Carbon-13 Chemical Shift Tensors in Polycyclic Aromatic Compounds. 2. Single-Crystal Study of Naphthalene†

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Abstract: Carbon-13 chemical shift tensors have been determined in single-crystal naphthalene. The high-field component of every tensor is oriented perpendicular to the molecular plane, as in other aromatic compounds. The bridgehead carbon tensor is nearly axially symmetric, with its low-field component approximately perpendicular to the central bridging bond, in agreement with theoretical predictions. Protonated carbon tensors in naphthalene are more asymmetric, with their low-field components directed approximately along the C–H bonds. The Pople model of chemical shielding with MNDO wave functions reproduces the experimental in-plane shielding components. These calculations show that the in-plane components of the carbon shift tensors are governed by the bond orders of the adjacent bonds, and the shift tensors thus provide valuable information relating to aromaticity. The measured tensors deviate significantly from the symmetry of an isolated naphthalene molecule because of the lower symmetry of the molcular site in the crystal.

Introduction

Measurement of ^{13}C chemical shift tensors has become a valuable technique for assessing the relative aromaticity of individual bonds in polycyclic aromatic molecules. A clear relationship between the in-plane shielding components and calculated bond order was established in pyrene[1] where the ^{13}C chemical shift tensors calculated from MNDO wave functions[2] with the Pople model of chemical shielding[3] were in good agreement with the measurements. This success led to a theoretical study of the in-plane shielding values in a series of polycyclic aromatic compounds.[4] Unfortunately the very long ^{1}H spin–lattice relaxation times in these compounds and the necessity of relatively large single crystals have limited the number of fused aromatics in which ^{13}C chemical shift tensors have been determined.

This work reports ^{13}C chemical shift tensors in single-crystal naphthalene. The measured tensors reflect the symmetry of the molecular site in the crystal but deviate significantly from the symmetry of an isolated naphthalene molecule. This result is particularly important because diffraction studies have been unable to detect any significant distortion of the naphthalene molecule in the solid. A comparison of the measurements with the results of theoretical calculations further justifies the use of MNDO wave functions to calculate the in-plane shielding components and thus to represent important aspects of π-electron structure in this class of compounds.

Naphthalene has historically been one of the most intensively studied molecular crystals,[5,6] and it was among the first organic compounds to be examined by X-ray diffraction methods. The early work of Sir William Bragg[7] clearly established the shape of the naphthalene molecules and their approximate orientations in the unit cell. The first detailed structure determination was by Robertson,[8] and naphthalene has since been the subject of numerous diffraction studies.[9–13] Figure 1 shows the positions of the two naphthalene molecules in the unit cell which are related by the space group symmetry $P2_1/a$ (C_{2h}^5). The two molecular orientations are interchanged by a two-fold rotation about the *b* crystal axis. The only symmetry element retained by the molecule in its crystal site is a center of inversion, and the molecular point group symmetry *mmm* (D_{2h}) may therefore be lowered to $\bar{1}$ (C_i) by the perturbing effects of nearby molecules. Figure 2 shows the labeling of the carbon positions in naphthalene.

The unit cell of naphthalene includes twenty carbons, but only five constitute the asymmetric unit, the others being related by the symmetry operations of the space group. Consequently solid naphthalene has five incongruent ^{13}C chemical shift tensors, in contrast to the three present in an isolated naphthalene molecule with *mmm* symmetry. Carbons C1, C2, C3, C4, and C4a (corresponding to carbons B, A, E′, D′, and C′, respectively, in ref 10 and 11) are selected as the asymmetric unit here.

The invariance of the chemical shift under inversion and the centrosymmetry of the naphthalene molecule in the solid result in only five resonance lines per molecule. Since the two molecules in the unit cell are oriented differently they can produce separate lines in the spectra, so that the ^{13}C spectrum of an arbitrarily oriented naphthalene crystal generally exhibits ten lines. The two groups of five tensors measured from these lines are related by the same symmetry operation which relates the orientations of the two molecules, a 2-fold rotation around the *b* crystal axis.

