4268

J. Am. Chem. Soc. **1986,** *108,* 4268–4272

narrow component in the slow-motion limit. Available formulas[5,8,15] predict a minimum line width of 80 Hz for the narrow component at 132.28 MHz assuming isotropic motion with $(e^2qQ/h)(1+\eta_Q^2/3)^{1/2}$ equal to 1.6 MHz and a 100 ppm chemical shift anisotropy. Although the calculated line width is smaller than that observed, the calculated minimum increases if a distribution of correlation times is assumed, or if larger values of the shift anisotropy or quadrupole coupling constant are assumed.

Conclusions

Our purpose was to identify the sources of non-Lorentzian (two component) ^{23}Na line shapes in two simple systems and to ascertain what information about molecular motion and quadrupole coupling constants can be obtained from measurements of relaxation times and line shapes, especially in the slow-motion region. On the basis of our observations of sodium chloride in glycerin and in sodium laurate/lauric acid we conclude that non-Lorentzian line shapes can be interpreted reliably only if one measures T_1, T_2, total signal intensity, and line shape as functions of τ_c and ω_0. The ^{23}Na data presented here for sodium chloride in glycerin (Figure 4) provide a guideline for the relaxation behavior expected if there is a single population of sodium nuclei in the sample. An estimate of $(e^2qQ/h)(1 + \eta_Q^2/3)^{1/2}$ can be obtained from relaxation measurements in the neighborhood of the T_1 minimum, while

the correlation time and individual spectral densities, $J(\omega_0)$ and $J(2\omega_0)$, can be obtained from analysis of relaxation times and line shapes in the slow-motion region. However, in practice, detection of the broad component will require a spectrometer having a short deadtime, <10 μs, and an intense radio frequency pulse, $\gamma B_1/2\pi$ = 100 kHz. Also, as noted, one must exclude glass from the vicinity of the receiver coil.

The line widths of the $\pm^1/_2 \leftrightarrow \pm^3/_2$ transitions of bound sodium ions are significantly reduced when the bound ions rapidly exchange with a large population of rapidly tumbling free ions.[16] Although fast exchange greatly reduces the problem of detecting the broad component, the price one pays is the introduction of a large number of unknown parameters that must be determined.[16] Complete analysis of even a simple fast exchange system such as sodium laurate requires the extensive relaxation measurements mentioned earlier.

(16) Bull, T. E. *J. Magn. Reson.* **1972,** *8,* 344–353.

Low-Temperature ^{13}C Magnetic Resonance in Solids. 6. Methine Carbons†

Julio C. Facelli, Anita M. Orendt, Mark S. Solum, Gisbert Depke, David M. Grant,* and Josef Michl

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received October 29, 1985

Abstract: The low-temperature static solid ^{13}C NMR spectra of the methine carbons of bicyclo[1.1.1]pentane, bicyclo[1.1.1]pentanone, norbornadiene, cubane, trimethoxymethane, and isobutane were measured. Calculations of the shielding tensors by the individual gauge localized orbitals (IGLO) method were also performed for these compounds and for tetrahedrane. Assignments of the principal values to the molecular frame were made on the basis of these calculations for cases in which they were not determined by symmetry. The analysis of the IGLO bond contributions either in the principal axis or in the local bond frames was used to obtain some insight into the origin of the chemical shielding.

I. Introduction

Low-temperature ^{13}C NMR spectroscopy in conjunction with quantum mechanical calculation of the shielding tensors[1,2] has been shown to validate the ab initio wave functions which provide information on the electronic structure of small molecules. In previous work the ^{13}C shielding tensors of unsaturated carbon atoms in linear and pseudolinear molecules,[1] of methylene carbons in a variety of compounds,[2] and of unsaturated carbons in a series of alkenes and cycloalkanes[3] have been reported. In this paper the methine ^{13}C shielding tensors in isobutane (1), trimethoxymethane (2), bicyclo[1.1.1]pentane (3), bicyclo[1.1.1]pentanone (4), norbornadiene (5), and cubane (6), measured on natural abundance samples are reported.

