

Carbon-13 chemical shielding tensors in single-crystal durene*

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The method of proton-enhanced nuclear induction spectroscopy [A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.* **59**, 569 (1973)] has been employed to find the eigenvalues and eigenvectors of the chemical shift tensors for the various ¹³C nuclei in a single crystal of durene (1, 2, 4, 5-tetramethylbenzene). For each type of carbon the trace of the shielding tensor, $\text{Tr}\sigma$ agrees well with the isotropic shift σ_i found from spectra of liquid solutions. The well-known tendency of σ_i to be smaller for aromatic than for aliphatic carbon is found to be ascribable largely to the very small shielding which occurs for the former when the applied field is in the plane of the ring and tangent to it at the C atom in question. The CH₃ carbons have much less anisotropic shielding than do the ring carbons. The rather close coincidences between nominal bond directions and the eigenvectors of σ suggest that nonbonded interactions in the crystal play an unimportant role.

I. INTRODUCTION

Magnetic screening of nuclei by induced electronic currents has effects on NMR spectra expressed by

$$\mathcal{H}_e = \sum_i \mathbf{H}_0 \cdot \sigma_i \cdot \mathbf{I}_i, \quad (1)$$

where σ_i is an effectively¹ symmetric second-rank tensor. In a liquid, the rapid tumbling of the principal axes of σ_i with respect to \mathbf{H}_0 and \mathbf{I}_i erases the influence of everything except the isotropic chemical shift $\sigma = \frac{1}{3} \text{Tr}\sigma$. Even this quantity has proven a very useful one to know, and an enormous body of lore has grown up concerning its relationship to molecular structure and reactivity, substituent and solvent effects, and the like. However, it is clear that a new dimension of knowledge and understanding would be added to all these matters if all six independent elements of σ could be determined experimentally. The way to make such measurements is clearly to observe the NMR spectra of molecules which are oriented in some known way with respect to \mathbf{H}_0 , and oriented molecules *par excellence* are found in crystals.

We have been interested to show that overwhelming dipolar broadening, which used to be thought an unavoidable obstacle to such studies, can be largely removed in many cases:

(a) If only one species of magnetic spins (e.g., ¹H or ¹⁹F) is present, its resonance can be narrowed by any of a number of multiple-pulse techniques²⁻⁷ and its shielding tensors determined.^{1, 8, 9}

(b) If two (or more) such species are abundantly present, similar techniques can be applied to the species of interest while at the same time subjecting the others to suitably pulsed decoupling fields.¹⁰

(c) If the species of interest is dilute (e.g., ¹³C in natural isotopic abundance) but immersed in a sea of other abundant spins (e.g., protons), the broadening can be reversed by relatively simple decoupling techniques¹¹ while at the same time the otherwise very weak signals from the rare spins can be greatly amplified by transferring polarization from the abundant spins.¹²⁻¹⁷ The principles of this method are described in Paper I (immediately preceding this one). In the present paper we illustrate its application to the determination of chemical shielding tensors.

We have chosen single crystals of durene, C₆H₂(CH₃)₄, as the experimental subject. This choice was made not in the hope of answering any particular questions about durene, but simply because it is an easily crystallized substance, containing C atoms of commonly occurring types, aliphatic and aromatic, and having enough complexity to illustrate the possibilities of the method but not so much as to becloud the underlying principles. We emphasize that the method in question is rather general and can be applied to a very wide variety of organic and biological substrates.

The crystal structure of durene was one of the earliest organic structures determined.¹⁸ It is a monoclinic prismatic structure with space group C_{2h}⁵(P2_{1/a}). The unit cell parameters are: $a = 11.57$, $b = 5.77$, $c = 7.03$ Å, and $\beta = 113.3^\circ$. The asymmetric structural unit consists of $\frac{1}{2}$ of a molecule. Hence there can be only five incongruent⁸ ¹³C shielding tensors: two in adjacent methyl groups, the two ring carbons to which these methyls are bonded, and one unsubstituted ring carbon. The other tensors are related to these by crystallographic symmetry operations. All carbon atoms, the two hy-

drogens of the nonsubstituted positions, and one hydrogen from each methyl group are coplanar. The methyl groups cause slight in-plane deformations of the benzene rings: the four included C-C-C angles where methyl groups are substituted are 118.6° and the remaining two are 122.7° . The C-C bond lengths in the ring are 1.4 \AA as for benzene. The angle between the CH_3 -C bond and the long axis of the molecule is about 32° . The two molecules in the unit cell are almost normal to the (001) plane. A refined crystal structure of durene¹⁹ has shown slight differences in crystal and molecular parameters.

