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Chiral recognition in a single molecule: A study of homo and heterochiral butan-2,3-ol by Fourier transform microwave spectroscopy

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4 **Chiral recognition in a single molecule: A study of homo and heterochiral**
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6 **butan-2,3-diol by Fourier transform microwave spectroscopy.**
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58 **Running title:** microwave spectroscopy of butandiol
59
60

Abstract

The microwave Fourier transform spectrum of butan-2,3-ol has been recorded in the range 5-18 GHz. The molecule possesses two chiral centres and exists in two distinct forms, one of which is homochiral ((*R, R*) or (*S, S*)) and is overall chiral, and the other which is heterochiral ((*R, S*) or (*S, R*)) and is overall meso. Detailed ab initio calculations enabled investigation of the relative stability of the many conformations exhibited by each form of the molecule. It is shown that the lowest energy forms in each case possess an internal hydrogen bond. The spectrum of the heterochiral (meso) form could be readily identified and analysed. The homochiral form, however, exhibits a tunnelling motion of about 1 GHz, in which the hydrogen bonded OH groups interchange their roles. Deuteration of one of these OH protons quenches the tunnelling motion, aiding the assignment of the spectrum. In all cases, deuteration of the hydroxyl groups was used to locate the positions of the OH hydrogen atoms and helped to confirm the identification of the conformers present.

1. Introduction

Butan-2,3-diol, is a fascinating molecule. It possesses two chiral centres and hence, exists as two pairs of enantiomers. These enantiomeric pairs differ only in their chirality, but should have very different properties. The lowest conformers in energy exhibit an intramolecular hydrogen bond, which should pronounce the chiral recognition effect in the molecule. Most interesting of all, however, the chiral recognition will affect the dynamic properties, as well as the rigid structure, because of the symmetries of the different isomers.

A considerable volume of work has been carried out on butan-2,3-diol. The conformations of chiral (*R, R* and *S, S*) and meso-butan-2,3-diol (*R, S*) in CCl_4 were compared by Kuhn [1, 2] via infrared spectroscopy. He concluded that the ratio of hydrogen bonded and non-hydrogen bonded OH was larger for the chiral species. This has been explained in terms of the steric interaction of the methyl groups. The chiral species can form an intramolecular hydrogen bond when the two methyl groups are trans to one another, but the hydroxyl groups in the meso species may only interact in this way when the methyl groups are forced into a gauche conformation (see figure 1). Kuhn also deduced that a stronger hydrogen bond was present in the chiral molecule by comparing the splittings between the free and bonded OH peaks.

Beyond the desire to study hydrogen bonding and chiral recognition, the stereochemistry of many molecules have been related to (*2R, 3R*)-butan-2,3-diol and its derivatives [3-6]. The conformational properties of this isomer are also of interest as it has been used as a model for investigations of the methyl ester of (*R, R*)-tartaric acid monoamide [7]. An investigation by Wang *et al.* [8] utilized infrared spectroscopy and *ab initio* molecular orbital calculations to probe the conformational properties of this isomer in the solution phase. These authors found that the gauche hydrogen bonded conformation of the chiral molecule was more stable than the trans conformer, in disagreement with the work of Kuhn [1, 2].

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There has been recent interest in the conformations of other glycol molecules. The microwave spectra of asymmetrically deuterated forms of ethylene glycol were first assigned by Caminati *et al.* in 1981 [9, 10], but attempts to assign the spectrum of the parent isotopomer concluded that the molecule exhibits a large amplitude motion, which produces a tunnelling splitting in the spectrum and complicates the analysis [11, 12]. Recently, however, Christen *et al.* have recorded microwave spectra of two conformers of ethylene glycol [13-16]. They found that the tunnelling splittings in the observed conformers were approximately 7 GHz and 1.4 GHz. Microwave spectra of two conformers of propan-1,2-diol were also studied by Caminati [17]. The spectra of these species were re-examined recently, and a third conformer was assigned, which was found to be the global minimum for the molecule [18].

This paper presents the first assignment of the microwave spectra of the ground state conformers of chiral and *meso* butan-2,3-diol. This work has been augmented with an *ab initio* study, which has been used to provide geometrical predictions and to help decide which spectra arise from which conformers.

2. The structure of butan-2,3-diol

The butan-2,3-diol molecule has conformational flexibility about three bonds; different conformers may be generated by rotations about the central, C₂-C₃, bond or either of the two C-O bonds, so the molecule possesses $3^3=27$ conformers. In addition, the presence of two chiral centres gives rise to four forms of the molecule, namely the (*R*, *R*), (*S*, *S*), (*R*, *S*) and (*S*, *R*) configurations. Microwave spectroscopy will distinguish only the homo and heterochiral forms of the molecule, so the *ab initio* study reviewed below considers 27x2 species. Initial geometry optimizations were performed on these systems with the Gaussian 98 package [19] at the HF/6-311G level. The geometries of the conformers lying lowest in energy were then re-optimized at the MP2/6-311++G** level.

2.1 The heterochiral species

The 27 conformers of (*R*, *S*) and (*S*, *R*)-butan-2,3-diol have been classified with a nomenclature of the form *XYZ*. The nomenclature used for both the hetero and homochiral species is illustrated in figure 2.

“*X*” represents the geometry of the carbon chain, and is assigned as follows; if the two methyl groups are trans to one another $X=T$. If the two methyl groups are gauche to one another $X=G_r$ or G_l . These two gauche orientations of the carbon chain are mirror images of one another. If the methyl and hydroxyl groups trans to one another are in the vertical plane, the methyl group points downwards and the molecule is viewed from the end nearest this methyl group, the classification is G_r if the methyl group and hydroxyl group gauche to one another are on the right hand side. If this positioning of the trans methyl and hydroxyl groups leaves the remaining methyl and hydroxyl groups on the left, the classification is G_l .

“*Y*” denotes the position of the hydroxyl group, which is trans to the methyl group on the other chiral carbon atom. If the carbon chain is in the *T* position the two hydroxyl groups are equivalent and the labels “*Y*” and “*Z*” are interchangeable. The classification then considers the position of the O-H bond relative to the groups attached to the chiral carbon to which the hydroxyl group is bonded. $X=M$ if the O-H bond is trans to the methyl group, *C* if the O-H bond is trans to the carbon chain or *H* if it is trans to the hydrogen atom.

“*Z*” is classified in the same way as “*Y*”, but denotes the position of the remaining hydroxyl group, which is gauche to the methyl group on the other chiral carbon atom.

Of these twenty-seven conformers nineteen were minima on the HF/6-311G potential surface (see table 1). These nineteen minima comprised all nine conformations where the methyl groups were trans to one another and five of each of the two gauche conformations. The minima were grouped in eight pairs of mirror images; the five G_rYZ minima being mirror

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3 images of the five G_1ZY minima and the trans conformers also forming mirror pairs
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5 (THC \equiv TCH), (TMC \equiv TCM) and (TMH \equiv THM). Only the TCC, TMM and THH conformers
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7
8 are unique.
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10 As one would expect, the four mirror pairs of conformers that display an
11
12 intramolecular hydrogen bond tend to be the lowest in energy. These species, and the TCC
13
14 conformer, were chosen for re-optimization at the MP2/6-311++G** level, which yielded the
15
16 rotational constants, relative energies and dipole moments displayed in table 2. The only large
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18 change during the re-optimization was the drop in energy of the GMM conformer. This was
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20 due to a large change in the angular orientation of the hydroxyl groups, resulting presumably
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22 from the inclusion of polarization functions in the basis set.
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29 2.2 The homochiral species

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31 The 27 conformers of (*R, R*) and (*S, S*)-butan-2,3-diol have been classified in a similar
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33 manner to that described above, for the heterochiral molecule. As for the heterochiral species,
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35 the nomenclature is of the form XYZ .
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38 “*X*” represents the geometry of the carbon chain. If the two methyl groups are trans to
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40 one another $X=T$. If the two methyl groups are gauche to one another $X=Gg$ or Gt . These two
41
42 gauche conformations of the carbon chain are non-equivalent and differ in that both methyl
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44 groups are either trans (Gt) or gauche (Gg) to both hydroxyl groups.
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48 Since the two hydroxyl groups are both either gauche or trans to the two methyl
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50 groups, for a specific orientation about the central C-C bond, they are equivalent. Hence, there
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52 is no way to distinguish between them, and “*Y*” and “*Z*” are interchangeable. As for the
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54 heterochiral molecule, Y or $Z=M$ if the O-H bond is trans to the methyl group, C if the O-H
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56 bond is trans to the carbon chain or H if it is trans to the hydrogen atom.
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Twenty-three of the twenty-seven starting structures are minima on the HF/6-311G potential surface (see table 3). The equivalence of the two hydroxyl groups means that nine of the twenty seven starting conformers are unique, and that there are nine identical pairs. For instance, for the Gg carbon chain rotamers, the GgMM, GgHH and GgCC conformers are unique and the (GgMC≡GgCM), (GgMH≡GgHM) and (GgHC≡GgCH) are the identical pairs. Of the twenty-three minima from the *ab initio* calculations, there are 7 unique conformers and 8 identical pairs. As in the heterochiral molecule, all conformers of the carbon chain orientation in which hydrogen bonding cannot occur (Gg), were minima. Of the T-type carbon chain conformers there were three pairs and two unique structures. Two of these pairs, the THC and THM rotamers, exhibit an intramolecular hydrogen bond. The remaining two minima and two pairs were Gt-type rotamers. Both pairs of Gt-type minima possess a hydrogen bond, and it was these conformers that were found to be the lowest in energy of all. The results of MP2 calculations are given in table 4. This is in agreement with the *ab initio* study of Wang *et al.* [8], but contradicts the arguments given in references 1 and 2.

It is interesting to consider the calculated energy differences between the hetero and homochiral forms of butan-2,3-diol. The GtCM homochiral conformer has an energy about 60 cm⁻¹ lower than the G_lCM and G_rMC heterochiral conformers. It seems likely that this energy difference arises for steric reasons; the projections of the conformers in figures 3 and 4 show that the sum of the angles between the bulky groups about the central C-C bond is only 180° in the four lowest heterochiral conformers, but is 270° in the two lowest homochiral conformers. The projections also show that the hydrogen bond in the GtCM conformer may be shortened by an increase in the separation of the two methyl groups, but in the G_lCM and G_rMC conformers the methyl group separation must decrease to shorten the hydrogen bond. Thus we might expect to find a stronger hydrogen bond in the homochiral species.

3. Experimental details

Microwave transitions of butan-2,3-diol were recorded with the Fourier transform spectrometer which has been described previously [20]. The sample was heated to about 70°C, in order to produce an appropriate concentration of butan-2,3-diol and the nozzle to about 75°C to prevent blocking. Helium at 1.5 bar was used as the backing gas for all spectroscopic investigations.

Samples of *meso* ((*R*, *S*), (*S*, *R*)) and racemic ((*R*, *R*), (*S*, *S*), (*R*, *S*), (*S*, *R*))-butan-2,3-diol were purchased from Sigma-Aldrich. A chiral sample of (*R*, *R*)-butan-2,3-diol was also acquired, from Acrōs Organics. The hydroxyl groups of the racemic sample were deuterated by distilling a mixture of 25ml of butan-2,3-diol and 10ml of D₂O. This procedure was only performed once, as the aim was to maximise the quantities of the mono-deutero-diols.

4.1 Experimental results I: Heterochiral butan-2,3-diol

The first spectra recorded were obtained by scanning over frequency ranges of about 200 MHz around the predicted $0_{00}-1_{11}$, $1_{01}-2_{12}$, $2_{02}-3_{13}$ and $2_{11}-3_{03}$ transitions of the G₁CM and G_rMC conformers of (*R*, *S*)-butan-2,3-diol. Several strong transitions were found in each frequency range but rotational constants derived from the set of four lines that gave the best fit to a rigid asymmetric top Hamiltonian enabled the $1_{01}-2_{02}$ and $3_{13}-3_{22}$ transitions to be accurately predicted. A further 46 lines were then recorded. All lines were fitted to a Watson A-type rotational Hamiltonian [21]. The fits are summarized in table 5.

The initial scans had been made with the racemic mixture of butan-2,3-diol so the assignment of the transitions to the heterochiral molecule was confirmed with the pure samples; it was found that the assigned transitions could be observed with the *meso* (*R*, *S* and *S*, *R*) sample but not with the chiral (*R*, *R*) sample.

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4 The next search focussed on the microwave spectra of the two mono-deutero-hydroxyl
5 forms of the G_lCM and G_rMC conformers. It was desirable to obtain information on
6 these species as it was hoped that a Kraitchman analysis [22] of the rotational constants would
7 confirm the assignment of the conformer to one of the *ab initio* predictions. It is likely
8 that the errors between the *ab initio* predictions and experimental rotational constants are
9 similar for the parent and deuterated isotopomers. Hence, assuming that the conformer already
10 observed was the G_lCM/ G_rMC species, it should be possible to improve the *ab initio*
11 predictions of the rotational constants of the mono-deutero-hydroxyl species by comparison
12 with the *ab initio* and experimental data on the parent isotopomer.
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25 This predictive technique appeared to work, and allowed microwave spectra of two
26 species with rotational constants similar to that of the parent isotopomer to be recorded. The
27 transitions of these species exhibited narrow quadrupole splittings, arising because of the
28 presence of the deuterium atom, which has a quadrupolar nucleus with a spin of 1. The
29 transitions of these species were fitted to a Hamiltonian identical to that used for the parent
30 isotopomer except that it included the diagonal quadrupole coupling parameters, χ_{aa} and χ_{bb} -
31 χ_{cc} . In total, 17 rotational transitions consisting of 47 hyperfine components were fitted for the
32 isotopomer which was believed to have the proton accepting hydroxyl group deuterated and 17
33 rotational transitions consisting of 56 hyperfine components for the for the isotopomer which
34 was believed to be deuterated at the proton donating hydroxyl group. The resulting spectral
35 parameters are given in table 5.
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53 4.2 Experimental results II: Homochiral butan-2,3-diol

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55 Initial searches for the spectra of the GtCM homochiral conformer did not lead to a
56 convincing assignment. This was believed to be due to a tunnelling motion of the hydroxyl
57 groups that could connect two equivalent minima of any of the four lowest energy conformers
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3 of homochiral butan-2,3-diol. Hence, scans were performed to locate the spectra of the two
4
5 mono-deutero-hydroxyl species, as the asymmetric deuteration should remove any effect of
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7 such tunnelling on the spectrum. It was hoped that the spectra of these deuterated species
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9 would yield accurate estimates of the rotational constants of the parent isotopomer.
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13 Searches around the *ab initio* predicted microwave transition frequencies for the
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15 deuterated isotopomers of the GtCM conformer yielded two sets of spectra. As for the
16
17 heterochiral species, narrow hyperfine splittings resulting from the quadrupole moment of the
18
19 deuterium nucleus were observable. Ten rotational transitions, divided into 26 hyperfine
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21 components, of each of these species were fitted to Watson A-type Hamiltonians. The spectral
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23 parameters are listed in table 6.
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29 30 **4.3 The tunnelling spectrum of homochiral butan-2,3-diol**

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32 As in the g'Ga conformer of ethylene glycol, the GtCM conformer of homochiral
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34 butan-2,3-diol was expected to undergo a tunnelling motion that reverses the direction of the
35
36 μ_a and μ_c components of the dipole moment. Thus, the a and c-type microwave transitions
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38 should connect the two tunnelling states of the GtCM conformer, and these transitions should
39
40 occur at frequencies approximately equal to a pure rotational transition difference plus or
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42 minus a tunnelling splitting. The b-type transitions link energy levels of the same tunnelling
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44 state and should be largely independent of the tunnelling splitting. The tunnelling motion is
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46 illustrated in figure 5.
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51 Coriolis forces complicate the spectrum by making the tunnelling splitting dependent
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53 on the rotational state of the molecule. If the spectrum of a molecule exhibiting a tunnelling
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55 motion through a potential barrier such as ethylene glycol or butan-2,3-diol is analysed with a
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57 rigid rotor approach then the rotational constants obtained will relate to the transition state, as
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59 this is the average structure. Hence, when the molecules are at their geometrical minima there
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are off-diagonal terms in the inertia tensors. In the rotational Hamiltonian, the rotational constants are the coefficients of the squares of the components of the total angular momentum. The off-diagonal inertial terms are the coefficients of the cross products of the angular momentum components.

