Carbon-13 Chemical Shift Tensors in *meso*-Erythritol, Measuring OH Dihedral Angles

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Abstract: The carbon-13 chemical shift tensors of *meso*-erythritol (1,2,3,4-butanetetrol, $C_4H_{10}O_4$) were measured from two one-dimensional NMR spectra taken with the applied field perpendicular to the (110) and (101) crystal faces. *Ab initio* gauge invariant atomic orbital (GIAO) chemical shielding computations were used to assign the spectral lines to the carbons in the erythritol molecule and the molecules in the unit cell. The conformational disorder in erythritol was treated by taking the weighted average of the GIAO results for the two different conformations. The icosahedral shieldings computed with various weighting factors were then fitted to the experimental icosahedral shifts. Using the neutron diffraction structure the GIAO computations produced shieldings which correlate to the experimental chemical shift tensors with a 1.53 ppm standard deviation. The weighting factor which produced the best fit agrees with the occupancy percentage determined by neutron diffraction. GIAO computations were done for hypothetical O–H bond conformations in erythritol to investigate the effect of the hydroxyl dihedral angles on carbon-13 tensors.

I. Introduction

Carbon-13 NMR spectroscopy is widely used to obtain structural and dynamical information in crystalline solids, where it has been found that ^{13}C chemical shift tensors are very sensitive to molecular conformations.[1–4] The chemical shift interaction is described by a second rank tensor, which can be specified with three principal values and the orientation of the principal axes system. Single crystal studies are necessary to measure the full chemical shift tensor, including its orientation. A number of techniques have been used to study single crystal chemical shifts, including 1D rotation patterns[5] and 2D chemical shift correlation spectroscopy.[6,7] The 2D technique has greatly extended the single crystal method to samples with a large number of carbons, and it has recently been applied to chemical shift tensors in carbohydrates[4] and methyl glycosides.[8,9] The 2D correlation method normally requires taking six 2D spectra, which can be time consuming for molecules such as *meso*-erythritol with long relaxation times. In this study the complete chemical shift tensors in *meso*-erythritol are obtained with an approach which exploits several unique properties specific to this crystal in conjunction with *ab initio* gauge invariant atomic orbital (GIAO) computations.[10,11]

meso-Erythritol crystals have several characteristics which make them both interesting and difficult to study. The neutron diffraction study of erythritol shows that the molecules in the crystal have conformational disorder about the C(2)–O(2) bond.[12] At 22.6 K, the H[O(2)] atom occupies site **A** 85% of the time and site **B** 15% of the time. Sets of four erythritol molecules in the two conformations are shown in Figure 1, where similar conformations are shown for both the inversion-symmetry-related H[O(2)] and H[O(3)] atoms. Figure 1 also reveals the interesting *homodromic* cycle[13] of the H[O(2)]–O(2) hydrogen bonds for both the **A** and **B** conformations. Because the hydrogen bonding pattern forms a closed loop, it is possible that the two conformations interchange either by a concerted flip-flop[14] conformational dihedral rotation or by a configurational intermolecular exchange with H[O(2)] jumping accross a hydrogen bond energy barrier, i.e. breaking one hydrogen bond and forming another. At room temperature, the motion between the two conformations is sufficiently fast to average the ^{13}C chemical shifts, but the motion is apparently too slow to effectively relax the spin system. The resultant 30-min proton relaxation time makes it impractical to obtain six 2D spectra. But fortunately, erythritol has symmetry properties which make it possible to determine the ^{13}C chemical shift tensors from only two 1D spectra. Erythritol crystals have a tetragonal lattice with the $I4_1/a$ space group, with eight molecules per unit cell arranged in four unique molecular orientations.[12] Furthermore, an inversion center is located at the midpoint of the C(2)–C(3) bond, and therefore C(2) and C(3) have identical tensors, as do C(1) and C(4). The two unique tensors in each of the four molecular orientations thus result in a maximum of eight spectral lines, a number accessible to 1D spectroscopy.