II. EXPERIMENTAL

A single crystal study of the ^{13}C chemical shift tensors of durene was done at room temperature, $22 \pm 1^\circ \text{C}$, by using the above-mentioned cross-polarization technique. The experiments were done with a pulse spectrometer described elsewhere²⁰ at 97.260 and 24.467 MHz for protons and carbons, respectively. To match the Hartmann-Hahn condition, $H_1 \sim 10 \text{ G}$ for protons and $\sim 40 \text{ G}$ for carbons. The recycle time was 8 sec during which only one contact between reservoir (protons) and rare spins (carbons) was established. About 100 accumulations ($\sim 15 \text{ min}$) were done to obtain a reasonable signal-to-noise ratio.

A single crystal of durene obtained from Princeton Organics, Incorporated, has been grown by zone refining. Because the crystal is very volatile at room temperature, we could not easily use x rays to align it. The very strong cleavage in the plane (001) and the NMR data were used to orient the crystal. For easier analysis of the NMR data a cube with edges of 4 mm and angles $90^\circ \pm 2^\circ$ was carefully cut from the crystal. One plane of the cube was the cleavage plane. Thus the rotations through 180° in steps of 10° were performed about three perpendicular axes of the cube. For this purpose a specially designed goniometer (Fig. 1) was used. The goniometer consists of a ring (R) which regulates precisely the rotation about an axis normal to the magnetic field, a gear (G) with 36 teeth, the angle between teeth being $10^\circ \pm 0.3^\circ$, a button (BU) on whose top the crystal (X) was glued using an acrylic coating, a base (BA), and a plate (P) with teeth at the end which couple with the gear's teeth when the gear is rotated precisely 10° about its axis. The gear and button were fixed with two screws. For the purpose of x-ray alignment of the crystal and changing the position of the crystal, the button can be easily dismantled and mounted on the goniometer. CC and PC are carbon and proton coils, respectively, the latter being of the Helmholtz type.

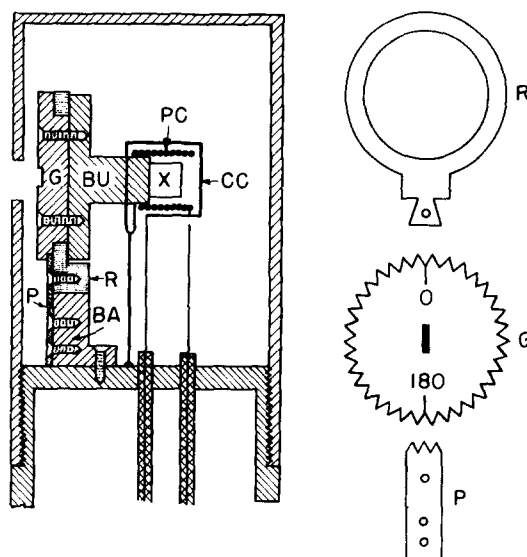


FIG. 1. Goniometer used for obtaining the orientation dependence of NMR spectra.

III. ANALYSIS OF NMR SPECTRA

As mentioned earlier, the symmetry of the unit cell permits the occurrence of five incongruent ^{13}C shielding tensors, three corresponding to ring carbons and two to methyl carbons. The unit cell contains four asymmetric units, so that in general one would expect 20 NMR lines for an arbitrarily oriented crystal. However, the two halves of each durene molecule are related by a center of symmetry and the chemical shift σ_{zz} is invariant to inversion, so only 10 lines are expected. In some orientations all 10 of these are in fact resolved. Figure 2 shows a representative spectrum obtained when H_0 makes angles with a , b , c^* 197° , 0° , 107° , respectively. The six lines at the left correspond to the three inequivalent ring carbons of each of the two molecules in the unit cell, and those at the right similarly arise from the methyl carbons.

