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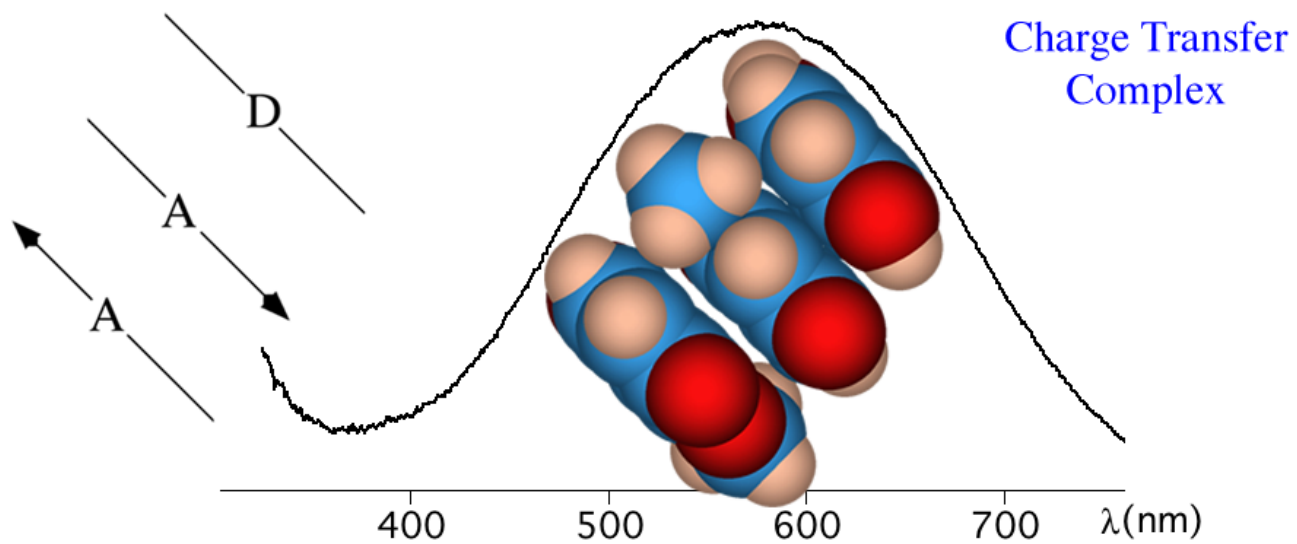
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Graphical abstract

A 2:1 2-methoxybenzoquinone–hydroquinone complex, obtained as single crystals by a solvent-free reaction, combines dipolar and π – π interactions, as well as hydrogen bonding.

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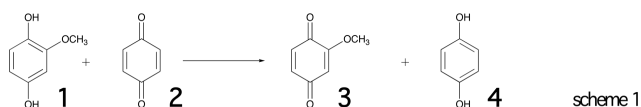
A Quinhydrone-Type 2:1 Acceptor-Donor Charge Transfer Complex Obtained Via a Solvent-free Reaction

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15 A 2:1 2-methoxybenzoquinone (BQ_{OMe}) - hydroquinone (H₂Q) complex (5) obtained as single crystals by a solvent-free reaction combines dipolar and π - π interactions, as well as H-bonding.