The four molecular orientations in the unit cell are related by the 4-fold rotational symmetry around the crystal *c* axis. Thus, a 1D spectrum of an erythritol single crystal, taken at an arbitrary field direction relative to the crystal, can reveal up to four different chemical shifts for the four magnetic field directions relative to the molecular frame. Two 1D spectra can

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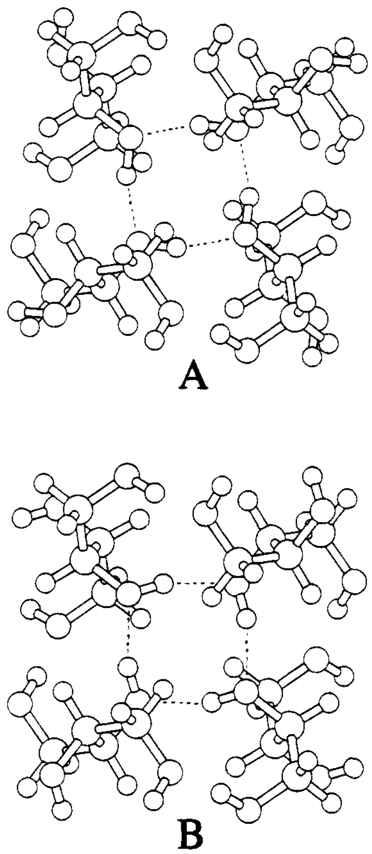

Figure 1. *meso*-Erythritol molecules in their **A** and **B** conformations; the conformations differ only by the positions of H[O(2)] and H[O(3)]. The hydrogen bonding between H[O(2)] and O(2) is shown with dashed lines.

thus provide up to eight different shifts for each chemically equivalent carbon. Symmetry may cause some shifts to be degenerate in certain field directions, but when the two 1D spectra reveal at least six measurable shifts per carbon the tensors may be determined from the positions of the peaks. The erythritol single crystal used in this study had remarkably well developed and identifiable {110} and {101} faces making it possible to unambiguously orient the crystal from its morphology. Fortunately, the necessary six independent frequencies required to obtain the shift tensors of erythritol are available from two 1D spectra with the magnetic field oriented perpendicular to the (110) and (101) crystal faces.

II. Theory

The experimental shift, δ, for a given carbon peak with a specified magnetic field direction is a function of the six measurable components of the symmetric chemical shift tensor, and can be expressed as

$$\delta = (C_x \quad C_y \quad C_z)\begin{bmatrix} \delta_{xx} & \delta_{xy} & \delta_{zx} \\ \delta_{xy} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{yz} & \delta_{zz} \end{bmatrix}\begin{pmatrix} C_x \\ C_y \\ C_z \end{pmatrix} = C_x^2\delta_{xx} + C_y^2\delta_{yy} + C_z^2\delta_{zz} + 2C_xC_y\delta_{xy} + 2C_yC_z\delta_{yz} + 2C_zC_x\delta_{zx} \quad (1)$$

where C_x, C_y, and C_z are the direction cosines of the applied magnetic field with respect to the three Cartesian axes. Because the orientations of the four molecules in the unit cell are related by a 4-fold axis parallel to the crystal *c* axis, the related tensors, in an *xyz* frame coincident with the orthogonal *abc* crystal frame, are given by

$$\underset{\textbf{I}}{\begin{bmatrix} +\delta_{xx} & +\delta_{xy} & +\delta_{zx} \\ +\delta_{xy} & +\delta_{yy} & +\delta_{yz} \\ +\delta_{zx} & +\delta_{yz} & +\delta_{zz} \end{bmatrix}} \quad \underset{\textbf{II}}{\begin{bmatrix} +\delta_{xx} & +\delta_{xy} & -\delta_{zx} \\ +\delta_{xy} & +\delta_{yy} & -\delta_{yz} \\ -\delta_{zx} & -\delta_{yz} & +\delta_{zz} \end{bmatrix}} \quad (2)$$

$$\underset{\textbf{III}}{\begin{bmatrix} +\delta_{yy} & -\delta_{xy} & -\delta_{yz} \\ -\delta_{xy} & +\delta_{xx} & +\delta_{zx} \\ -\delta_{yz} & +\delta_{zx} & +\delta_{zz} \end{bmatrix}} \quad \underset{\textbf{IV}}{\begin{bmatrix} +\delta_{yy} & -\delta_{xy} & +\delta_{yz} \\ -\delta_{xy} & +\delta_{xx} & -\delta_{zx} \\ +\delta_{yz} & -\delta_{zx} & +\delta_{zz} \end{bmatrix}}$$