A representative rotation plot is shown in Fig. 3. The points are experimental and the solid curves are least squares fits to a trigonometric dependence of period π . Similar data were obtained for rotations about two other orthogonal axes. These results served to define the chemical shielding tensors in laboratory frames (L), defined so that Z_L lies along H_0 , Y_L along the axis of rotation, and X_L is chosen to complete a right-handed system. The data thus obtained were used as input to a computer program, written by Mehring and described elsewhere,²¹ which calculates the components of σ in a frame fixed in the crystallographic unit cell. The orientation of the unit cell with respect to the faces of the cubical sample used was partly known from the fact that one

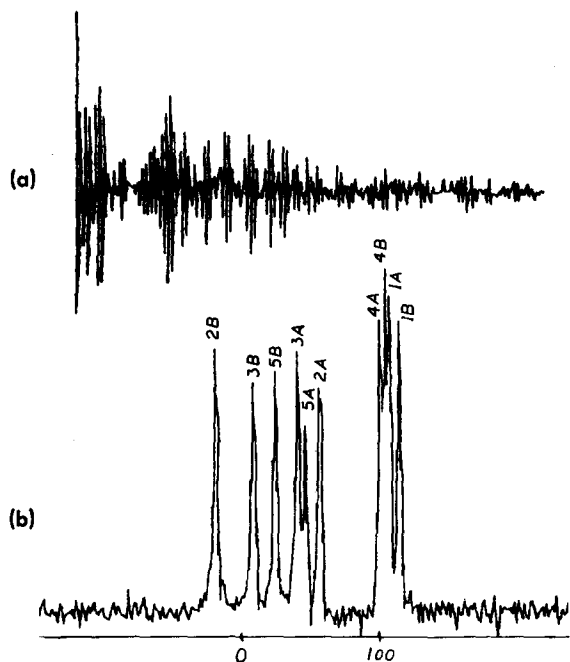


FIG. 2. Representative proton-enhanced free induction decay and absorption spectrum for natural-abundance ^{13}C spins in a durene crystal. At this orientation (see text) all 10 theoretically possible lines are resolved. Aromatic resonances lie at the left and methyl resonances comprise the dense group at the right.

of the faces of the latter coincided with the prominent cleavage plane of durene. The remaining angles were determined from the NMR results on the basis of the fact that the NMR spectra of both molecules in the unit cell must coincide, under the symmetries enforced by the $2P_{1/a}$ space group, when H_0 is along either the (100) or the (010) axis.

Since the crystal structure is fully known, the various shielding tensors could now be transformed into frames fixed in a symmetric way in one molecule or the other in the unit cell. When this was done, the tensors naturally fell into two groups, each being closely related to the bonding geometry and symmetry of one molecule. Symmetry demands that the eigenvalues of σ for a particular C atom on one molecule be the same as those for the corresponding C atom on the other molecule. Since this requirement had not yet been enforced in the analysis, small differences (of ~ 2 ppm in the eigenvalues and $\sim 2^\circ$ in the eigenvectors) appeared. The pairs of tensors were therefore averaged together. The final results are presented in Table I and shown pictorially in Fig. 4.

IV. DISCUSSION

From Table I it is evident that $\bar{\sigma} = \frac{1}{3}\text{Tr}\sigma$ agrees quite well, for each of the chemically different