Two methods that have been developed to account for these effects are the internal axis method (IAM) of Hougen [23, 24] and the reduced axis system (RAS) of Pickett [25]. The IAM approach removes the tunnelling-rotation mixing via a suitable choice of axes and thus considers the wavefunctions of the two vibrational species to be localized in their potential wells. The IAM Hamiltonian contains a constant term for the tunnelling between the wells and coupling terms to take account of the dependence of the tunnelling on the rotational state. The RAS technique solves the problem including the tunnelling-rotation mixing via a stepwise diagonalization of the Hamiltonian matrix. Thus, the RAS technique considers the symmetric and antisymmetric tunnelling states and the terms involving the cross products of the angular momentum components. The RAS Hamiltonian is of the form:

$$\hat{\mathbf{H}}_{vv} = E_v + AJ_a^2 + BJ_b^2 + CJ_c^2 \quad [1]$$

$$\hat{\mathbf{H}}_{vv'} = (F_{bc}(J_b J_c + J_c J_b)) + (F_{ab}(J_a J_b + J_b J_a)) + (F_{ac}(J_a J_c + J_c J_a)) \quad [2]$$

where E_v is the energy of the vibrational state, $\hat{\mathbf{H}}_{vv}$ connects levels of the same vibrational state and $\hat{\mathbf{H}}_{vv'}$ connects levels of different vibrational states. Pickett has determined the required symmetric top matrix elements for equations 1 and 2, which are given in reference 25.

Christen *et al.* have employed both the IAM and RAS methods for their work on ethylene glycol [13 - 16]. The main advantages of the RAS method are that it can provide information on the tunnelling splitting even if no transitions across the tunnelling splitting have been recorded and that it can be applied without knowledge of the tunnelling path, whereas the IAM method must be set up differently for each tunnelling path considered. For

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3 these reasons the analysis of homochiral butan-2,3-diol presented in this chapter has utilized
4
5 the RAS method, implemented with the SPFIT computer program of Pickett [26].
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8 A useful diagnostic, which aids the assignment of microwave spectra, occurs when it is
9
10 possible to observe “cycles” of transitions, which link two rotational energy levels by more
11
12 than one path. If the assignment of the transitions is correct, the sum of the transition
13
14 frequencies in each path should be equal to within the experimental error.
15
16

17 The predicted rotational constants provided by work on the mono-deutero-hydroxyl
18
19 species indicated that two cycles of b-type transitions lay within the range of the spectrometer.
20
21 Scans over frequency ranges centred on the predictions of these transitions yielded four cycles
22
23 in total. These sixteen transitions were then fitted to an RAS Hamiltonian
24
25 that included a set of rotational constants for each of the two tunnelling states, a tunnelling
26
27 frequency and the Coriolis coupling constants F_{ab} and F_{bc} .
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31 Only two combinations of trial fits were then needed to deduce which two cycles of
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33 lines belonged to the lower, and which to the upper, tunnelling state. The cycles are illustrated
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35 in figure 6. A reasonable starting value of the tunnelling splitting (Δ_{tun}) was deduced by fitting
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37 the sixteen transitions with values of Δ_{tun} between 0 and 7 GHz in 0.5 GHz steps. It was found
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39 that starting values of 1.0 and 1.5 GHz both yielded a fit with a root mean square error of 9.6
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41 kHz and $\Delta_{tun}=1024.39$ (65) MHz. The small error of this fit appeared to confirm that the two
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43 pairs of cycles had been correctly matched.
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48 Using the parameters from this fit it proved possible to record transitions across the
49
50 tunnelling; 20 a-type and 12 c-type transitions were found. A further 48 b-type
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52 lines were also observed and included in the final fit.
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55 The five A-reduced quartic centrifugal distortion terms were also derived from this fit
56
57 but, the differences between the centrifugal distortion constants of the two tunnelling states
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3 were too small to be determined from the observed transitions. The constants derived from the
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5 fit of the four b-type cycles and the final fit are displayed in table 7.
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10 6. Discussion

11 6.1 Mass substitution analysis

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13 The position of a specific atom within a molecule may be deduced if the rotational
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15 constants, which arise when different isotopes are present at this position, are known. This is
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17 achieved via Kraitchman's substitution method [22]. This technique will be utilized below in
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19 an attempt to confirm which of the *ab initio* structures most closely resembles the species
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21 that have been observed in the supersonic molecular beam. The difference in the moment of
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23 inertia between two isotopomers may be written [27]:
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$$28 \Delta I_i = \left(\frac{m\Delta m}{m + \Delta m} \right) r_i^2 \quad [3]$$

29
30 where ΔI_i is the difference in the *a*, *b* or *c* moment of inertia of the two species, *m* is the mass
31
32 of the parent species (approximately 90 u in the case of butan-2,3-diol), Δm is the change of
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34 mass involved in the substitution (approximately 1 u for H substituted by D) and r_i is the
35
36 distance of the substituted atom from the principal axis to which ΔI_i relates.
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43 This analysis assumes that the observed structures are not affected by the mass
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45 dependence of the vibrations of the molecule and also that the inertial axes are not
46
47 significantly shifted by the change in mass. Co-ordinates relative to the three principal axes
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49 were thus deduced for the two hydrogen atoms in the observed homo and heterochiral
50
51 conformers of butan-2,3-diol, and are displayed in tables 8 and 9 alongside the equivalent *ab*
52
53 *initio* results for the conformers predicted to have the lowest energies.
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57 The experimental results for the two conformers match very well with the co-ordinates
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59 for the lowest energy homo and heterochiral conformers respectively. As can be seen from
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3 figures 3 and 4, the only significant difference between the GtCM and GtMH homochiral
4 conformers and the G_lCM / G_rMC and G_lMM / G_rMM heterochiral conformers is a rotation of
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6 the HOCC dihedral angle for the proton accepting OH group. The coordinates above reflect
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8 this; as expected, it is only the coordinates of the proton acceptor hydroxyl hydrogen that
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10 allow us to distinguish which conformer of each of these pairs has been observed.
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15 The predicted dipole moment components of the heterochiral conformers, displayed in
16 table 2, also support the conclusion that the G_lCM / G_rMC conformer is the one observed. In
17 both the G_lHC / G_rCH and the G_lMM / G_rMM conformers two of the dipole components are
18 small. There is no way to measure the dipoles quantitatively in the microwave experiment that
19 has been performed, but the fact the a, b and c-type transitions were all easily observable
20 suggests that none of the dipole components were near zero. In the homochiral conformer the
21 lowest energy *ab initio* structures all have similar dipoles and do not add further evidence to
22 support the Kraitchman analysis
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36 6.2 Deuterium quadrupole coupling constants

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38 The inertial axis quadrupole coupling constants obtained from the microwave spectra
39 provide information on the effect of the hydrogen bond on the hydroxyl groups in butan-2,3-
40 diol. These coupling constants are elements of the inertial axis quadrupole coupling tensor. If
41 this tensor is transformed to its principal axes the coupling constants of the four deuterium
42 atoms will be comparable. It seems reasonable to assume that the quadrupole tensor is
43 approximately symmetric about the O-D bond. If this is the case it will have a coupling
44 constant, χ , associated with the bond axis and two non-unique coupling constants, $-\chi/2$,
45 perpendicular to the bond. The value of χ can then be found by substituting the *ab initio*
46 predicted angle between the O-D bond and the a-principal inertial axis into the equation [28]
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$$\chi_{aa} = \chi \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad [4]$$

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3 where θ is the angle between the O-D bond and the a-inertial axis. The angles relating the four
4 O-D bonds to this inertial axis and the derived values of χ are displayed in table 10.
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6

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8 The lowest energy homo and heterochiral conformers of butan-2,3-diol are so similar
9 in structure that one would hope to obtain similar values of χ for the two deuterium
10 environments in both species. For the deuterium in the proton accepting hydroxyl group this
11 occurs and the two values of χ differ by only 3 kHz. In the donor deuterium environment this
12 is not the case. An anomalous value occurs for the GtCM donor environment because the
13 angle between the O-D bond and the a-inertial axis is close to 54.7° . At this angle the term
14 $(3\cos^2\theta_{az}-1)$ in equation is near to zero and hence the inertial axis quadrupole coupling terms,
15 deduced from the spectrum are poorly determined. The other three values of χ are similar to
16 that of the deuterium quadrupole coupling in the trans OD rotamer of isopropanol, reported by
17 Hirota and Kawashima [29], who found that χ is equal to 269.3 kHz.
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32 A comparison of the two proton environments in the hydrogen bond is limited to the
33 heterochiral conformer, because of the anomalous value of χ that occurs for the GtCM donor
34 environment. The values of the principal quadrupole coupling constant for the heterochiral
35 species suggest that the difference in χ produced by the two deuteron environments is close to
36 50 kHz.
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46 **6.3 The tunnelling path of the GtCM conformer**

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48 There are four possible combinations of 120° and 240° rotations of the hydroxyl groups
49 that will interconvert the two equivalent minima of the GtCM/GtMC conformer. These paths
50 are illustrated in figure 7. Intuitively the path that involves a 120° rotation of both hydroxyl
51 groups appears to be the most favourable as it requires both hydroxyl hydrogens to pass over
52 C-H bonds, rather than C-C bonds.
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This guess at the most likely tunnelling path is supported by the microwave work of Christen *et al.*, which has shown that the *g'*Ga conformer of ethylene glycol undergoes a concerted 120°, 120° tunnelling path, at a frequency of 7GHz [13]. The decrease in the tunnelling splitting between the two systems is assumed to indicate that the positions of the methyl groups in butan-2,3-diol must change slightly during the tunnelling process. This will increase the reduced mass involved in the tunnelling motion and decrease the tunnelling splitting.

7. Concluding remarks

The assignment of the two observed conformers of butan-2,3-diol to the conformational ground states of the homo and heterochiral species is supported by the Kraitchman analyses and the tunnelling properties of the homochiral species. These species have also accounted for all of the most intense observed transitions, as would be expected if they are indeed the most populated conformational states. The microwave spectrum of butan-2,3-diol is, however, very dense and many weaker lines, which could arise from excited conformational states, uncommon isotopomers, rare gas-butan-2,3-diol complexes, dimers and higher clusters, are still unassigned.

Acknowledgements

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Table 1: The energies of the conformers of (*R*, *S*)-butan-2,3-diol geometry optimized at the HF/6-311G level.

Conformer	E/ E_h	E_{rel}/ cm^{-1}	H bond
G ₁ CM≡G _r MC	-306.8810923	0	Yes
G ₁ CC≡G _r CC	Converted to G ₁ CM≡G _r MC		No
G ₁ HM≡G _r MH	Converted to G ₁ CM≡G _r MC		No
G ₁ HC≡G _r CH	-306.8797009	305	Yes
G ₁ MC≡G _r CM	Converted to G ₁ HC≡G _r CH		No
TCC	-306.8790738	443	No
G ₁ MM≡G _r MM	-306.8790667	445	Yes
G ₁ MH≡G _r HM	Converted to G ₁ HH≡G _r HH		No
G ₁ HH≡G _r HH	-306.8776857	748	Yes
THC≡TCH	-306.8773939	812	No
TMC≡TCM	-306.8773328	825	No
TMM	-306.8767426	955	No
THH	-306.8760264	1112	No
THM≡TMH	-306.8752805	1276	No
G ₁ CH≡G _r HC	-306.8701875	2393	No

Table 2: The properties of the lowest energy conformers of (*R*, *S*)-butan-2,3-diol optimized at MP2/6-311++G**.

Conformer	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	μ_a /D	μ_b /D	μ_c /D	<i>E</i> / <i>E</i> _h	<i>E</i> _{rel} / cm ⁻¹
G ₁ CM≡G _r MC	4665.9	2871.9	2350.2	1.7	1.9	1.0	-308.1263317	0
G ₁ HC≡G _r CH	4607.4	2843.9	2360.0	2.9	0.4	0.0	-308.1249394	306
G ₁ MM≡G _r MM	4669.1	2830.7	2344.8	0.2	0.5	2.5	-308.125464	190
G ₁ HH≡G _r HH	4557.6	2852.7	2331.7	1.9	2.2	0.9	-308.1241772	473
TCC	4572.7	3107.8	1999.6	0.0	0.0	0.0	-308.1232344	680

Table 3: The energies of the conformers of (*S, S*) and (*R, R*)-butan-2,3-diol geometry optimized at the HF/6-311G level.

Conformer	E/E_H	E_{rel}/cm^{-1}	H bond
GtCM	-306.8815422	0	Yes
GtHC	Converted to GtCM		No
THC	-306.8807831	167	Yes
GtMH	-306.8794134	467	Yes
THM	-306.8788301	595	Yes
GtCC	Converted to GtMM		No
GtMM	-306.8786928	625	No
GgCC	-306.877986	780	No
THH	-306.8778043	820	No
TCC	Converted to THH		No
GgMC	-306.876508	1105	No
GgHC	-306.8759726	1222	No
GgHM	-306.8753539	1358	No
GgMM	-306.8750526	1424	No
TMM	-306.737299	1715	No
GtHH	-306.736728	1727	No
GgHH	-306.733768	1792	No
TMC	-306.713747	2231	No

Table 4: The properties of the lowest energy conformers of (*S, S*) and (*R, R*)-butan-2,3-diol optimized at MP2 / 6-311++G**.

Conformer	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	μ_a /D	μ_b /D	μ_c /D	<i>E</i> / <i>E</i> _h	<i>E</i> _{rel} / cm ⁻¹
GtCM	4578.7	3090.9	1994.6	2.5	1.6	0.7	-308.126606	0
GtMH	4571.1	3061.2	1987.8	1.6	2.0	1.4	-308.1260706	117
THC	4773.1	2765.2	2414.4	1.9	1.4	1.3	-308.1255081	240
THM	4763.2	2739.6	2399.1	0.5	2.0	0.7	-308.1243612	492
GtMM	4612.6	3007.5	1985.0	0.0	0.7	0.0	-308.1241789	533

Table 5: Spectral parameters of the G_rCM/ G_rCM conformer of heterochiral butan-2,3-diol.

	Parent Isotopomer	Proton Donor Group Deuterated	Proton Acceptor Group Deuterated
A /MHz	4640.0465 (2)	4497.4826 (8)	4629.2594 (8)
B /MHz	2840.8899 (2)	2832.7649 (7)	2745.8061 (9)
C /MHz	2343.3848 (2)	2312.9114 (7)	2278.3988 (8)
Δ_J /kHz	0.932 (9)	0.993 (23)	0.850 (30)
Δ_{JK} /kHz	-1.165 (5)	-1.06 (9)	-0.94 (13)
Δ_K /kHz	1.616 (11)	0.63 (20)	1.47 (19)
δ_J /kHz	0.240 (6)	0.251 (13)	0.316 (22)
δ_K /kHz	3.481 (11)	3.10 (24)	2.95 (36)
χ_{aa} /kHz	-	117.1 (14)	219.5 (15)
$(\chi_{bb} - \chi_{cc})$ /kHz	-	100.4 (40)	43.5 (38)
N^a	52	56	47
σ_{rms} /kHz	1.7	4.3	3.1

^a The total number of lines included in the fit.

Table 6: Spectral parameters of the deuterohydroxyl isotopomers of the GtCM conformer of homochiral butan-2,3-diol.

	Proton Donor Group Deuterated	Proton Acceptor Group Deuterated
A /MHz	4437.9005 (9)	4505.6211 (13)
B /MHz	3061.3386 (10)	2987.7452 (7)
C /MHz	1956.2602 (4)	1940.6420 (7)
Δ_J /kHz	0.455 (20)	0.442 (28)
Δ_{JK} /kHz	-0.580	-0.56 (11)
Δ_K /kHz	1.41 (25)	1.3 (8)
δ_J /kHz	0.170 (17)	0.18 (2)
δ_K /kHz	0.361 ^a	0.361 ^a
χ_{aa} /kHz	16.9 (34)	166.9 (19)
$(\chi_{bb} - \chi_{cc})$ /kHz	275.8 (34)	-80.0 (52)
N	26	26
σ_{rms} /kHz	2.6	1.9

^a Constrained to the value for the parent isotopomer (table 4.7).

