Acta Cryst. (1995). B51, 540–546

Relationship of ^{13}C NMR Chemical Shift Tensors to Diffraction Structures

By David M. Grant, Fang Liu, Robbie J. Iuliucci, Cu G. Phung, Julio C. Facelli* and D. W. Alderman

*Department of Chemistry and *Utah Supercomputing Institute, University of Utah, Salt Lake City, Utah* 84112, *USA*

(*Received* 19 *October* 1994; *accepted* 26 *January* 1995)

Abstract

^{13}C chemical shift tensor measurements on single crystals provide a powerful method to study changes in the electron environment of nuclei with changes in molecular structure. Thus, diffraction structures are critical to an understanding of chemical shift tensors. This work explores the general reliability of using structural data to predict components of the symmetrical chemical shift tensor. Imprecision in the hydrogen positions introduces considerable scatter in the simulated ^{13}C shift tensors, and optimized C—H bond distances in methyl-β-D-glucopyranoside used with the X-ray positions of the heavier C and O atoms greatly improve the simulated chemical shifts. Acenaphthene, with two crystallographically different molecules per unit cell, offers an excellent example for comparing and contrasting structural differences in the two molecules. A recently improved X-ray structure of naphthalene obtained at low temperature provides chemical shift simulations which are comparable to those from neutron diffraction methods and appear to reflect breaks in the D_{2h} symmetry measured in the NMR chemical shift tensors. These data illustrate the close relationship between NMR and diffraction structures.

Introduction

^{13}C chemical shift tensors (Carter, Alderman, Facelli & Grant, 1987; Carter, Facelli, Alderman & Grant, 1988; Sherwood, Facelli, Alderman & Grant, 1991; Sherwood, Alderman & Grant, 1993; Facelli *et al.*, 1994) have now been determined in a wide variety of molecular crystals, and they provide valuable three-dimensional information on chemical structure as it affects the associated electronic distributions in molecules. The measurable part of the chemical shift tensor is described by a 3 × 3 symmetric matrix with up to six independent parameters (Buckingham & Malm, 1971; Facelli, Orendt, Grant & Michl, 1984). These components are very sensitive to the three-dimensional arrangement of the molecular nuclei, because the chemical shift depends on the inverse cubic distance between the electrons and the shielded nucleus, and on the magnetic polarizability of the electrons. As both these electronic properties reflect the underlying nuclear positions, a connection between NMR chemical shift tensors and molecular structures is established. Hence the relationship between NMR shifts and diffraction structures.

The high sensitivity of chemical shifts to molecular structure and the relatively high precision with which chemical shifts may be measured in single crystals allow us to explore quantitatively the molecular structures obtained from diffraction techniques. Such comparisons depend critically on the accuracy of quantum chemical computations for obtaining nuclear shielding from a diffraction structure. Since the introduction of the IGLO method (Kutzelnigg, 1980; Kutzelnigg, Fleischer & Schindler, 1990), in 1980 several quantum mechanical methods have been presented that calculate the chemical shift with local gauge origins (Hansen & Bouman, 1985; Facelli, Grant, Bouman & Hansen, 1990). These methods, as well as the efficient implementation (Wolinski, Hinton & Pulay, 1990) of the GIAO method (Ditchfield, 1974), have allowed quantum chemical calculations of ^{13}C shielding tensors to advance in recent years to the point where it is possible to correlate, within a few parts per million (p.p.m.), the experimental ^{13}C chemical shift tensors with diffraction structures (Grant, Facelli, Alderman & Sherwood, 1993; Facelli & Grant, 1993). Since ^{13}C chemical shifts usually fall within *ca* 200 p.p.m., this accuracy implies correlations that are reliable to 1–2% of typical shift ranges. It would appear in some cases that the reliability of these numerical methods is now comparable to the accuracy of the experimental diffraction coordinates required to generate the molecular wave functions. Thus, single-crystal solid-state NMR methods, when combined with quantum mechanical calculations, promise to be a valuable new and complementary tool for examining and perhaps refining diffraction structures.

It is generally accepted that neutron diffraction techniques are superior to X-ray methods for establishing the position of H atoms in organic molecules (Jeffrey, 1992), although recent low-temperature X-ray data provide thermally corrected proton positions that rival the neutron diffraction results. Since chemical shifts depend strongly on proton positions, it is not surprising that experimental ^{13}C chemical shifts correlate better with shielding calculations based upon neutron diffraction structures than with those derived from typical X-ray structures. Thus, the high sensitivity of chemical shifts upon the C—H bond lengths and directions can provide additional information on hydrogen positions. This paper also presents an example in which quantum mechanically optimized hydrogen positions superimposed on the X-ray diffraction positions of the heavier atoms improve the shift correlations. This approach offers an alternative when neutron diffraction or higher quality low-temperature X-ray data are unavailable.