where the **I**, **II**, **III**, and **IV** labels refer to the four molecular orientations in the unit cell. When the field direction is perpendicular to the (110) crystal face, the direction cosines are $C_x = C_y = 1/\sqrt{2}$, $C_z = 0$, and the chemical shifts for each carbon are

$$\delta_{[110]}{}^{\mathrm{I}} = \delta_{[110]}{}^{\mathrm{II}} = 0.5\delta_{xx} + 0.5\delta_{yy} + \delta_{xy} \quad (3)$$

$$\delta_{[110]}{}^{\mathrm{III}} = \delta_{[110]}{}^{\mathrm{IV}} = 0.5\delta_{xx} + 0.5\delta_{yy} - \delta_{xy} \quad (4)$$

Thus, only two peaks for C(1,4) and two peaks for C(2,3) appear at this field direction. When the field direction is perpendicular to the (101) crystal face, the direction cosines calculated from the unit cell dimensions are $C_x = 0.4688$, $C_y = 0$, $C_z = 0.8833$, and the shifts for each carbon are

$$\delta_{[101]}{}^{\mathrm{I}} = 0.2198\delta_{xx} + 0.7802\delta_{zz} + 0.8282\delta_{zx} \quad (5)$$

$$\delta_{[101]}{}^{\mathrm{II}} = 0.2198\delta_{xx} + 0.7802\delta_{zz} - 0.8282\delta_{zx} \quad (6)$$

$$\delta_{[101]}{}^{\mathrm{III}} = 0.2198\delta_{yy} + 0.7802\delta_{zz} - 0.8282\delta_{yz} \quad (7)$$

$$\delta_{[101]}{}^{\mathrm{IV}} = 0.2198\delta_{yy} + 0.7802\delta_{zz} + 0.8282\delta_{yz} \quad (8)$$

Thus, four peaks for C(1,4) and four peaks for C(2,3) appear at this field direction. Once the six experimental shifts for each carbon are obtained, eqs 3–8 constitute six linear equations which can be solved for the required six tensor components at that carbon.

In order to obtain the shifts in eqs 3–8 it is first necessary to identify which carbon in the unit cell gives rise to each line in the two spectra. Since the spectra themselves provide no hint of these assignments, additional independent information is necessary. By employing GIAO computations to approximate the two unique tensors, theoretical shifts at the specified field directions can be computed for the two sets of four congruent tensors and the results used to assign the experimental lines. Extensive experience in this laboratory with GIAO computations on carbohydrates[4] and methyl glycosides[8] with the Dunning D95 basis set has shown that these computations produce shieldings which correlate to experimental shifts within ±3 ppm. The GIAO computations require nuclear coordinates, and these are provided by the neutron diffraction study.[12] The neutron study found the respective **A** and **B** conformations for the erythritol molecule to have 85% and 15% occupancy percentages at 22.6 K. Boltzmann statistics yield a 78 cal/mol energy difference between the **A** and **B** conformations, and occupancy percentages of 53% and 47%, respectively, at ambient temperature. The results of the chemical shielding computations for each conformation are thus combined with 53% and 47% weighting factors to obtain the average chemical shift tensors as the

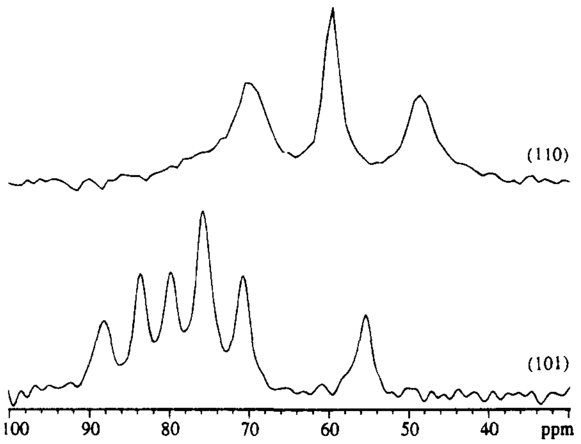

Figure 2. Experimental spectra of the erythritol single crystal with the field perpendicular to the (110) face and the (101) face.

hydrogens H[O(2)] and H[O(3)] move between their **A** and **B** conformations. These simulated tensors are then employed to compute shifts which are used to assign the experimental lines at the specified field directions.

