0.101(3) -0.0155(6) 0.0381(14) 0.385(13) Uiso . . P . . .
loop_
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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0355(11) 0.0300(11) 0.0217(8) -0.0040(9) 0.0143(8) -0.0061(11)
O2 0.0295(10) 0.0298(12) 0.0260(9) -0.0032(9) 0.0096(8) -0.0089(10)
C1 0.0211(7) 0.0220(9) 0.0159(6) -0.0003(6) 0.0062(6) -0.0018(7)
C2 0.0193(7) 0.0157(8) 0.0155(6) 0.0010(6) 0.0059(6) -0.0020(6)
C3 0.0245(8) 0.0265(10) 0.0253(8) -0.0044(8) 0.0087(6) -0.0049(8)
```

C4 0.0230(8) 0.0253(10) 0.0317(9) -0.0052(8) 0.0063(7) -0.0055(8)
C5 0.0296(9) 0.0212(9) 0.0249(8) -0.0054(7) 0.0017(7) -0.0012(8)
C6 0.0335(10) 0.0275(10) 0.0184(7) -0.0033(7) 0.0076(6) -0.0013(8)
C7 0.0254(8) 0.0216(9) 0.0180(7) -0.0008(6) 0.0083(6) -0.0036(8)
H3 0.048(3) 0.057(3) 0.049(2) -0.007(2) 0.027(2) -0.015(3)
H4 0.042(2) 0.052(3) 0.066(3) -0.018(3) 0.021(2) -0.024(2)
H5 0.055(3) 0.050(3) 0.042(2) -0.023(2) 0.004(2) -0.011(3)
H6 0.067(3) 0.053(3) 0.040(2) -0.017(2) 0.028(2) -0.016(3)
H7 0.046(2) 0.049(3) 0.042(2) -0.006(2) 0.0249(18) -0.018(2)

_refine_ls_extinction_coef 2.2(2)

_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1278(6)

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_geom_bond_site_symmetry_2

_geom_bond_distance

_geom_bond_publ_flag

O1 . C1 . 1.269(3) yes
O1 . H2 . 0.958(17) no
O2 . H1 2_555 0.990(11) no
O2 . C1 . 1.279(3) yes
C1 . C2 . 1.487(3) yes
C2 . C3 . 1.404(3) yes
C2 . C7 . 1.399(2) yes
C3 . C4 . 1.392(3) yes
C3 . H3 . 1.081(5) no
C4 . C5 . 1.401(3) yes

C4 . H4 . 1.093(5) no
C5 . C6 . 1.396(3) yes
C5 . H5 . 1.096(5) no
C6 . C7 . 1.389(3) yes
C6 . H6 . 1.088(4) no
C7 . H7 . 1.087(5) no
H1 . H2 . 0.674(14) no

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C1 . O1 . H2 . 119.7(8) no
H1 2_555 O2 . C1 . 115.1(5) no
O2 . C1 . O1 . 123.3(2) yes
O2 . C1 . C2 . 117.63(17) yes
O1 . C1 . C2 . 119.11(19) yes
C1 . C2 . C3 . 120.14(15) yes
C1 . C2 . C7 . 119.79(15) yes
C3 . C2 . C7 . 120.07(16) yes
C2 . C3 . C4 . 119.51(16) yes
C2 . C3 . H3 . 119.1(3) no
C4 . C3 . H3 . 121.4(3) no
C3 . C4 . C5 . 120.38(18) yes
C3 . C4 . H4 . 120.1(3) no
C5 . C4 . H4 . 119.5(4) no
C4 . C5 . C6 . 119.79(19) yes

C4 . C5 . H5 . 120.2(3) no
 C6 . C5 . H5 . 120.0(3) no
 C5 . C6 . C7 . 120.17(17) yes
 C5 . C6 . H6 . 119.7(4) no
 C7 . C6 . H6 . 120.2(4) no
 C2 . C7 . C6 . 120.09(17) yes
 C2 . C7 . H7 . 118.5(3) no
 C6 . C7 . H7 . 121.4(3) no
 O2 2_555 H1 . H2 . 174.6(16) no
 H1 . H2 . O1 . 176.6(20) no

175 K

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 _chemical_name_systematic ?
 _chemical_melting_point ?

 _cell_length_a 5.4555(10)
 _cell_length_b 5.0738(10)
 _cell_length_c 21.8745(10)
 _cell_angle_alpha 90
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 _symmetry_cell_setting 'Monoclinic'

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    '-x,-y,-z'
    '-x,y+1/2,-z+1/2'
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loop_
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  _atom_type_scatter_dispersion_imag
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  _atom_type_scatter_Cromer_Mann_b1
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  _atom_type_scatter_Cromer_Mann_b2
  _atom_type_scatter_Cromer_Mann_a3
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  _atom_type_scatter_Cromer_Mann_a4
  _atom_type_scatter_Cromer_Mann_b4
  _atom_type_scatter_Cromer_Mann_c
  _atom_type_scatter_source
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O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

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# Given Formula = C1.75 H1.50 O0.50
# Dc =      0.34 Ffoo =    148.00 Mu =      0.25 M =    30.53
# Found Formula = C7 H6.00 O2
# Dc =      1.35 F000 =    148.00 Mu =      1.00 M =   122.12

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_chemical_formula_moiety       'C7 H6.00 O2'
_chemical_compound_source      'commercial'
_chemical_formula_weight       122.12

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_cell_measurement_theta_min     0
_cell_measurement_theta_max     0
_cell_measurement_temperature   175

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_exptl_crystal_colour          'white'
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_exptl_crystal_size_mid        '3mm'
_exptl_crystal_size_max        '10mm'

_exptl_crystal_density_diffn   1.353
_exptl_crystal_density_meas

# Non-dispersive F(000):
_exptl_crystal_F_000           148.000
_exptl_absorpt_coefficient_mu   0.100

# Sheldrick geometric approximat 1.00 1.00

```

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_exptl_absorpt_correction_type      none
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_exptl_absorpt_correction_T_max     1.0000
_diffrn_measurement_device_type      'Unknown'
_diffrn_radiation_monochromator      'copper 220'
_diffrn_radiation_type               ' neutrons '
_diffrn_radiation_wavelength         0.83200
_diffrn_measurement_method           \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.

