Carbon-13 Chemical Shift Tensors in Pentaerythritol

Fang Liu, Anita M. Orendt, D. W. Alderman, and David M. Grant*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received January 7, 1997. Revised Manuscript Received May 16, 1997[⊗]

Abstract: The carbon-13 chemical shift tensors of pentaerythritol ($C(CH_2OH)_4$, tetrakis(hydroxymethyl)methane) are measured with use of the two-dimensional chemical shift correlation technique. The results are interpreted with quantum-chemical *ab initio* gauge invariant atomic orbital computations of the nuclear shielding tensors based on X-ray and neutron diffraction structures, and on corresponding structures modified by optimizing the CH_2 proton positions with the Gaussian 94 program. The X-ray based computations correlate with the experimental tensors with a root-mean-square deviation of 4.45 ppm, while the neutron structure gives a root-mean-square deviation of 0.86 ppm. After optimizing the CH_2 proton positions for the X-ray and neutron structures, root-mean-square deviations of 1.19 and 0.84 ppm, respectively, are calculated. Tensor computations for the central carbon were done with hypothetical structures obtained by altering the C−C−C angle. The difference between the two computed principal values of this axially symmetric tensor varies at a rate of 2.7 ppm/deg as the angle changes. The experimentally measured chemical shift difference of 14.6 ppm corresponds to a C−C−C bond angle of 106.6°, in good agreement with the X-ray diffraction value of 107.3° and the neutron diffraction value of 107.1°.

I. Introduction

Carbon-13 chemical shift tensors provide a powerful technique for studying molecular structure.[1] The complete chemical shift tensor is described by a 3×3 real-symmetric matrix with up to six independent components[2−4] that are very sensitive to the arrangement of the directly-bonded nuclei,[5] and may also depend on the positions of distant nuclei.[6−10] Complete chemical shift tensors can be accurately measured in single crystals with a 2D NMR technique.[11] The necessary theoretical link between molecular structure and nuclear shielding is established by *ab initio* quantum-chemical computations. Gauge-invariant atomic orbital (GIAO) computations[12,13] of ^{13}C shielding tensors have recently advanced to the point where they correlate well with the experimental chemical shift tensors in certain molecules (e.g. to within 3 ppm in a variety of monosaccharides, methyl glycosides, and alcohols)[6−9] whenever the molecular structure is accurately known. Thus, single crystal

solid state NMR methods, when combined with diffraction data and quantum-chemical computations, are a valuable tool for examining and refining molecular structures.

In a previous study of six methyl glycosides,[7] the complete chemical shift tensors correlated much better with shielding tensors computed from structures in which the proton coordinates had been optimized with use of the Gaussian program.[14] These results are consistent with the fact that uncorrected X-ray C−H bond lengths appear to be too short due to the displacement of valence electrons.[15,16] Conformational effects on ^{13}C chemical shift tensors have also been studied in mesoerythritol,[6] where it was shown that the measured ^{13}C chemical shift tensors agree best with the GIAO computations made with hydroxyl H−O−C−C dihedral angles close to those obtained from neutron diffraction.

Pentaerythritol, $C(CH_2OH)_4$, was studied in early X-ray diffraction work that determined the carbon and oxygen atom positions.[17−20] The hydrogens were then located by a pioneering neutron diffraction study using deuterium substitution.[21] More recently a new X-ray dataset has been collected at ambient temperature and refined with modern methods,[22] and in the past decade a sophisticated neutron diffraction study has been completed.[23] These last two modern structures of pentaerythritol are used here. Pentaerythritol has a tetragonal lattice and an $I\bar{4}$ space group with two molecules per unit cell. The first molecule is located at the unit cell origin, and the second at the body-centered position. Both molecules are in the same orientation

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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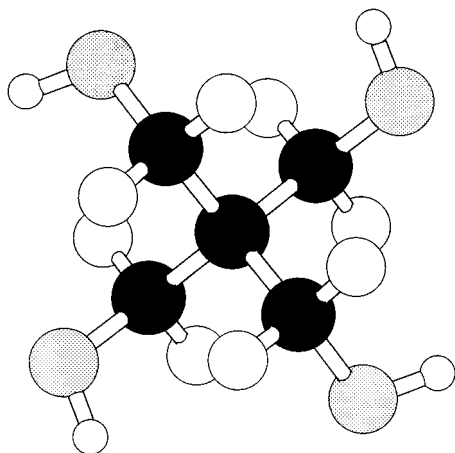(23) Semmingsen, D. *Acta Chem. Scand. Ser. A* **1988**, *42*, 279.