To orient the measured tensors with respect to the molecular framework and to perform the theoretical calculations, it is necessary to employ structural results obtained from diffraction studies. Since naphthalene has been the subject of much work, a choice must be made between the various diffraction studies in the literature. The most recent X-ray work[13] shows that the lattice parameters are quite temperature dependent, and thus that the molecular orientation may change with temperature, but unfortunately this study provides only low-temperature structures. X-ray diffraction results are also of limited value here because the accuracy with which they locate protons is inadequate to support the theoretical calculations. A room temperature neutron diffraction study of perdeuterionaphthalene[1] shows that the lattice constants of naphthalene and perdeuterionaphthalene are nearly identical and provides a structure which accurately locates the deuterons. This neutron structure of perdeuterionaphthalene is consistent with the most recent room temperature X-ray structure of naphthalene.[10] The neutron work hints that the nuclear positions of the perdeuterionaphthalene molecule in the solid break the isolated molecule symmetry, but ultimately it reports that "these deviations are insignificant" and lists nuclear coordinates which possess *mmm* symmetry. For these reasons the *mmm* molecular symmetry neutron diffraction structure of perdeuterionaphthalene[11] was chosen as the most suitable for the present purposes and was used both to orient the experimental

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† See ref 1 for paper 1 of this series.

(1) Carter, C. M.; Alderman, D. W.; Facelli, J. C.; Grant, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2639.
(2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(3) Pople, J. A. *J. Chem. Phys.* **1962**, *37*, 53.
(4) Facelli, J. C.; Grant, D. M. *Theor. Chim. Acta* **1987**, *71*, 277.
(5) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic: New York, 1973.
(6) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*; Oxford University: New York, 1982.
(7) Bragg, W. H. *Proc. Phys. Soc.* **1921**, *34*, 33.
(8) Robertson, J. M. *Proc. R. Soc. A* **1933**, *142*, 674.
(9) Abrahams, S. C.; Robertson, J. M.; White, J. S. *Acta Crystallogr.* **1949**, *2*, 233.
(10) Cruickshank, D. W. J. *Acta Crystallogr.* **1957**, *10*, 504.
(11) Pawley, G. S.; Yeats, E. A. *Acta Crystallogr.* **1969**, *B25*, 2009.
(12) Ponomarev, V. I.; Filipenko, O. S.; Atovmyan, L. O. *Sov. Phys. Crystallogr.* **1976**, *21*, 215.
(13) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr.* **1982**, *B38*, 2218.

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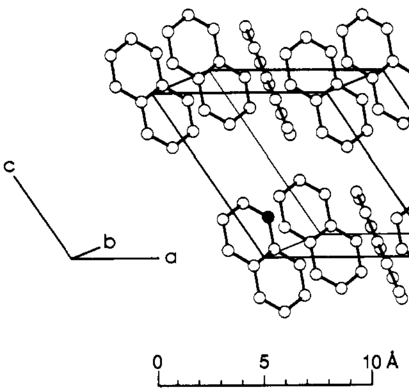

Figure 1. Naphthalene molecules in the unit cell. The view is the same as in Figure 3 of ref 10. Carbon 1 of the molecule at the origin of the unit cell is blackened.

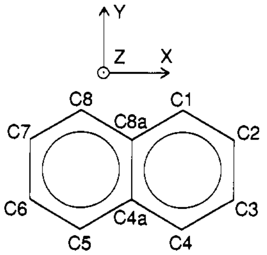

Figure 2. Naphthalene molecule with carbon numbering and molecular coordinate system. The correspondence to ref 10 numbering is C1 = B, C2 = A, C3 = E′, C4 = D′, and C4a = C′.

tensors on the molecule and to provide the bond distances and angles required for the theoretical calculations.

Experimental Section

Commercially obtained naphthalene was purified by recrystallization from methanol, followed by sublimation and zone refining. A single crystal 1 cm in diameter and approximately 5 cm long was grown by the Bridgman method.[14] In order to maximize the filling factor, the crystal was cleaved into three sections and each section was ground into a cylinder whose outside diameter just filled the inside of a 5-mm NMR sample tube. Care was taken to mount the samples such that the axes of the cylinders lay along three mutually orthogonal directions in the original crystal, and in one mounting that the cleavage plane lay perpendicular to the axis of rotation.

All experiments were performed at room temperature on a Bruker CXP-200 spectrometer operating at 200 and 50.3 MHz for protons and carbons, respectively. The combined techniques of cross polarization and high-power proton decoupling[15] were used to acquire spectra from the stationary single crystals. As the proton T_1 in the naphthalene crystal was longer than 1 h, the pulse sequence was terminated with a 90° "flip back" pulse[16] which returned the spin-locked ^{1}H magnetization to the z axis, thereby shortening the delay required between acquisitions.