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_computing_cell_refinement           'USER DEFINED CELL REFINEMENT'
_computing_data_reduction            'USER DEFINED DATA REDUCTION'
_computing_structure_solution        'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement      'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material      'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics        'CAMERON (Watkin et al., 1996)'

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_diffrn_standards_decay_%            0

_diffrn_ambient_temperature          175
_diffrn_reflns_number                3607
_reflns_number_total                 2300
_diffrn_reflns_av_R_equivalents      0.105

# Number of reflections with Friedels Law is 2300
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2311
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_diffnrn_measured_fraction_theta_max 0.992

_diffnrn_reflms_theta_full 39.053
_diffnrn_measured_fraction_theta_full 1.000

_diffnrn_reflms_limit_h_min -8
_diffnrn_reflms_limit_h_max 8
_diffnrn_reflms_limit_k_min -7
_diffnrn_reflms_limit_k_max 3
_diffnrn_reflms_limit_l_min -33
_diffnrn_reflms_limit_l_max 13
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_reflms_limit_k_min 0
_reflms_limit_k_max 7
_reflms_limit_l_min 0
_reflms_limit_l_max 33

_oxford_diffnrn_Wilson_B_factor 0.00
_oxford_diffnrn_Wilson_scale 0.00

_atom_sites_solution_primary direct #heavy,direct,difmap,geom
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min -0.58

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_refine_diff_density_max          0.64

_refine_ls_number_reflns          951
_refine_ls_number_restraints      1
_refine_ls_number_parameters      137

#_refine_ls_R_factor_ref 0.0412
_refine_ls_wR_factor_ref          0.0369
_refine_ls_goodness_of_fit_ref    1.1009

#_reflns_number_all 2256
_refine_ls_R_factor_all           0.1521
_refine_ls_wR_factor_all          0.1330

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
_reflns_threshold_expression      I>3.0\s(I)
_reflns_number_gt                 951
_refine_ls_R_factor_gt            0.0412
_refine_ls_wR_factor_gt           0.0369

_refine_ls_shift/su_max           0.000092

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
```

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_refine_ls_matrix_type          full
_refine_ls_hydrogen_treatment  mixed      # none, undef, noref, refall,
                                         # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme    calc
_refine_ls_weighting_details
;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
A~i~ are:
0.137 -0.792E-01 -0.296E-01 -0.413E-01
;

_publ_section_references
;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

```

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

_atom_site_refinement_flags_posn

_atom_site_refinement_flags_adp

_atom_site_refinement_flags_occupancy

_atom_site_disorder_assembly


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_atom_site_disorder_group
_atom_site_attached_hydrogens
O1 O 0.2181(5) 0.2415(5) 0.01299(9) 0.0331 1.0000 Uani . . . . .
O2 O -0.0941(5) 0.1413(5) 0.06494(10) 0.0328 1.0000 Uani . . . . .
C1 C 0.0974(3) 0.2770(4) 0.05753(7) 0.0228 1.0000 Uani . . . . .
C2 C 0.1782(3) 0.4849(3) 0.10370(7) 0.0207 1.0000 Uani . . . . .
C3 C 0.3852(3) 0.6390(4) 0.09762(8) 0.0279 1.0000 Uani . . . . .
C4 C 0.4594(4) 0.8341(4) 0.14122(9) 0.0325 1.0000 Uani . . . . .
C5 C 0.3280(4) 0.8728(4) 0.19086(9) 0.0312 1.0000 Uani . . . . .
C6 C 0.1220(4) 0.7175(4) 0.19708(8) 0.0311 1.0000 Uani . . . . .
C7 C 0.0466(3) 0.5240(4) 0.15331(7) 0.0256 1.0000 Uani . . . . .
H3 H 0.4834(9) 0.6083(11) 0.0588(2) 0.0543 1.0000 Uani . . . . .
H4 H 0.6198(10) 0.9568(12) 0.1366(3) 0.0588 1.0000 Uani . . . . .
H5 H 0.3876(10) 1.0245(11) 0.2259(2) 0.0559 1.0000 Uani . . . . .
H6 H 0.0204(11) 0.7512(12) 0.2360(2) 0.0610 1.0000 Uani . . . . .
H7 H -0.1157(9) 0.4032(11) 0.1571(2) 0.0525 1.0000 Uani . . . . .
H1 H 0.1374(13) -0.0070(17) -0.0350(3) 0.0392(12) 0.589(10) Uiso . . P . . .
H2 H 0.1706(19) 0.105(2) -0.0152(5) 0.0392(12) 0.411(10) Uiso . . P . . .
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_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0402(11) 0.0359(11) 0.0267(8) -0.0056(9) 0.0169(8) -0.0088(11)
O2 0.0365(11) 0.0341(11) 0.0303(9) -0.0023(9) 0.0132(8) -0.0098(10)
C1 0.0254(8) 0.0248(8) 0.0191(6) -0.0002(6) 0.0064(5) -0.0020(7)
C2 0.0254(7) 0.0190(7) 0.0185(6) 0.0000(5) 0.0057(5) -0.0002(6)
C3 0.0260(8) 0.0287(9) 0.0307(7) -0.0027(7) 0.0101(6) -0.0053(8)
```

C4 0.0291(9) 0.0315(9) 0.0369(9) -0.0068(8) 0.0054(7) -0.0059(8)
C5 0.0347(9) 0.0285(9) 0.0296(8) -0.0068(7) 0.0012(7) -0.0009(8)
C6 0.0402(10) 0.0293(9) 0.0251(7) -0.0053(7) 0.0090(7) -0.0030(8)
C7 0.0297(9) 0.0272(9) 0.0220(7) -0.0018(6) 0.0107(6) -0.0034(7)
H3 0.052(2) 0.065(3) 0.052(2) -0.014(2) 0.029(2) -0.020(2)
H4 0.052(3) 0.059(3) 0.068(3) -0.017(3) 0.018(2) -0.026(2)
H5 0.065(3) 0.052(3) 0.051(2) -0.027(2) 0.007(2) -0.012(2)
H6 0.079(3) 0.062(3) 0.048(2) -0.023(2) 0.031(2) -0.014(3)
H7 0.054(3) 0.057(3) 0.053(2) -0.010(2) 0.031(2) -0.019(2)

_refine_ls_extinction_coef 2.1(2)

_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1266(5)

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O2 . H1 2_555 0.952(9) no

O2 . C1 . 1.280(3) yes

C1 . C2 . 1.484(2) yes

C2 . C3 . 1.395(2) yes

C2 . C7 . 1.397(2) yes

C3 . C4 . 1.394(3) yes

C3 . H3 . 1.076(4) no

C4 . C5 . 1.397(3) yes

C4 . H4 . 1.091(5) no
C5 . C6 . 1.395(3) yes
C5 . H5 . 1.102(5) no
C6 . C7 . 1.392(3) yes
C6 . H6 . 1.093(4) no
C7 . H7 . 1.090(5) no
H1 . H2 . 0.721(11) no

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C1 . O1 . H2 . 119.0(6) no
H1 2_555 O2 . C1 . 115.2(5) no
O2 . C1 . O1 . 123.0(2) yes
O2 . C1 . C2 . 117.73(16) yes
O1 . C1 . C2 . 119.29(17) yes
C1 . C2 . C3 . 119.99(14) yes
C1 . C2 . C7 . 119.60(15) yes
C3 . C2 . C7 . 120.40(15) yes
C2 . C3 . C4 . 119.54(16) yes
C2 . C3 . H3 . 119.6(3) no
C4 . C3 . H3 . 120.9(3) no
C3 . C4 . C5 . 120.03(18) yes
C3 . C4 . H4 . 120.1(3) no
C5 . C4 . H4 . 119.9(3) no
C4 . C5 . C6 . 120.35(17) yes

C4 . C5 . H5 . 120.3(3) no
C6 . C5 . H5 . 119.3(3) no
C5 . C6 . C7 . 119.67(16) yes
C5 . C6 . H6 . 119.5(3) no
C7 . C6 . H6 . 120.9(3) no
C2 . C7 . C6 . 120.01(16) yes
C2 . C7 . H7 . 119.4(3) no
C6 . C7 . H7 . 120.5(3) no
O2 2_555 H1 . H2 . 173.6(13) no
H1 . H2 . O1 . 175.8(15) no

200 K

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_audit_creation_method CRYSTALS_ver_12.84

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_chemical_melting_point ?

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_cell_length_b 5.1000(10)
_cell_length_c 22.0200(10)
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_cell_angle_beta 97.900(10)
_cell_angle_gamma 90
_cell_volume 611.80(17)

_symmetry_cell_setting 'Monoclinic'

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    '-x,y+1/2,-z+1/2'
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D      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  6.6710 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
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 0.0000 0.0000 5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

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Given Formula = C1.75 H1.75 O0.50
 # Dc = 0.33 F000 = 148.00 Mu = 0.24 M = 30.78
 # Found Formula = C7 H6 O2
 # Dc = 1.33 F000 = 148.00 Mu = 0.98 M = 122.12

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 _chemical_formula_weight 122.12

_cell_measurement_reflns_used 0
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 _cell_measurement_theta_max 0
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 _exptl_crystal_size_mid '3mm'
 _exptl_crystal_size_max '10mm'

_exptl_crystal_density_diffn 1.326
 _exptl_crystal_density_meas
 # Non-dispersive F(000):