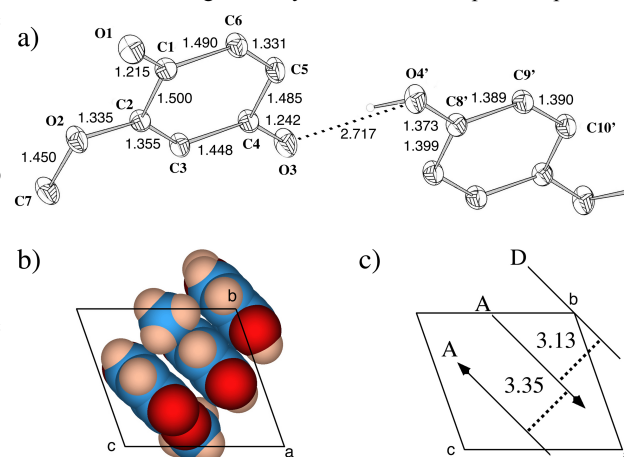
Non-covalent interactions, namely hydrogen bonding, halogen bonding, π - π and dipole-dipole interactions stabilize numerous organic, organometallic and biological molecular networks.¹⁻⁶ Considering the example of quinhydrone, a well-known charge transfer complex between benzoquinone (BQ) and H₂Q, π - π interactions exist inside the donor-acceptor stacks, while infinite molecular chains form through hydrogen bonds between neighboring stacks.^{7,8} Elsewhere, charge transfer complexes of the quinhydrone-type were involved in recognition processes⁹ and recently used to self-organize calixarenes.¹⁰ In unsymmetrically substituted quinhydrones, interconversion by hydrogen transfer was shown to occur between the two components of the complex in the solid state,¹¹⁻¹³ but only one crystal structure was reported.¹² Concerning the association of BQ_{OMe} and H₂Q, a charge transfer band has been observed but without any information about the stoichiometry of the interaction.¹⁴



In this paper, we describe a new synthetic route to obtain single crystals of quinhydrones through a solvent-free reaction. The starting materials, 2-methoxyhydroquinone H₂Q_{OMe} (1) and BQ (2), undergo a redox reaction to lead to BQ_{OMe} (3) and H₂Q (4) (scheme 1) that evolve to give 5[‡] as black needles (space group: P-1).[‡] The asymmetric unit is composed of one molecule of 3 and half a molecule of 4 (Fig. 1). Hydroquinone lies on an inversion center. So, compound 5 has to be considered as a 2:1 acceptor/donor (AAD) complex. Molecules arrange in columns with repeated AAD sequences, parallel to the $(c-b)$ vector, and make an angle of 30° with this axis. The distance between the molecular planes of A and D components in a column varies between 3.09 and 3.17 Å (mean value: 3.13 Å), which indicates a strong π - π interaction (Fig. 1). This A-D π stacking distance is comparable to that observed in the unsubstituted quinhydrone (3.2 Å).⁸ We note however that A and D are tilted by 2°. Further, the distance between two neighboring moieties A (3.35 Å) is typical of a π - π interaction, comparable to the intermolecular distance observed in pure 3.¹⁵ The AA pairs in which each molecule corresponds to its twin by an inversion center are

† Electronic Supplementary Information (ESI) available: 1. Crystallographic data for compound 5 are available free of charge from the Cambridge Data Center via Internet at http://www.ccdc.cam.ac.uk/data_request/cif (CCDC 294809). 2. Optical absorption spectra of a thin film of 1 in PMMA exposed to 2, as a function of time (2a) and difference from the starting film showing the charge transfer band (2b). See <http://dx.doi.org/10.1039/b000000x/>

stabilized by a dipole-dipole interaction. The dipole moment of 3 has been calculated to be 0.81 Debye (MNDO).¹⁵ Hydrogen bonds exist between H₂Q and BQ_{OMe} molecules belonging to adjacent columns, defining planes parallel to the plane (011); $dO3-O4' = 2.717(2)$ Å, angle $O3-H1'-O4' = 164^\circ$ (Fig. 1). These hydrogen bonds involve the carbonyl group in meta position with respect to the methoxy group. Interatomic distances of subunits 3 in 5 are slightly different from those measured in single crystals of free 3 (space group P2₁/c).¹⁵ Due to the existence of H bonding involving O3, the difference between the two carbonyl distances (C4-O3 - C1-O1) suffers a slight increase from 0.005(5) to 0.027(5) Å, while the C-OH distance is not significantly shortened as compared to pure 4.



80 **Fig.1** X-ray crystal structure of 5: a) ORTEP (30% probability level) representation of the asymmetric unit including atomic numbering and bond lengths in Å, the prime (') symbol indicates that these atoms are at equivalent position (1-x, 2-y, -z), b) view of a triad AAD (100% van der Waals radii) and c) a schematic view of the structure with interplanar distances in Å (projection on the plane (011), segments indicate the main axis of molecules, and arrows the direction of the dipolar moment of A).