Figure 1. Pentaerythritol molecular conformation shown in a view along the *c* crystallographic axis that forms the intersection of the two O−C−C−O planes.

and conformation, shown in Figure 1. The carbon and oxygen atoms in each molecule are arranged in two intersecting *all-trans* O−C−C−O chains that share their central carbon's tetrahedral bonding, making the planes of the two chains perpendicular to one another. The molecule is superimposed on itself by a 90° rotation around a line located at the intersection of the two perpendicular planes passing through the central carbon, followed by a reflection through a mirror plane perpendicular to this axis. This symmetry axis is parallel to the crystallographic *c* axis. The hydroxyl hydrogens are tipped out of the intersecting planes, and thus the molecule resembles a pinwheel. The molecules centered on planes perpendicular to the *c* axis are bound together with *homodromic* cycles[24] of 1.790 Å hydrogen bonds.[23] The strong intraplanar hydrogen bonds and weak interplanar forces result in librations of the molecules with root-mean-square librational amplitudes of 7.65° about the *a* and *b* axes and of 3.90° about the *c* axis.[22]

The $I\bar{4}$ symmetry of the pentaerythritol molecule requires that the chemical shift tensor of the central carbon be axially symmetric with its unique principal axis along the *c* crystallographic axis. The four CH_2OH hydroxymethyl carbons are chemically equivalent but magnetically nonequivalent. Thus, while their tensors are related by the crystal symmetry, their resonance lines are shifted differently due to the different orientations of the tensors. Thus, a spectrum of a pentaerythritol single crystal exhibits five lines.

II. Experimental Section

Pentaerythritol from Matheson, Coleman and Bell was purified by recrystallization and grown into single crystals by slowly evaporating 95% ethanol−water solutions at room temperature.

The ^{13}C chemical shift tensors were measured from six 2D chemical shift correlation (CSC) spectra and a single 1D spectrum analyzed as described previously.[8,9] The CSC technique has also been described in detail elsewhere.[11]

All of the data were obtained on a Chemagnetics CMX-200 spectrometer operating at 50.304 MHz for ^{13}C with use of a home-built probe[11] in an Oxford 200/89 vertical bore magnet. For the CSC experiments one of the single crystals was shaped by sanding to fit into a shortened 5 mm NMR tube for installation in the multiple-axis sample-reorientation probe. The cross-polarization and decoupling fields were 70 kHz, the contact time was 1 ms, the cycle time was 20 s, and a flip-back pulse was used to return any remaining proton magnetization to the $+z$ axis.[25] Six hypercomplex 2D FIDs were obtained with 512 complex points in the acquisition dimension and 64

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Table 1. Carbon-13 Chemical Shift Tensors in Pentaerythritol[a]

carbon	δ_{xx}	δ_{yy}	δ_{zz}	δ_{xy}	δ_{yz}	δ_{zx}	δ_{11}	δ_{22}	δ_{33}	δ_{iso}
central	45.3	45.3	59.9	0.0	0.0	0.0	59.9	45.3	45.3	50.2
CH_2OH[b]	50.6	67.5	57.2	−31.7	−15.5	−15.0	92.2	67.8	15.3	58.4

[a] Tensor shifts are given in the Cartesian representation in ppm from TMS. The coordinate system has the *x* axis along the *a* crystallographic axis, the *y* axis along the *b* axis, and the *z* axis along the *c* axis. The errors in the values are estimated to be ±0.35 ppm. [b] This tensor is for the hydroxymethyl carbon.

complex points in the evolution dimension. These 2D FIDs were Gaussian line-broadened by 0.6 ppm full-width at half-maximum in both dimensions, zero filled, and Fourier transformed to 2048 × 2048 point spectra with 10 000 Hz spectral widths in both dimensions. The single-crystal shifts with the sample-positioning mechanism in the up and down positions were referenced to the average shift found from 1D tetramethylsilane (TMS) spectra taken in both positions before and after the data acquisition; the TMS shifts observed in each position changed over this time by less than 0.04 ppm. To obtain a spectrum with the applied field in a known direction a large bipyramidal single crystal was examined and the faces were identified as {101} faces. A 1-D spectrum was then obtained with this crystal mounted with its {101} face perpendicular to the field direction in a probe that has been described previously.[26] It is estimated that the crystal face was perpendicular to the field direction to within ±2°. The 1D spectrum was obtained with cross-polarization and repetition times identical with those used for the 2D CSC spectra. The cross-polarization and decoupling fields were both 36 KHz.