```
_exptl_crystal_F_000          148.000
_exptl_absorpt_coefficient_mu  0.098

# Sheldrick geometric approximat 1.00 1.00
_exptl_absorpt_correction_type none
_exptl_absorpt_correction_T_min 1.0000
_exptl_absorpt_correction_T_max 1.0000
_diffn_measurement_device_type  'Unknown'
_diffn_radiation_monochromator  'copper 220'
_diffn_radiation_type          ' neutrons '
_diffn_radiation_wavelength    0.83200
_diffn_measurement_method      \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection      'USER DEFINED DATA COLLECTION'
_computing_cell_refinement      'USER DEFINED CELL REFINEMENT'
_computing_data_reduction       'USER DEFINED DATA REDUCTION'
_computing_structure_solution   'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement 'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material 'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics   'CAMERON (Watkin et al., 1996)'

_diffn_standards_interval_time  0
_diffn_standards_interval_count 0
_diffn_standards_number         0
_diffn_standards_decay_%        0

_diffn_ambient_temperature      200
_diffn_reflns_number            3502
_reflns_number_total             2714
```

```
_diffn_reflsv_R_equivalents 0.103
# Number of reflections with Friedels Law is 2714
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2723

_diffn_reflsv_theta_min 2.186
_diffn_reflsv_theta_max 42.362
_diffn_measured_fraction_theta_max 0.996

_diffn_reflsv_theta_full 42.362
_diffn_measured_fraction_theta_full 0.996

_diffn_reflsv_limit_h_min -8
_diffn_reflsv_limit_h_max 1
_diffn_reflsv_limit_k_min 0
_diffn_reflsv_limit_k_max 8
_diffn_reflsv_limit_l_min -35
_diffn_reflsv_limit_l_max 35
_reflsv_limit_h_min -8
_reflsv_limit_h_max 8
_reflsv_limit_k_min 0
_reflsv_limit_k_max 8
_reflsv_limit_l_min 0
_reflsv_limit_l_max 35

_oxford_diffn_Wilson_B_factor 0.00
_oxford_diffn_Wilson_scale 0.00

_atom_sites_solution_primary direct #heavy,direct,difmap,geom
```



```
# _atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min -0.56
_refine_diff_density_max 0.64

_refine_ls_number_reflns 1031
_refine_ls_number_restraints 1
_refine_ls_number_parameters 137

#_refine_ls_R_factor_ref 0.0690
_refine_ls_wR_factor_ref 0.0445
_refine_ls_goodness_of_fit_ref 1.0326

#_reflns_number_all 2714
_refine_ls_R_factor_all 0.2039
_refine_ls_wR_factor_all 0.0569

# The I/u(I) cutoff below was used for refinement as
# well as the  $\gt$  R-factors:
_reflns_threshold_expression I>3.0\s(I)
_reflns_number_gt 1031
_refine_ls_R_factor_gt 0.0690
_refine_ls_wR_factor_gt 0.0445
_refine_ls_shift/su_max 0.004277

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
```

```

_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     mixed      # none, undef, noref, refall,
                                           # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details

;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2~
A~i~ are:
0.856 0.243 0.981 0.157 0.401
;

_publ_section_references

;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.

```

Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_U_iso_or_equiv

_atom_site_occupancy

_atom_site_adp_type