III. Experimental Section

meso-Erythritol obtained from Pfanstiehl Laboratories, Inc. was used without further purification. A beautiful single crystal of volume 0.5 cm^3 with remarkably well-developed {110} and {101} faces was obtained by slow solvent evaporation from a saturated 95% ethanol solution.

Two 1D spectra of erythritol were obtained on a modified Varian VXR-200 instrument operating at 50.309 MHz for carbon and 200.06 MHz for protons using a home-built probe. The crystal was first mounted by gluing its (110) face to a 5-mm glass rod whose end was ground flat perpendicular to the rod axis. It is estimated that the rod axis was perpendicular to the (110) crystal face to within ±2°. The rod axis was then aligned parallel to the field in the magnet. The same procedure was repeated for the (101) face. A standard cross-polarization pulse sequence was used with a 45-kHz decoupling amplitude and a 1-ms contact time. Sixty four scans with a 40-min recycle delay were taken for each spectrum. The spectra were referenced externally to TMS by replacing the single-crystal sample with a vial of TMS.

The erythritol carbon chemical shielding tensors were computed from the neutron diffraction structure[12] using the GIAO chemical shielding method with the Dunning D95 basis set as implemented in the TEXAS program[11] run on an IBM RS 6000 POWERstation 370.

IV. Results

The spectra taken with the field direction perpendicular to crystal faces (110) and (101) are shown in Figure 2. Three of the four peaks in the (110) spectra are resolved, as are six of the eight peaks in the (101) spectra.

The chemical shielding tensors for erythritol were computed for both the **A** and **B** conformations shown in Figure 1. The results of the two shielding computations for both H[O(2)] and H[O(3)] in the **A** positions and for both in the **B** positions were averaged with 53% and 47% weighting factors respectively, and then converted to shifts from TMS with an empirical value of 208 ppm for the shielding of TMS relative to the bare nucleus.[8] The computed results at the two experimental field directions are given in parentheses in Table 1 for the two independent tensors in the four molecular orientations designated by Roman numerals. The experimental shifts, assigned to the carbons and molecules by their correspondence to the computed shifts, are also given in Table 1. Note that these assignments are based only on the order of the lines, so that uncertainties in the 208-ppm value used to convert shielding to shift cannot influence the peak designations. The assignments indicate that the peak with the highest shift at 70.2 ppm in the (110) spectrum contains two resonances, while the tallest peak at 75.8 ppm in the (101) spectrum includes three overlapping resonances.

Table 1. The Experimental and Theoretical Chemical Shifts (in parentheses) of Erythritol at Two Different Field Directions

	chemical shift							
field direction	C(1) and C(4)				C(2) and C(3)			
	I	II	III	IV	I	II	III	IV
$\perp$ to (110)	59.3	59.3	48.4	48.4	70.2	70.2	70.2	70.2
	(59.6)	(59.6)	(51.1)	(51.1)	(69.4)	(69.4)	(69.4)	(69.4)
$\perp$ to (101)	75.8	70.8	75.8	88.2	79.9	75.8	83.7	55.4
	(74.4)	(67.9)	(73.4)	(85.3)	(80.1)	(73.5)	(82.6)	(53.7)

Table 2. The Experimental ^{13}C Chemical Shift Tensors of Erythritol in the Crystal Frame (in ppm) from TMS

carbon	δ_{xx}	δ_{yy}	δ_{zz}	δ_{xy}	δ_{yz}	δ_{zx}
C(1) and C(4)	33.9	73.8	84.3	5.4	7.5	3.1
C(2) and C(3)	89.1	51.3	74.7	-0.0	-17.1	2.5

Table 3. The Experimental ^{13}C Principal Values and Isotropic Shifts of Erythritol (in ppm) from TMS

carbon	δ_{11}	δ_{22}	δ_{33}	δ_{iso}
C(1) and C(4)	88.7	70.2	33.1	64.0
C(2) and C(3)	89.9	82.9	42.3	71.7

Table 4. Distances (in ppm) between Chemical Shielding Tensors for C(1) and C(2) (in-parentheses) Calculated with H[O(2)] and H[O(3)] in all Combinations of Their **A** and **B** Positions

	AA[a]	**AB**	**BA**
AB	0.82 (0.73)		
BA	1.51 (3.94)	1.87 (4.19)	
BB	1.60 (3.79)	1.55 (3.92)	0.85 (0.78)

[a] The first letter gives the position of H[O(2)] and the second letter the position of H[O(3)]; thus **AB** means H[O(2)] is in position **A** and H[O(3)] is in position **B**.