Individual gauge for localized orbitals (IGLO)[4,5] calculations of the shielding tensors were performed on these compounds as well as on tetrahedrane (7). The calculations of the ^{13}C shielding tensor have provided a basis for the assignment of principal components to the molecular frame in cases for which the orientation cannot be determined by the molecular symmetry. The IGLO results agree with the ordering of the shielding magnitudes

found experimentally in all cases in which the orientation can be determined from the experiment except in isobutane where the perpendicular and parallel components differ by only 4 ppm.

II. Experimental and Computational Methods

The spectra were taken at a temperature of about 20 K with an Air Products displex 202-B refrigeration unit.[3] The spectrum of cubane was also measured at about 6 K with a Heli-tran (Air Products Co.) because the spectrum at 20 K did not exhibit sharp features, suggesting that the molecule may have some degree of movement at this temperature. The 6 K spectrum shows a slightly different broad pattern, but the fitted tensorial values extracted from the spectra obtained at the two temperatures agreed within experimental error. A modest improvement is noted

(1) Beeler, A. J.; Cutts, P.; Orendt, A.; Grant, D. M.; Michl, J.; Zilm, K. W.; Downing, J. W.; Facelli, J. C.; Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1984,** *106,* 7672.

(2) 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. *J. Am. Chem. Soc.* **1985,** *107,* 6749.

(3) Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980,** *102,* 6672.

(4) Kutzelnigg, W. *Isr. J. Chem.* **1980,** *19,* 193.

(5) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983,** *105,* 1360.

---

†Part 5 of this series: ref 2.

Low-Temperature ^{13}C Magnetic Resonance in Solids. 6

J. Am. Chem. Soc., Vol. 108, No. 15, 1986 4269

Table I. Experimental and Calculated Principal Values of ^{13}C Shielding Tensors for Trigonal Carbons[a,c]

no.	compound	σ_{11}	σ_{22}	σ_{33}	$\langle\sigma\rangle$	σ_{liq}
1	isobutane	26 (11,8)	26 (11,8)	22 (19,15)	25 (14,10)	25.0
2	trimethoxymethane	123 (-,115)	116 (-,103)	99 (-,80)	113 (-,99)	115.2
3	bicyclo[1.1.1]pentane	42 (40,39)	42 (40,39)	17 (22,25)	34 (34,34)	33.57
4	bicyclo[1.1.1]pentanone	101 (-,89)	47 (-,68)	21 (-,22)	56 (-,60)	55.1
5	norbornadiene	58 (61,59)	56 (58,58)	32 (19,19)	49 (46,45)	50.9
6	cubane 6 K	71 (66,75)	35 (17,25)	35 (17,25)	47 (33,42)	47.3
	cubane 20 K	62	35	35	44	
7	tetrahedrane[b]	- (33,42)	- (-35,-40)	- (-35,-40)	- (-12,-13)	-

[a] Experimental values referenced to Me_4Si; calculated (basis set I, basis set II) to CH_4 as is explained in the text. [b] An unknown compound. [c] Note Added in Proof: A recent calculation for 1 using a (9,5;5) basis set gave $\sigma_{11} = \sigma_{22} = 26$ ppm and $\sigma_{33} = 25$ ppm in agreement with the above experimental serial order.

Chart I
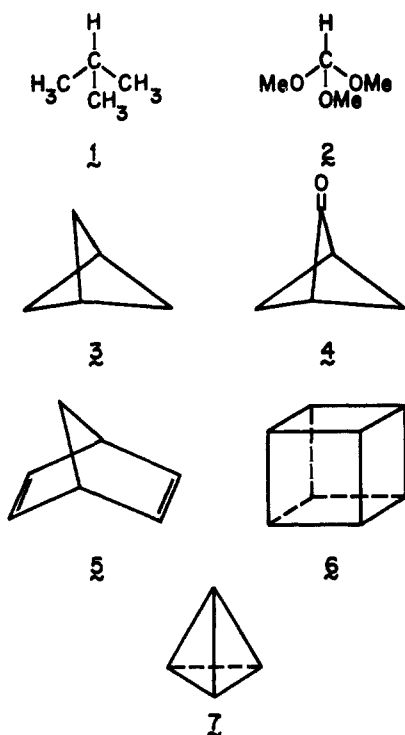
in the agreement of the isotropic chemical shift at 6 K with the liquid value of 47.3 ppm.[6]