Single-crystal rotation patterns were obtained with a Bruker double-tuned solids probe modified by replacing the spinner assembly with a single-axis goniometer. The goniometer was constructed from a 60:1 ratio brass worm-gear set held in a Teflon assembly facilitating precise rotation of the sample about an axis perpendicular to the magnetic field. A Teflon sleeve pressed into the center of the gear accepted a shortened NMR tube containing the sample. Extensive electronic modifications to the probe to maximize sensitivity are described elsewhere.[17] Each of the three 180° rotation patterns were taken in 10° increments. The individual spectra resulted from 12 accumulations of the FID using a single 5 ms contact per accumulation and a repetition time of 1200 s. The Hartmann-Hahn matching condition[18] was achieved with $H_1 \sim 100$ G and $H_2 \sim 25$ G. This same H_2 field was used for decoupling during acquisition.

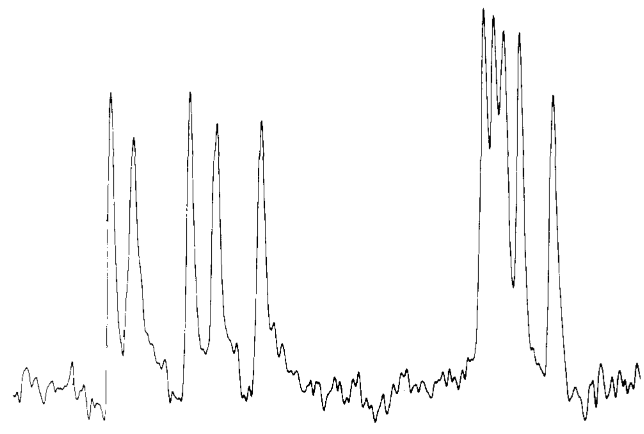

Figure 3. Representative ^{13}C spectrum of single-crystal naphthalene in which all ten theoretically possible lines are resolved. The spectral width shown is 10 kHz.

A ^{13}C MAS spectrum[19] was obtained using another modified Bruker probe[17] with a 5 kHz spinning frequency, 1200 s repetition time, 5 ms contact time, 80 accumulations, and rf fields of $H_1 \sim 80$ G and $H_2 \sim 20$ G.

All ^{13}C chemical shifts are reported in ppm relative to liquid tetramethylsilane (TMS) with positive values assigned to downfield shifts. The nearly isotropic methyl resonance of solid hexamethylbenzene (17.6 ppm) was taken as an external reference standard. By convention the principal values are designated δ_{11}, δ_{22}, and δ_{33} in order of increasing field strength.

Results

A naphthalene single-crystal spectrum containing all ten possible lines is shown in Figure 3.

Preliminary analysis traced the evolution of each line through the spectra of the three rotations, connected lines between rotations, and identified which lines corresponded to congruent tensors on the two molecules. All 570 frequencies measured in the three rotations were then least-squares fitted simultaneously with a FORTRAN program similar to one described before.[20] This program enforces the 2-fold symmetry between congruent tensors, while adjusting two angles describing the 2-fold axis direction and six angles describing slight tilts of the mountings of the crystal between the rotations, to obtain the thirty elements of the five non-congruent tensors. The standard deviation of the fit to the naphthalene data is 0.378 ppm. This first fit determines the five tensors and finds the apolar direction of the 2-fold b crystal axis from the tensor data, but it neither orients the crystal around the axis nor gives the vector sense of the axis.

The δ_{33} components of aromatic carbon tensors lie perpendicular to the plane of the ring,[1] and the directions of the ten δ_{33} components of the naphthalene tensors in the fit were found to be closely grouped in two sets of five. By assuming that a single composite δ_{33} direction for each set of five components would lie perpendicular to the plane of each of the two naphthalene molecules it becomes possible to orient the crystal around the 2-fold axis with use of the tensors themselves. A second fit was made for this purpose by adding the constraint that the tensors' δ_{33} components lie in only two directions at equal angles from the 2-fold axis in a plane containing that axis. The results of this fit combined with the known orientation of the cleavage plane also resolve the sense of the 2-fold axis. Finally, the neutron diffraction structure was used to give the orientation of the naphthalene molecule in the plane normal to the composite δ_{33} directions to obtain the complete transformation between the sample reference frame and the molecular axis system. Figure 2 shows the orientation of the molecular axes, identical with that used in the

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(14) Sherwood, J. N. In *Purification of Inorganic and Organic Materials*; *Techniques of Fractional Solidification*; Zief, M., Ed.; Marcel Dekker: New York, 1969; Chapter 15.