The pentaerythritol chemical shielding tensors were computed from the diffraction structures[22,23] by using the GIAO method[12,13] with a D95 basis set[27] as implemented in the Gaussian 94 program[14] on an IBM RISC/6000 POWERstation 560.

III. Results and Discussion

The experimental chemical shift tensors in the crystallographic frame are given in Table 1. The measured chemical shift tensors and the GIAO nuclear shielding results are correlated by converting them both into the icosahedral representation[4] to yield six shift-versus-shielding pairs for each tensor. All of these points are then least-squares fitted with a straight line[8,9] that establishes an additive offset and a multiplicative factor between the chemical shift and the nuclear shielding scales. The root-mean-square deviation of the points from the line is a scalar measure of the correlation effectiveness and, along with the slope and intercept of the line, it reflects the reliability of the computations. The correlation plot weights the central carbon tensor and the hydroxymethyl carbon tensor equally, even though the latter appears four times in the symmetric pentaerythritol molecule.

The GIAO shielding tensors computed for an isolated molecule whose nuclear coordinates are defined by the X-ray diffraction structure correlate with the experimental shift tensors with a root-mean-square deviation of 4.45 ppm. The shieldings from an isolated molecule defined by the neutron diffraction structure correlate with a root-mean-square deviation of 0.86 ppm. Figure 2a presents the correlation plot for the tensors computed from the X-ray structure, and Figure 2b shows the correlation plot from the neutron structure along with the least-squares straight line. The slope of the line in Figure 2b is 1.0245, and its intercept is 212.5 ppm. The superiority of the correlation obtained with the neutron diffraction structure is immediately evident. Unlike previous cases, the experimental error of ±0.35 ppm now makes a significant contribution to the overall correlation error. The pentaerythritol ^{13}C tensor data

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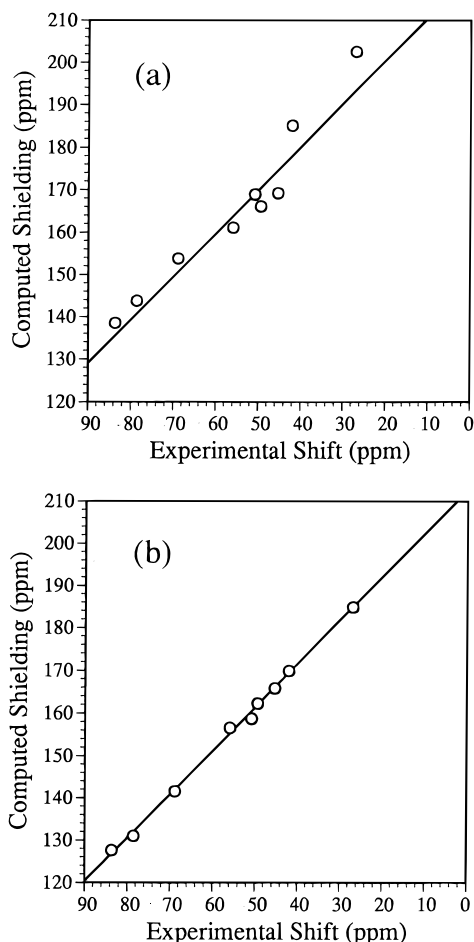
Figure 2. (a) Plot of the X-ray diffraction structure computed icosahedral shieldings versus the experimental icosahedral shifts for pentaerythritol. The least-squares straight line shown has a root-mean-square deviation of 4.45 ppm. (b) Plot of the neutron diffraction structure computed shieldings versus the experimental icosahedral shifts for pentaerythritol. The least-squares straight line shown has a root-mean-square deviation of 0.86 ppm. The experimental shifts are in ppm from TMS and the computed shieldings are in ppm from the bare nucleus.

indicate that the neutron structure is good for the purpose of computing chemical shift tensors, and that the GIAO method with the D95 basis set works successfully on this small molecule.