```
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_atom_site_attached_hydrogens
O1 O 0.2188(5) 0.2399(6) 0.01310(11) 0.0402 1.0000 Uani . . . . .
O2 O -0.0924(5) 0.1405(6) 0.06506(12) 0.0385 1.0000 Uani . . . . .
C1 C 0.0976(4) 0.2750(4) 0.05758(8) 0.0273 1.0000 Uani . . . . .
C2 C 0.1784(4) 0.4819(4) 0.10360(8) 0.0257 1.0000 Uani . . . . .
C3 C 0.3857(4) 0.6357(5) 0.09770(10) 0.0343 1.0000 Uani . . . . .
C4 C 0.4588(4) 0.8294(5) 0.14095(11) 0.0390 1.0000 Uani . . . . .
C5 C 0.3291(4) 0.8677(5) 0.19114(10) 0.0388 1.0000 Uani . . . . .
C6 C 0.1231(4) 0.7140(5) 0.19683(10) 0.0396 1.0000 Uani . . . . .
C7 C 0.0476(4) 0.5210(5) 0.15340(8) 0.0319 1.0000 Uani . . . . .
H3 H 0.4843(10) 0.6050(13) 0.0585(3) 0.0628 1.0000 Uani . . . . .
H4 H 0.6201(11) 0.9518(14) 0.1364(3) 0.0692 1.0000 Uani . . . . .
H5 H 0.3906(12) 1.0209(13) 0.2248(3) 0.0659 1.0000 Uani . . . . .
H6 H 0.0186(13) 0.7455(15) 0.2353(3) 0.0721 1.0000 Uani . . . . .
H7 H -0.1158(11) 0.4016(11) 0.1569(3) 0.0560 1.0000 Uani . . . . .
H1 H 0.1398(15) -0.007(2) -0.0344(4) 0.0451(14) 0.583(12) Uiso . . P . . .
H2 H 0.175(2) 0.099(3) -0.0150(6) 0.0451(14) 0.417(12) Uiso . . P . . .
loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0463(13) 0.0452(15) 0.0327(11) -0.0093(12) 0.0178(10) -0.0117(13)
```

O2 0.0396(13) 0.0417(15) 0.0363(11) -0.0051(11) 0.0121(10) -0.0107(12)
C1 0.0326(9) 0.0259(10) 0.0240(8) 0.0003(7) 0.0061(7) -0.0035(8)
C2 0.0289(8) 0.0249(11) 0.0235(8) 0.0026(7) 0.0045(6) 0.0003(8)
C3 0.0308(9) 0.0362(12) 0.0377(10) -0.0057(9) 0.0114(8) -0.0067(9)
C4 0.0328(10) 0.0389(13) 0.0455(11) -0.0075(10) 0.0063(8) -0.0065(9)
C5 0.0447(12) 0.0357(13) 0.0343(10) -0.0089(9) -0.0008(8) -0.0016(10)
C6 0.0471(12) 0.0428(14) 0.0299(9) -0.0069(9) 0.0090(8) -0.0026(11)
C7 0.0380(10) 0.0323(12) 0.0272(9) -0.0015(8) 0.0105(8) -0.0038(9)
H3 0.060(3) 0.069(4) 0.066(3) -0.023(3) 0.035(3) -0.020(3)
H4 0.055(3) 0.067(4) 0.087(4) -0.017(3) 0.018(3) -0.027(3)
H5 0.079(4) 0.059(4) 0.057(3) -0.024(3) 0.002(3) -0.016(3)
H6 0.088(4) 0.080(4) 0.056(3) -0.027(3) 0.038(3) -0.013(4)
H7 0.065(3) 0.051(3) 0.057(3) -0.006(2) 0.028(2) -0.021(3)

_refine_ls_extinction_coef 2.6(9)

_refine_ls_extinction_method

'Larson (1970), Equation 22'

_oxford_refine_ls_scale 0.1547(8)

loop_

_geom_bond_atom_site_label_1

_geom_bond_site_symmetry_1

_geom_bond_atom_site_label_2

_geom_bond_site_symmetry_2

_geom_bond_distance

_geom_bond_publ_flag

O1 . C1 . 1.271(3) yes

O1 . H2 . 0.955(18) no

O2 . H1 2_555 0.969(13) no

O2 . C1 . 1.279(3) yes

C1 . C2 . 1.488(3) yes

C2 . C3 . 1.405(3) yes

C2 . C7 . 1.406(2) yes
C3 . C4 . 1.393(3) yes
C3 . H3 . 1.091(5) no
C4 . C5 . 1.409(3) yes
C4 . H4 . 1.100(6) no
C5 . C6 . 1.398(4) yes
C5 . H5 . 1.098(6) no
C6 . C7 . 1.395(3) yes
C6 . H6 . 1.099(5) no
C7 . H7 . 1.097(5) no
H1 . H2 . 0.702(13) no
loop_
 _geom_angle_atom_site_label_1
 _geom_angle_site_symmetry_1
 _geom_angle_atom_site_label_2
 _geom_angle_site_symmetry_2
 _geom_angle_atom_site_label_3
 _geom_angle_site_symmetry_3
 _geom_angle
 _geom_angle_publ_flag
C1 . O1 . H2 . 119.4(7) no
H1 2_555 O2 . C1 . 115.7(5) no
O2 . C1 . O1 . 123.2(2) yes
O2 . C1 . C2 . 117.71(19) yes
O1 . C1 . C2 . 119.1(2) yes
C1 . C2 . C3 . 120.21(17) yes
C1 . C2 . C7 . 119.68(17) yes
C3 . C2 . C7 . 120.11(18) yes
C2 . C3 . C4 . 119.66(19) yes
C2 . C3 . H3 . 119.4(3) no
C4 . C3 . H3 . 120.9(4) no

C3 . C4 . C5 . 120.3(2)	yes
C3 . C4 . H4 . 120.1(4)	no
C5 . C4 . H4 . 119.6(4)	no
C4 . C5 . C6 . 119.8(2)	yes
C4 . C5 . H5 . 119.1(4)	no
C6 . C5 . H5 . 121.1(4)	no
C5 . C6 . C7 . 120.18(19)	yes
C5 . C6 . H6 . 120.2(4)	no
C7 . C6 . H6 . 119.6(4)	no
C2 . C7 . C6 . 119.94(19)	yes
C2 . C7 . H7 . 119.2(3)	no
C6 . C7 . H7 . 120.9(3)	no
O2 2_555 H1 . H2 . 173.5(16)	no
H1 . H2 . O1 . 177.0(18)	no

250 K

data_CRYSTALS_cif

_audit_creation_date 10-07-01

_audit_creation_method CRYSTALS_ver_12.84

_oxford_structure_analysis_title 'benzoic acid 250K'

_chemical_name_systematic ?

_chemical_melting_point ?

_cell_length_a 5.5000(10)

_cell_length_b 5.1000(10)

_cell_length_c 22.0200(10)

_cell_angle_alpha 90

_cell_angle_beta 97.900(10)