In this contribution, examples of shift–structure correlations include methyl-β-D-glucopyranoside hemihydrate, acenaphthene and naphthalene. The ^{13}C chemical shifts in carbohydrates represent an excellent opportunity to test correlations between theoretical and experimental chemical shifts, because of the great variety of molecular configurations and conformations found in this class of compounds. Fortunately, carbohydrates have received considerable attention from both neutron and X-ray diffraction workers, and extensive databases now exist for both chemical shift tensors and diffraction structures (Chu & Jeffrey, 1968; Jeffrey, McMullan & Takagi, 1977; Takagi & Jeffrey, 1977, 1979), which can be used to test the above concepts. For example, conformational variations in a C—^{13}C—O—H dihedral angle may lead to changes of *ca* 10–15 p.p.m. in some of the ^{13}C shift components of specific carbons. Polycyclic aromatic hydrocarbons (PAH's), have long attracted the interest of diffraction workers, in part due to readily available crystals, but also due to interest in the nature of aromaticity and its dependence and influence on structural features. Naphthalene is one of the most extensively studied PAH crystals, with a history dating back to the early work of Bragg (Bragg, 1921) and more recently Cruickshank (1957). Since this earlier work naphthalene has been the subject of some very accurate diffraction work, including both a high-quality neutron diffraction structure (Pawley & Yeats, 1969) and a very accurate low-temperature X-ray structure (Brock, Dunitz & Hirshfield, 1991). This abundance of structural information makes naphthalene an ideal compound for NMR study. The presence of a nonaromatic five-membered ring in acenaphthene allows the study of ring strain. Strain on both the aromatic naphthalene residues and on the aliphatic moiety produces an unusual CH_2—CH_2 bond length and several unique C—C—C bond angles. The solution isotropic chemical shifts at the three aromatic carbons in the five-membered ring are notably increased. Single-crystal NMR studies of acenaphthene also are especially interesting because the unit cell contains two crystallographically different molecules with measurably different sets of chemical shift tensors, which allows important crystal packing effects on chemical shifts to be observed. Such NMR data on the two different acenaphthene molecules in the same unit cell provide an ideal case for analyzing the shift–structure relationship and testing the reliability of quantum chemical theoretical methods.

All the ^{13}C chemical shielding calculations presented here were performed using the *GIAO* method (Ditchfield, 1974), as implemented in the *TEXAS* program (Wolinski, Hinton & Pulay, 1990).

Table 1. *Comparison of fitting parameters and statistical information for diffraction and quantum-mechanical structures for methyl-*D*-pyranosides*

Compound	Slope	Intercept	Scatter
Methyl-α-D-galactopyranoside (neutron)	0.96	205.8	2.67
Methyl-β-D-galactopyranoside (neutron)	1.02	210.6	3.65
Methyl- α-D-glucopyranodisde (neutron)	1.03	212.8	2.73
Methyl-β-D-glucopyranoside (X-ray)	1.19	233.2	3.17
Methyl-β-D-glucopyranoside (QM optimized)	1.00	210.6	2.11

Results and discussion

*Optimized proton positions in methyl-β-*D*-glucopyranoside hemihydrate*

Work in this laboratory on a variety of carbohydrates (Liu *et al.*, 1995; Liu, Alderman, Phung & Grant, 1995) has established the correlation between the experimental chemical shift tensors and the theoretically simulated tensors based upon calculated wavefunctions that use molecular geometries taken from diffraction data. Table 1 for four representative methyl glycosides contains a brief summary of the correlation slope (ideally unity), the intercept (representing the theoretical shielding of ^{13}C in tetramethylsilane, TMS, relative to a bare nucleus) and the r.m.s. scatter (expressed as the root mean square of the deviations from the best fit line). These chemical shift correlations have been performed in the icosahedral representation of the tensor in the unit-cell frame (Alderman, Sherwood & Grant, 1993). Only one compound in this series, methyl-β-D-glucopyranoside hemihydrate, lacks a neutron diffraction structure. Note in Table 1 that both the slope and intercept for methyl-β-D-glucopyranoside hemihydrate, based on only X-ray structural data, deviate significantly from the corresponding results for the other three molecules with neutron diffraction structures. While the experimental data correspond to the hemihydrate, all geometry optimizations and the computation of chemical shifts have been calculated for methylated sugar molecules without bound water.

In exploring alternative ways to improve the molecular geometry necessary to calculate the ^{13}C chemical shifts, we have quantum-mechanically optimized the proton positions in methyl-β-D-glucopyranoside using the *GAUSSIAN*92 program (Frisch *et al.*, 1992) at the Hartree–Fock (HF) level with a D95* basis set (Dunning & Hay, 1977). The positions of the heavier carbon and oxygen nuclei were locked to those determined by the X-ray study. Fig. 1 presents graphically the optimized C—H bond distances in methyl-β-D-glucopyranoside *versus* the corresponding diffraction distances. Fig. 2 presents the results of the correlations of experimental chemical shifts and calculated shieldings for these quantities when the X-ray structure alone is used and when it is corrected by optimization of the proton positions. The fitting parameters in the calculations depicted in Fig. 2 are also shown in Table 1, they indicate a significant improvement when the proton positions are optimized. Note in Table 1 the movement of the slope towards unity and the reduced scatter achieved by the optimization. In addition, the partially optimized X-ray-based theoretical simulation of shielding values has a TMS intercept, which better corresponds to the values found for simulations based on the neutron diffraction structures. Clearly, the recognized inadequacies of hydrogen distances from the X-ray data have impacted the quantum-mechanical calculations, and the single-crystal chemical shift data provides an independent experimental result that may be used to validate the optimized proton positions employed in the calculations.