Table 7: Spectral parameters of the GtCM conformer of homochiral butan-2,3-diol.

	Full Fit	Fit of b-type cycles
A /MHz	4574.8694 (2)	4574.8330 (11)
B /MHz	3072.5964 (2)	3072.5832 (3)
C /MHz	1987.0638 (2)	1987.0550 (3)
ΔA /kHz	12.46 (8)	23.6 (9)
ΔB /kHz	14.62 (4)	26.1 (4)
ΔC /kHz	4.28 (6)	2.5 (3)
Δ_J /kHz	0.468 (6)	-
Δ_{JK} /kHz	-0.580 (8)	-
Δ_K /kHz	1.446 (7)	-
δ_J /kHz	0.1672 (14)	-
δ_K /kHz	0.361 (7)	-
Δ_{tun} /MHz	1011.9781 (6)	1024.4 (7)
F_{ab} /MHz	10.9472 (13)	11.444 (18)
F_{bc} /MHz	8.3800 (4)	8.356 (14)
N	96	16
σ_{rms} /kHz	0.67	9.6

Table 8: Principal axis coordinates of the hydroxyl hydrogen atoms in the conformers of heterochiral butan-2,3-diol from isotopic substitution and *ab initio* calculations.

	Donor OH hydrogen			Acceptor OH hydrogen		
	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$
Exp.	0 ^a	± 1.710	± 0.753	± 2.469	± 0.352	± 0.365
G _l CM \equiv G _r MC	-0.053	-1.659	0.817	2.469	-0.415	-0.243
G _l HC \equiv G _r CH	1.424	-1.310	0.232	-1.515	-1.606	0.87
G _l MM \equiv G _r MM	-0.019	-1.583	0.886	1.619	-1.206	-1.169
G _l HH \equiv G _r HH	1.352	-1.352	0.230	-0.998	-0.630	1.518

^a The square of this coordinate was determined to be small and negative, so it has been set to zero.

Table 9: Principal axis coordinates of the hydroxyl hydrogen atoms in the conformers of homochiral butan-2,3-diol from isotopic substitution and *ab initio* calculations.

	Donor OH hydrogen			Acceptor OH hydrogen		
	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$
Exp.	± 0.779	± 1.856	± 0.069	± 2.140	± 1.254	± 0.380
G _t CM	0.760	-1.857	-0.023	-2.121	-1.287	0.393
G _t MH	-0.720	-1.853	-0.032	1.678	-1.083	0.916
THC	0.595	-0.589	1.503	-1.631	1.395	0.923

Table 10: Calculated axial deuterium quadrupole coupling constants of the conformers of butan-2,3-diol.

	$G_{\text{ICM}} / G_{\text{rMC}}$		G_{tCM}	
	Donor	Acceptor	Donor	Acceptor
θ	35.8°	23.7°	49.2°	31.8°
χ/kHz	240	290	121	287

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Figure captions.

Figure 1. The hydrogen bonded conformations of meso and racemic butan-2,3-diol.

Figure 2. A nomenclature for the conformations of butan-2,3-diol.

Figure 3. The lowest energy structural minima of the heterochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

Figure 4. The three lowest energy structural minima of homochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

Figure 5. The tunnelling motion and approximate principal inertial axes of the GtCM conformer of butan-2,3-diol.

Figure 6. The b-type cycles of upper and lower tunnelling states of the GtCM conformer of butan-2,3-diol.

Figure 7. The four likely tunnelling paths of the GtCM conformer of butan-2,3-diol.

Figure 1. The hydrogen bonded conformations of meso and racemic butan-2,3-diol.

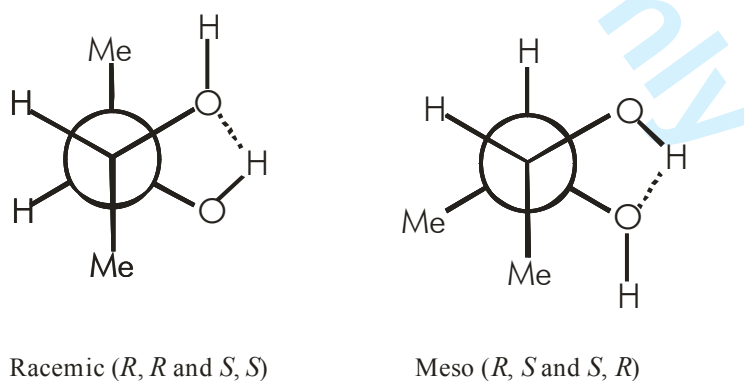


Figure 2. A nomenclature for the conformations of butan-2,3-diol.

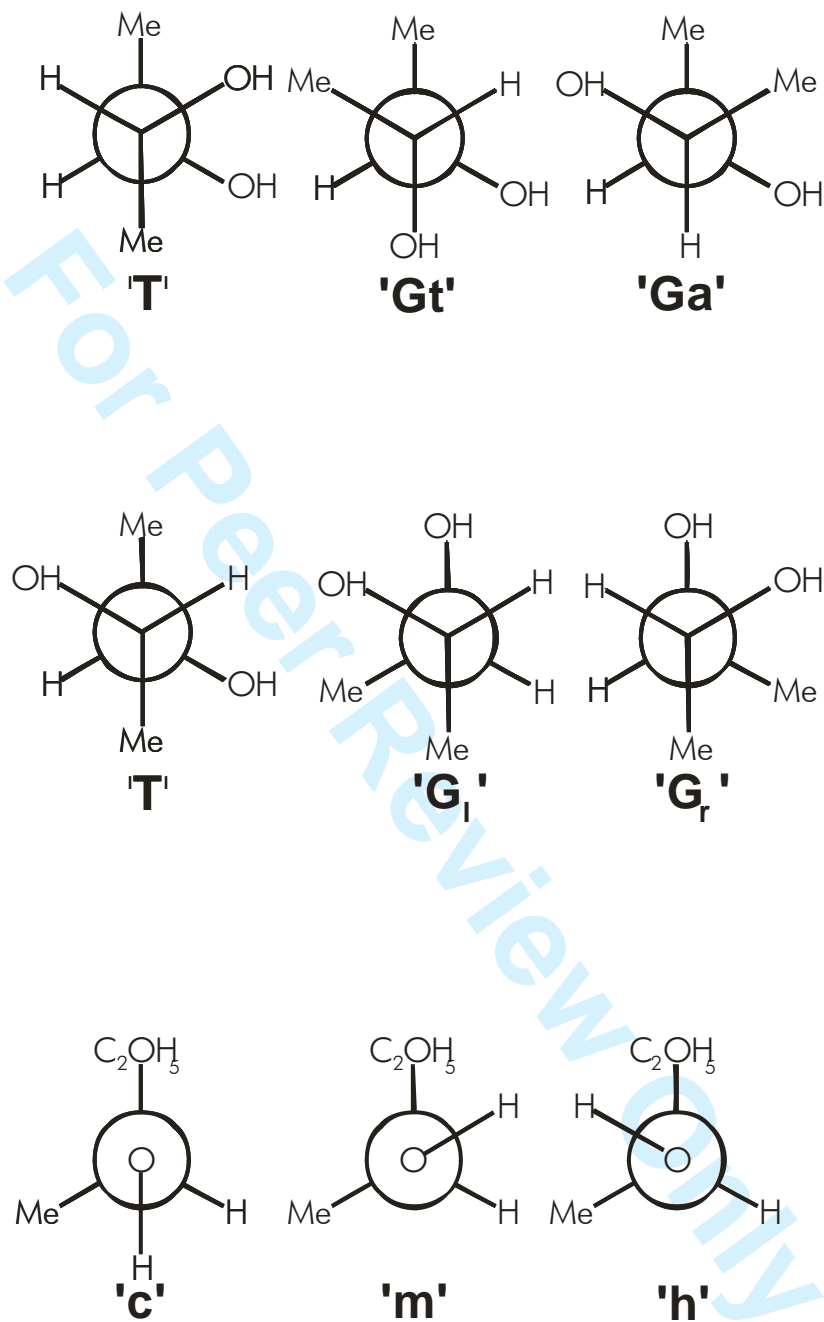


Figure 3. The lowest energy structural minima of the heterochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

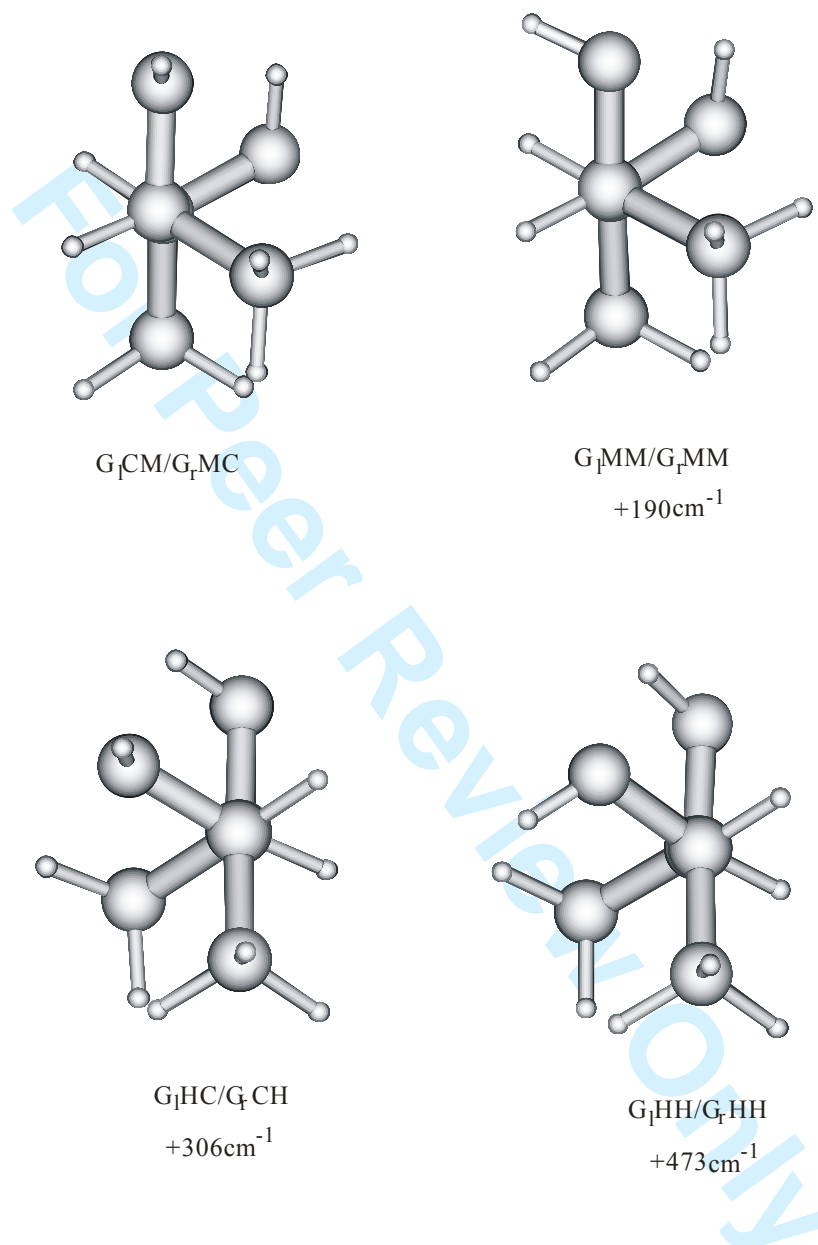


Figure 4. The three lowest energy structural minima of homochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

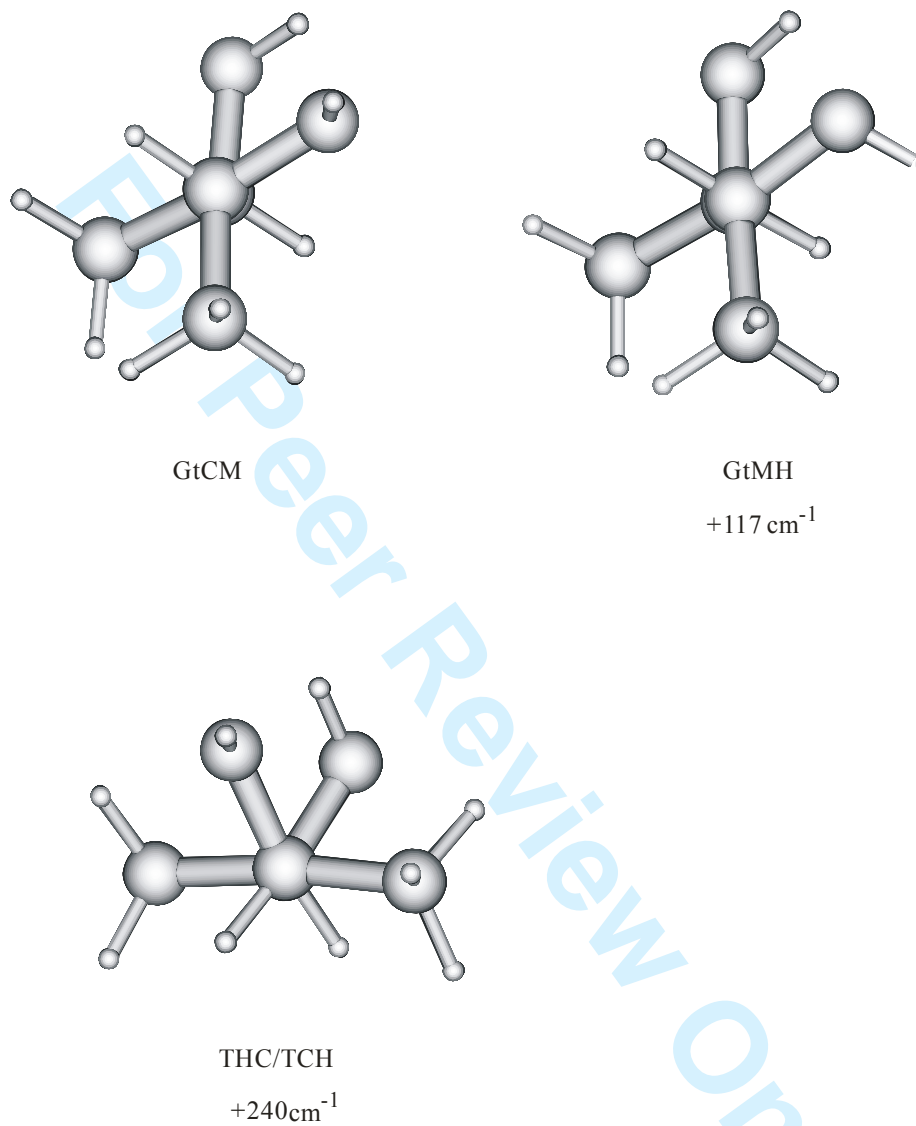


Figure 5. The tunnelling motion and approximate principal inertial axes of the GtCM conformer of butan-2,3-diol.

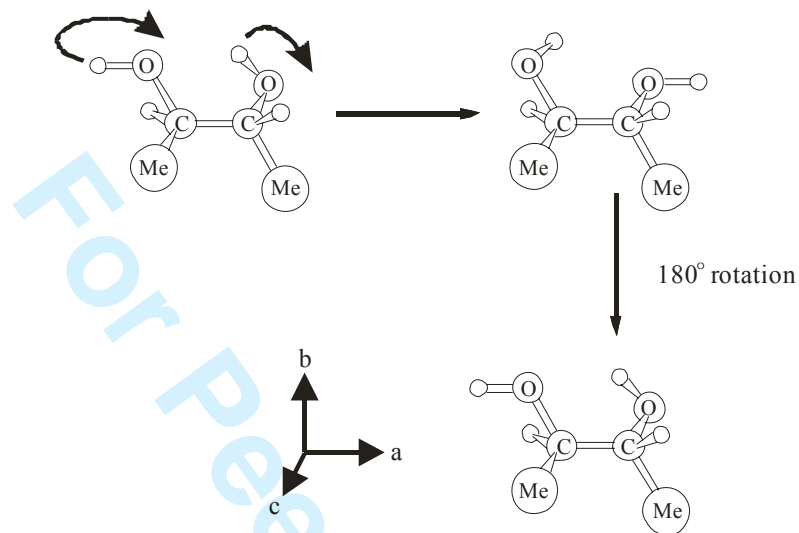


Figure 6. The b-type cycles of upper and lower tunnelling states of the GtCM conformer of butan-2,3-diol.