CH$_2$ Proton Positions. The proton positions in the CH$_2$ groups of pentaerythritol were optimized with use of the Gaussian 94 program[14] with the D95 basis set[27] and the resultant structure was used to compute the shieldings. The coordinates of the carbon and oxygen nuclei and the hydroxyl protons were locked to those determined by diffraction, and the $I\bar{4}$ symmetry was enforced. The CH$_2$ proton optimization was carried out twice, once with the carbon, oxygen, and hydroxyl proton coordinates from the X-ray structure, and a second time with these coordinates from the neutron structure. The effects of the two optimizations on the CH$_2$ bond lengths are presented schematically in Figure 3. The neutron diffraction bond lengths are changed very little by the optimization, while the X-ray diffraction lengths adjust to values very close to the neutron lengths. The computed shielding tensors based on the two optimized structures correlate with the experimental shift tensors with root-mean-square deviations of 1.19 and 0.84 ppm, respectively. The significant improvement of the X-ray root-mean-square deviation from 4.45 to 1.19 ppm illustrates that the CH$_2$ proton coordinates are largely responsible for the poor
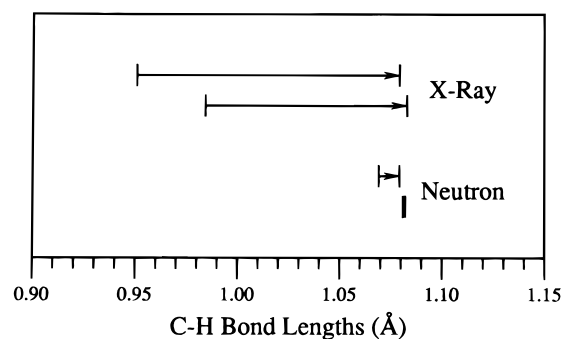

Figure 3. The effect of the optimizations on the C−H bond lengths for the X-ray and neutron structures. For the X-ray structure and the neutron diffraction structure, the arrows are drawn from the original to the proton optimized values (one of the neutron arrows is too short to draw on this scale). The two hydrogens in one CH$_2$ group are not equivalent because of the $I\bar{4}$ pinwheel shape of the molecule, and thus each has its own entry in the figure.

fit of the first computations. On the other hand, the neutron structure results indicate that optimization does not significantly improve the neutron structure coordinates. A full optimization of an isolated pentaerythritol molecule, with $I\bar{4}$ symmetry as the only constraint, produces a 1.42-ppm root-mean-square deviation. This increased deviation over the 0.86 ppm neutron structure value is attributed to the inability of the isolated-molecule optimization to properly place the hydroxy protons, whose positions in the actual crystal structure are set primarily by intermolecular hydrogen bonds.

C−C−C Bond Angle. Because of the $I\bar{4}$ symmetry, the positions of all five carbons in pentaerythritol are defined by a single C−C bond length and the C−C−C geminal angle between carbons in the plane of the *all-trans* O−C−C−C−O chain. The axially-symmetric chemical shift tensor of the central carbon has its principal axes parallel and perpendicular to the 4-fold symmetry axis along the *c* crystallographic axis. To study the effect of varying the C−C−C geminal angle on the central carbon tensor, the shielding components in pentaerythritol were computed from hypothetical molecular geometries with various C−C−C angles. These molecular coordinates were derived from the neutron diffraction structure by changing the two initial in-plane C−C−C angles by an identical amount, thus preserving the $I\bar{4}$ symmetry. All other bond distances and angles were held fixed, except those defining the positions of the CH$_2$ protons, which were optimized after setting the C−C−C angles. The principal values of the computed shielding tensors obtained from the GIAO method by using the D95 basis set are plotted in Figure 4. The difference between the parallel and perpendicular components depends linearly on the C−C−C geminal angle at a rate of 2.7 ppm/deg. Liquid pentaerythritol would on average be a tetrahedrally symmetric molecule, as a consequence of its rapid internal motion. In the solid, however, the central carbon tensor is not spherically symmetric when the geminal angle is the 109.5° tetrahedral angle because of the oxygen atoms' fixed *trans* configuration. The experimentally measured 14.6-ppm difference in the parallel and perpendicular shifts for the central carbon corresponds to a C−C−C bond angle of 106.6°, in good agreement with the neutron diffraction geminal angle of 107.1°.