The components of the Cartesian representation of the erythritol tensors in the crystal frame obtained with eqs 3-8 are given in Table 2, and their principal values and isotropic shifts are given in Table 3. The single-crystal isotropic shifts of 64.0 ppm for C(1) and C(4) and 71.7 ppm for C(2) and C(3) compare to values of 62.0 and 70.5 ppm, respectively, obtained from a CP/MAS spectrum referenced to hexamethylbenzene.

V. Discussion

Full chemical shift tensors specified by six numbers may be compared by computing the distance between them.[15] An example of such a comparison is given in Table 4 which gives the distances in ppm among chemical shielding tensors of erythritol computed with H[O(2)] and H[O(3)] in different combinations of the **A** and **B** positions.

The chemical shielding tensors were computed for erythritol in both the **A** and **B** conformations determined by the diffraction study.[12] These computed results were then combined using the 53−47% thermal weighting factors to produce a composite tensor corresponding to the rapid-exchange limit for erythritol at room temperature. The resulting correlation plot for erythritol is shown in Figure 3; the intercept is 205 ppm and the slope is −0.96 (the minus sign results from the reversed scale on the shift axis), and the rms residual is 1.40 ppm. Allowing for the two fitting parameters the standard deviation of the fit to the 12 points in Figure 3 is $[12/(12 - 2)]^{1/2} \times 1.40$ ppm = 1.53 ppm.

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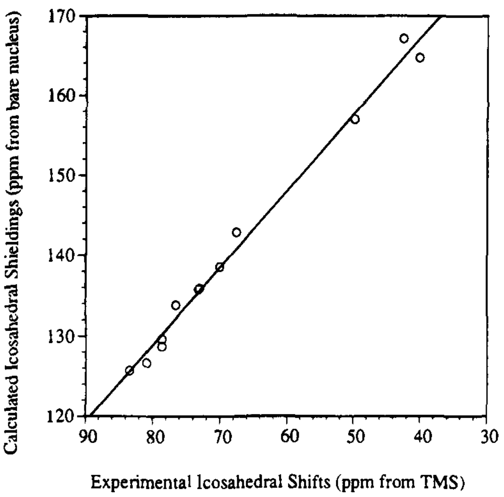

Figure 3. Icosahedral shieldings computed with 53–47% occupancy percentages for **A** and **B** conformations versus experimental icosahedral shifts.

The plot of theoretical and experimental tensors, in Figure 3, provides a way to visualize the correlation between the predicted and experimental shifts.[15] The statistical measures of the correlation are obtained by fitting the points with a straight line. The rms residual of the straight-line fit gives the minimum rms average distance between the experimental shift tensors and the computed shielding tensors adjusted with an additive offset (the intercept) and a multiplicative factor (the slope).[15] Fitting computed shieldings to experimental shifts in this way is designed to reveal the extent to which the computations reflect the anisotropy in the chemical shifts, while avoiding experimental referencing problems and some of the theoretical difficulties inherent in referencing and scaling the shieldings. This technique is particularly valuable when using shielding computations to make assignments of experimental tensors.[8] The use of an adjustable intercept and slope is inappropriate for assaying the absolute accuracy of either computed shieldings or measured shifts.

Straight-line fits of composite shielding tensors using various weighting factors were also made, and the resulting rms average distances are plotted in Figure 4 as a function of the **A** conformation weighting factor. The rms average distance for the 100% **A** conformation computation is 1.81 ppm, while that for the 100% **B** conformation is 2.15 ppm. The minimum rms distance is found at an **A** conformation weighting factor of 59%, where the distance reaches 1.39 ppm. Because the curve of Figure 4 is relatively flat between 50% and 65%, the weighting factor minimum agrees satisfactorily with the 53% occupancy percentage calculated from the neutron diffraction results using Boltzmann statistics to adjust for the different sample temperatures. The curve in Figure 4 illustrates how composite chemical shift tensors differ distinctly from either the **A** or **B** tensors. This result confirms that the positions of the H[O(2)] and H[O(3)] protons, even though not directly bonded to the shielded carbons, influence the carbon chemical shift tensor. Presumably the proton positions impact the shifts through their influence on the orientation of the electron free pair on the connecting oxygen atom.