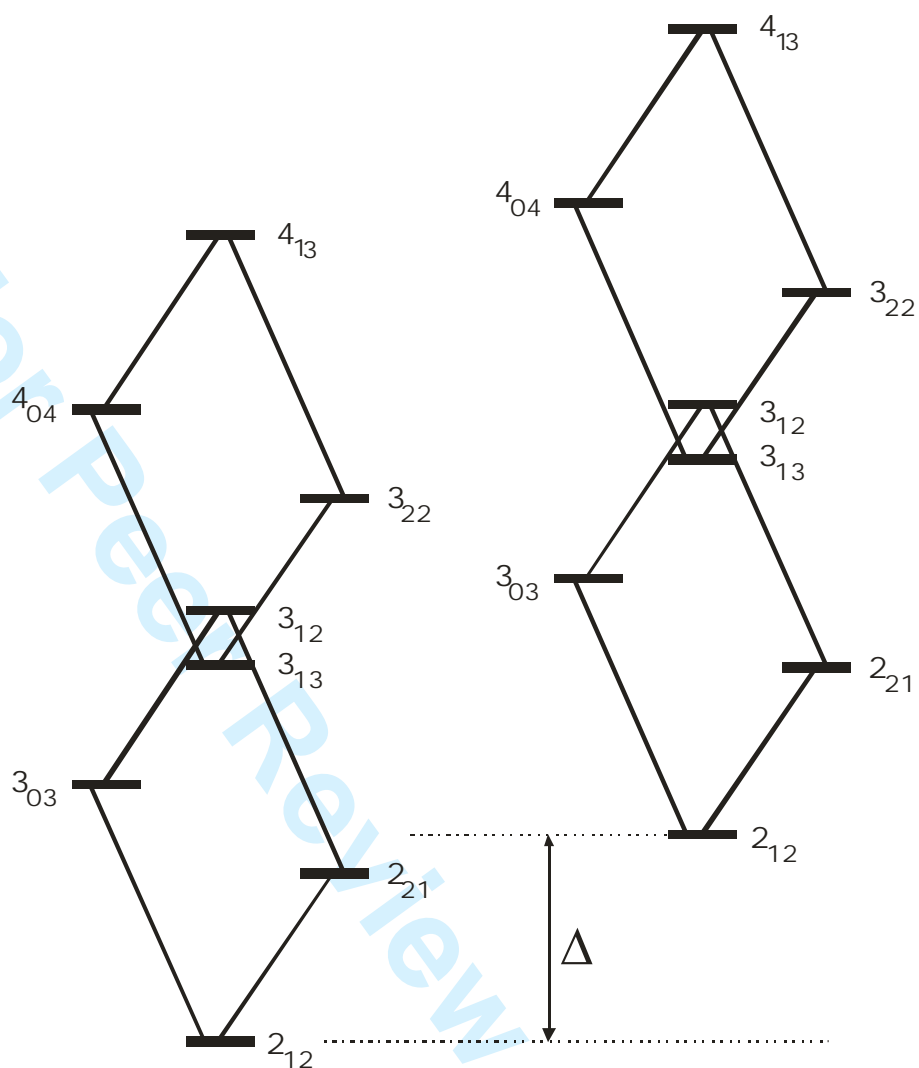
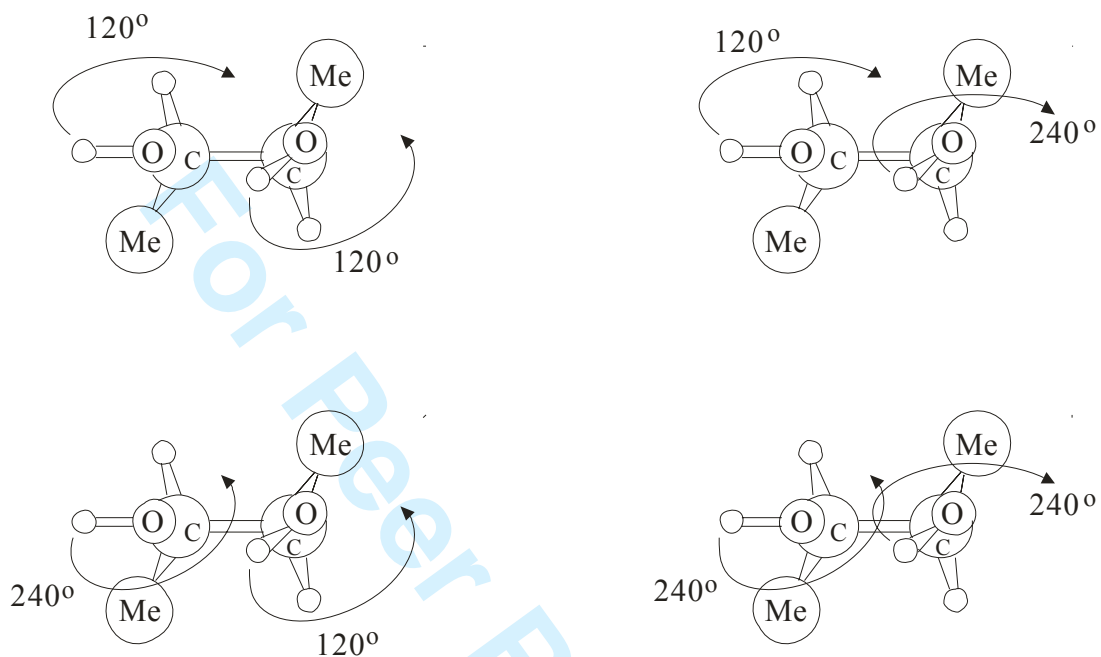


Figure 7. The four likely tunnelling paths of the GtCM conformer of butan-2,3-ol.



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2 **Chiral recognition in a single molecule: A study of homo and heterochiral**
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4 **butan-2,3-diol by Fourier transform microwave spectroscopy.**
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48 **Running title:** microwave spectroscopy of butandiol
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Abstract

The microwave Fourier transform spectrum of butan-2,3-ol has been recorded in the range 5-18 GHz. The molecule possesses two chiral centres and exists in two distinct forms, one of which is homochiral ((*R, R*) or (*S, S*)) and is overall chiral, and the other which is heterochiral ((*R, S*) or (*S, R*)) and is overall meso. Detailed ab initio calculations enabled investigation of the relative stability of the many conformations exhibited by each form of the molecule. It is shown that the lowest energy forms in each case possess an internal hydrogen bond. The spectrum of the heterochiral (meso) form could be readily identified and analysed. The homochiral form, however, exhibits a tunnelling motion of about 1 GHz, in which the hydrogen bonded OH groups interchange their roles. Deuteration of one of these OH protons quenches the tunnelling motion, aiding the assignment of the spectrum. In all cases, deuteration of the hydroxyl groups was used to locate the positions of the OH hydrogen atoms and helped to confirm the identification of the conformers present.

1. Introduction

Butan-2,3-diol, is a fascinating molecule. It possesses two chiral centres and hence, exists as two pairs of enantiomers. These enantiomeric pairs differ only in their chirality, but should have very different properties. The lowest conformers in energy exhibit an intramolecular hydrogen bond, which should pronounce the chiral recognition effect in the molecule. Most interesting of all, however, the chiral recognition will affect the dynamic properties, as well as the rigid structure, because of the symmetries of the different isomers.

A considerable volume of work has been carried out on butan-2,3-diol. The conformations of chiral (*R, R* and *S, S*) and meso-butan-2,3-diol (*R, S*) in CCl_4 were compared by Kuhn [1, 2] via infrared spectroscopy. He concluded that the ratio of hydrogen bonded and non-hydrogen bonded OH was larger for the chiral species. This has been explained in terms of the steric interaction of the methyl groups. The chiral species can form an intramolecular hydrogen bond when the two methyl groups are trans to one another, but the hydroxyl groups in the meso species may only interact in this way when the methyl groups are forced into a gauche conformation (see figure 1). Kuhn also deduced that a stronger hydrogen bond was present in the chiral molecule by comparing the splittings between the free and bonded OH peaks.

Beyond the desire to study hydrogen bonding and chiral recognition, the stereochemistry of many molecules have been related to (*2R, 3R*)-butan-2,3-diol and its derivatives [3-6]. The conformational properties of this isomer are also of interest as it has been used as a model for investigations of the methyl ester of (*R, R*)-tartaric acid monoamide [7]. An investigation by Wang *et al.* [8] utilized infrared spectroscopy and *ab initio* molecular orbital calculations to probe the conformational properties of this isomer in the solution phase. These authors found that the gauche hydrogen bonded conformation of the chiral molecule was more stable than the trans conformer, in disagreement with the work of Kuhn [1, 2].

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There has been recent interest in the conformations of other glycol molecules. The microwave spectra of asymmetrically deuterated forms of ethylene glycol were first assigned by Caminati *et al.* in 1981 [9, 10], but attempts to assign the spectrum of the parent isotopomer concluded that the molecule exhibits a large amplitude motion, which produces a tunnelling splitting in the spectrum and complicates the analysis [11, 12]. Recently, however, Christen *et al.* have recorded microwave spectra of two conformers of ethylene glycol [13-16]. They found that the tunnelling splittings in the observed conformers were approximately 7 GHz and 1.4 GHz. Microwave spectra of two conformers of propan-1,2-diol were also studied by Caminati [17]. The spectra of these species were re-examined recently, and a third conformer was assigned, which was found to be the global minimum for the molecule [18].

This paper presents the first assignment of the microwave spectra of the ground state conformers of chiral and *meso* butan-2,3-diol. This work has been augmented with an *ab initio* study, which has been used to provide geometrical predictions and to help decide which spectra arise from which conformers.

2. The structure of butan-2,3-diol

The butan-2,3-diol molecule has conformational flexibility about three bonds; different conformers may be generated by rotations about the central, C₂-C₃, bond or either of the two C-O bonds, so the molecule possesses $3^3=27$ conformers. In addition, the presence of two chiral centres gives rise to four forms of the molecule, namely the (*R*, *R*), (*S*, *S*), (*R*, *S*) and (*S*, *R*) configurations. Microwave spectroscopy will distinguish only the homo and heterochiral forms of the molecule, so the *ab initio* study reviewed below considers 27x2 species. Initial geometry optimizations were performed on these systems with the Gaussian 98 package [19] at the HF/6-311G level. The geometries of the conformers lying lowest in energy were then re-optimized at the MP2/6-311++G** level.

2.1 The heterochiral species

The 27 conformers of (*R*, *S*) and (*S*, *R*)-butan-2,3-diol have been classified with a nomenclature of the form *XYZ*. The nomenclature used for both the hetero and homochiral species is illustrated in figure 2.

“*X*” represents the geometry of the carbon chain, and is assigned as follows; if the two methyl groups are trans to one another $X=T$. If the two methyl groups are gauche to one another $X=G_r$ or G_l . These two gauche orientations of the carbon chain are mirror images of one another. If the methyl and hydroxyl groups trans to one another are in the vertical plane, the methyl group points downwards and the molecule is viewed from the end nearest this methyl group, the classification is G_r if the methyl group and hydroxyl group gauche to one another are on the right hand side. If this positioning of the trans methyl and hydroxyl groups leaves the remaining methyl and hydroxyl groups on the left, the classification is G_l .

“*Y*” denotes the position of the hydroxyl group, which is trans to the methyl group on the other chiral carbon atom. If the carbon chain is in the *T* position the two hydroxyl groups are equivalent and the labels “*Y*” and “*Z*” are interchangeable. The classification then considers the position of the O-H bond relative to the groups attached to the chiral carbon to which the hydroxyl group is bonded. $X=M$ if the O-H bond is trans to the methyl group, *C* if the O-H bond is trans to the carbon chain or *H* if it is trans to the hydrogen atom.

“*Z*” is classified in the same way as “*Y*”, but denotes the position of the remaining hydroxyl group, which is gauche to the methyl group on the other chiral carbon atom.

Of these twenty-seven conformers nineteen were minima on the HF/6-311G potential surface (see table 1). These nineteen minima comprised all nine conformations where the methyl groups were trans to one another and five of each of the two gauche conformations. The minima were grouped in eight pairs of mirror images; the five G_rYZ minima being mirror

1
2 images of the five G_iZY minima and the trans conformers also forming mirror pairs
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4 (THC \equiv TCH), (TMC \equiv TCM) and (TMH \equiv THM). Only the TCC, TMM and THH conformers
5
6 are unique.
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8 As one would expect, the four mirror pairs of conformers that display an
9
10 intramolecular hydrogen bond tend to be the lowest in energy. These species, and the TCC
11
12 conformer, were chosen for re-optimization at the MP2/6-311++G** level, which yielded the
13
14 rotational constants, relative energies and dipole moments displayed in table 2. The only large
15
16 change during the re-optimization was the drop in energy of the GMM conformer. This was
17
18 due to a large change in the angular orientation of the hydroxyl groups, resulting presumably
19
20 from the inclusion of polarization functions in the basis set.
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23 24 2.2 The homochiral species

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26 The 27 conformers of (*R, R*) and (*S, S*)-butan-2,3-diol have been classified in a similar
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28 manner to that described above, for the heterochiral molecule. As for the heterochiral species,
29
30 the nomenclature is of the form *XYZ*.

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32 “X” represents the geometry of the carbon chain. If the two methyl groups are trans to
33
34 one another $X=T$. If the two methyl groups are gauche to one another $X=Gg$ or Gt . These two
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36 gauche conformations of the carbon chain are non-equivalent and differ in that both methyl
37
38 groups are either trans (Gt) or gauche (Gg) to both hydroxyl groups.

39
40 Since the two hydroxyl groups are both either gauche or trans to the two methyl
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42 groups, for a specific orientation about the central C-C bond, they are equivalent. Hence, there
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44 is no way to distinguish between them, and “Y” and “Z” are interchangeable. As for the
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46 heterochiral molecule, Y or $Z=M$ if the O-H bond is trans to the methyl group, C if the O-H
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48 bond is trans to the carbon chain or H if it is trans to the hydrogen atom.
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Twenty-three of the twenty-seven starting structures are minima on the HF/6-311G potential surface (see table 3). The equivalence of the two hydroxyl groups means that nine of the twenty seven starting conformers are unique, and that there are nine identical pairs. For instance, for the Gg carbon chain rotamers, the GgMM, GgHH and GgCC conformers are unique and the (GgMC≡GgCM), (GgMH≡GgHM) and (GgHC≡GgCH) are the identical pairs. Of the twenty-three minima from the *ab initio* calculations, there are 7 unique conformers and 8 identical pairs. As in the heterochiral molecule, all conformers of the carbon chain orientation in which hydrogen bonding cannot occur (Gg), were minima. Of the T-type carbon chain conformers there were three pairs and two unique structures. Two of these pairs, the THC and THM rotamers, exhibit an intramolecular hydrogen bond. The remaining two minima and two pairs were Gt-type rotamers. Both pairs of Gt-type minima possess a hydrogen bond, and it was these conformers that were found to be the lowest in energy of all. The results of MP2 calculations are given in table 4. This is in agreement with the *ab initio* study of Wang *et al.* [8], but contradicts the arguments given in references 1 and 2.

It is interesting to consider the calculated energy differences between the hetero and homochiral forms of butan-2,3-diol. The GtCM homochiral conformer has an energy about 60 cm^{-1} lower than the G_lCM and G_rMC heterochiral conformers. It seems likely that this energy difference arises for steric reasons; the projections of the conformers in figures 3 and 4 show that the sum of the angles between the bulky groups about the central C-C bond is only 180° in the four lowest heterochiral conformers, but is 270° in the two lowest homochiral conformers. The projections also show that the hydrogen bond in the GtCM conformer may be shortened by an increase in the separation of the two methyl groups, but in the G_lCM and G_rMC conformers the methyl group separation must decrease to shorten the hydrogen bond. Thus we might expect to find a stronger hydrogen bond in the homochiral species.