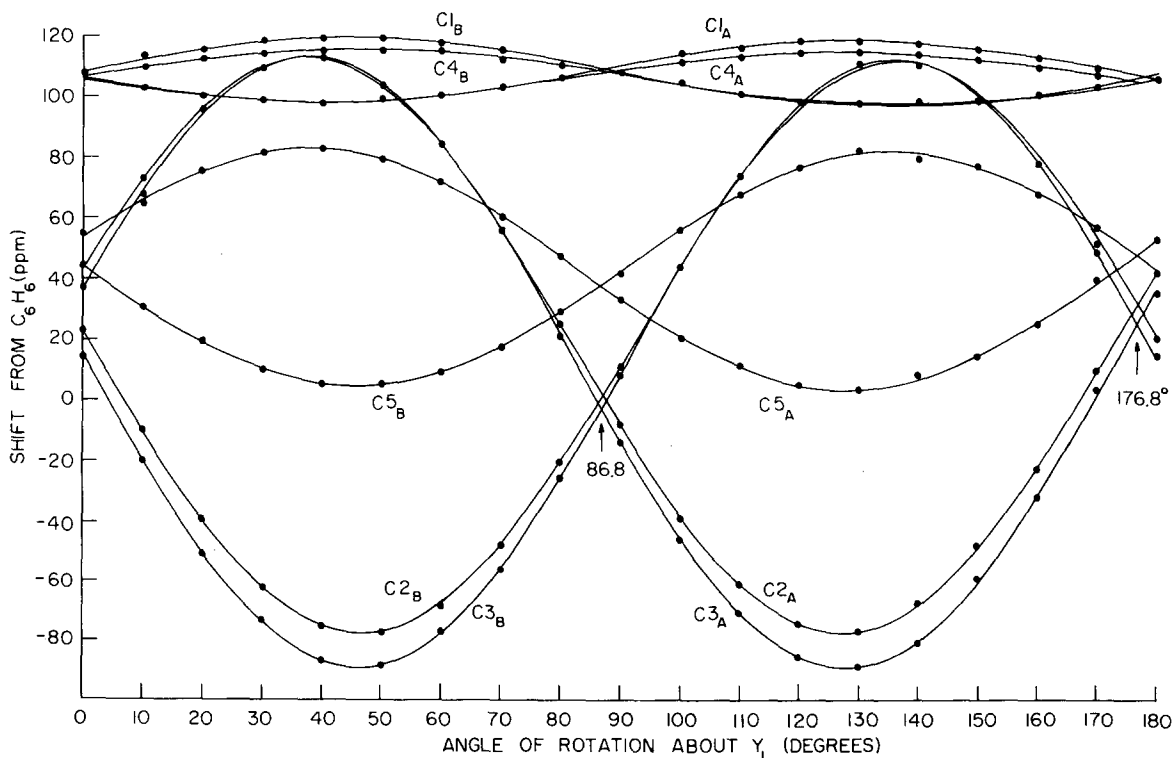


FIG. 3. Representative plot of angle dependence of the absorption spectrum of durene.

TABLE I. Shielding tensors for the carbon atoms of durene, referred to the $\{LMN\}$ coordinate system fixed in the molecule. See Fig. 4.

Carbon	Eigenvalues			Eigenvectors			$\bar{\sigma}$	σ_i
C1	σ_{11}	126.8 ± 1.0	-0.7700	-0.6370	-0.0375		110.0	109.2
	σ_{22}	105.3 ± 1.0	-0.6376	0.7635	0.0887			
	σ_{33}	98.0 ± 1.0	0.0285	-0.1034	0.9961			
C2	σ_{11}	112.0 ± 3.4	0.0087	-0.0454	0.9994		-5.8	-5.0
	σ_{22}	-27.7 ± 3.4	-0.4609	0.8854	0.0070			
	σ_{33}	-101.6 ± 4.1	-0.8878	-0.4610	-0.0105			
C3	σ_{11}	110.9 ± 2.2	0.0087	-0.0384	0.9997		-4.3	-5.0
	σ_{22}	-26.8 ± 2.2	0.5164	0.8559	0.0238			
	σ_{33}	-97.1 ± 3.6	-0.8563	0.5143	0.0323			
C4	σ_{11}	125.6 ± 1.0	-0.7553	0.6548	0.0078		109.7	109.2
	σ_{22}	105.0 ± 1.0	-0.6541	-0.7548	0.0661			
	σ_{33}	98.4 ± 1.0	0.0471	-0.0212	0.9989			
C5	σ_{11}	82.6 ± 1.3	0.0061	-0.0404	0.9994		-1.7	-2.8
	σ_{22}	6.4 ± 1.5	-0.9960	0.0122	0.0027			
	σ_{33}	-94.1 ± 1.5	0.0125	0.9999	-0.0556			

types of carbon in the durene molecule, with the effective isotropic shifts σ_i for the same substance in solution. It is also clear that the tensors σ have eigenvectors which are oriented in simple ways with respect to the chemical bonding structure, and in fact have no perceptible departures from orientations which might be imposed in an isolated molecule. This is in contradistinction to some ^{19}F shielding tensors reported earlier⁸ which show definite perturbations which must arise from intermolecular ("nonbonded") interactions, (and could be used as the first empirical steps toward an understanding of solvent effects on chemical shifts). It is perhaps not surprising that ^{19}F atoms, which reside on the molecular exterior, show greater intermolecular perturbations than the relatively buried ^{13}C atoms. In any case, it seems probable that the ^{13}C shielding tensors found here reflect quite accurately the properties of the isolated durene molecule itself. As such, they form a far more detailed experimental basis for the understanding of chemical shielding via molecular theory than do the much-studied average chemical shifts which are observed in liquids.