For subunit 4, we compared data measured in 5 with the mean value obtained from the three independent molecules constituting the asymmetric unit in 4, obtained as single crystals by sublimation under vacuum (α -form).[†] The C-C distances measured in 5 are 0.007(4) Å longer than those measured in free 4 (mean values on all the C-C bonds). In spite of the marginal significance of this value, one can note that the difference is 0.014 Å when going from 4 to the BQ/H₂Q quinhydrone, both determined at RT.^{8,16}

The ¹H NMR spectrum of an equimolar mixture of 1 and 2 in CD₃CN indicates that the reaction depicted in scheme 1 is quantitative after few minutes. The spectrum of crystals of 5 dissolved in CD₃CN confirms that 3 and 4 are in a ratio 2 to 1. Peaks attribution of 3 was achieved from the different coupling constants and homogeneous decoupling experiments. In contrast with previously published works, the signal at 6.71 is not a singlet,^{17,18} but remains as two

doublets (Fig. 2). The methoxy group does not appear as a singlet but as one doublet. Irradiation at 3.8 ppm induces a modification of the peak at 6.0 ppm, which then appears as a doublet of doublet, without modification of the other signals. Reverseably, irradiation at 6.0 ppm transforms the signal at 3.8 ppm into a singlet. So, a coupling phenomenon exists between protons of methoxy group and H5. That could be also observed in pure CDCl₃ and when solution was diluted ten times in CD₃CN. No variation of chemical shift was observed between pure **3**[¶] and mixtures of **3** and **4** in CD₃CN, indicating no intermolecular interaction between acceptor and donor components in that solvent.

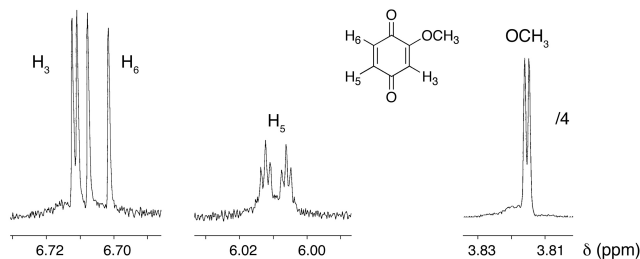


Fig.2 ¹H NMR spectra of **3** in CD₃CN.

In acetonitrile, reaction occurs rapidly between **1** and **2** at room temperature, but absorption spectra of equimolar mixtures of **1** and **2** correspond to the superimposition of individual spectra of **3** and **4** (Fig. 3) indicating that products **3** and **4** do not interact.

The absorption spectrum of **5** obtained in the solid state from a KBr pellet shows a strong and broad absorption band centered at 575 nm (Fig. 3). Films are violet in color. Solid mixtures of **1** and **2** and of **3** and **4** show the same spectra as **5**, indicating that the redox reaction occurs rapidly, in the minute range, at room temperature.

We also prepared films from acetonitrile solutions of **1** and poly(methyl metacrylate) (PMMA), which after exposure to **2** at RT exhibit the same charge transfer band. We are now applying the same synthetic route to other more elaborated molecules.

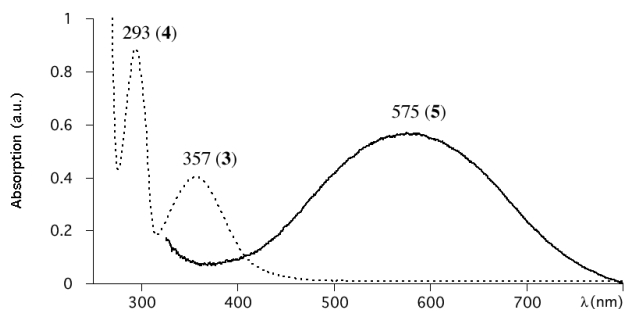


Fig. 3 Absorption spectrum of an equimolar mixture of **1** and **2** in acetonitrile (dotted line), and in the solid state (KBr pellet) (solid line).