```

_cell_angle_gamma          90
_cell_volume               611.80(17)

_symmetry_cell_setting     'Monoclinic'
_symmetry_space_group_name_H-M 'P 1 21/c 1 '
_symmetry_space_group_name_Hall '?'

loop_
  _symmetry_equiv_pos_as_xyz
    'x,y,z'
    '-x,-y,-z'
    '-x,y+1/2,-z+1/2'
    'x,-y+1/2,z+1/2'

loop_
  _atom_type_symbol
  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
  _atom_type_scatter_Cromer_Mann_a1
  _atom_type_scatter_Cromer_Mann_b1
  _atom_type_scatter_Cromer_Mann_a2
  _atom_type_scatter_Cromer_Mann_b2
  _atom_type_scatter_Cromer_Mann_a3
  _atom_type_scatter_Cromer_Mann_b3
  _atom_type_scatter_Cromer_Mann_a4
  _atom_type_scatter_Cromer_Mann_b4
  _atom_type_scatter_Cromer_Mann_c
  _atom_type_scatter_source
D      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  6.6710 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

```



```

H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
N      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000  9.3600 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

```

```
_cell_formula_units_Z      4
```

```
# Given Formula = C1.75 H1.75 O0.50
```

```
# Dc =      0.33 F000 =      148.00 Mu =      0.24 M =      30.78
```

```
# Found Formula = C7 H6.00 O2
```

```
# Dc =      1.33 F000 =      148.00 Mu =      0.98 M =      122.12
```

```
_chemical_formula_sum      'C7 H6.00 O2'
```

```
_chemical_formula_moiety  'C7 H6.00 O2'
```

```
_chemical_compound_source  'commercial'
```

```
_chemical_formula_weight   122.12
```

```
_cell_measurement_reflns_used      0
```

```
_cell_measurement_theta_min      0
```

```
_cell_measurement_theta_max      0
```

```
_cell_measurement_temperature    250
```

```
_exptl_crystal_description  'needle'
```

```
_exptl_crystal_colour       'white'
```

```
_exptl_crystal_size_min      '3mm'
```

```
_exptl_crystal_size_mid      '3mm'
```

```
_exptl_crystal_size_max      '10mm'
```

```
_exptl_crystal_density_diffn      1.326
_exptl_crystal_density_meas
# Non-dispersive F(000):
_exptl_crystal_F_000              148
_exptl_absorpt_coefficient_mu     0.098

# Sheldrick geometric approximat 1.00 1.00
_exptl_absorpt_correction_type    none
_exptl_absorpt_correction_T_min   1.0000
_exptl_absorpt_correction_T_max   1.0000
_diffn_measurement_device_type     'Unknown'
_diffn_radiation_monochromator     'copper 220'
_diffn_radiation_type              ' neutrons '
_diffn_radiation_wavelength        0.83200
_diffn_measurement_method          \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection         'USER DEFINED DATA COLLECTION'
_computing_cell_refinement         'USER DEFINED CELL REFINEMENT'
_computing_data_reduction          'USER DEFINED DATA REDUCTION'
_computing_structure_solution      'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement    'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material    'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics      'CAMERON (Watkin et al., 1996)'

_diffn_standards_interval_time     0
_diffn_standards_interval_count    0
_diffn_standards_number            0
_diffn_standards_decay_%           0
```

```
_diffrn_ambient_temperature      250
_diffrn_reflns_number            3828
_reflns_number_total             2748
_diffrn_reflns_av_R_equivalents  0.066
# Number of reflections with Friedels Law is 2748
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2783

_diffrn_reflns_theta_min         2.186
_diffrn_reflns_theta_max         42.745
_diffrn_measured_fraction_theta_max 0.989

_diffrn_reflns_theta_full        41.890
_diffrn_measured_fraction_theta_full 1.000

_diffrn_reflns_limit_h_min       -8
_diffrn_reflns_limit_h_max        8
_diffrn_reflns_limit_k_min       -1
_diffrn_reflns_limit_k_max        8
_diffrn_reflns_limit_l_min        0
_diffrn_reflns_limit_l_max       35
_reflns_limit_h_min              -8
_reflns_limit_h_max               8
_reflns_limit_k_min               0
_reflns_limit_k_max               8
_reflns_limit_l_min               0
_reflns_limit_l_max              35
```

```
_oxford_diffn_Wilson_B_factor      0.00
_oxford_diffn_Wilson_scale         0.00

_atom_sites_solution_primary        direct #heavy,direct,difmap,geom
# _atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens      geom

_refine_diff_density_min            -0.56
_refine_diff_density_max            0.64

_refine_ls_number_reflns            755
_refine_ls_number_restraints        1
_refine_ls_number_parameters        137

#_refine_ls_R_factor_ref 0.0488
_refine_ls_wR_factor_ref            0.0320
_refine_ls_goodness_of_fit_ref      1.1133

#_reflns_number_all 2748
_refine_ls_R_factor_all              0.2340
_refine_ls_wR_factor_all            0.0694

# The I/u(I) cutoff below was used for refinement as
# well as the _gt R-factors:
_reflns_threshold_expression        I>3.0\s(I)
_reflns_number_gt                   755
_refine_ls_R_factor_gt              0.0488
_refine_ls_wR_factor_gt             0.0320

_refine_ls_shift/su_max             0.000756
```

```

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment    mixed      # none, undef, noref, reffall,
                                           # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme      calc
_refine_ls_weighting_details

;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~]*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
A~i~ are:
0.462 0.303 0.496 0.178 0.207
;