The GIAO computations for the above analysis were all done on erythritol molecules with both H[O(2)] and H[O(3)] in the same conformation, either **A** or **B**. The data of Table 4 indicate that the C(2) tensor depends primarily on the conformation of H[O(2)] and is relatively insensitive (*ca.* 0.7 ppm) to the conformation of H[O(3)]. Thus, it is unnecessary to include mixed conformations in the analysis. Consequently, the chemical shift tensor data is unable to address the question of whether the H[O(2)] conformation correlates with the H[O(3)] conformation.

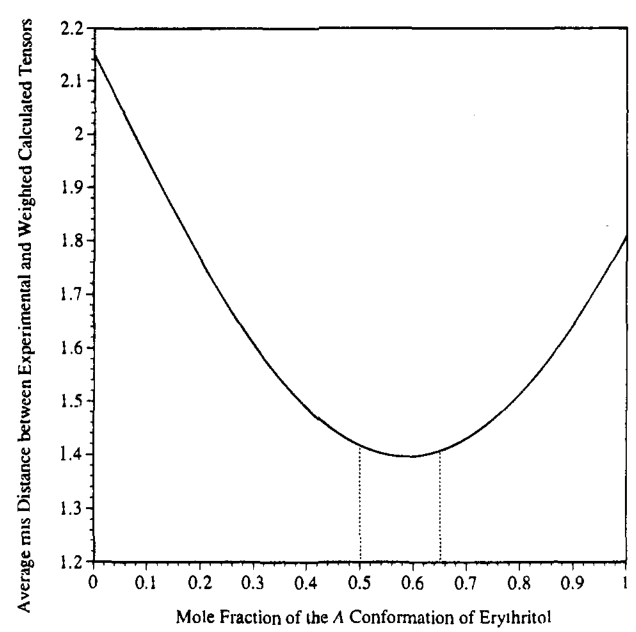

Figure 4. The rms distance between the experimental chemical shifts and the computed shieldings as a function of the occupancy percentage of the **A** configuration of the erythritol molecule.

The GIAO computations for the assignment of the lines in the 1D spectra were weighted with the 53% occupancy percentage computed from the neutron diffraction data with Boltzmann statistics, even though a 59% weighting factor was found to best fit the experimental shifts. Fortunately, the line assignments are independent of this difference in weighting factors, as the predicted line frequencies have the same order for 100% **A**, 100% **B**, and all intermediate conformational weighting factors. The experimental peak positions depend on the crystal orientations relative to the field direction. Thus, the peak positions will shift if the field directions are slightly off the crystal face perpendiculars. To determine whether such mounting errors could change the peak assignments, chemical shifts were calculated at field directions varying in the neighborhood of the nominal experimental field directions. Hypothetical mounting errors of up to 5° had no effect on the order of the resolved lines, indicating that the assignments are secure given the estimated ±2° mounting error. These same computations show that, on average, the lines move by about 0.3 ppm per degree. Therefore, from the 2° mounting error, the tensor results are estimated to have errors on the order of ±0.6 ppm.

The integrals of the lines in the spectra of Figure 2 deviate from the number of carbons involved, presumably because of the different efficiencies of cross polarization and decoupling for each type of carbon nucleus. These limitations are especially noticeable in $-CH_2$ carbons. It is difficult to establish from the spectral intensities alone how many resonances are represented by each line, and this is another reason that the GIAO computations were essential.

The C(1) and C(2) chemical shift tensors in erythritol are quite typical in that the principal axes are closely determined by the local symmetry defined by the directly bonded carbon and oxygen atoms. The δ_{33} principal axis in C(1) is only 4° from the C(1)–O(1) bond and the δ_{11} principal axis is 11° from the direction perpendicular to the C(2)–C(1)–O(1) plane. For C(2), the δ_{33} principal axis is 7° away from the C(2)–O(2) bond and the δ_{22} principal axis is 17° from the perpendicular to the plane bisecting the attached carbons.