3. Experimental details

Microwave transitions of butan-2,3-diol were recorded with the Fourier transform spectrometer which has been described previously [20]. The sample was heated to about 70°C, in order to produce an appropriate concentration of butan-2,3-diol and the nozzle to about 75°C to prevent blocking. Helium at 1.5 bar was used as the backing gas for all spectroscopic investigations.

Samples of *meso* ((*R*, *S*), (*S*, *R*)) and racemic ((*R*, *R*), (*S*, *S*), (*R*, *S*), (*S*, *R*))-butan-2,3-diol were purchased from Sigma-Aldrich. A chiral sample of (*R*, *R*)-butan-2,3-diol was also acquired, from Acrōs Organics. The hydroxyl groups of the racemic sample were deuterated by distilling a mixture of 25ml of butan-2,3-diol and 10ml of D₂O. This procedure was only performed once, as the aim was to maximise the quantities of the mono-deutero-diols.

4.1 Experimental results I: Heterochiral butan-2,3-diol

The first spectra recorded were obtained by scanning over frequency ranges of about 200 MHz around the predicted $0_{00}-1_{11}$, $1_{01}-2_{12}$, $2_{02}-3_{13}$ and $2_{11}-3_{03}$ transitions of the G_{rCM}/G_{rMC} conformers of (*R*, *S*)-butan-2,3-diol. Several strong transitions were found in each frequency range but rotational constants derived from the set of four lines that gave the best fit to a rigid asymmetric top Hamiltonian enabled the $1_{01}-2_{02}$ and $3_{13}-3_{22}$ transitions to be accurately predicted. A further 46 lines were then recorded. All lines were fitted to a Watson A-type rotational Hamiltonian [21]. The fits are summarized in table 5, [and in tables S1, S2 and S3 of the Supplementary Material](#).

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The initial scans had been made with the racemic mixture of butan-2,3-diol so the assignment of the transitions to the heterochiral molecule was confirmed with the pure samples; it was found that the assigned transitions could be observed with the *meso* (*R*, *S* and *S*, *R*) sample but not with the chiral (*R*, *R*) sample.

1
2 The next search focussed on the microwave spectra of the two mono-deutero-hydroxyl
3 forms of the G₁CM/G₁MC conformers. It was desirable to obtain information on
4 these species as it was hoped that a Kraitchman analysis [22] of the rotational constants would
5 confirm the assignment of the conformer to one of the *ab initio* predictions. It is likely
6 that the errors between the *ab initio* predictions and experimental rotational constants are
7 similar for the parent and deuterated isotopomers. Hence, assuming that the conformer already
8 observed was the G₁CM/ G₁MC species, it should be possible to improve the *ab initio*
9 predictions of the rotational constants of the mono-deutero-hydroxyl species by comparison
10 with the *ab initio* and experimental data on the parent isotopomer.
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20 This predictive technique appeared to work, and allowed microwave spectra of two
21 species with rotational constants similar to that of the parent isotopomer to be recorded. The
22 transitions of these species exhibited narrow quadrupole splittings, arising because of the
23 presence of the deuterium atom, which has a quadrupolar nucleus with a spin of 1. The
24 transitions of these species were fitted to a Hamiltonian identical to that used for the parent
25 isotopomer except that it included the diagonal quadrupole coupling parameters, χ_{aa} and χ_{bb} -
26 χ_{cc} . In total, 17 rotational transitions consisting of 47 hyperfine components were fitted for the
27 isotopomer which was believed to have the proton accepting hydroxyl group deuterated and 17
28 rotational transitions consisting of 56 hyperfine components for the isotopomer which was
29 believed to be deuterated at the proton donating hydroxyl group. The resulting spectral
30 parameters are given in table 5.
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43 4.2 Experimental results II: Homochiral butan-2,3-diol

44 Initial searches for the spectra of the GtCM homochiral conformer did not lead to a
45 convincing assignment. This was believed to be due to a tunnelling motion of the hydroxyl
46 groups that could connect two equivalent minima of any of the four lowest energy conformers
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2 of homochiral butan-2,3-diol. Hence, scans were performed to locate the spectra of the two
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4 mono-deutero-hydroxyl species, as the asymmetric deuteration should remove any effect of
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6 such tunnelling on the spectrum. It was hoped that the spectra of these deuterated species
7
8 would yield accurate estimates of the rotational constants of the parent isotopomer.
9

10 Searches around the *ab initio* predicted microwave transition frequencies for the
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12 deuterated isotopomers of the GtCM conformer yielded two sets of spectra. As for the
13
14 heterochiral species, narrow hyperfine splittings resulting from the quadrupole moment of the
15
16 deuterium nucleus were observable. Ten rotational transitions, divided into 26 hyperfine
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18 components, of each of these species were fitted to Watson A-type Hamiltonians. The spectral
19
20 parameters are listed in table 6, [and the fits in tables S5 and S6](#).
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22 23 24 4.3 The tunnelling spectrum of homochiral butan-2,3-diol

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26 As in the *g'*Ga conformer of ethylene glycol, the GtCM conformer of homochiral
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28 butan-2,3-diol was expected to undergo a tunnelling motion that reverses the direction of the
29
30 μ_a and μ_c components of the dipole moment. Thus, the a and c-type microwave transitions
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32 should connect the two tunnelling states of the GtCM conformer, and these transitions should
33
34 occur at frequencies approximately equal to a pure rotational transition difference plus or
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36 minus a tunnelling splitting. The b-type transitions link energy levels of the same tunnelling
37
38 state and should be largely independent of the tunnelling splitting. The tunnelling motion is
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40 illustrated in figure 5 [and is related to the original structure by a rotation by 180° around the b-](#)
41
42 [axis](#).
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44 Coriolis forces complicate the spectrum by making the tunnelling splitting dependent
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46 on the rotational state of the molecule. If the spectrum of a molecule exhibiting a tunnelling
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48 motion through a potential barrier such as ethylene glycol or butan-2,3-diol is analysed with a
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50 rigid rotor approach then the rotational constants obtained will relate to the transition state, as
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2 this is the average structure. Hence, when the molecules are at their geometrical minima there
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4 are off-diagonal terms in the inertia tensors. In the rotational Hamiltonian, the rotational
5
6 constants are the coefficients of the squares of the components of the total angular momentum.
7
8 The off-diagonal inertial terms are the coefficients of the cross products of the angular
9
10 momentum components.

11
12 Two methods that have been developed to account for these effects are the internal axis
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14 method (IAM) of Hougen [23, 24] and the reduced axis system (RAS) of Pickett [25]. The
15
16 IAM approach removes the tunnelling-rotation mixing via a suitable choice of axes and thus
17
18 considers the wavefunctions of the two vibrational species to be localized in their potential
19
20 wells. The IAM Hamiltonian contains a constant term for the tunnelling between the wells and
21
22 coupling terms to take account of the dependence of the tunnelling on the rotational state. The
23
24 RAS technique solves the problem including the tunnelling-rotation mixing via a stepwise
25
26 diagonalization of the Hamiltonian matrix. Thus, the RAS technique considers the symmetric
27
28 and antisymmetric tunnelling states and the terms involving the cross products of the angular
29
30 momentum components. The RAS Hamiltonian is of the form:

$$\hat{H}_{vv} = E_v + AJ_a^2 + BJ_b^2 + CJ_c^2 \quad [1]$$

$$\hat{H}_{v'v} = (F_{bc}(J_b J_c + J_c J_b)) + (F_{ab}(J_a J_b + J_b J_a)) + (F_{ac}(J_a J_c + J_c J_a)) \quad [2]$$

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38 where E_v is the energy of the vibrational state, \hat{H}_{vv} connects levels of the same vibrational state
39
40 and $\hat{H}_{v'v}$ connects levels of different vibrational states. Pickett has determined the required
41
42 symmetric top matrix elements for equations 1 and 2, which are given in reference 25.
43

44
45 Christen *et al.* have employed both the IAM and RAS methods for their work on
46
47 ethylene glycol [13 - 16]. The main advantages of the RAS method are that it can provide
48
49 information on the tunnelling splitting even if no transitions across the tunnelling splitting
50
51 have been recorded and that it can be applied without knowledge of the tunnelling path,
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1
2 whereas the IAM method must be set up differently for each tunnelling path considered. For
3 these reasons the analysis of homochiral butan-2,3-diol presented in this chapter has utilized
4 the RAS method, implemented with the SPFIT computer program of Pickett [26].
5
6

7
8 A useful diagnostic, which aids the assignment of microwave spectra, occurs when it is
9 possible to observe “cycles” of transitions, which link two rotational energy levels by more
10 than one path. If the assignment of the transitions is correct, the sum of the transition
11 frequencies in each path should be equal to within the experimental error.
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13

14
15 The predicted rotational constants provided by work on the mono-deutero-hydroxyl
16 species indicated that two cycles of b-type transitions lay within the range of the spectrometer.
17 Scans over frequency ranges centred on the predictions of these transitions yielded four cycles
18 in total. These sixteen transitions were then fitted to an RAS Hamiltonian
19 that included a set of rotational constants for each of the two tunnelling states, a tunnelling
20 frequency and the Coriolis coupling constants F_{ab} and F_{bc} .
21
22

23
24 Only two combinations of trial fits were then needed to deduce which two cycles of
25 lines belonged to the lower, and which to the upper, tunnelling state. The cycles are illustrated
26 in figure 6. A reasonable starting value of the tunnelling splitting (Δ_{tun}) was deduced by fitting
27 the sixteen transitions with values of Δ_{tun} between 0 and 7 GHz in 0.5 GHz steps. It was found
28 that starting values of 1.0 and 1.5 GHz both yielded a fit with a root mean square error of 9.6
29 kHz and $\Delta_{tun}=1024.39$ (65) MHz. The small error of this fit appeared to confirm that the two
30 pairs of cycles had been correctly matched.
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34 Using the parameters from this fit it proved possible to record transitions across the
35 tunnelling; 20 a-type and 12 c-type transitions were found. A further 48 b-type
36 lines were also observed and included in the final fit.
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40 The five A-reduced quartic centrifugal distortion terms were also derived from this fit
41 but, the differences between the centrifugal distortion constants of the two tunnelling states
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2 were too small to be determined from the observed transitions. The constants derived from the
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4 fit of the four b-type cycles and the final fit are displayed in table 7, [and the fits to the](#)
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6 [spectrum in table S4.](#)
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8

9 10 **6. Discussion**

11 12 **6.1 Mass substitution analysis**

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14 The position of a specific atom within a molecule may be deduced if the rotational
15 constants, which arise when different isotopes are present at this position, are known. This is
16 achieved via Kraitchman's substitution method [22]. This technique will be utilized below in
17
18 an attempt to confirm which of the *ab initio* structures most closely resembles the species
19
20 that have been observed in the supersonic molecular beam. The difference in the moment of
21
22 inertia between two isotopomers may be written [27]:
23
24

$$25 \quad \Delta I_i = \left(\frac{m\Delta m}{m + \Delta m} \right) r_i^2 \quad [3]$$

26
27 where ΔI_i is the difference in the *a*, *b* or *c* moment of inertia of the two species, *m* is the mass
28
29 of the parent species (approximately 90 u in the case of butan-2,3-diol), Δm is the change of
30
31 mass involved in the substitution (approximately 1 u for H substituted by D) and r_i is the
32
33 distance of the substituted atom from the principal axis to which ΔI_i relates.
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35

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37 This analysis assumes that the observed structures are not affected by the mass
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39 dependence of the vibrations of the molecule and also that the inertial axes are not
40
41 significantly shifted by the change in mass. Co-ordinates relative to the three principal axes
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43 were thus deduced for the two hydrogen atoms in the observed homo and heterochiral
44
45 conformers of butan-2,3-diol, and are displayed in tables 8 and 9 alongside the equivalent *ab*
46
47 *initio* results for the conformers predicted to have the lowest energies.
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2 The experimental results for the two conformers match very well with the co-ordinates
3
4 for the lowest energy homo and heterochiral conformers respectively. As can be seen from
5
6 figures 3 and 4, the only significant difference between the GtCM and GtMH homochiral
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8 conformers and the G_lCM / G_rMC and G_lMM / G_rMM heterochiral conformers is a rotation of
9
10 the HOCC dihedral angle for the proton accepting OH group. The coordinates above reflect
11
12 this; as expected, it is only the coordinates of the proton acceptor hydroxyl hydrogen that
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14 allow us to distinguish which conformer of each of these pairs has been observed.

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16 The predicted [electric](#) dipole moment components of the heterochiral conformers,
17
18 displayed in table 2, also support the conclusion that the G_lCM / G_rMC conformer is the one
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20 observed. In both the G_lHC / G_rCH and the G_lMM / G_rMM conformers two of the dipole
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22 components are small. There is no way to measure the dipoles quantitatively in the microwave
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24 experiment that has been performed, but the fact the a, b and c-type transitions were all easily
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26 observable suggests that none of the dipole components were near zero. In the homochiral
27
28 conformer the lowest energy *ab initio* structures all have similar dipoles and do not add further
29
30 evidence to support the Kraitchman analysis. [Full ab initio geometries of the observed](#)
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32 [conformers are given in tables S7 and S8 of the Supplementary Material.](#)

33 34 35 **6.2 Deuterium quadrupole coupling constants**

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37 The inertial axis quadrupole coupling constants obtained from the microwave spectra
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39 provide information on the effect of the hydrogen bond on the hydroxyl groups in butan-2,3-
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41 diol. These coupling constants are elements of the inertial axis quadrupole coupling tensor. If
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43 this tensor is transformed to its principal axes the coupling constants of the four deuterium
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45 atoms will be comparable. It seems reasonable to assume that the quadrupole tensor is
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47 approximately symmetric about the O-D bond. If this is the case it will have a coupling
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49 constant, χ , associated with the bond axis and two non-unique coupling constants, $-\chi/2$,
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perpendicular to the bond. The value of χ can then be found by substituting the *ab initio* predicted angle between the O-D bond and the a-principal inertial axis into the equation [28]

$$\chi_{aa} = \chi \left(\frac{3 \cos^2 \theta - 1}{2} \right) \quad [4]$$

where θ is the angle between the O-D bond and the a-inertial axis. The angles relating the four O-D bonds to this inertial axis and the derived values of χ are displayed in table 10.

The lowest energy homo and heterochiral conformers of butan-2,3-diol are so similar in structure that one would hope to obtain similar values of χ for the two deuterium environments in both species. For the deuterium in the proton accepting hydroxyl group this occurs and the two values of χ differ by only 3 kHz. In the donor deuterium environment this is not the case. An anomalous value occurs for the GtCM donor environment because the angle between the O-D bond and the a-inertial axis is close to 54.7°. At this angle the term $(3 \cos^2 \theta_{az} - 1)$ in equation is near to zero and hence the inertial axis quadrupole coupling terms, deduced from the spectrum are poorly determined. The other three values of χ are similar to that of the deuterium quadrupole coupling in the trans OD rotamer of isopropanol, reported by Hirota and Kawashima [29], who found that χ is equal to 269.3 kHz.

A comparison of the two proton environments in the hydrogen bond is limited to the heterochiral conformer, because of the anomalous value of χ that occurs for the GtCM donor environment. The values of the principal quadrupole coupling constant for the heterochiral species suggest that the difference in χ produced by the two deuterium environments is close to 50 kHz.