_publ_section_references
;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

```

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

...refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_atom_site_attached_hydrogens
O1 O 0.2199(6) 0.2381(7) 0.01337(12) 0.0548 1.0000 Uani
O2 O -0.0909(5) 0.1398(7) 0.06535(13) 0.0517 1.0000 Uani
C1 C 0.0982(4) 0.2734(5) 0.05740(9) 0.0395 1.0000 Uani
C2 C 0.1799(4) 0.4786(5) 0.10343(9) 0.0374 1.0000 Uani
C3 C 0.3851(4) 0.6322(5) 0.09745(10) 0.0479 1.0000 Uani
C4 C 0.4590(5) 0.8225(6) 0.14088(12) 0.0548 1.0000 Uani
C5 C 0.3311(5) 0.8600(6) 0.19052(11) 0.0517 1.0000 Uani
C6 C 0.1260(5) 0.7078(6) 0.19667(10) 0.0548 1.0000 Uani
C7 C 0.0503(4) 0.5172(5) 0.15338(9) 0.0441 1.0000 Uani
H3 H 0.4852(11) 0.5993(14) 0.0584(3) 0.0816 1.0000 Uani
H4 H 0.6200(12) 0.9458(15) 0.1355(3) 0.0912 1.0000 Uani
H5 H 0.3908(12) 1.0099(14) 0.2251(3) 0.0817 1.0000 Uani
H6 H 0.0200(14) 0.7416(15) 0.2346(3) 0.0900 1.0000 Uani
H7 H -0.1114(11) 0.3946(13) 0.1572(3) 0.0737 1.0000 Uani
H1 H 0.1419(18) -0.003(3) -0.0340(6) 0.0595(19) 0.570(17) Uiso . . P
H2 H 0.172(2) 0.103(4) -0.0151(8) 0.0595(19) 0.430(17) Uiso . . P
loop_
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_atom_site_aniso_U_22
_atom_site_aniso_U_33

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_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
O1 0.0618(16) 0.064(2) 0.0430(12) -0.0121(16) 0.0218(11) -0.0163(16)
O2 0.0529(15) 0.058(2) 0.0461(13) -0.0090(15) 0.0136(11) -0.0152(15)
C1 0.0415(10) 0.0451(15) 0.0321(9) 0.0009(10) 0.0049(8) -0.0038(10)
C2 0.0376(10) 0.0404(15) 0.0343(10) 0.0031(10) 0.0052(8) 0.0015(10)
C3 0.0432(11) 0.0509(17) 0.0510(12) -0.0082(12) 0.0117(10) -0.0112(12)
C4 0.0442(12) 0.0558(18) 0.0636(14) -0.0074(13) 0.0051(10) -0.0131(12)
C5 0.0565(14) 0.0479(17) 0.0473(12) -0.0076(12) -0.0043(10) 0.0001(13)
C6 0.0638(15) 0.0589(18) 0.0436(12) -0.0153(13) 0.0138(10) -0.0056(14)
C7 0.0503(13) 0.0468(16) 0.0375(12) -0.0054(11) 0.0143(9) -0.0070(12)
H3 0.072(3) 0.097(5) 0.085(3) -0.024(3) 0.041(3) -0.029(3)
H4 0.067(3) 0.098(6) 0.112(5) -0.020(4) 0.024(3) -0.037(4)
H5 0.093(4) 0.072(4) 0.076(3) -0.036(3) -0.002(3) -0.013(3)
H6 0.120(5) 0.093(5) 0.066(3) -0.025(4) 0.045(3) -0.014(4)
H7 0.081(4) 0.079(4) 0.067(3) -0.016(3) 0.032(3) -0.030(3)

_refine_ls_extinction_coef 1.8(6)
_refine_ls_extinction_method
  'Larson (1970), Equation 22'
_oxford_refine_ls_scale 0.1399(7)
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  _geom_bond_atom_site_label_2
  _geom_bond_site_symmetry_2
  _geom_bond_distance
  _geom_bond_publ_flag
O1 . C1 . 1.264(3)    yes
O1 . H2 . 0.94(3)    no
```


O2 . H1 2_555 0.99(2) no
O2 . C1 . 1.276(4) yes
C1 . C2 . 1.483(3) yes
C2 . C3 . 1.395(3) yes
C2 . C7 . 1.404(3) yes
C3 . C4 . 1.384(4) yes
C3 . H3 . 1.096(6) no
C4 . C5 . 1.392(4) yes
C4 . H4 . 1.105(7) no
C5 . C6 . 1.391(4) yes
C5 . H5 . 1.096(7) no
C6 . C7 . 1.385(4) yes
C6 . H6 . 1.096(6) no
C7 . H7 . 1.100(6) no
H1 . H2 . 0.690(17) no
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_geom_angle_site_symmetry_2
_geom_angle_atom_site_label_3
_geom_angle_site_symmetry_3
_geom_angle
_geom_angle_publ_flag
C1 . O1 . H2 . 118.8(8) no
H1 2_555 O2 . C1 . 115.9(6) no
O2 . C1 . O1 . 123.8(3) yes
O2 . C1 . C2 . 117.3(2) yes
O1 . C1 . C2 . 118.8(2) yes
C1 . C2 . C3 . 120.31(18) yes
C1 . C2 . C7 . 119.7(2) yes

C3 . C2 . C7 . 120.0(2)	yes
C2 . C3 . C4 . 119.6(2)	yes
C2 . C3 . H3 . 119.3(4)	no
C4 . C3 . H3 . 121.2(4)	no
C3 . C4 . C5 . 120.4(2)	yes
C3 . C4 . H4 . 119.3(4)	no
C5 . C4 . H4 . 120.3(4)	no
C4 . C5 . C6 . 120.3(2)	yes
C4 . C5 . H5 . 120.3(4)	no
C6 . C5 . H5 . 119.4(4)	no
C5 . C6 . C7 . 119.7(2)	yes
C5 . C6 . H6 . 120.7(4)	no
C7 . C6 . H6 . 119.6(4)	no
C2 . C7 . C6 . 120.1(2)	yes
C2 . C7 . H7 . 118.9(3)	no
C6 . C7 . H7 . 121.0(3)	no
O2 2_555 H1 . H2 . 172.9(19)	no
H1 . H2 . O1 . 175(2)	no

293 K

data_CRYSTALS_cif

_audit_creation_date 10-07-01

_audit_creation_method CRYSTALS_ver_12.84

_oxford_structure_analysis_title 'benzoic acid 293K'

_chemical_name_systematic ?

_chemical_melting_point ?

_cell_length_a 5.5000(10)

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_cell_length_c          22.0200(10)
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_cell_angle_beta        97.900(10)
_cell_angle_gamma       90
_cell_volume            611.80(17)

_symmetry_cell_setting  'Monoclinic'
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_symmetry_space_group_name_Hall  '??'