(15) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

(16) Tegenfeldt, J.; Haeberlen, U. *J. Magn. Reson.* **1979**, *36*, 453.

(17) Jiang, Y. J.; Pugmire, R. J.; Grant, D. M. *J. Magn. Reson.* **1987**, *71*, 485.

(18) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.

(19) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.

(20) Sherwood, M. H.; Alderman, D. W.; Grant, D. M. *J. Magn. Reson.* **1989**, *84*, 466.

(21) Jameson, C. J.; Osten, H. J. *Ann. Rep. NMR Spectrosc.* **1986**, *17*, 1.

Table I. Experimental ^{13}C Shift Tensors of Naphthalene in the Molecular Axis System[a,b]

nucleus	δ_{iso}[c]	δ_{XX}	δ_{YY}	δ_{ZZ}	δ_{XY}	δ_{YZ}	δ_{ZX}
C1	129.3	143.2	221.8	22.8	15.5	−0.6	−0.4
C2	126.0	196.8	170.0	11.1	42.0	0.8	0.8
C3	125.4	195.9	169.9	10.4	−42.8	−0.1	1.2
C4	129.9	148.1	221.3	20.4	−13.8	0.5	−0.8
C4a	134.9	208.3	202.4	−5.9	1.1	0.0	−0.9

[a] The isotropic shift δ_{iso} and the diagonal terms, δ_{XX}, δ_{YY}, and δ_{ZZ}, are in ppm downfield from TMS. The remaining terms, δ_{XY}, δ_{YZ}, and δ_{ZX}, are off diagonal and thus independent of reference. [b] The molecular axis system is shown in Figure 2. [c] Isotropic shift; $\delta_{iso} = (\delta_{XX} + \delta_{YY} + \delta_{ZZ})/3 = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

neutron diffraction work.[11] The transformation obtained from the second fit and the diffraction data was used to convert the tensors obtained from the first fit into the molecular axis system. The results are presented in Table I.

The second fit which orients the crystal around the 2-fold axis had a standard deviation of 0.542 ppm, indicating a small, but statistically significant, deviation of the five δ_{33} directions from the assumed composite directions. The angle between the 2-fold axis and the two constrained normal directions obtained by the tensor data fit was 63.59°, while the neutron diffraction data gave 63.53°. That these two independently determined angles are nominally identical is a necessary, though not sufficient, condition for the δ_{33} directions to be perpendicular to the molecular planes. The direction perpendicular to the cleavage plane was found by the fit to be 2.64° from one of the rotation directions, a value consistent with the accuracy with which the crystal was mounted. Thus the orientation of the crystal from the tensors is consistent with all other available information.

The tensor with diagonal values $\delta_{XX} = 209$, $\delta_{YY} = 202$, and $\delta_{ZZ} = -6$ ppm was unambiguously assigned to the bridgehead carbon C4a because it lacked a similar partner among the other four tensors. The C2 and C3 assignments were made by diagonalizing the remaining tensors and requiring that the δ_{11} directions lie approximately along the C2–H and C3–H bonds. As the C1–H and C4–H bonds are nearly parallel, the assignment was made based on the theoretical calculations of the next section.

Calculations

The in-plane components of the ^{13}C chemical shielding tensors in naphthalene have been calculated previously[4] by using the Pople model of chemical shielding[3] employing the MNDO method[2] to evaluate the wave functions. Within the Pople model, the elements of the shift tensor are given by

$$\delta_{\alpha\alpha}^{\mathrm{calc}} = Af_{\alpha\alpha}(\mathbf{P}_{\mu\nu}) + B$$

$$\delta_{\alpha\beta}^{\mathrm{calc}} = Af_{\alpha\beta}(\mathbf{P}_{\mu\nu}) \qquad (\alpha \neq \beta)$$

where $\delta_{\alpha\beta}$ is the $\alpha\beta$ component of the shift tensor referenced to TMS, $f_{\alpha\beta}$ is a function of the MNDO calculated electron density matrix $\mathbf{P}_{\mu\nu}$ given previously,[4] and the parameters A and B are empirical constants related to the molecular electronic excitation spectrum of the molecule.