6.3 The tunnelling path of the GtCM conformer

There are four possible combinations of 120° and 240° rotations of the hydroxyl groups that will interconvert the two equivalent minima of the GtCM/GtMC conformer. These paths are illustrated in figure 7. Intuitively the path that involves a 120° rotation of both hydroxyl

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2 groups appears to be the most favourable as it requires both hydroxyl hydrogens to pass over
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4 C-H bonds, rather than C-C bonds.
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6 This guess at the most likely tunnelling path is supported by the microwave work of
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8 Christen *et al.*, which has shown that the *g*'Ga conformer of ethylene glycol undergoes a
9
10 concerted 120°, 120° tunnelling path, at a frequency of 7GHz [13]. The decrease in the
11
12 tunnelling splitting between the two systems is assumed to indicate that the positions of the
13
14 methyl groups in butan-2,3-diol must change slightly during the tunnelling process. This will
15
16 increase the reduced mass involved in the tunnelling motion and decrease the tunnelling
17
18 splitting.
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20 21 22 **7. Concluding remarks**

23 The assignment of the two observed conformers of butan-2,3-diol to the
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25 conformational ground states of the homo and heterochiral species is supported by the
26
27 Kraitchman analyses and the tunnelling properties of the homochiral species. These species
28
29 have also accounted for all of the most intense observed transitions, as would be expected if
30
31 they are indeed the most populated conformational states. The microwave spectrum of butan-
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33 2,3-diol is, however, very dense and many weaker lines, which could arise from excited
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35 conformational states, uncommon isotopomers, rare gas-butan-2,3-diol complexes, dimers and
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37 higher clusters, are still unassigned.
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39

40 41 **Acknowledgements**

42 The support of the EPSRC is gratefully acknowledged. We also thank Professor D. Christen
43
44 for helpful discussions.
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Table 1: The energies of the conformers of (*R*, *S*)-butan-2,3-diol geometry optimized at the HF/6-311G level.

Conformer	E/ E_h	E_{rel}/ cm^{-1}	H bond
$G_rCM \equiv G_rMC$	-306.8810923	0	Yes
$G_lCC \equiv G_rCC$	Converted to $G_lCM \equiv G_rMC$		No
$G_lHM \equiv G_rMH$	Converted to $G_lCM \equiv G_rMC$		No
$G_lHC \equiv G_rCH$	-306.8797009	305	Yes
$G_lMC \equiv G_rCM$	Converted to $G_lHC \equiv G_rCH$		No
TCC	-306.8790738	443	No
$G_lMM \equiv G_rMM$	-306.8790667	445	Yes
$G_lMH \equiv G_rHM$	Converted to $G_lHH \equiv G_rHH$		No
$G_lHH \equiv G_rHH$	-306.8776857	748	Yes
THC \equiv TCH	-306.8773939	812	No
TMC \equiv TCM	-306.8773328	825	No
TMM	-306.8767426	955	No
THH	-306.8760264	1112	No
THM \equiv TMH	-306.8752805	1276	No
$G_lCH \equiv G_rHC$	-306.8701875	2393	No

Table 2: The properties of the lowest energy conformers of (*R*, *S*)-butan-2,3-diol optimized at MP2/6-311++G**.

Conformer	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	μ_a /D	μ_b /D	μ_c /D	<i>E</i> / <i>E</i> _h	<i>E</i> _{rel} /cm ⁻¹
G ₁ CM≡G _r MC	4665.9	2871.9	2350.2	1.7	1.9	1.0	-308.1263317	0
G ₁ HC≡G _r CH	4607.4	2843.9	2360.0	2.9	0.4	0.0	-308.1249394	306
G ₁ MM≡G _r MM	4669.1	2830.7	2344.8	0.2	0.5	2.5	-308.125464	190
G ₁ HH≡G _r HH	4557.6	2852.7	2331.7	1.9	2.2	0.9	-308.1241772	473
TCC	4572.7	3107.8	1999.6	0.0	0.0	0.0	-308.1232344	680

Table 3: The energies of the conformers of (*S, S*) and (*R, R*)-butan-2,3-diol geometry optimized at the HF/6-311G level.

Conformer	E/E_H	E_{rel}/cm^{-1}	H bond
GtCM	-306.8815422	0	Yes
GtHC	Converted to GtCM		No
THC	-306.8807831	167	Yes
GtMH	-306.8794134	467	Yes
THM	-306.8788301	595	Yes
GtCC	Converted to GtMM		No
GtMM	-306.8786928	625	No
GgCC	-306.877986	780	No
THH	-306.8778043	820	No
TCC	Converted to THH		No
GgMC	-306.876508	1105	No
GgHC	-306.8759726	1222	No
GgHM	-306.8753539	1358	No
GgMM	-306.8750526	1424	No
TMM	-306.737299	1715	No
GtHH	-306.736728	1727	No
GgHH	-306.733768	1792	No
TMC	-306.713747	2231	No

Table 4: The properties of the lowest energy conformers of (*S, S*) and (*R, R*)-butan-2,3-diol optimized at MP2 / 6-311++G**.

Conformer	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	μ_a /D	μ_b /D	μ_c /D	<i>E</i> / <i>E</i> _h	<i>E</i> _{rel} / cm ⁻¹
GtCM	4578.7	3090.9	1994.6	2.5	1.6	0.7	-308.126606	0
GtMH	4571.1	3061.2	1987.8	1.6	2.0	1.4	-308.1260706	117
THC	4773.1	2765.2	2414.4	1.9	1.4	1.3	-308.1255081	240
THM	4763.2	2739.6	2399.1	0.5	2.0	0.7	-308.1243612	492
GtMM	4612.6	3007.5	1985.0	0.0	0.7	0.0	-308.1241789	533

Table 5: Spectral parameters of the G₁CM/ G₂CM conformer of heterochiral butan-2,3-diol.

	Parent Isotopomer	Proton Donor Group Deuterated	Proton Acceptor Group Deuterated
A /MHz	4640.0465 (2)	4497.4826 (8)	4629.2594 (8)
B /MHz	2840.8899 (2)	2832.7649 (7)	2745.8061 (9)
C /MHz	2343.3848 (2)	2312.9114 (7)	2278.3988 (8)
Δ_J /kHz	0.932 (9)	0.993 (23)	0.850 (30)
Δ_{JK} /kHz	-1.165 (5)	-1.06 (9)	-0.94 (13)
Δ_K /kHz	1.616 (11)	0.63 (20)	1.47 (19)
δ_J /kHz	0.240 (6)	0.251 (13)	0.316 (22)
δ_K /kHz	3.481 (11)	3.10 (24)	2.95 (36)
χ_{aa} /kHz	-	117.1 (14)	219.5 (15)
$(\chi_{bb} - \chi_{cc})$ /kHz	-	100.4 (40)	43.5 (38)
N^a	52	56	47
σ_{rms} /kHz	1.7	4.3	3.1

^a The total number of lines included in the fit.

Table 6: Spectral parameters of the deuterohydroxyl isotopomers of the GtCM conformer of homochiral butan-2,3-diol.

	Proton Donor Group Deuterated	Proton Acceptor Group Deuterated
A /MHz	4437.9005 (9)	4505.6211 (13)
B /MHz	3061.3386 (10)	2987.7452 (7)
C /MHz	1956.2602 (4)	1940.6420 (7)
Δ_J /kHz	0.455 (20)	0.442 (28)
Δ_{JK} /kHz	-0.580	-0.56 (11)
Δ_K /kHz	1.41 (25)	1.3 (8)
δ_J /kHz	0.170 (17)	0.18 (2)
δ_K /kHz	0.361 ^a	0.361 ^a
χ_{aa} /kHz	16.9 (34)	166.9 (19)
$(\chi_{bb} - \chi_{cc})$ /kHz	275.8 (34)	-80.0 (52)
N	26	26
σ_{rms} /kHz	2.6	1.9

^a Constrained to the value for the parent isotopomer (table 4.7).

Table 7: Spectral parameters of the GtCM conformer of homochiral butan-2,3-diol.

	Full Fit	Fit of b-type cycles
A /MHz	4574.8694 (2)	4574.8330 (11)
B /MHz	3072.5964 (2)	3072.5832 (3)
C /MHz	1987.0638 (2)	1987.0550 (3)
ΔA /kHz	12.46 (8)	23.6 (9)
ΔB /kHz	14.62 (4)	26.1 (4)
ΔC /kHz	4.28 (6)	2.5 (3)
Δ_J /kHz	0.468 (6)	-
Δ_{JK} /kHz	-0.580 (8)	-
Δ_K /kHz	1.446 (7)	-
δ_J /kHz	0.1672 (14)	-
δ_K /kHz	0.361 (7)	-
Δ_{un} /MHz	1011.9781 (6)	1024.4 (7)
F_{ab} /MHz	10.9472 (13)	11.444 (18)
F_{bc} /MHz	8.3800 (4)	8.356 (14)
N	96	16
σ_{rms} /kHz	0.67	9.6

Table 8: Principal axis coordinates of the hydroxyl hydrogen atoms in the conformers of heterochiral butan-2,3-diol from isotopic substitution and *ab initio* calculations.

	Donor OH hydrogen			Acceptor OH hydrogen		
	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$
Exp.	0 ^a	± 1.710	± 0.753	± 2.469	± 0.352	± 0.365
G _l CM≡G _r MC	-0.053	-1.659	0.817	2.469	-0.415	-0.243
G _l HC≡G _r CH	1.424	-1.310	0.232	-1.515	-1.606	0.87
G _l MM≡G _r MM	-0.019	-1.583	0.886	1.619	-1.206	-1.169
G _l HH≡G _r HH	1.352	-1.352	0.230	-0.998	-0.630	1.518

^a The square of this coordinate was determined to be small and negative, so it has been set to zero.

Table 9: Principal axis coordinates of the hydroxyl hydrogen atoms in the conformers of homochiral butan-2,3-diol from isotopic substitution and *ab initio* calculations.

	Donor OH hydrogen			Acceptor OH hydrogen		
	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$
Exp.	± 0.779	± 1.856	± 0.069	± 2.140	± 1.254	± 0.380
GtCM	0.760	-1.857	-0.023	-2.121	-1.287	0.393
GtMH	-0.720	-1.853	-0.032	1.678	-1.083	0.916
THC	0.595	-0.589	1.503	-1.631	1.395	0.923

Table 10: Calculated axial deuterium quadrupole coupling constants of the conformers of butan-2,3-diol.

	G _r CM / G _r MC		GtCM	
	Donor	Acceptor	Donor	Acceptor
θ	35.8°	23.7°	49.2°	31.8°
χ /kHz	240	290	121	287

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Figure captions.

Figure 1. The hydrogen bonded conformations of meso and racemic butan-2,3-diol.

Figure 2. A nomenclature for the conformations of butan-2,3-diol.

Figure 3. The lowest energy structural minima of the heterochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

Figure 4. The three lowest energy structural minima of homochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

Figure 5. The tunnelling motion and approximate principal inertial axes of the GtCM conformer of butan-2,3-diol.

Figure 6. The b-type cycles of upper and lower tunnelling states of the GtCM conformer of butan-2,3-diol.

Figure 7. The four likely tunnelling paths of the GtCM conformer of butan-2,3-diol.

Figure 1. The hydrogen bonded conformations of meso and racemic butan-2,3-diol.

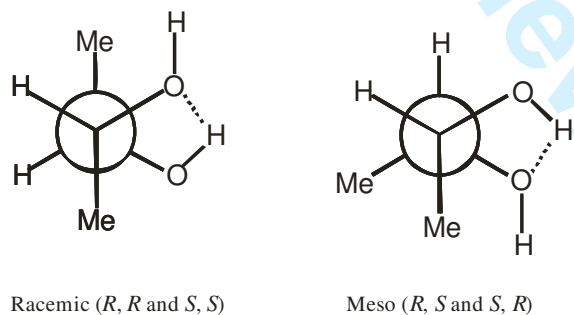


Figure 2. A nomenclature for the conformations of butan-2,3-diol.

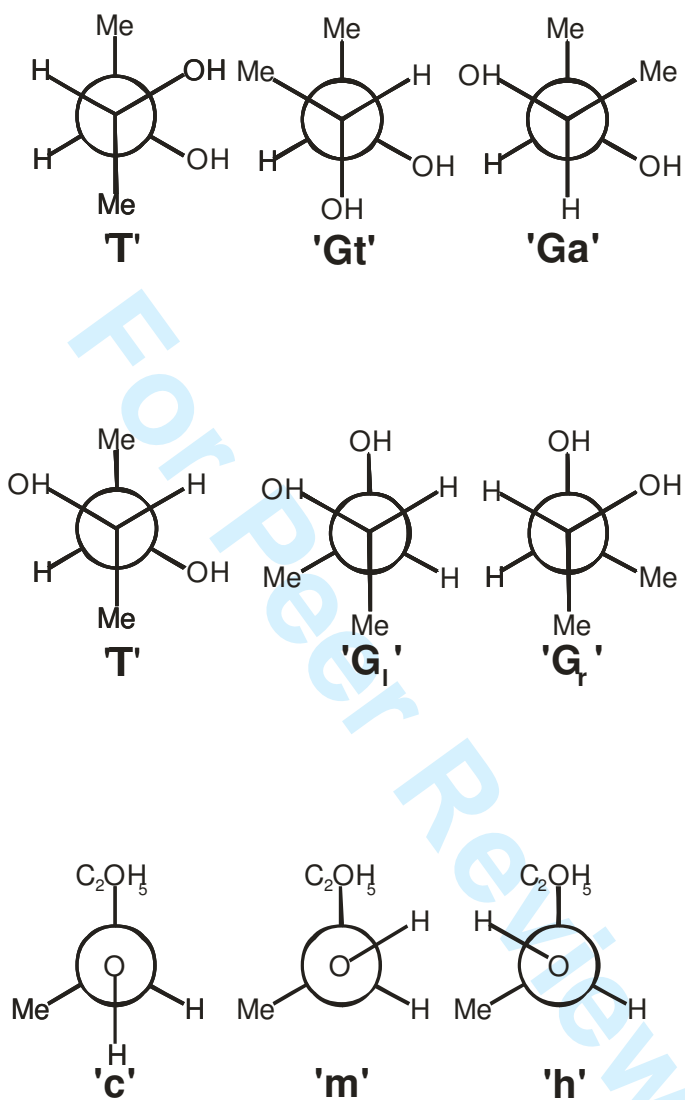


Figure 3. The lowest energy structural minima of the heterochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

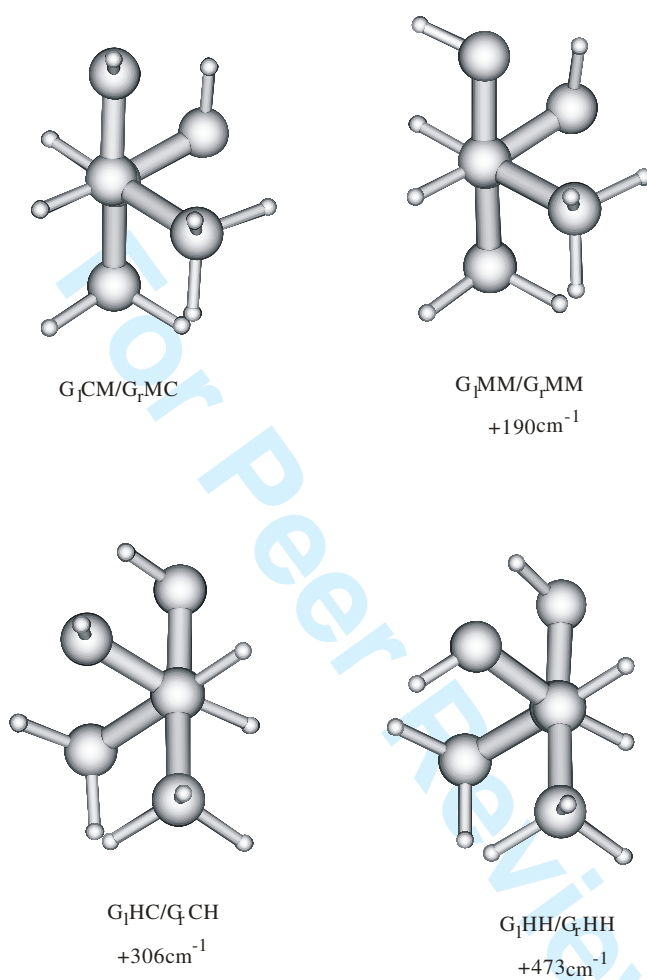


Figure 4. The three lowest energy structural minima of homochiral butan-2,3-diol (together with relative MP2/6-311++G** energies).