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    '-x,-y,-z'
    '-x,y+1/2,-z+1/2'
    'x,-y+1/2,z+1/2'

loop_
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  _atom_type_scatter_dispersion_real
  _atom_type_scatter_dispersion_imag
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  _atom_type_scatter_Cromer_Mann_b1
  _atom_type_scatter_Cromer_Mann_a2
  _atom_type_scatter_Cromer_Mann_b2
  _atom_type_scatter_Cromer_Mann_a3
  _atom_type_scatter_Cromer_Mann_b3
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  _atom_type_scatter_source
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0.0000  0.0000  6.6710 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
C      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000  6.6460 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
H      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000 -3.7390 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
N      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000  9.3600 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
O      0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
0.0000  0.0000  5.8030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'

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_cell_formula_units_Z      4

# Given Formula = C1.75 H1.75 O0.50
# Dc =      0.33 F000 =      368.00 Mu =      0.24 M =      30.78
# Found Formula = C7 H1 D5 O2
# Dc =      1.27 F000 =      368.00 Mu =      0.96 M =      117.08

_chemical_formula_sum      'C7 H1 D5 O2'
_chemical_formula_moiety    'C7 H1 D5 O2'
_chemical_compound_source    'commercial'
_chemical_formula_weight     117.08
# Structure does not match formula

_cell_measurement_reflns_used      0
_cell_measurement_theta_min        0
_cell_measurement_theta_max        0
_cell_measurement_temperature      293

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_exptl_crystal_description      'needle'
_exptl_crystal_colour          'white'
_exptl_crystal_size_min        '3mm'
_exptl_crystal_size_mid        '3mm'
_exptl_crystal_size_max        '10mm'

_exptl_crystal_density_diffn   1.271
_exptl_crystal_density_meas

# Non-dispersive F(000):
_exptl_crystal_F_000           368.000
_exptl_absorpt_coefficient_mu   0.096

# Sheldrick geometric approximat 1.00 1.00
_exptl_absorpt_correction_type  none
_exptl_absorpt_correction_T_min 1.0000
_exptl_absorpt_correction_T_max 1.0000
_diffn_measurement_device_type  'Unknown'
_diffn_radiation_monochromator  'copper 220'
_diffn_radiation_type           ' neutrons '
_diffn_radiation_wavelength     0.83200
_diffn_measurement_method       \w

# If a reference occurs more than once, delete the author
# and date from subsequent references.
_computing_data_collection      'USER DEFINED DATA COLLECTION'
_computing_cell_refinement      'USER DEFINED CELL REFINEMENT'
_computing_data_reduction       'USER DEFINED DATA REDUCTION'
_computing_structure_solution   'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement 'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material 'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics   'CAMERON (Watkin et al., 1996)'
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_diffn_standards_decay_% 0

_diffn_ambient_temperature 293
_diffn_reflns_number 3401
_reflns_number_total 2630
_diffn_reflns_av_R_equivalents 0.078
# Number of reflections with Friedels Law is 2630
# Number of reflections without Friedels Law is 0
# Theoretical number of reflections is about 2760

_diffn_reflns_theta_min 2.186
_diffn_reflns_theta_max 42.601
_diffn_measured_fraction_theta_max 0.953

_diffn_reflns_theta_full 39.619
_diffn_measured_fraction_theta_full 0.997

_diffn_reflns_limit_h_min 0
_diffn_reflns_limit_h_max 8
_diffn_reflns_limit_k_min -8
_diffn_reflns_limit_k_max 1
_diffn_reflns_limit_l_min -33
_diffn_reflns_limit_l_max 33
_reflns_limit_h_min -8
_reflns_limit_h_max 8
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_reflns_limit_k_max          8
_reflns_limit_l_min          0
_reflns_limit_l_max          33

_oxford_diffn_Wilson_B_factor 0.00
_oxford_diffn_Wilson_scale    0.00

_atom_sites_solution_primary  direct #heavy,direct,difmap,geom
# _atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom

_refine_diff_density_min      -0.53
_refine_diff_density_max      0.62

_refine_ls_number_reflns      511
_refine_ls_number_restraints  0
_refine_ls_number_parameters  146

#_refine_ls_R_factor_ref      0.0505
_refine_ls_wR_factor_ref      0.0297
_refine_ls_goodness_of_fit_ref 1.1013

#_reflns_number_all           2630
_refine_ls_R_factor_all        0.2884
_refine_ls_wR_factor_all        0.0538

# The I/u(I) cutoff below was used for refinement as
# well as the > R-factors:
_reflns_threshold_expression    I>3.0\s(I)
```

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_reflns_number_gt          511
_refine_ls_R_factor_gt     0.0505
_refine_ls_wR_factor_gt    0.0297

_refine_ls_shift/su_max    0.000432

# choose from: rm (reference molecule of known chirality),
# ad (anomalous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'

_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     mixed      # none, undef, noref, refall,
                                           # refxyz, refU, constr or mixed

_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details

;
Method, part 1, Chebychev polynomial, (Watkin, 1994, Prince, 1982)
[weight] = 1.0/[A~0~*T~0~(x)+A~1~*T~1~(x) ... +A~n-1~*T~n-1~(x)]
where A~i~ are the Chebychev coefficients listed below and x= Fcalc/Fmax
Method = Robust Weighting (Prince, 1982)
W = [weight] * [1-(deltaF/6*sigmaF)^2]^2^
A~i~ are:
0.580 -0.218 0.648 -0.581E-01 0.260
;

_publ_section_references

```


;

Betteridge, P.W., Carruthers, J.R., Cooper, R.I.,
Prout, K. & Watkin, D.J. (2003). J. Appl. Cryst. 36, 1487.

Larson, A.C. (1970) Crystallographic Computing, Ed Ahmed, F.R.,
Munksgaard, Copenhagen, 291-294.

Prince, E.
Mathematical Techniques in Crystallography
and Materials Science
Springer-Verlag, New York, 1982.

Watkin D.J. (1994).
Acta Cryst, A50, 411-437.

Watkin, D.J., Prout, C.K. & Pearce, L.J. (1996). CAMERON, Chemical
Crystallography Laboratory, Oxford, UK.

;

Uequiv = arithmetic mean of U_i i.e. $U_{equiv} = (U_1+U_2+U_3)/3$

Replace last . with number of unfound hydrogen atoms attached to an atom.

..._refinement_flags...