Previous calculations in naphthalene[4] were performed with the parameters A and B determined in pyrene and an idealized geometry based on the experimental bond distances in benzene. Since the experimentally determined structure of naphthalene shows significant deviations from this idealized geometry, the calculations were repeated with the structure derived from the neutron diffraction data with the presumed *mmm* symmetry and with all C–H bond lengths set to 1.08 Å. The calculated MNDO bond orders[2] are given in Figure 4.

A and B were determined empirically with a linear correlation by computing experimental shifts, δ_n^{exp}, and theoretical shieldings, σ_n^{calc}, for the magnetic field in three in-plane trigonal directions with the equations

$$\delta_n^{\mathrm{exp}} = \sum_{\alpha\beta} c_{n\alpha}\delta_{\alpha\beta}c_{n\beta}$$

$$\sigma_n^{\mathrm{calc}} = \sum_{\alpha\beta} c_{n\alpha}f_{\alpha\beta}(\mathbf{P}_{\mu\nu})c_{n\beta}$$

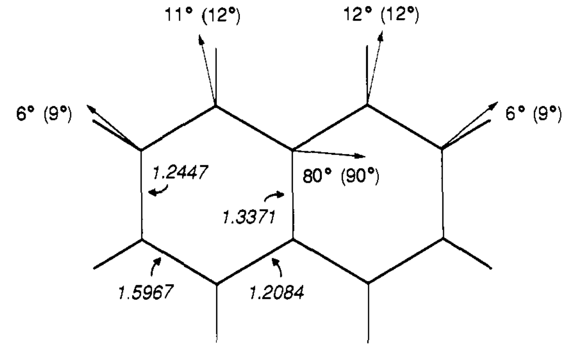

Figure 4. Orientation of the in-plane principal axes of the ^{13}C shift tensors relative to the C–H bonds in naphthalene. Arrows show the directions of the δ_{11} components. Calculated angles are given in parentheses. All δ_{33} components are oriented perpendicular to the molecular plane. Calculated MNDO bond orders are shown in italics.

Table II. Experimental and Calculated Principal Values of the ^{13}C Shift Tensors of Naphthalene in ppm Downfield from TMS[a]

nucleus	δ_{iso}[b]	δ_{11}	δ_{22}	δ_{33}
C1	129.3	224.7 (226.1)	140.3 (141.9)	22.8
C2	126.0	227.6 (229.9)	139.3 (139.4)	11.1
C3	125.4	227.6 (229.9)	138.2 (139.4)	10.4
C4	129.9	223.9 (226.1)	145.6 (141.9)	20.4
C4a	134.9	208.5 (206.6)	202.2 (196.7)	−5.9

[a] The calculated values given in parentheses are expressed in ppm downfield from TMS using the determined values $A = 168.3$ ppm/au and $B = -41.6$ ppm. [b] Isotropic shift; $\delta_{iso} = (\delta_{XX} + \delta_{YY} + \delta_{ZZ})/3 = (\delta_{11} + \delta_{22} + \delta_{33})/3$.

where the trigonal directions are indicated by the index n, α and β take the values X and Y, and the $c_{n\alpha}$ are the directional cosines of the nth direction. The trigonal directions are given by

$$c_{1X} = 0 \qquad c_{1Y} = 1$$

$$c_{2X} = -\sqrt{3/4} \qquad c_{2Y} = -1/2$$

$$c_{3X} = +\sqrt{3/4} \qquad c_{3Y} = -1/2$$

The set of δ_n^{exp} are thus given by

$$\delta_1^{\mathrm{exp}} = \delta_{YY}$$

$$\delta_2^{\mathrm{exp}} = 3/4\,\delta_{XX} + 1/4\,\delta_{YY} + \sqrt{3/4}\,\delta_{XY}$$

$$\delta_3^{\mathrm{exp}} = 3/4\,\delta_{XX} + 1/4\,\delta_{YY} - \sqrt{3/4}\,\delta_{XY}$$

and similarly for the σ_n^{calc} with $f_{\alpha\beta}(\mathbf{P}_{\mu\nu})$ in place of $\delta_{\alpha\beta}$.