All spectra were recorded at 20.12 MHz on the previously described home-built spectrometer.[3] The cross-polarization technique[7] was used, and 10 000 to 15 000 transients were collected with use of a contact time of about 3 ms and recycle times of 3 to 5 s. Experimental shieldings were referenced to an external sample of Me_4Si as described previously,[3] with no attempt to correct the results for bulk susceptibility. The experimental spectra were analyzed either by direct simulation[3] or by using a SIMPLEX fitting method.[8] An error of 2–5 ppm is estimated in the reported values.

Research-grade commercial samples of isobutane (1), trimethoxymethane (2), and norbornadiene (5) were used without further purification. Bicyclo[1.1.1]pentane (3) was prepared by using the method of Wiberg and Connor[9] from a precursor kindly provided by Prof. Wiberg (Yale University), bicyclo[1.1.1]pentanone[10] (4) was obtained from Prof. Dougherty (California Institute of Technology), and cubane[11] (6) was obtained from Prof. Eaton (University of Chicago). All chemicals were degassed before deposition with the freeze–pump–thaw technique. All spectra were run on neat solids.

The ab initio calculations of the shielding tensors were performed by using the IGLO method[4,5] based on the coupled Hartree–Fock perturbation theory[12] with localized molecular orbitals. Huzinaga[13] Gaussian

basis sets were used in the calculations as follows: carbon, (6,3) contracted to (411,21) in basis set I and (7,3) contracted to (4111,21) in basis set II; oxygen, (7,3) contracted to (4111,21); hydrogen, (3) contracted to (2,1). Geometries used in the calculations were obtained from the following sources: isobutane (1);[14] bicyclo[1.1.1]pentane (3);[15] bicyclo[1.1.1]pentanone (4);[10] norbornadiene (5);[16] cubane (6);[17] tetrahedrane (7).[18] For trimethoxymethane (2), the structure reported[19] for the TGG conformer (see below) was used. For comparison with the experimental results, the principal values of the calculated shielding tensors were converted to the CH_4 scale as described previously.[1,2] Methane shielding values of 211 and 219 ppm were used for basis sets I and II, respectively. Only the symmetric part of the shielding tensors was taken into account for comparison with the experimental results.[2,20] All calculations were performed on a VAX 11/750 computer.

III. Results and Discussion

In Table I the experimental and calculated shielding tensors are shown. The agreement between the liquid and average solid shifts is within the experimental error. The agreement between theory and experiment is good. The average difference is about 10 ppm, and the maximum difference is 21 ppm. The agreement of the calculated average value is better than the agreement for the individual components of the shielding tensors. The theoretical fit must be considered to be very good when it is realized that the experimental anisotropy of the shielding tensor ranges from 4 ppm in isobutane (1) to 67 ppm in bicyclo[1.1.1]pentanone (4). These values fall within a typical spectral region for aliphatic carbons.[2,3] The large calculated anisotropy, 68 ppm, for tetrahedrane is included for the sake of completeness, even though the experimental values are not available.

In isobutane (1), bicyclo[1.1.1]pentane (3), and cubane (4) the assignment of the experimental principal values with respect to the molecular frame can be done without ambiguity since axial symmetry renders two of the components equal.[21] The unique component along the C–H bond is upfield in 1 and 3 but downfield in 6. The other two degenerate components lie in the plane perpendicular to the C–H bond. In the case of 1, the calculated results place the downfield component parallel to the C–H bond. This is not surprising because it is well documented that the IGLO method, with double-ζ type of basis sets, does not reproduce the α-substituent effect on the ^{13}C isotropic shielding in hydrocarbons.[5] In the other two cases the serial order of the calculated results agreed with the order of the experimental assignments. These results give confidence to the use of theoretical assignments when axial symmetry is absent,[1,2] providing the tensorial components differ from one another by at least 20–25 ppm. In tetrahedrane (7), the calculated downfield component is parallel to the C–H axis, as it is in cubane (6).