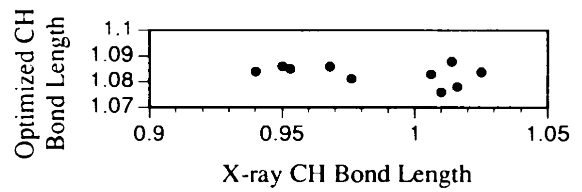


Fig. 1. The optimized C—H bond lengths are graphically portrayed *versus* the X-ray bond lengths in methyl-β-D-glucopyranoside.

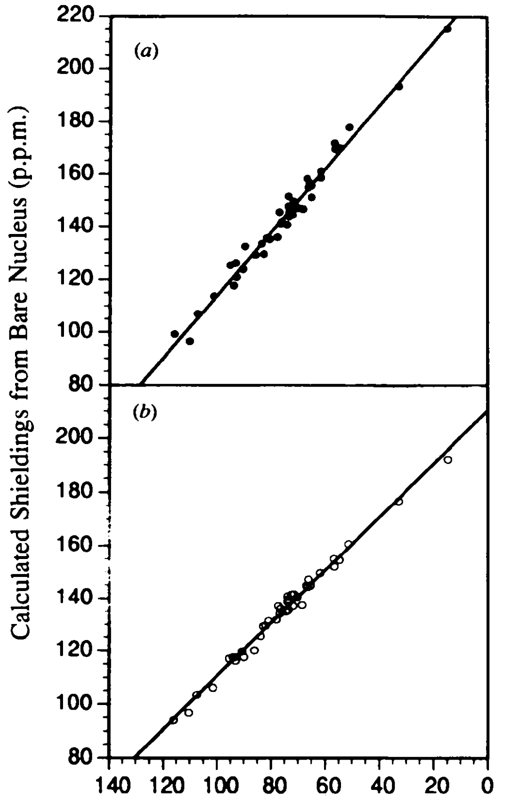


Fig. 2. The calculated shieldings *versus* experimental shifts for the chemical shift tensors in methyl-β-D-glucopyranoside hemihydrate. (*a*) The X-ray diffraction structure is used to provide the atomic coordinates in the shielding simulations. (*b*) The X-ray structure is partially optimized with quantum mechanical methods. The hydrogen positions are established with the *GAUSSIAN* 92 program (Frisch *et al.*, 1992) at the HF level with a D95* basis set.

To explore the impact of bond distances upon shielding tensors the shieldings of the central carbon in isobutane were calculated as a function of a variable C—H bond distance. Fig. 3 represents results for the $\sigma_{\parallel}$ and $\sigma_{\perp}$ components of this axially symmetric tensor in isobutane. Note, the $\sigma_{\parallel}$ component, lying along the C—H bond, is essentially independent of changes in the C—H bond distance, while the perpendicular $\sigma_{\perp}$ component exhibits a $\mathrm{d}\sigma_{\perp}/\mathrm{d}r = 110\,\mathrm{p.p.m.}\,\mathrm{Å}^{-1}$ dependence on the bond distance. These results can be compared with similar calculations reported by Chestnut (1989). These theoretical results thus indicate that inaccuracies of 0.02–0.03 Å in the C—H bond distance may introduce 2–3 p.p.m. discrepancies into theoretically predicted tensor components lying perpendicular, or nearly perpendicular, to a C—H bond. The value of $\mathrm{d}\sigma_{\perp}/\mathrm{d}r$ explains why HF calculations of H positions are sufficient to improve the chemical shift correlations. Boggs (1986) has estimated that HF calculations predict C—H bonds which are *ca* 0.005 Å shorter than the best experimental values. Therefore, the neglect of the electron correlation in the calculations of the position