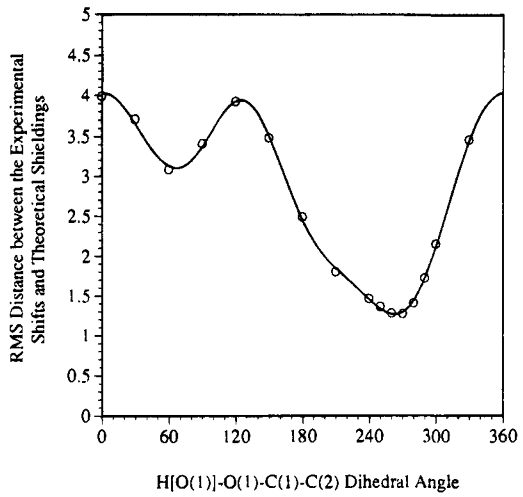

Figure 5. The rms distance between the experimental chemical shifts and the computed shieldings as a function of the H[O(1)]−O(1)−C(1)−C(2) dihedral angle.

To explore the dependence of the chemical shift tensors of erythritol on the conformation of the hydroxyl proton H[O(1)], a series of computations were performed with hypothetical H[O(1)]−O(1)−C(1)−C(2) dihedral angles in both conformations of H[O(2)]. The results were linearly combined with the 53−47% neutron diffraction ambient temperature weighting factors and then correlated by straight-line fitting to the experimental chemical shift tensors. The minimum distance between the experimental C(1) shift tensor and the computed C(1) shielding tensor as a function of the hypothetical dihedral angle is plotted in Figure 5. There is an overall minimum in the distance plot at a hypothetical dihedral angle near 270°, which is in good agreement with the 279° obtained by neutron diffraction.

In order to reveal the dependence of the shift on the exchanging H[O(2)] position, computations were done for erythritol with hypothetical values for the H[O(2)]−O(2)−C(2)−H[C(2)] dihedral angle at 10° intervals from 0° to 350°. The computed shielding tensors for all combinations of the dihedral angles were linearly combined with the 53−47% neutron diffraction weighting factors and then fitted to the experimental chemical shift tensors. Figure 6 is a two-dimensional contour plot in which one axis corresponds to the dihedral angle of H[O(2)]−O(2)−C(2)−H[C(2)] for the 53% occupied **A** conformation, and the other axis gives the 47% occupied **B** conformation dihedral angle. The contour levels represent the rms distance of the fitting between the experimental chemical shift tensors and the corresponding theoretical shielding computations for pairs of hypothetical conformations. Even though the weighting factors, 0.53 for **A** and 0.47 for **B**, differ only slightly from $^1/_2$, this small difference breaks the symmetry with respect to the diagonal in the contour plot. The results in Figure 4 indicate that neither the pure **A** conformation nor the **B** conformation correlate best with the experimental data. The global minimum with a rms distance of 0.95 ppm in Figure 6 occurs at a point where the dihedral angles of the H[O(2)]−O(2)−C(2)−H[C(2)] for the **A** and **B** conformations are 70° and 190°, respectively. These NMR results are felt to be in reasonable agreement with the diffraction results where the H[O(2)]−O(2)−C(2)−H[C(2)] dihedral angle is 39° for the **A** and 157° for the **B** conformation. It is interesting that both of these results are similar to the 60° and 180° staggered conformations expected if only the total energy of the isolated molecule is considered.

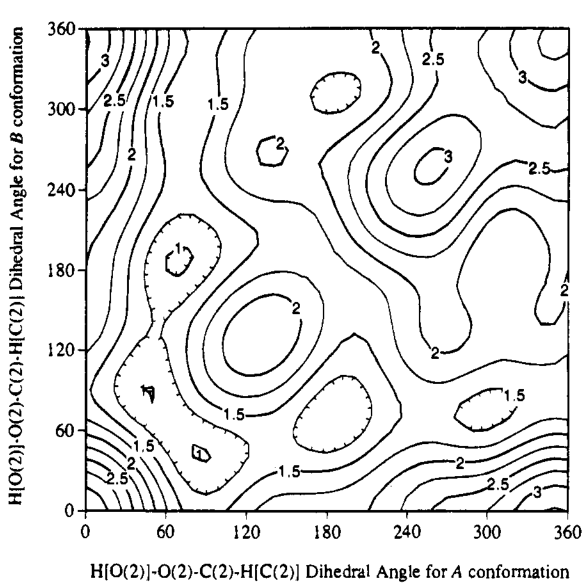

Figure 6. Two-dimensional contour plot of the rms distance between the experimental chemical shifts and the computed shieldings as a function of hypothetical H[O(2)]−O(2)−C(2)−H[C(2)] dihedral angles for both the **A** and the **B** conformations. The rms distance is for the composite tensor obtained by weighting conformation **A** and **B** tensors with the 53−47% occupancy percentages.