The five experimental tensors were finally assigned to the carbons by evaluating the standard deviations of straight lines fitted to the trigonal experimental shifts and calculated shieldings for all 5! = 120 possible assignment permutations. The standard deviation for the given assignment is 3.4 ppm, while that for the next-best permutation was 16.5 ppm. An excellent correlation is obtained for the given assignment, as is evident in Figure 5 where three in-plane shift-shielding pairs for each tensor are plotted. This treatment provided the C1 and C4 assignments and confirmed the C2, C3, and C4a assignments made above.

The experimentally determined principal values are given in Table II along with the results of the theoretical calculations. The orientations of the experimental and theoretical tensors in the molecular frame are depicted in Figure 4 and favorable agreement is noted.

Discussion

Rules relating the in-plane components of ^{13}C chemical shift tensors in polycyclic aromatic compounds to Kekule and MNDO bond orders have been derived previously.[1,4]

The near-axial symmetry of the C4a tensor in naphthalene may be rationalized in terms of the number of formal double bonds that can be drawn to the bridgehead carbon in the Kekule structures. Each of the three bonds connecting the bridgehead to adjacent carbons appears as a double bond in only one of the

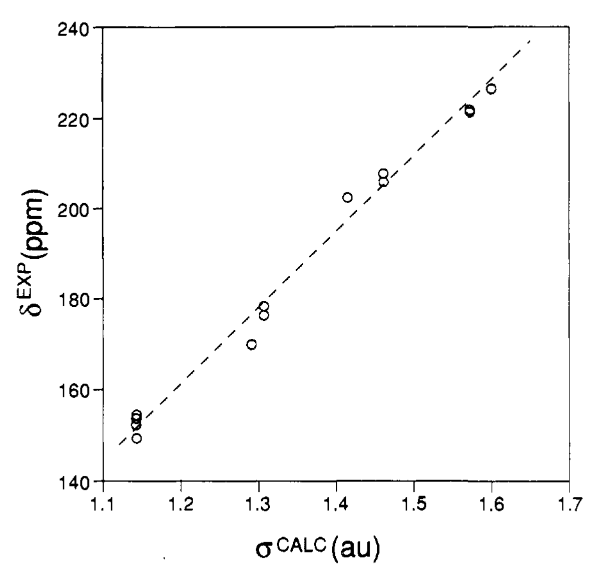

Figure 5. Correlation of calculated shieldings and experimental shifts for the given assignment. Shieldings and shifts are plotted for the magnetic field in trigonal directions in the plane of the naphthalene molecule. The dashed line is the best-fit straight line which minimizes the sum of the squares of the theoretical residuals with slope A = 168.3 ppm/au and intercept B = −41.6 ppm.

three Kekule structures of naphthalene. Thus the bond between the two bridgehead carbons will have the same weighting as the two remaining bonds, predicting that the bridgehead carbon tensor should be axially symmetric in naphthalene. The near-axial symmetry found here is consistent with this picture. When MNDO-derived bond orders are employed they predict that the δ_{11} principal axis for the bridgehead carbon C4a will be oriented perpendicular to the central C4a–C8a bond in naphthalene. Indeed such an orientation is found experimentally, although a 10° deviation (see below) is present.

In all higher members of the homologous series naphthalene, anthracene, naphthacene, pentacene, etc., one of the nonbridge bonds always appears as a formal double bond in more than one of the possible Kekule structures. Thus in all higher members of the series the δ_{11} component is never predicted to align perpendicular to the bridging bond, making the naphthalene result unique. The MNDO calculated bond orders for these compounds agree with this simple Kekule explanation.[4]

The calculated bond orders, given in Figure 4, can also explain the small but significant deviations of the δ_{11} directions from the C–H bond directions. For all the protonated carbons the experimental and calculated angles between the δ_{11} and C–H directions are in good agreement. Furthermore, the δ_{11} axes move toward the direction perpendicular to the adjacent C–C bond with the larger bond order. This experimental result confirms that C1–C2 has a higher double bond character than either the C2–C3 or C4–C4a bonds, in accordance with the MNDO calculation. The simple valence-bond picture is in agreement, as there are two Kekule structures with a C1–C2 double bond, while C2–C3, C4–C4a, and C4a–C8a double bonds appear in only one structure.