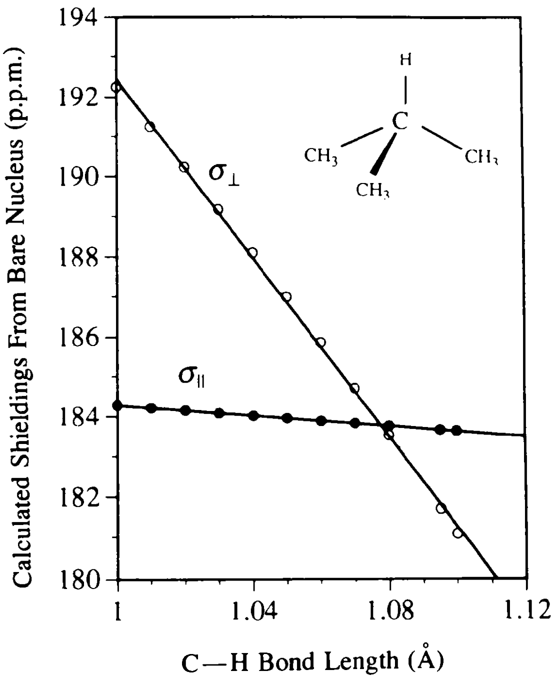


Fig. 3. Calculated shieldings for the central carbon in *iso*-butane as a function of a hypothetical C—H bond distance. The parallel component is relatively insensitive to the C—H bond length, but the perpendicular component exhibits a $110\,\mathrm{p.p.m.}\,\mathrm{Å}^{-1}$ dependence on the bond distance.

of H atoms would introduce an error of only *ca* 0.5 p.p.m. in the calculated shielding. This error is similar to the NMR measurement errors and most likely smaller than the error introducted by the neglect of electron correlation in the actual calculation of the shielding tensors.

Possible molecular deformations of the aliphatic moiety in acenaphthene

The unit cell of acenaphthene (Hazell, Hazell, Horskov-Lauritsen, Briant & Jones, 1986) has four molecules, consisting of two *A* and two *B* molecules, in different structural environments (see Fig. 4). As a consequence of the different crystalline environment, the chemically equivalent nuclei have two sets of measurably different ^{13}C chemical shift tensors (Iuliucci, Facelli, Alderman & Grant, 1995). While reported errors in the diffraction data are larger than the structural differences noted between the *A* and *B* molecules, the NMR single-crystal chemical shift tensors differ (Pawley & Yeats, 1969) from each other by a r.m.s. amount, 1.82 p.p.m., which significantly exceeds the 0.52 p.p.m. experimental uncertainties in the chemical shift measurements. Thus, single-crystal ^{13}C shift data clearly document the differences between the two different *A* and *B* molecules in acenaphthene.

The differences between the *A* and *B* tensors can originate from two distinct but related crystalline effects. One is the direct effect of the fields generated by neighboring molecules which alter the chemical shifts, the second is an indirect affect arising from a change in the molecular geometry due to crystalline forces. Model calculations suggest that the direct effects (de Dios & Jameson, 1995) are insufficient to explain the large changes observed on the chemical shifts. We, therefore, argue that small deformations of the molecular geometry are sufficient to account for measurable shift differences between the *A* and *B* molecules.

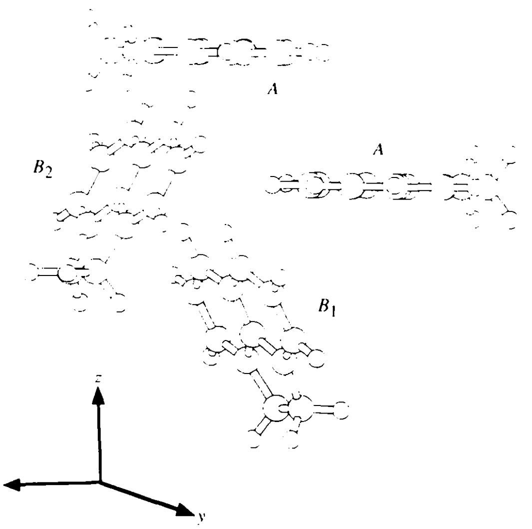
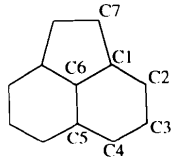


Fig. 4. Geometrical representation of the orientation of the *A* and *B* molecules in the unit cell of acenaphthene. The inversion relationship between the two *A* molecules doubles the NMR line intensities of the ^{13}C peaks, while the herringbone structure for the two *B* molecules provides two peaks for each carbon position which are related to each other through congruent chemical shift tensors.

Table 2. *The angle between the perpendicular principal axis* in the acenaphthene unit cell of the A and B molecules*



Position	Principal components *A*/*B*	Directional cosine between *A*/*B* directions	Angle between *A*/*B* directions (°)
C1	35.24/38.70	0.4670	62.16
C2	11.39/13.58	0.4716	61.86
C3	11.87/11.34	0.4677	62.11
C4	17.21/16.76	0.4607	62.57
C5	−3.43/−2.79	0.4647	62.31
C6	[illegible]1.96/14.55	0.4683	62.08
C7	48.92/50.46	0.5726	55.07

* All tensor components, directional cosines and angles are between the perpendicular tensor components of the *A* and *B* molecules. All perpendicular components for the *A* molecule lie along the *z*-axis within experimental uncertainty.