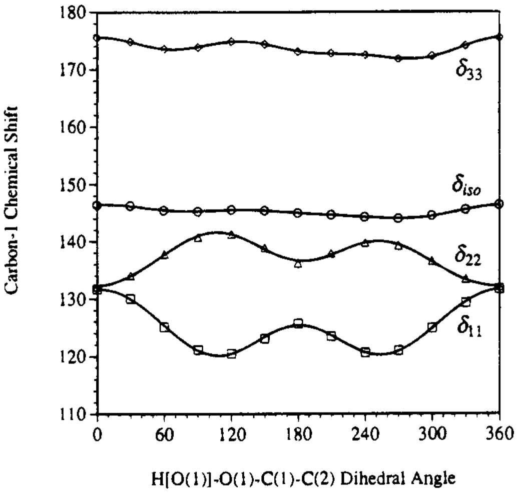

Figure 7. Principal values and isotropic chemical shieldings of C(1) as a function of the H[O(1)]−O(1)−C(1)−C(2) dihedral angle.

Intermolecular hydrogen bonding effects on the carbon-13 chemical shift have been estimated by "dressing" an erythritol molecule with small alcohol and water molecules in place of the its neighbors. These initial efforts suggest that the direct effect of hydrogen bonding on the ^{13}C shifts is only about 0.5 ppm. On the other hand, variations of 12−15 ppm are noted in the theoretical estimates of shift tensors depending on the dihedral angle. These results lead to the tentative conclusion that the primary effect of hydrogen bonding on the ^{13}C chemical shift tensor is to establish the O−H dihedral angle and that the electronic structure of the C−O bond accounts for the observed shifts. This result suggests that good shielding-shift correlations can be computed solely from the dominant intramolecular effects present in the wave function of an isolated molecule, providing it is constrained to its crystal conformation.

Computed principal values and isotropic shieldings for C(1) of erythritol as a function of hypothetical values for the H[O(1)]−O(1)−C(1)−C(2) dihedral angle are plotted in Figure 7. Neither the isotropic shieldings nor the δ_{33} principal values are sensitive to the conformation of H[O(2)]. The δ_{11} and δ_{22} principal values, however, change in opposite directions by more than 10 ppm. The δ_{11} and δ_{22} components move together near 0° and differ most at 120° and 240° where the O−H bond eclipses the vicinal C−H bonds. The curves for δ_{11} and δ_{22} in Figure 7 suggest that, while powder solid state NMR measurements of primary alcohol principal values may provide some insight into hydroxyl proton positions, they are unable to provide a unique conformational determination when a number of dihedral angles produce the same δ_{11} and δ_{22} principal values. This situation is in contrast to that found for the full tensor correlation given in Figure 5, where a unique dihedral angle of 270° is defined by the minimum in the plot.

The tensors of erythritol, as in related monosaccharides and methyl glycosides, confirm that carbohydrate carbon chemical shift tensors are dominated by proximate carbons and oxygens. The principal axes are dominated by the positions of directly bonded carbon, oxygen, and hydrogen atoms, while the more precisely measured principal values may also reflect the nature and position of next-nearest-neighboring atoms.

Like the neutron diffraction data,[12] the NMR data presented here cannot distinguish the mechanism of the H[O(2)] hydrogen-bonding rearrangement, be it a flip-flop[14] conformational reorientation or a configurational transfer of the hydrogen across or through a hydrogen bond energy barrier.

VI. Conclusions

The results presented here serve as another illustration of how carbon chemical shift tensors are very sensitive to the three-dimensional structure of molecules. The full tensor results, in concert with GIAO computations, uniquely determine the H[O(1)]−O(1)−C(1)−C(2) dihedral angle. The two conformations of the *meso*-erythritol molecule provide an interesting example of how the position of the hydrogen in the C(2) hydroxyl group influences the chemical shift tensor of the bonded carbon, observed here as an average over the conformations, and how this effect is reproduced well enough by the GIAO computations to correlate the observed tensor to the occupancy percentage of the two conformations.

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