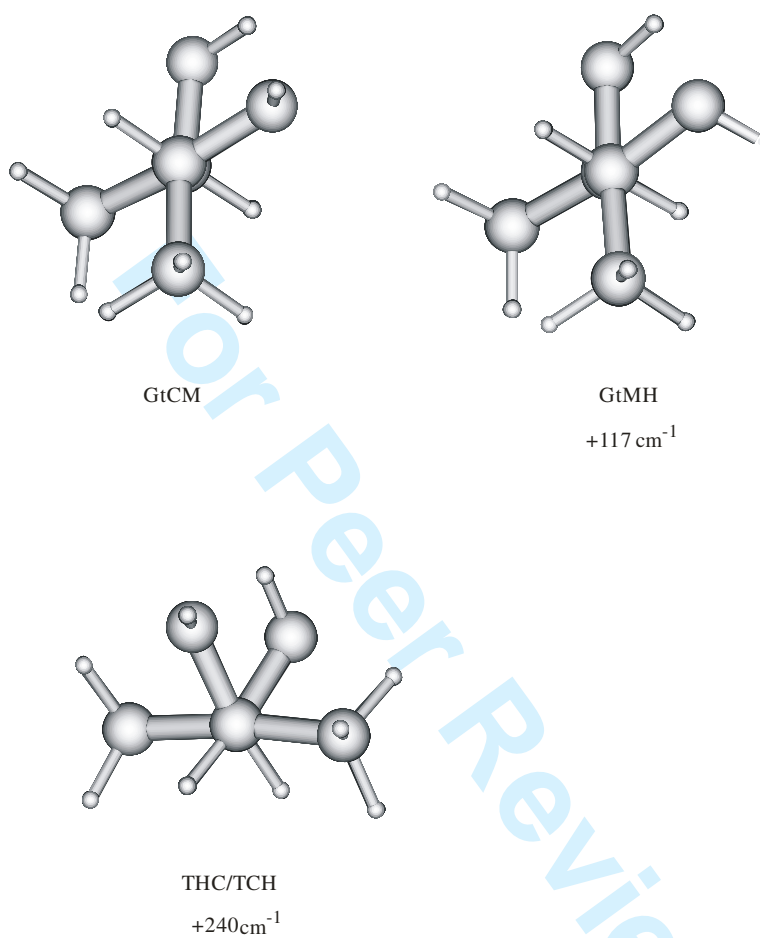


Figure 5. The tunnelling motion and approximate principal inertial axes of the GtCM conformer of butan-2,3-diol.

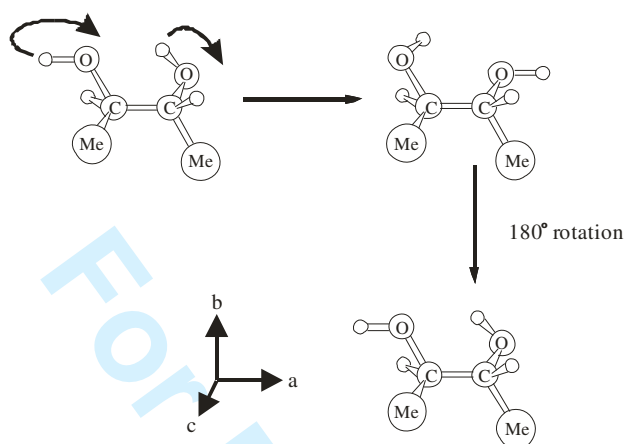


Figure 6. The b-type cycles of upper and lower tunnelling states of the GtCM conformer of butan-2,3-diol.

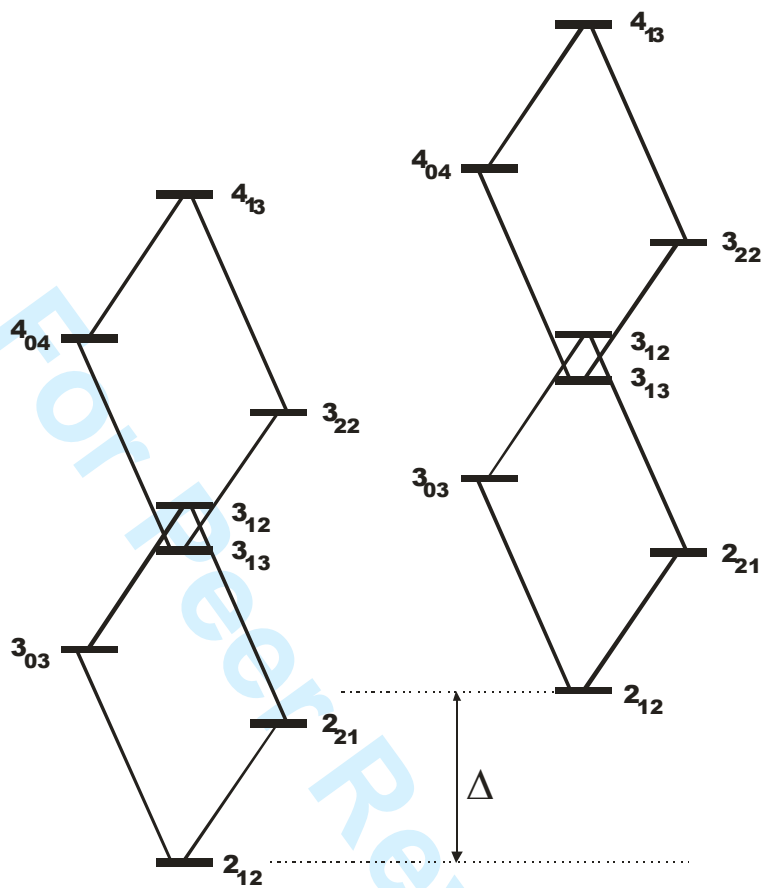
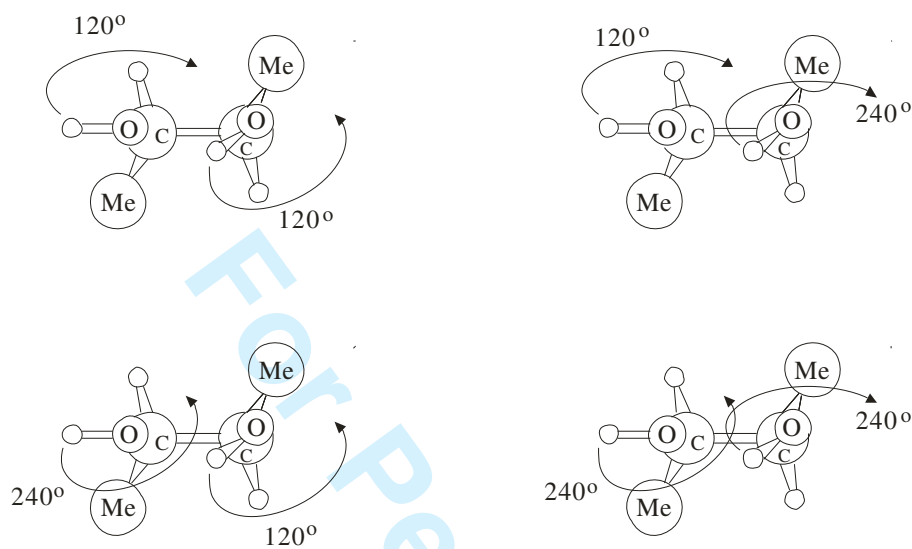


Figure 7. The four likely tunnelling paths of the GtCM conformer of butan-2,3-ol.



Supplementary Material

Chiral recognition in a single molecule: A study of homo and heterochiral butan-2,3-diol by Fourier transform microwave spectroscopy.

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Microwave transitions of heterochiral butan-2,3-diol.

Table S1: Fitted microwave transitions of the parent isotopomer of the G_rCM/ G_rMC conformer of butan-2,3-diol.

J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
2	2	1	2	1	2	6889.9522	-0.0001
1	1	1	0	0	0	6983.4357	-0.0005
5	1	4	5	0	5	7480.6408	0.0002
1	1	0	0	0	0	7480.9263	0.0009
3	2	2	3	1	3	7687.9390	-0.0016
3	2	1	3	1	3	8118.4675	0.0006
5	3	3	5	2	3	8458.1902	0.0000
2	0	2	1	1	1	8479.7020	-0.0003
9	3	6	9	2	7	8492.9441	0.0008
3	2	2	3	0	3	8622.1922	-0.0009
4	2	3	4	1	4	8765.1702	-0.0002
4	2	3	4	0	4	9314.5210	-0.0000
4	3	2	4	2	2	9322.0121	0.0000
4	3	1	4	2	2	9392.7108	0.0004
3	3	1	3	2	1	9860.7390	-0.0021
2	1	2	1	1	1	9871.0407	-0.0000
2	0	2	1	0	1	10278.8678	0.0002
3	3	1	3	2	2	10291.2655	-0.0019
5	2	4	5	0	5	10401.9173	0.0027
4	3	2	4	2	3	10514.1085	0.0004
4	3	1	4	2	3	10584.8073	0.0008
2	1	1	1	1	0	10866.0081	0.0005

	J'	K_a'	K_c'	J''	K_a''	K_c''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1								
2								
3								
4	5	3	3	5	2	4	10928.4808	0.0009
5								
6	5	3	2	5	2	4	11200.4100	0.0012
7								
8	2	1	2	1	0	1	11670.2057	-0.0003
9								
10	6	2	5	6	1	6	11697.2907	0.0010
11								
12	9	2	7	9	1	8	12325.1072	-0.0017
13								
14	3	0	3	2	1	1	12328.0538	-0.0006
15	8	3	6	8	2	7	13717.6081	0.0004
16								
17	3	0	3	2	1	2	13820.5112	0.0007
18								
19	5	3	3	5	1	4	13849.7545	0.0006
20								
21	5	4	2	5	3	2	13912.1566	0.0005
22								
23	4	4	1	4	3	1	14130.5068	-0.0017
24	4	4	0	4	3	1	14131.4873	0.0014
25								
26	5	4	2	5	3	3	14184.0861	0.0010
27								
28	5	4	1	5	3	3	14192.7711	0.0003
29								
30	4	4	1	4	3	2	14201.2059	-0.0010
31	4	4	0	4	3	2	14202.1854	0.0012
32								
33	3	1	3	2	1	2	14754.7636	0.0006
34								
35	3	0	3	2	0	2	15211.8499	0.0010
36								
37	3	2	2	2	2	1	15552.7531	0.0018
38								
39	3	2	1	2	2	0	15893.6280	0.0023
40	4	0	4	3	1	2	16065.4788	-0.0001
41								
42	3	1	3	2	0	2	16146.1025	0.0011
43								
44	3	1	2	2	1	1	16236.8898	0.0014
45								
46	2	2	1	1	1	0	16263.5038	-0.0001
47								
48	2	2	0	1	1	0	16353.1558	0.0001
49								
50	4	1	3	3	2	1	16374.9674	0.0028
51								
52	2	2	1	1	1	1	16760.9933	0.0002
53								
54	4	1	3	3	2	2	16805.4857	-0.0052
55								
56	2	2	0	1	1	1	16850.6374	-0.0076
57								
58	12	5	7	12	4	8	13861.7169	-0.0008
59								
60								

Table S2: Fitted microwave transitions of the isotopomer of the G₁CM/ G_rMC conformer of butan-2,3-diol with deuteration at the proton donor hydroxyl group.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1	0	1	1	0	0	0	1	5145.6937	-0.0079
1	0	1	0	0	0	0	1	5145.6191	0.0053
1	0	1	2	0	0	0	1	5145.6652	-0.0013
1	1	0	1	0	0	0	1	7330.2081	-0.0026
1	1	0	2	0	0	0	1	7330.2462	0.0029
1	1	1	0	0	0	0	1	6810.4087	0.0057
1	1	1	1	0	0	0	1	6810.3858	-0.0109
1	1	1	2	0	0	0	1	6810.3985	-0.0007
2	0	2	1	1	0	1	1	10187.3653	0.0015
2	0	2	1	1	0	1	0	10187.4528	0.0011
2	0	2	2	1	0	1	1	10187.4268	-0.0007
2	0	2	3	1	0	1	2	10187.4174	-0.0043
2	1	1	1	1	1	0	0	10811.0980	-0.0037
2	1	1	2	1	1	0	1	10811.1974	0.0099
2	1	1	3	1	1	0	2	10811.1526	0.0004
2	1	2	1	1	0	1	1	11436.1619	-0.0001
2	1	2	2	1	0	1	2	11436.2476	-0.0039
2	1	2	1	1	0	1	0	11436.2476	-0.0022
2	1	2	2	1	0	1	1	11436.2142	-0.0022
2	1	2	3	1	0	1	2	11436.2142	-0.0023
2	1	1	1	1	0	1	0	12995.7823	0.0021
2	1	1	2	1	0	1	1	12995.6941	-0.0024
2	1	1	3	1	0	1	2	12995.7325	0.0035
2	2	1	1	1	1	0	1	15805.4072	0.0021
2	2	1	2	1	1	0	2	15805.3191	0.0052
2	2	1	2	1	1	0	1	15805.3492	0.0026
2	2	1	3	1	1	0	2	15805.3492	-0.0024

	J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1										
2										
3										
4										
5	3	2	1	2	2	2	0	1	15827.7127	-0.0006
6	3	2	1	3	2	2	0	2	15827.7583	-0.0081
7										
8	3	2	1	4	2	2	0	3	15827.7398	0.0065
9										
10	2	1	2	1	1	1	1	0	9771.4666	0.0059
11										
12	2	1	2	3	1	1	1	2	9771.4834	-0.0004
13										
14	3	1	3	3	2	1	2	3	14597.6997	0.0029
15	3	1	3	2	2	1	2	1	14597.6471	-0.0057
16										
17	3	1	3	3	2	1	2	2	14597.6640	0.0022
18										
19	3	1	3	4	2	1	2	3	14597.6471	-0.0028
20										
21	3	0	3	2	2	0	2	2	15046.0669	-0.0016
22										
23	3	0	3	3	2	0	2	3	15046.1702	-0.0024
24										
25	3	0	3	2	2	0	2	1	15046.1335	0.0014
26										
27	3	0	3	3	2	0	2	2	15046.1335	0.0018
28										
29	3	0	3	4	2	0	2	3	15046.1235	-0.0023
30										
31	3	2	2	2	2	2	1	2	15436.9742	-0.0023
32										
33	3	2	2	3	2	2	1	3	15436.9429	0.0041
34										
35	3	2	2	2	2	2	1	1	15436.9118	-0.0061
36										
37	3	2	2	3	2	2	1	2	15436.9742	-0.0023
38										
39	3	2	2	4	2	2	1	3	15436.9429	0.0041
40										
41	3	1	3	2	2	0	2	1	15846.4625	0.0115
42										
43	3	1	3	3	2	0	2	2	15846.4445	-0.0063
44										
45	3	1	3	4	2	0	2	3	15846.4445	-0.0002
46										
47	3	1	2	2	2	1	1	1	16143.8266	0.0026
48										
49	3	1	2	3	2	1	1	2	16143.8394	0.0010
50										
51	3	1	2	4	2	1	1	3	16143.8266	-0.0007
52										
53	2	2	1	2	1	1	1	1	16325.1537	-0.0069
54										
55	2	2	1	3	1	1	1	2	16325.1957	0.0000
56										
57	2	2	0	2	1	1	1	1	16429.0548	0.0008
58										
59	2	2	0	3	1	1	1	2	16429.0911	-0.0013
60										

Table S3: Fitted microwave transitions of the isotopomer of the G₁CM/ G_rMC conformer of butan-2,3-diol with deuteration at the proton acceptor hydroxyl group.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1	0	1	1	0	0	0	1	5024.2599	0.0035
1	0	1	0	0	0	0	1	5024.0937	0.0019
1	0	1	2	0	0	0	1	5024.1903	-0.0003
1	1	0	1	0	0	0	1	7375.0210	-0.0014
1	1	0	0	0	0	0	1	7375.1268	0.0057
1	1	0	2	0	0	0	1	7375.0603	-0.0016
1	1	1	0	0	0	0	1	6907.7024	-0.0040
1	1	1	1	0	0	0	1	6907.6459	0.0055
1	1	1	2	0	0	0	1	6907.6670	0.0002
2	1	2	2	1	1	1	1	9581.0579	0.0020
2	1	2	3	1	1	1	2	9580.9867	-0.0006
2	0	2	1	1	0	1	0	9971.7398	-0.0098
2	0	2	3	1	0	1	2	9971.6915	0.0014
2	1	1	2	1	1	0	1	10515.8264	-0.0003
2	1	1	3	1	1	0	2	10515.7589	-0.0000
2	1	2	1	1	0	1	1	11464.3712	-0.0029
2	1	2	2	1	0	1	2	11464.5020	-0.0037
2	1	2	1	1	0	1	0	11464.5460	0.0072
2	1	2	3	1	0	1	2	11464.4648	0.0013
2	1	1	1	1	0	1	1	12866.5507	0.0020
2	1	1	1	1	0	1	0	12866.7153	0.0020
2	1	1	2	1	0	1	1	12866.5918	-0.0009
2	1	1	3	1	0	1	2	12866.6294	-0.0009
3	0	3	3	2	1	2	2	13285.7975	0.0044
3	0	3	4	2	1	2	3	13285.7608	-0.0007