It is well established in PAH's that the smaller shift component (δ_{33}) lies perpendicular to the plane of the molecule (Carter, Alderman, Facelli & Grant, 1987) and in CH$_2$ groups that the largest shift component (δ_{11}) lies perpendicular to the C—CH$_2$—C plane in five-membered rings (Facelli *et al.*, 1985). In Table 2 the δ_{33} components for the aromatic carbons and δ_{11} for the CH$_2$ carbons in acenaphthene are presented along with the angles between the corresponding components in the *A* and *B* molecules. The coplanarity in the two *A* molecules along with the C_{2z} screw-symmetry axis relate corresponding nuclei in the two *A* molecules by an inversion symmetry element, as shown in Fig. 4. This symmetry leaves the shifts of corresponding nuclei doubly degenerate. The herringbone structure of the two *B* molecules lacks the effective inversion property noted for the *A* molecules and introduces congruent pairs of tensors (chemically equivalent, but magnetically non-equivalent) for each unique carbon position in the two separate *B* molecules. A publication from our laboratory (Iuliucci, Facelli, Alderman & Grant, 1995) gives extensive details on the chemical shift tensors in acenaphthene. It is sufficient to indicate that the coplanarity in the two *A* molecules and the coincidence that the normals to these two *A* rings lies along the C_{2z} screw axis combine to leave the principle components, perpendicular to the molecular plane, lying along the *z*-axis of the unit cell for all *A* carbons, both aromatic and aliphatic carbons. The corresponding aromatic δ_{33} and aliphatic δ_{11} components for the *B* molecule again lie generally perpendicular to the molecular plane, but the δ_{11} direction of the aliphatic portion of the *B* molecule is slightly different from the δ_{33} direction in the *B* aromatic carbons.

The direction of these perpendicular components is given in Table 2 along with the corresponding principal values of both the *A* and *B* molecules. Note in Table 2 that all δ_{33} components for the aromatic *B* carbons, within experimental error, are coparallel and thus presumably perpendicular to the *B* aromatic rings. These data indicate that the aromatic plane of the *B* molecule lies on average 62.2° from the aromatic plane of the *A* molecule, in good agreement with the 61.6° angle obtained from the diffraction data (Hazell, Hazell, Horskov-Lauritsen, Briant & Jones, 1986). However, the direction of δ_{11} of the aliphatic component in the *B* molecule is only 55.1° from the corresponding direction in the *A* molecule. This 7.1° deviation of δ_{11} from the molecular plane is significant and well outside our experimental error. A rotation of the tensor forcing the aliphatic δ_{11} to be parallel to the aromatic δ_{33} direction of the *B* molecule implies on average a shift in the resonance frequencies of 2.6 p.p.m., with individual tensor components varying by 0.5–4.3 p.p.m., depending upon the relative orientation of the tensor components and the axis of rotation that produces the 7.1° displacement in the aliphatic δ_{11} component. These shifts are well above the accuracy in the experimental NMR measurements. The full explanation of this effect must await further work, in which the thermal vibrations can be assessed. However, the atomic displacement ellipsoid (ADP) factors for the aliphatic H atoms in the *B* molecule suggest increased vibrational amplitudes for this portion of the molecule in comparison with the aromatic portion, thereby further obscuring the structural data that might explain the significant difference in the angular orientation of the aliphatic δ_{11} shift component in the *B versus A* molecules.

Possible explanations for this anomaly include deformations or anharmonic averaging of the two geminal C—H bond distances at the aliphatic carbon. Other types of structural deformations, which could contribute to the anomalous effect at the aliphatic carbon in acenaphthene, include angular rocking or twisting deformations of the geminal hydrogens relative to the plane of the five-membered ring. This would destroy the plane of symmetry of the *B* molecule in the $—CH_2CH_2—$ vicinity of the five-membered ring. Possibly a combination of several such distortions are needed to account for the anomalous δ_{11} direction at C7. The diffraction data (Hazell, Hazell, Horskov-Lauritsen, Briant & Jones, 1986) hint of some nonequivalence of the two geminal C—H bonds, but unfortunately the error limits in these data prevent a verification of possible deformations which could explain the shift anomaly. Calculation for the C—H bond distances, which differ by 0.015 Å in the neutron diffraction structure, give a tilt of *ca* 1° in the aliphatic δ_{11}. However, if the difference of these bond lengths is increased to the maximum allowed by the marginal standard deviations reported in the neutron diffraction paper, *i.e.* 0.048 Å, then the tilt increases to 3.6°, while the δ_{33} components at C1 and C6 remain perpendicular to the aromatic ring within 0.5°.

It is unlikely, however, that the aliphatic carbons will deform much from the plane of the five-membered ring, as such structural effects change not only the direction of the C7 perpendicular principal value, but also the direction of the δ_{33} perpendicular tensor components for C1 and C6. An out-of-plane bending of C7 sufficient to produce the 7° change in δ_{11} at C7 also changes the δ_{33} direction of C1 and C6 by 3.5° from the normal to the aromatic ring, even though the aromatic ring carbons remain planar. This variation of 3.5° would introduce changes in the C1 peak positions, which is several-fold larger than our measurement uncertainties. These considerations suggest that one may eliminate any structural deformations that alter the orientation in the principal axis of the aromatic δ_{33} component by more than 0.5°.