Ab initio calculations of the ^{13}C shielding tensors in naphthalene performed in this laboratory will be discussed in detail elsewhere. They are in reasonable agreement with the experimental results and reproduce well the trends observed in δ_{33}.

An interesting feature of the experimental tensors is their deviation from *mmm* symmetry. The most significant effects are in the C1 and C4 tensors, where the δ_{22} values differ by 5.3 ppm and the δ_{33} values differ by 2.4 ppm, well outside the standard deviation of the fit of 0.378 ppm. The δ_{11} values for C1 and C4 differ by only 0.8 ppm which is of questionable significance given the above estimation of error. The difference in the C1 and C4 isotropic chemical shifts is only 0.6 ppm, which was unresolved in the ^{13}C MAS spectrum due to the widths of the lines. The deviation of the C4a δ_{11} direction by 10° from the in-plane perpendicular to the C4a–C8a bond is also a departure from *mmm* symmetry. However, as a result of the near-axial symmetry of the tensor, the orientation of the δ_{11} principal axis is determined so poorly that the significance of this deviation remains in question. Fortunately, these symmetry-breaking effects are small enough that the theoretical tensors obtained with an assumed *mmm* molecular symmetry still closely resemble the experimental tensors for the $\bar{1}$ symmetry and can be used for establishing the assignments.

Similar effects on solid-state chemical shifts have been detected in the ^{19}F CRAMPS spectrum of perfluoronaphthalene.[22] In naphthalene, the packing effects are not exhibited in the ^{13}C MAS spectrum due to the coincidental cancellation of changes in the principal values of the shift tensors.

The presence of *mmm* symmetry breaking perturbations in naphthalene is consistent with the symmetry of the molecular site, but it is somewhat surprising considering the diffraction results which show no distortion of the molecule. The intermolecular closest approaches within the lattice may account for this symmetry breaking in the NMR data. The hydrogen atom H(C1) in the reference molecule centered at the origin of the unit cell is approached within 2.4 Å by H(C2) in the molecule centered at ($^1/_2$, $^1/_2$, 1). In addition, carbons C4 and C4a in the reference molecule are both approached within 2.8 Å by H(C4) in the molecule positioned at (−$^1/_2$, $^1/_2$, 0). The breaking of *mmm* symmetry observed in the shift tensors can arise from two possible contributions. The magnetic environment of a carbon nucleus may be altered by direct shielding from the electrons associated with a closely positioned neighboring molecule. In an aromatic molecule such as naphthalene these effects might be due to ring currents, which could be modeled with point dipoles centered in the rings of neighboring molecules. Such an approach including many neighbors was tried, but it failed to reproduce the trends observed. Alternatively, the molecular structure may actually be distorted from *mmm* symmetry under the influence of the crystal field, thus altering the local electronic structure. For small molecules it is well established that $|\partial\delta/\partial R|$ can be of the order of 10^2 to 10^3 ppm/Å,[21] thus $\Delta\delta$ of only a few ppm, as observed in this study, could be explained with ΔR values on the order of 10^{-2}–10^{-3} Å, distances comparable to the uncertainties of the diffraction data. Since the effects of molecular distortions cannot be separated from the effects of shielding from neighboring molecules, the relative magnitudes of these two contributions are not experimentally measurable. Understanding of these effects awaits diffraction data of greater accuracy along with more detailed and precise theoretical models.

The breaking of the *mmm* molecular symmetry by the naphthalene tensors, indicating the high sensitivity of chemical shifts to subtle changes in the electronic environment, portends high promise for ^{13}C NMR studies of such effects in solids. Moreover, single-crystal studies detect effects on the chemical shifts which are not measurable by MAS NMR when changes in tensor principal values coincidentally cancel. These results suggest that joint single-crystal NMR and diffraction studies would be valuable for substances whose crystal size and molecular composition are within the capabilities of the NMR method.

Acknowledgment. Helpful discussions with Kent Dalley on the diffraction literature of naphthalene are gratefully acknowledged. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy under Grant DE-FG02-86ER13510.

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[22] Harris, R. K.; Jackson, P.; Nesbitt, G. J. *J. Magn. Reson.* **1989**, *85*, 294.