	J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1										
2										
3										
4										
5	3	1	3	3	2	1	2	3	14326.9750	-0.0008
6	3	1	3	3	2	1	2	2	14326.9387	0.0052
7										
8	3	1	3	4	2	1	2	3	14326.9084	-0.0051
9										
10	3	0	3	2	2	0	2	2	14778.4368	-0.0014
11										
12	3	0	3	3	2	0	2	2	14778.5352	-0.0027
13										
14	3	0	3	4	2	0	2	3	14778.5352	0.0004
15										
16	3	2	2	3	2	2	1	2	15072.5994	-0.0011
17										
18	3	2	2	4	2	2	1	3	15072.5301	0.0002
19										
20	2	2	1	2	1	1	0	2	16166.0963	0.0023
21										
22	2	2	1	3	1	1	0	2	16166.1652	0.0006
23										
24	3	2	1	2	2	2	0	1	15366.4752	-0.0012
25										
26	3	2	1	3	2	2	0	2	15366.5848	-0.0008
27										
28	3	2	1	4	2	2	0	3	15366.5179	0.0024
29										
30	3	1	3	3	2	0	2	3	15819.7481	-0.0010
31										
32	3	1	3	2	2	0	2	1	15819.7090	0.0046
33										
34	3	1	3	3	2	0	2	2	15819.6798	0.0015
35										
36	3	1	3	4	2	0	2	3	15819.6798	-0.0071
37										
38	2	2	0	2	1	1	0	1	16242.8165	-0.0046
39										
40	2	2	0	3	1	1	0	2	16242.8546	0.0022
41										
42	2	2	0	1	1	1	1	1	16710.3116	-0.0017
43										
44										
45										
46										
47										
48										
49										
50										
51										
52										
53										
54										
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56										
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Microwave transitions of homochiral butan-2,3-diol.

Table S4: Fitted microwave transitions of the parent isotopomer of the GtCM conformer of butan-2,3-diol.

J'	K_a'	K_c'	v'^a	J''	K_a''	K_c''	v''^a	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
3	1	2	0	3	0	3	0	6748.4595	0.0004
3	1	2	1	3	0	3	1	6747.9610	-0.0004
5	3	2	1	5	2	3	1	7323.6892	0.0005
5	3	2	0	5	2	3	0	7324.1719	0.0007
4	3	1	0	4	2	2	0	7752.8982	-0.0003
4	3	1	1	4	2	2	1	7754.0804	0.0006
2	2	1	0	2	1	2	0	7764.7910	-0.0001
2	2	1	1	2	1	2	1	7764.1571	0.0002
2	0	2	0	1	1	1	0	8205.2069	0.0013
2	0	2	1	1	1	1	1	8207.1127	0.0019
3	3	0	0	3	2	1	0	8778.6604	0.0002
3	3	0	1	3	2	1	1	8779.3344	0.0002
3	2	2	1	3	1	3	1	9614.4980	-0.0001
3	2	2	0	3	1	3	0	9615.5415	0.0001
4	1	3	1	4	0	4	1	10297.9331	-0.0012
4	1	3	0	4	0	4	0	10299.0309	0.0001
3	3	1	0	3	2	2	0	10448.1415	-0.0011
3	3	1	1	3	2	2	1	10449.1759	-0.0008
2	1	2	0	1	0	1	0	10535.0964	-0.0012
2	1	2	1	1	0	1	1	10535.9336	-0.0002
3	1	2	1	2	2	1	1	11970.6411	-0.0000
3	1	2	0	2	2	1	0	11971.0377	0.0004

	J'	K_a'	K_c'	v'^a	J''	K_a''	K_c''	v''^a	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1										
2										
3										
4	4	2	3	0	4	0	4	1	11157.3701	0.0006
5										
6	4	2	3	1	4	1	4	1	12052.2026	-0.0004
7										
8	4	2	3	0	4	1	4	0	12053.7252	-0.0003
9										
10	3	1	3	0	2	1	2	1	12315.6267	-0.0005
11										
12	3	0	3	0	2	0	2	1	12801.9343	-0.0010
13										
14	3	0	3	1	2	1	2	1	12986.8360	-0.0007
15										
16	3	0	3	0	2	1	2	0	12987.3696	0.0003
17										
18	4	2	3	1	4	0	4	0	13179.7818	-0.0005
19										
20	5	1	4	0	5	0	5	0	14098.4468	-0.0010
21										
22	5	1	4	1	5	0	5	1	14102.3872	-0.0010
23										
24	3	1	3	1	2	0	2	1	14154.8291	-0.0006
25										
26	3	1	3	0	2	0	2	0	14155.6227	-0.0005
27										
28	3	2	2	0	2	2	1	1	14167.0120	0.0004
29										
30	3	1	3	1	2	1	2	0	14340.2638	0.0001
31										
32	3	0	3	1	2	0	2	0	14826.8324	-0.0003
33										
34	2	2	0	0	1	1	0	1	15111.1885	-0.0000
35										
36	3	1	2	0	2	1	1	1	15466.3483	0.0003
37										
38	3	2	1	0	2	2	0	1	15531.3024	0.0003
39										
40	2	2	1	0	1	1	0	0	15711.0931	-0.0006
41										
42	2	2	1	1	1	1	0	1	15712.0010	0.0001
43										
44	2	2	1	0	1	1	1	1	15786.4683	0.0004
45										
46	3	2	2	1	2	2	1	0	16189.9708	0.0001
47										
48	4	1	4	0	3	1	3	1	16457.0573	0.0001
49										
50	4	0	4	0	3	0	3	1	16682.2110	-0.0002
51										
52	2	2	0	1	1	1	0	0	17134.3878	-0.0006
53										
54	2	2	0	0	1	1	1	0	17208.5453	-0.0008
55										
56	2	2	0	1	1	1	1	1	17209.7617	-0.0010
57										
58	4	0	4	0	3	1	3	0	17353.4213	0.0006
59										
60	4	0	4	1	3	1	3	1	17353.4122	-0.0011
	3	1	2	1	2	1	1	0	17489.7610	0.0002

	J'	K_a'	K_c'	v'^a	J''	K_a''	K_c''	v''^a	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1										
2										
3										
4										
5	3	2	1	1	2	2	0	0	17554.7657	0.0006
6	2	2	1	1	1	1	1	0	17809.3585	0.0000
7										
8	4	1	4	1	3	0	3	1	17809.7897	-0.0008
9										
10	4	1	4	0	3	0	3	0	17809.9525	0.0008
11										
12	4	1	3	0	3	2	2	0	18036.9099	-0.0002
13										
14	4	1	3	1	3	2	2	1	18036.8502	0.0007
15										
16	4	1	4	1	3	1	3	0	18481.0001	0.0001
17										
18	4	0	4	1	3	0	3	0	18706.3078	0.0001
19	6	4	2	1	6	3	3	1	10609.5591	-0.0001
20										
21	6	4	2	0	6	3	3	0	10605.3428	-0.0013
22										
23	4	4	1	0	4	3	2	0	13826.3032	-0.0005
24										
25	4	4	1	1	4	3	2	1	13825.9295	-0.0006
26										
27	5	4	2	0	5	3	3	0	14069.3802	0.0004
28										
29	5	4	2	1	5	3	3	1	14071.0964	0.0011
30										
31	5	2	4	0	5	1	5	0	14930.0083	0.0004
32										
33	5	2	4	1	5	1	5	1	14933.6355	0.0002
34										
35	4	4	0	0	4	3	1	0	13177.3891	0.0002
36										
37	4	4	0	1	4	3	1	1	13176.7838	0.0001
38										
39	2	1	1	0	1	0	1	1	12780.9716	0.0006
40										
41	2	1	1	1	1	0	1	0	14804.5793	0.0013
42										
43	5	4	1	1	5	3	3	0	15270.5920	0.0005
44										
45	5	4	1	0	5	3	3	1	13248.6144	0.0008
46										
47	5	3	3	1	5	2	4	1	12940.1138	0.0010
48										
49	5	3	3	0	5	2	4	0	12945.6141	0.0008
50										
51	5	4	1	1	5	3	2	1	12043.4786	0.0005
52										
53	5	4	1	0	5	3	2	0	12042.3641	0.0001
54										
55	5	4	2	1	5	3	2	0	12864.8464	0.0006
56										
57	5	5	0	1	5	4	1	1	17397.3177	0.0003
58										
59	5	5	0	0	5	4	1	0	17397.0725	0.0011
60										
61	5	5	1	0	5	4	2	0	17582.1092	-0.0005

	J'	K_a'	K_c'	v'^a	J''	K_a''	K_c''	v''^a	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1										
2										
3										
4	5	5	1	1	5	4	2	1	17582.4500	-0.0007
5										
6	7	4	4	1	7	3	5	1	16096.2741	0.0002
7										
8	7	4	4	0	7	3	5	0	16094.9755	0.0009
9										
10	8	5	4	1	8	4	5	1	18056.2262	-0.0017
11										
12	8	5	4	0	8	4	5	0	18041.4574	0.0009
13										
14	8	5	3	1	8	4	4	1	13522.2503	-0.0000
15										
16	8	5	3	0	8	4	4	0	13508.8206	0.0000
17										
18	8	5	3	0	8	4	5	1	17953.2310	-0.0011
19										
20	6	3	4	1	6	1	5	0	16484.7566	0.0002
21										
22	6	3	4	0	6	1	5	1	14463.0537	0.0015
23										
24	2	1	1	1	1	1	0	0	12215.7828	-0.0002
25										
26	2	1	1	0	1	1	0	1	10192.8810	-0.0002
27										
28	8	5	4	0	8	4	4	1	11578.2059	0.0001
29										
30	8	5	4	1	8	4	4	0	13611.8161	-0.0002

^a $v=0$ signifies the lower and $v=1$ signifies the upper tunnelling state.

Table S5: Fitted microwave transitions of the isotopomer of the GtCM conformer of butan-2,3-diol with deuteration at the proton donor hydroxyl group.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1	1	1	0	0	0	0	1	6394.096	0.0008
1	1	1	1	0	0	0	1	6394.190	-0.00148
1	1	1	2	0	0	0	1	6394.153	0.00015
1	1	0	0	0	0	0	1	7499.306	-0.00254
1	1	0	1	0	0	0	1	7499.199	0.00076
1	1	0	2	0	0	0	1	7499.243	0.00054
2	1	2	1	1	1	1	0	8930.143	0.00165
2	1	2	3	1	1	1	2	8930.111	0.00185
3	2	2	2	3	1	3	2	9343.704	0.00408
3	2	2	3	3	1	3	3	9343.623	-0.00129
3	2	2	4	3	1	3	4	9343.676	-0.00429
2	1	2	2	1	0	1	1	10306.70	-0.00113
2	1	2	3	1	0	1	2	10306.66	0.00214
3	1	3	2	2	1	2	1	13153.99	-0.00771
3	1	3	3	2	1	2	2	13154.00	0.00195
3	1	3	4	2	1	2	3	13153.99	-0.0012
3	1	2	2	2	1	1	1	16343.52	-0.00314
3	1	2	3	2	1	1	2	16343.55	0.0037
3	1	2	4	2	1	1	3	16343.53	0.00065
2	2	0	1	1	1	1	0	16823.78	0.00133
2	2	0	2	1	1	1	1	16823.64	0.00108
2	2	0	3	1	1	1	2	16823.71	-0.00078
4	0	4	4	3	0	3	3	17409.98	0.00262
4	0	4	5	3	0	3	4	17409.96	-0.00203
4	1	4	4	3	0	3	3	17497.43	0.00352
4	1	4	5	3	0	3	4	17497.40	-0.00243

Table S6: Fitted microwave transitions of the isotopomer of the GtCM conformer of butan-2,3-diol with deuteration at the proton acceptor hydroxyl group.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{obs}} - \nu_{\text{calc}}/\text{MHz}$
1	0	1	0	0	0	0	1	4928.2997	-0.0023
1	0	1	1	0	0	0	1	4928.4271	-0.0001
1	0	1	2	0	0	0	1	4928.3768	-0.0003
1	1	1	0	0	0	0	1	6446.3248	0.0006
1	1	1	1	0	0	0	1	6446.2309	-0.0008
1	1	1	2	0	0	0	1	6446.2679	-0.0008
1	1	0	2	0	0	0	1	7493.3661	0.0010
2	1	1	2	1	1	0	2	10903.8825	-0.0048
2	1	1	1	1	1	0	0	10903.8115	0.0055
2	1	1	2	1	1	0	1	10903.9006	0.0003
2	1	1	3	1	1	0	2	10903.8464	-0.0012
2	0	2	1	1	0	1	1	9471.9981	0.0009
2	0	2	2	1	0	1	2	9472.1131	-0.0012
2	0	2	1	1	0	1	0	9472.1238	0.0014
2	0	2	3	1	0	1	2	9472.0721	0.0009
2	1	2	2	1	1	1	1	8809.7094	0.0013
2	1	2	3	1	1	1	2	8809.6565	-0.0006
2	1	2	1	1	0	1	0	10327.6171	0.0010
2	1	2	3	1	0	1	2	10327.5472	-0.0015
3	1	2	3	2	1	1	2	16051.0865	0.0009
3	1	2	4	2	1	1	3	16051.0745	-0.0010
3	0	3	3	2	1	2	2	12642.5773	0.0016
3	0	3	4	2	1	2	3	12642.5522	-0.0021
4	2	3	3	4	0	4	3	11950.4214	-0.0003
4	2	3	4	4	0	4	4	11950.4040	-0.0026
4	2	3	5	4	0	4	5	11950.4214	0.0028

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Table S7. Structural coordinates of the G₁CM/ G_rMC conformer of heterochiral butan-2,3-diol derived from MP2 6-311++G** ab initio calculations (after counterpoise correction).

Atom	<i>a</i>	<i>b</i>	<i>c</i>
C	0.7022	-0.0364	-0.3224
C	1.5807	1.1338	0.0802
C	-0.6803	0.0042	0.3181
C	-1.5015	1.2213	-0.0785
O	1.3779	-1.2232	0.079
O	-1.3157	-1.2083	-0.1198
H	0.558	-0.0419	-1.4146
H	-0.5416	-0.0322	1.4084
H	-2.5189	1.1382	0.3174
H	-1.0636	2.1402	0.3203
H	-1.5636	1.2945	-1.1684
H	2.5898	0.9704	-0.3053
H	1.203	2.0755	-0.3257
H	1.6376	1.2072	1.1707
H	0.7332	-1.9326	-0.0304
H	-2.138	-1.3045	0.3692

Table S8. Structural coordinates of the G₁CM/ G_rMC conformer of homochiral butan-2,3-diol derived from MP2 6-311++G** ab initio calculations (after counterpoise correction).

Atom	<i>a</i>	<i>b</i>	<i>c</i>
C	0.7022	-0.0364	-0.3224
C	1.5807	1.1338	0.0802
C	-0.6803	0.0042	0.3181
C	-1.5015	1.2213	-0.0785
O	1.3779	-1.2232	0.079
O	-1.3157	-1.2083	-0.1198
H	0.558	-0.0419	-1.4146
H	-0.5416	-0.0322	1.4084
H	-2.5189	1.1382	0.3174
H	-1.0636	2.1402	0.3203
H	-1.5636	1.2945	-1.1684
H	2.5898	0.9704	-0.3053
H	1.203	2.0755	-0.3257
H	1.6376	1.2072	1.1707
H	0.7332	-1.9326	-0.0304
H	-2.138	-1.3045	0.3692