Naphthalene revisited

During the presentation at the ACA Symposium 94 in Atlanta, considerable discussion centered upon thermal corrections to the shift tensor calculations, and some attention was focused on the accuracy of the diffraction data used in our molecular quantum-mechanical simulation of the chemical shift tensors. Unlike the more mature diffraction fields, the field of single-crystal NMR has yet to progress to the level where thermal averaging is introduced into the chemical shift tensor simulations, although clearly this must be an important area of future work. The recommendation that NMR studies progress to the point where thermal effects can be determined is, therefore, well taken. It was pointed out by Professor C. P. Brock, at the ACA Symposium, that a considerably improved and unconstrained X-ray structure for naphthalene is available, including corrections for the thermal effects on the diffraction parameters arising from molecular vibrations and from the anisotropy of the electronic charge distributions (Brock, Dunitz & Hirshfeld, 1991). This excellent X-ray work on naphthalene appeared after we had completed our experimental chemical shift work, and we were unaware of some of the important details in the supplementary materials. Professor Brock has now graciously provided us with a copy of the atomic coordinates contained in the supplementary structural data, and we have been able to confirm that the shielding tensors simulated with these data exhibit breaks in the D_{2h} structural symmetry previously presumed (Pawley & Yeats, 1969) for bond parameters in naphthalene.

Using the unconstrained refinements from the supplementary material we have calculated the ^{13}C chemical shift tensors for naphthalene using the X-ray structures reported for five different temperatures, ranging from 92 to 239 K. The structures at all temperatures produce significant departures from D_{2h} symmetry in the calculated ^{13}C shielding tensors. The temperature dependence of the calculated tensors is also significant. For some of the more sensitive components, the temperature dependence is larger than 1 p.p.m. over the temperature range studied and, as expected, is larger for the protonated carbons than for the bridgehead carbons. These calculated shieldings clearly indicate that the temperature dependence of shifts should be measurable, and suggest the need for future variable-temperature NMR studies of single crystals.

For simplicity, we present here only the analysis of the theoretical chemical shift tensors using the structure reported at 239 K by Brock, Dunitz & Hirshfeld (1991) and compare them with the neutron diffraction results. Fig. 5 plots only the principal values to remove the ambiguity associated with minor differences in the X-ray and neutron diffraction descriptions of the unit cell of naphthalene. The principal values lack the spatial orientational information associated with the chemical shift tensor and as such allow comparisons to be made between the two sets of diffraction results without concern for the exact positions and molecular orientations in the two diffraction structures. Thus, this plot of only principal values is not quite comparable to the results by Facelli & Grant (1993) which report the r.m.s. value for the distance between the experimental and theoretical simulations of the full tensor. Nevertheless, Fig. 5 clearly indicates that high-quality X-ray methods can produce structures that lead to correlation plots of shielding *versus* chemical shift that are at least of the same quality as those obtained from neutron diffraction studies.

To view the departures from D_{2h} symmetry, the δ_{33} portion of Fig. 5 is magnified to yield the information shown in Fig. 6. The small differences between the shielding calculation based on the X-ray and neutron diffraction structures exhibit the modest differences still present in these high-quality diffraction structures. The ability to predict breaks in the D_{2h} symmetry by the low-temperature X-ray structure appear to be better than the corresponding neutron diffraction simulations. The symmetry reduction is clearly evident in the NMR tensor data, where the 0.52 p.p.m. measurement errors are considerably less than the 2.5 p.p.m. observed deviations from D_{2h} symmetry. It is rewarding to note that this break in the tensor symmetry is also reflected in the structural features found in these new X-ray simulations. Such information is critical to the question of the relative importance of intramolecular and intermolecular contributions. These temperature-dependent X-ray results predict significant thermal changes in the chemical shift tensors and focus attention again on the need for future study of motional and temperature effect upon chemical shift tensors.

Concluding remarks

Diffraction structures are critical to our present understanding of nuclear shielding, and it is important to develop accurate methods for relating chemical shift

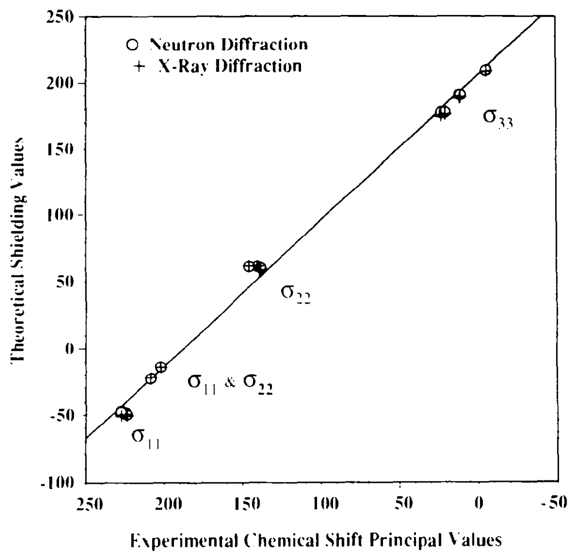


Fig. 5. The theoretical simulations based on both the neutron diffraction and low-temperature X-ray structures are both exhibited and compared. Both methods appear to provide comparable results and their differences appear to fall below the structural uncertainties between the two methods.