(6) Della, E. W.; Hine, P. T.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940.

(7) Mehring, M. *NMR: Basic Princ. Prog.* **1976**, *11*, 1.

(8) Solum, M. Ph.D. Dissertation, University of Utah, 1986.

(9) Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437.

(10) Sponster, M. B.; Dougherty, D. A. *J. Org. Chem.* **1984**, *49*, 4978.

(11) Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964**, *86*, 3158.

(12) Stevens, R. M.; Pitzer, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *38*, 550.

(13) Huzinaga, S. *Approximate Atomic Wave Functions*; University of Alberta: Edmonton, Alberta, 1971.

(14) Sutton, L. E. *Tables of Interatomic Distances and Configurations of Molecules and Ions*; The Chemical Society: London, 1958.

(15) Chiang, J. F.; Baver, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 1614.

(16) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356.

(17) Fleischer, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3889.

(18) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.

(19) Spelbos, A.; Mijhoff, F. C.; Faber, D. H. *J. Mol. Struct.* **1977**, *41*, 47.

(20) Facelli, J. C.; Orendt, A. M.; Grant, D. M.; Michl, J. *Chem. Phys. Lett.* **1984**, *112*, 147.

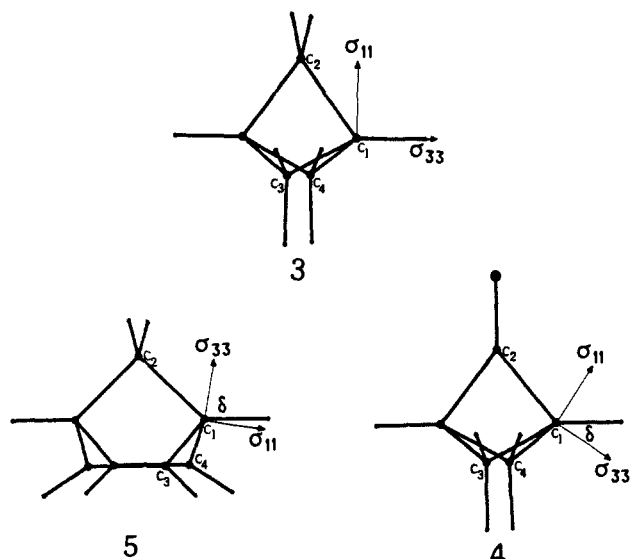(21) Buckingham, A. D.; Malm, S. M. *Mol. Phys.* **1971**, *22*, 1127.

Figure 1. Orientation of the shielding tensor components in compounds 1 to 3. σ_{22} is always perpendicular to the HCCCH symmetry plane of the molecules. $\delta = 80°$ in norbornadiene and $\delta = 34°$ in bicyclo-[1.1.1]pentanone.

In the absence of single crystal or dipolar studies[2,22,23] for compounds **2**, **4**, and **5**, it is only possible to tentatively assign the principal values of the shielding tensor to the molecular frame by using the tensorial assignments obtained from the theoretical calculations. In compounds **4** and **5**, the plane passing through the methine and either the carbonyl or the methylene carbons, respectively, is a symmetry plane of the molecule, forcing the normal to this plane to be one of the principal axes of the shielding tensor.[21] The calculations place σ_{22} as the principal value along this perpendicular direction in both compounds. One should hasten to note that in **5** σ_{11} is indistinguishable from σ_{22} and therefore the theoretical results can only be taken to be reflective of a very modest break in the symmetry which is below the experimental resolution. For both **4** and **5**, the calculated σ_{11} and σ_{33} values correspond to axes located in the symmetry plane (Figure 1). In bicyclo[1.1.1]pentanone (**4**) the calculated angle between the σ_{33} direction and the C–H bond axis is 34° (Figure 1). In nor-bornadiene (**5**) the calculation places σ_{33} at an angle of 80° from the C–H bond (Figure 1).