Long-Range Substituent Effect. The orientation of the ^{13}C tensor of the pentaerythritol CH$_2$OH hydroxymethyl group is typical in that it conforms closely to the local bond symmetry of the adjacent atoms. The δ_{33} principal axis is only 4.4° from the C−O bond, while the δ_{11} principal axis lies only 7.8° from the direction perpendicular to the C−C−O plane. The 15.3 ppm δ_{33} principal value of the pentaerythritol hydroxymethyl
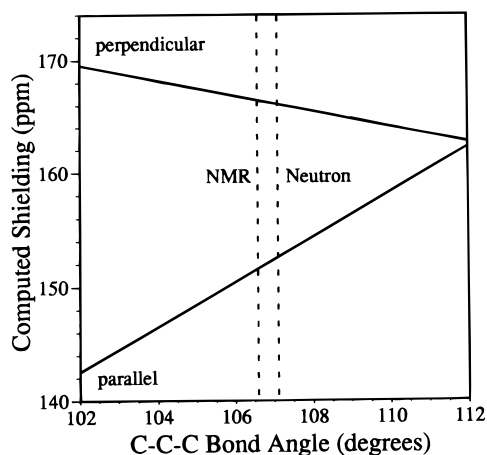
Figure 4. The parallel and perpendicular components of GIAO-computed shieldings for the central carbon in pentaerythritol plotted as a function of a hypothetical C−C−C bond angle. Both the 107.1° value from the neutron diffraction structure and the 106.6° value determined from the observed difference in the parallel and perpendicular principal values of the central carbon tensor are marked with vertical dashed lines.

Table 2. Hydroxymethyl ^{13}C Chemical Shift Tensor Principal Values[7]

molecule	δ_{11}	δ_{22}	δ_{33}	δ_{iso}
methyl-α-D-galactopyranoside	86.6	68.0	29.4	61.4
methyl-α-D-glucopyranoside	89.2	69.6	32.5	63.8
methyl-α-D-mannopyranoside	84.4	65.3	27.2	58.9
methyl-β-D-galactopyranoside	89.5	69.7	29.2	62.8
methyl-β-D-glucopyranoside	90.3	71.1	32.3	64.5
glycoside average	88.0	68.7	30.1	62.3
pentaerythritol	92.2	67.8	15.3	58.4

tensor is unusual, however, as it is much smaller than the 30.1 ppm average δ_{33} of the five methyl glycoside hydroxymethyl carbons[7] given in Table 2. The variation in the glycoside principal values, on the order of 5 ppm, arises from conformational differences. The large 14.8 ppm difference between the pentaerythritol δ_{33} and the glycoside average δ_{33} arises from the different structures at the β, or next nearest neighbor atoms. The α carbon to the methylenes in pentaerythritol is the central carbon that is bonded to three other carbon atoms. In the glycosides, the α carbon is C(5) that is directly bonded to one carbon, C(4), one oxygen, O(5), and one hydrogen H[C(5)].

Thus, it is the β-hydrogen and β-oxygen atoms that change the δ_{33} component of the hydroxymethyl group by 14.8 ppm in these glycosides.

Effect of Surrounding Molecules. Tensors computed in an isolated molecule take into account the conformation of the molecule, but do not include charge polarization and inductive effects from surrounding molecules. These effects would be expected to be particularly large when extensive hydrogen bonding is present, as in pentaerythritol. The 0.86-ppm correlation obtained from an isolated pentaerythritol molecule indicates that hydrogen bonding affects chemical shift tensors primarily through its influence on the conformation of the molecule, rather than by altering its electronic structure. To approximately account for neighboring molecules the shielding tensors were also computed in a pentaerythritol molecule surrounded by four 1,3-propanediol molecules placed so that their CH_2OH groups are in the same positions as those surrounding pentaerythritol in the crystal. The resulting tensors correlate with the data with a 1.27-ppm root-mean-square deviation. As these enhanced tensors should be more accurate, the 0.86-ppm correlation obtained from the isolated molecule can be viewed as fortuitous, and 1.27 ppm taken as a better reflection of the accuracy of the GIAO computations.

IV. Conclusions

The GIAO-computed ^{13}C chemical shielding tensors of pentaerythritol based on the neutron diffraction structure are significantly better than those based on the best X-ray diffraction structure, as measured by their correlation with experimental chemical shift tensors. Optimization of the CH_2 proton positions in the X-ray structure significantly improves the correlation, but such an optimization has essentially no effect on the already excellent neutron structure correlation. When interpreted with GIAO computations, the chemical shift principal values of the central carbon in pentaerythritol uniquely estimate the C−C−C bond angle. In the pentaerythritol hydroxymethyl group, the identity of the β-atoms establishes a unique δ_{33} principal value of 15.3 ppm, compared with the average value of 30.1 ppm for a set of methyl glycosides.