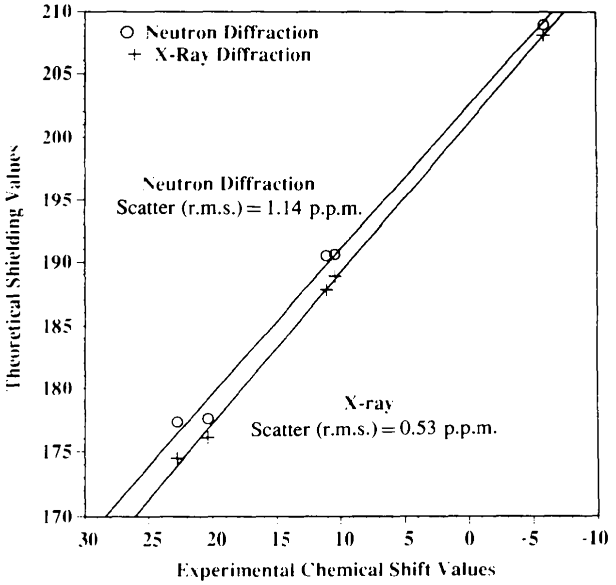


Fig. 6. Plotted on an expanded scale the δ_{33} components from Fig. 5 now exhibit the minor differences in their simulated shieldings. The X-ray simulations reflect the breaks in the D_{2h} symmetry found in the NMR slightly better than those observed in the neutron simulations.

tensors with diffraction structures. The success of the correlation between these experimental quantities depends entirely upon the reliability of the quantum-mechanical calculations of the shielding tensors, as well as upon the errors inherent in both the experimental NMR and diffraction data. The intrinsic accuracy of NMR shifts, which depend only upon frequency measurements, can augment diffraction information as these limitations are understood and included in the structure–shift correlations. This paper has explored the important issues of hydrogen positions and thermal corrections to diffraction structures. The selected examples illustrate how diffraction and single-crystal NMR methods work together to achieve considerable synergism in an elucidation of detailed molecular structural features. A recent high-quality X-ray structure of naphthalene taken at various low temperatures appears to predict chemical shift tensors as well as or better than the neutron structure. Should the positions of the H atoms not be located precisely because of the absence of neutron diffraction and low-temperature X-ray stuctures, the partial quantum-mechanical optimization of the hydrogen positions offers a reasonably reliable alternative for obtaining suitable structures to calculate ^{13}C chemical shifts. Use of traditional X-ray structures in this instance is adequate to establish the positions of heavier atoms. The X-ray structure data also manifest deviations from D_{2h} symmetry which are reflected in the shielding simulations and agree with the measurable and confirmed deviations from the D_{2h} symmetry in the NMR shifts. These results illustrate the close relationship that exists between diffraction structures and the ^{13}C chemical shift tensor components and indicate a promising future relationship between these two diverse experimental methods.

Our appreciation is expressed to Professors P. Pulay, J. F. Hinton and K. Wolinski for a copy of their *TEXAS*93 program. Helpful conversations and correspondence with Professor Cruickshank and C. P. Brock, and receipt of a copy of her supplementary material, are acknowledged. This work was supported by the office of Basic Energy Sciences, DOE, under grant number DE-FG-86ER13510 and by the Institute of General Medical Sciences, NIH, under grant number GM 08521-34. The Utah Supercomputing Institute provided some of the computing time used in the calculation of the nuclear shieldings.

References

ALDERMAN, D. W., SHERWOOD, M. H. & GRANT, D. M. (1993). *J. Magn. Reson. A*, **101**, 188–197.

BOGGS, Y. E. (1986). *Accurate Molecular Structures, Their Determination and Importance*, edited by A. DOMENICANO & I. HARGITTAI, pp. 322–335. Oxford Science Publications.

BRAGG, W. H. (1921). *Proc. Phys. Soc. A*, **34**, 33–50.

BROCK, C. P., DUNITZ, J. D. & HIRSHFELD, F. L. (1991). *Acta Cryst.* B**47**, 789–797.

BUCKINGHAM, A. D. & MALM, S. M. (1971). *Mol. Phys.* **22**, 1127–1130.

CARTER, C. M., ALDERMAN, D. W., FACELLI, J. C. & GRANT, D. M. (1987). *J. Am. Chem. Soc.* **109**, 2639–2644.

CARTER, C. M., FACELLI, J. C., ALDERMAN, D. W. & GRANT, D. M. (1988). *J. Chem. Soc. Faraday Trans.* **84**, 3673–3690.