In this connection, note from Fig. 4 and Table I, that (a) the methyl shift tensors are not very anisotropic; (b) their eigenvalues are not very different from elements σ_{11} of the shift tensors of the ring carbons (these corresponding to H_0 being normal to the molecular plane); (c) the least shielding of the ring carbons occurs when H_0 is in the molecular plane, and particularly so when it is tangent to the ring at the carbon atom in question. That is, the distinction between methyl carbon and ring carbon is not a general one, but one largely associated with the circulation of diatomic charge about special directions in the molecule. Not be-

ing specialists in the various degrees of neglect of differential overlap, we defer to those who are for an *a posteriori* rationalization of these facts.

In a more empirical vein, note that our measurements would have formed a basis for a partial determination of the crystal structure of durene had it been necessary. As remarked in the previous section, the shift tensors fall into two families, each corresponding to one of the molecules in the unit cell. One of the eigenvectors of each ring C atom lies normal to the molecular plane, within our experimental error. Assuming this to be exactly so, our diagonalization of the various ring-carbon shielding tensors says that the angles between the molecular axes of the two molecules in the unit cell are (see Fig. 4) $L: 82.4^\circ \pm 0.6^\circ$; $M: 175.8^\circ \pm 2.0^\circ$; $N: 98.3^\circ \pm 1.3^\circ$. The corresponding angles from x-ray diffraction are 82.8° , 177.8° , and 97.3° , respectively. The NMR results were obtained rather quickly and economically, without the large amounts of computation which are required for exact quantitative structural information through diffraction. We should also add parenthetically that information concerning internuclear distances, as well as angles, can be obtained through high-resolution NMR of solids if the dilute spins studied lie close to other spins (of the same or of a third species) which produce a resolved dipole-dipole splitting. In this sense, studies of the type we report here may revive some of the promise for structural studies envisioned many years ago in the pioneering work of Pake²² and others.

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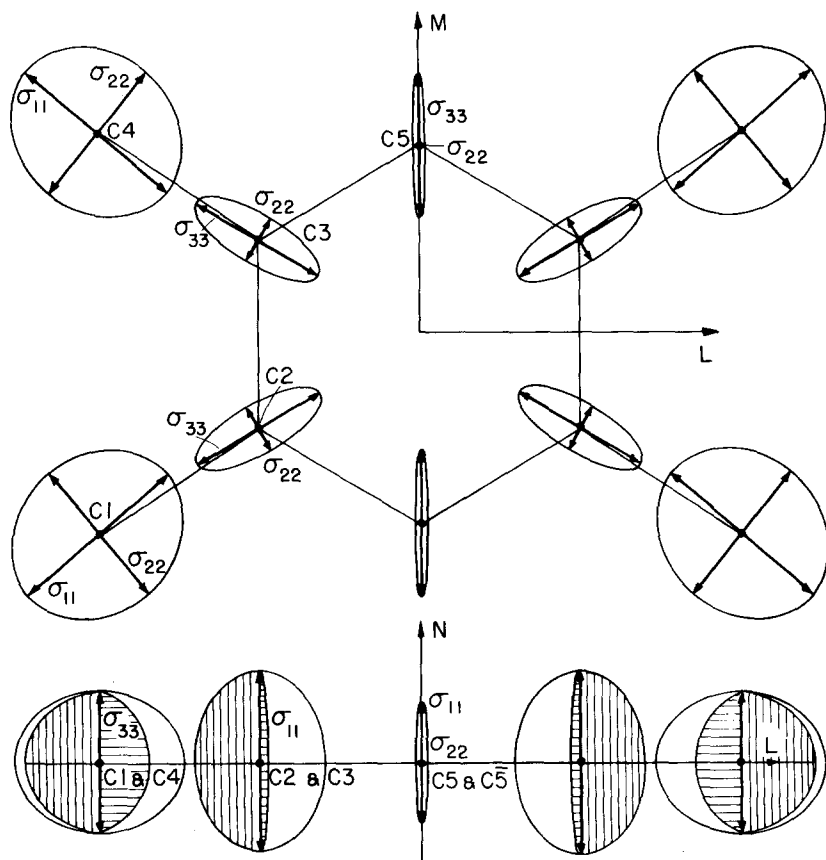


FIG. 4. Representation of the ^{13}C shielding tensors in durene listed in Table I. The shielding ellipsoids, shown in two projections, are such that the diameter in any direction is linear in the chemical shift for the applied field H_0 in that direction. The origin of chemical shifts is chosen arbitrarily.

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