. no refinement constraints S special position constraint on site

G rigid group refinement of site R riding atom

D distance or angle restraint on site T thermal displacement constraints

U Uiso or U_{ij} restraint (rigid bond) P partial occupancy constraint

loop_
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_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_atom_site_attached_hydrogens

O1	O	0.2208(10)	0.2394(12)	0.0131(2)	0.0641	1.0000	Uani
O2	O	-0.0899(9)	0.1408(11)	0.0652(2)	0.0578	1.0000	Uani
C1	C	0.0996(7)	0.2702(7)	0.05720(14)	0.0441	1.0000	Uani
C2	C	0.1815(6)	0.4756(7)	0.10399(15)	0.0419	1.0000	Uani
C3	C	0.3850(8)	0.6260(8)	0.0969(2)	0.0566	1.0000	Uani
C4	C	0.4603(8)	0.8164(8)	0.14052(19)	0.0614	1.0000	Uani
C5	C	0.3315(8)	0.8541(8)	0.19027(19)	0.0635	1.0000	Uani
C6	C	0.1284(8)	0.7025(8)	0.19658(18)	0.0623	1.0000	Uani
C7	C	0.0522(7)	0.5158(7)	0.15353(15)	0.0495	1.0000	Uani
D3	D	0.4827(10)	0.5965(12)	0.0580(3)	0.0910	1.0000	Uani
D4	D	0.6161(11)	0.9351(13)	0.1357(4)	0.1103	1.0000	Uani
D5	D	0.3900(12)	1.0007(13)	0.2236(3)	0.0946	1.0000	Uani
D6	D	0.0269(13)	0.7328(13)	0.2349(2)	0.1050	1.0000	Uani
D7	D	-0.1061(10)	0.3937(11)	0.1575(2)	0.0837	1.0000	Uani
H10	H	0.137(5)	-0.004(4)	-0.0368(11)	0.0628	0.5039	Uani
H11	H	0.173(4)	0.094(5)	-0.0165(10)	0.0650	0.4962	Uani

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  _atom_site_aniso_U_22
  _atom_site_aniso_U_33
  _atom_site_aniso_U_23
  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
O1 0.080(3) 0.058(3) 0.059(3) -0.015(3) 0.029(3) -0.021(3)
O2 0.063(3) 0.059(3) 0.055(3) -0.013(2) 0.020(2) -0.024(3)
C1 0.052(2) 0.0402(19) 0.0412(17) -0.0017(15) 0.0094(17) -0.0039(16)
C2 0.0455(19) 0.0368(18) 0.0437(18) 0.0054(15) 0.0067(16) -0.0016(16)
C3 0.053(2) 0.054(2) 0.066(2) -0.004(2) 0.017(2) -0.0108(19)
C4 0.062(3) 0.048(3) 0.073(3) -0.014(2) 0.006(2) -0.014(2)
C5 0.073(3) 0.053(3) 0.060(2) -0.020(2) -0.008(2) -0.003(2)
C6 0.083(3) 0.056(3) 0.0504(19) -0.0162(19) 0.018(2) -0.004(2)
C7 0.061(2) 0.044(2) 0.046(2) -0.0096(18) 0.0172(18) -0.0090(19)
D3 0.083(4) 0.094(4) 0.105(4) -0.032(3) 0.043(3) -0.031(3)
D4 0.087(4) 0.099(4) 0.147(6) -0.041(4) 0.027(4) -0.044(4)
D5 0.109(4) 0.072(3) 0.099(4) -0.033(3) 0.000(4) -0.007(3)
D6 0.145(5) 0.098(5) 0.082(3) -0.035(3) 0.049(3) -0.022(4)
D7 0.092(4) 0.086(3) 0.081(3) -0.019(3) 0.042(3) -0.030(3)
H10 0.071(13) 0.045(12) 0.076(16) -0.009(9) 0.024(12) -0.010(9)
H11 0.071(13) 0.073(17) 0.053(11) -0.015(9) 0.018(9) -0.012(12)
_refine_ls_extinction_coef 2.6(5)
_refine_ls_extinction_method
  'Larson (1970), Equation 22'
_oxford_refine_ls_scale 0.1412(9)
loop_
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_geom_bond_site_symmetry_2
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_geom_bond_publ_flag
O1 . C1 . 1.260(5) yes
O1 . H11 . 1.00(3) no
O2 . H10 2_555 0.95(3) no
O2 . C1 . 1.266(6) yes
C1 . C2 . 1.495(5) yes
C2 . C3 . 1.383(5) yes
C2 . C7 . 1.397(4) yes
C3 . C4 . 1.388(6) yes
C3 . D3 . 1.083(6) yes
C4 . C5 . 1.397(6) yes
C4 . D4 . 1.066(7) yes
C5 . C6 . 1.381(6) yes
C5 . D5 . 1.066(6) yes
C6 . C7 . 1.368(5) yes
C6 . D6 . 1.085(6) yes
C7 . D7 . 1.083(5) yes
H10 . H11 . 0.68(2) no
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_geom_angle_site_symmetry_3
_geom_angle
_geom_angle_publ_flag

C1 . 01 . H11 . 118.4(14) no
H10 2_555 02 . C1 . 116.5(13) no
02 . C1 . 01 . 125.1(5) yes
02 . C1 . C2 . 116.4(4) yes
01 . C1 . C2 . 118.5(4) yes
C1 . C2 . C3 . 118.9(3) yes
C1 . C2 . C7 . 120.2(3) yes
C3 . C2 . C7 . 120.9(3) yes
C2 . C3 . C4 . 118.6(4) yes
C2 . C3 . D3 . 120.6(5) yes
C4 . C3 . D3 . 120.7(5) yes
C3 . C4 . C5 . 120.2(4) yes
C3 . C4 . D4 . 119.7(5) yes
C5 . C4 . D4 . 120.1(5) yes
C4 . C5 . C6 . 120.4(4) yes
C4 . C5 . D5 . 119.9(6) yes
C6 . C5 . D5 . 119.7(6) yes
C5 . C6 . C7 . 119.7(4) yes
C5 . C6 . D6 . 120.5(5) yes
C7 . C6 . D6 . 119.8(6) yes
C2 . C7 . C6 . 120.2(4) yes
C2 . C7 . D7 . 118.6(4) yes
C6 . C7 . D7 . 121.2(4) yes
02 2_555 H10 . H11 . 179(5) no
H10 . H11 . 01 . 178(5) no