CHESTNUT, D. B. (1989). *Ann. Rep. NMR Spectrosc.* **21**, 51–97.

CHU, S. S. C. & JEFFREY, G. A. (1968). *Acta Cryst.* B**24**, 830–838.

CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.

DIOS, A. C. DE & JAMESON, C. J. (1995). *Ann. Rep. NMR Spectrosc.* **29**, 1–69.

DITCHFIELD, R. (1974). *Mol. Phys.* **27**, 789–807.

DUNNING, T. H. & HAY, P. J. (1977). *Methods of Electronic Structure Theory*, edited by H. F. SCHAEFER III, pp. 1–27. New York: Plenum Press.

FACELLI, J. C. & GRANT, D. M. (1993). *Nature*, **365**, 325–327.

FACELLI, J. C., GRANT, D. M., BOUMAN, T. D. & HANSEN, AA. E. (1990). *J. Comp. Chem.* **11**, 32–44.

FACELLI, J. C., HU, J. Z., ORENDT, A. M., ARIF, A. M., PUGMIRE, R. J. & GRANT, D. M. (1994). *J. Phys. Chem.* **98**, 12186–12190.

FACELLI, J. C., ORENDT, A. M., BEELER, A. J., SOLUM, M. S., DEPKE, G., MALSCH, K. D., DOWNING, J. W., MURTHY, P. S., GRANT, D. M. & MICHL, J. (1985). *J. Am. Chem. Soc.* **107**, 6749–6754.

FACELLI, J. C., ORENDT, A. M., GRANT, D. M. & MICHL, J. (1984). *Chem. Phys. Lett.* **112**, 147–149.

FRISCH, M. J., TRUCKS, G. W., HEAD-GORDON, M., GILL, P. M. W., WONG, M. W., FORESMAN, J. B., JOHNSON, B. G., SCHLEGEL, H. B., ROBB, M. A., REPLOGLE, E. S., GOMPERTS, R., ANDRES, J. L., RAGHAVACHARI, K., BINKLEY, J. S., GONZALEZ, C., MARTIN, R. L., FOX, D. J., DEFREES, D. J., BAKER, J., STEWART, J. J. P. & POPLE, J. A. (1992). *GAUSSIAN*92, Revision C. Gaussian Inc., Pittsburgh, USA.

GRANT, D. M., FACELLI, J. C., ALDERMAN, D. W. & SHERWOOD, M. H. (1993). NATO Advanced Research Workshop, *Nuclear Magnetic Shieldings and Molecular Structure*, edited by J. TOSSELL, pp. 367–384. Dordrecht: Kluwer Academic Publishers.

HANSEN, AA. E. & BOUMAN, T. D. (1985). *J. Chem. Phys.* **82**, 5035–5047.

HAZELL, A. D., HAZELL, R. G., HORSKOV-LAURITSEN, L., BRIANT, C. E. & JONES, D. W. (1986). *Acta Cryst.* C**42**, 690–693.

IULIUCCI, R. J., FACELLI, J. C., ALDERMAN, D. W. & GRANT, D. M. (1995). *J. Am. Chem. Soc.* In the press.

JEFFREY, G. A. (1992). *Accurate Molecular Structures, Their Determination and Importance*, edited by A. DOMENICANO & I. HARGITTAI, pp. 270–298. Oxford Science Publication.

JEFFREY, G. A., MCMULLAN, R. K. & TAKAGI, S. (1977). *Acta Cryst.* B**33**, 728–737.

KUTZELNIGG, W. (1980). *Isr. J. Chem.* **19**, 193–200.

KUTZELNIGG, W., FLEISCHER, U. & SCHINDLER, M. (1990). *NMR Basic Princ. Prog.* **23**, 167–262.

LIU, F., ALDERMAN, D. W., PHUNG, C. G. & GRANT, D. M. (1995). Submitted for publication.

LIU, F., PHUNG, C. G., HU, Z.-Z., FACELLI, J. C., ALDERMAN, D. W. & GRANT, D. M. (1995). In preparation.

PAWLEY, G. S. & YEATS, E. A. (1969). *Acta Cryst.* B**25**, 2009–2013.

SHERWOOD, M. H., ALDERMAN, D. W. & GRANT, D. M. (1993). *J. Magn. Reson. A*, **104**, 132–145.

SHERWOOD, M. H., FACELLI, J. C., ALDERMAN, D. W. & GRANT, D. M. (1991). *J. Am. Chem. Soc.* **113**, 750–753.

TAKAGI, S. & JEFFREY, G. A. (1977). *Acta Cryst.* B**33**, 3033–3040.

TAKAGI, S. & JEFFREY, G. A. (1979). *Acta Cryst.* B**35**, 902–906.

WOLINSKI, K., HINTON, J. F. & PULAY, P. (1990). *J. Am. Chem. Soc.* **112**, 8251–8260.