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Notes

‡*Synthesis of compound 5*: A Schlenk tube containing a mixture of **1** (50 mg, 0.35 mmol) and **2** (50 mg, 0.46 mmol) was purged under argon, then

evacuated under primary vacuum and closed. The Schlenk is heated in a home-made vertical oven from room temperature to 100 °C, at an heating rate of 0.1 ° min⁻¹, then maintained at 100 °C for 13 h. Black needles, 2 cm long, were formed 2 cm above the oven. **5**: M.P.: 136 °C (dec.) IR (KBr): 1677, 1640 (s) (C=O) cm⁻¹, UV-Visible: λ_{max} (KBr) 575 nm, ¹H NMR of dissolved crystals (300 MHz, CD₃CN): δ = 3.81 [d, J_{OCH₃-5} = 0.4 Hz, 3H, OCH₃]; 6.01 [ddq, J₅₋₆ = 1.9 Hz, J₅₋₃ = 0.4 Hz, J_{5-OCH₃} = 0.4 Hz, 2H, H₅]; 6.46 [s broad, 2H, OH], 6.70 [s, 4H, ArH], 6.705 [d, J₅₋₆ = 1.9 Hz, 2H, H₆], 6.71 [d, J₃₋₅ = 0.4 Hz, 2H, H₃], ¹³C NMR (75.47 MHz, CD₃CN) 57.2 (OCH₃), 108.7 (C3), 116.9 (CH, H₂Q), 135.7 and 138.0 (C5, C6), 151.1 (COH, H₂Q), 160.1 (C2), 183.0 and 189.0 (C1 and C4). Anal. Calcd for C₂₀H₁₈O₈: C, 62.18%; H, 4.70%. Found: C, 61.54%; H, 4.92%.

¶ Compound **3** was synthesized from **1** (130 mg, 0.93 mmol) and **2** (100 mg, 0.92 mmol) in CH₃CN and purified on silicagel (eluent: CH₂Cl₂). Yield = 70%. **3**: M.P.: 136 °C (dec.), lit. 134¹⁵ IR (KBr): 1679 (s), 1647 (s) (C=O) cm⁻¹, UV-Visible: λ_{max} (CH₃CN) 252 nm (log ε = 4.0), 357 nm (log ε = 3.2), ¹H NMR (300 MHz, CD₃CN): δ = 3.81 [d, J_{OCH₃-5} = 0.4 Hz, 3H, OCH₃]; 6.01 [ddq, J₅₋₆ = 1.9 Hz, J₅₋₃ = 0.4 Hz, J_{5-OCH₃} = 0.4 Hz, 1H, H₅]; 6.705 [d, J₅₋₆ = 1.9 Hz, 1H, H₆], 6.71 [d, J₃₋₅ = 0.4 Hz, 1H, H₃].

§ *Crystal data for 5*: C₂₀H₁₈O₈, Fw = 386.36, triclinic, P-1, a = 6.6793 (14), b = 8.117 (2), c = 9.238 (2) Å, α = 69.157 (14), β = 69.931 (19), γ = 81.34 (2)°, V = 439.42 (19) Å³, Z = 1, D_c = 1.46 g cm⁻³, were measured on a KAPPACCD-Enraf Nonius diffractometer. λ (MoKα) = 0.71073 Å, μ (MoKα) = 1.14 cm⁻¹, 8218 reflections (T = 200 K, 2<θ<32 °), nb of independent data collected: 2825, nb of independent data used for refinement: 1387 ((Fo)² > 1.5σ(Fo)², merging R = 0.034, R = Σ|Fo| - |Fc| / Σ|Fo|, Fo = 0.0578, Rw* = [Σw(|Fo| - |Fc|)² / ΣwFo²]^{1/2} = 0.0597, -0.297 < Δρ < 0.424.

¶ *Crystal data for 4*: R-3, at 200 K a = b = 38.567, c = 5.6650 Å (α-form, lit.¹⁶ at 300 K, a = b = 38.46, c = 5.650 Å), α = β = 90 and γ = 120 °, and Z = 18.

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