From the seven spectroscopically different conformers of tri-methoxymethane (**2**),[24] four can be eliminated because of ener-getically unfavorable steric interactions. The remaining three, TGG (point symmetry C_1), TGG' (C_s symmetry), and GGG (C_3 symmetry), have been found to be predominant in different phases.[19] In the solid phase the compound assumes C_3 symmetry,[24] while recent studies by electron diffraction and molecular me-chanics calculations point to the TGG conformer (C_1 symmetry) as the most stable in the gas phase.[19] The GGG conformer will exhibit an axially symmetric tensor, due to the C_3 symmetry, while the TGG and TGG' will not. The observed tensor for trimeth-oxymethane is definitely not axially symmetric. This indicates that the deposition process preserves, at least to some extent, the conformational equilibrium present in the gas phase.[25] However, the possibility that the deposited solid contains a mixture of different conformers cannot be excluded. Calculations have been done for the TGG conformation, and they place σ_{11} at 16° from the C–H bond.

Quantum mechanical calculations not only allow tentative assignments of the shielding components in the molecular frame to be made when symmetry fails to provide this information but

(22) Zilm, K. W.; Grant, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 2913.
(23) Linder, M.; Hohener, A.; Ernst, R. R. *J. Chem. Phys.* **1980**, *73*, 1980.
(24) Lee, H.; Wilnshurst, J. K. *Spectrochim. Acta* **1966**, *23A*, 347.
(25) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry: Application of Flow and Flash Vacuum Pyrolytic Techniques*; Academic Press: New York, 1980.

Table II. IGLO Bond Contribution Analysis for the ^{13}C Methine Chemical Shielding in Tetrahedrane, Bicyclo[1.1.1]pentane, Cubane, and Isobutane[a]

	^{13}C–H bond		^{13}C–C bonds[b]	
	$\sigma_\parallel$	$\sigma_\perp$	$\sigma_\parallel$	$\sigma_\perp$
Diamagnetic Contributions				
(1) isobutane	14	12	34	37
(3) bicyclo[1.1.1]pentane	15	11	34	35
(6) cubane	14	11	33	35
(7) tetrahedrane	16	13	36	37
Paramagnetic Contributions				
(1) isobutane	0	−14	−39	−29
(3) bicyclo[1.1.1]pentane	0	−33	−59	−33
(6) cubane	0	−27	−97	−20
(7) tetrahedrane	0	−3	−87	9
Total Shielding Contributions				
(1) isobutane	14	−2	−5	8
(3) bicyclo[1.1.1]pentane	15	−22	−25	2
(6) cubane	14	−16	−64	15
(7) tetrahedrane	16	10	−51	46

[a] All values in ppm. Contributions from all the other bonds of the molecule are below 2 ppm. The 1s carbon shell gives constant isotropic contribution of 200 ppm to the ^{13}C shielding tensor. Values calculated with basis set II. [b] Sum of the contribution from the three equivalent C–C bonds.

they also give some insight to the origin of the chemical shifts and their relation to the molecular structure. In Table II the IGLO bond contribution analysis[4,26] is presented for the methine carbons in isobutane (**1**), bicyclo[1.1.1]pentane (**3**), cubane (**6**), and tetrahedrane (**7**). Only the larger contributions projected onto the overall principal shielding axes of the molecule are listed. Only modest contributions, less than 3 ppm, are obtained from more remote bonds. The constant isotropic 200-ppm contribution arising from the 1s carbon shell is not included in Table II. The dia-magnetic bond contributions are found to be almost constant for both C–H and C–C bonds in all the compounds studied here. Furthermore, the anisotropy in the diamagnetic term lies in a narrow range of only 3 ppm. This agrees with the well-known fact that variations of ^{13}C chemical shifts with structure are dominated by paramagnetic contributions.[27]

The paramagnetic contribution of the C–H bond to the parallel component of the shielding tensor is zero, thus variations in the parallel component are determined almost completely by the contributions from the three adjacent C–C bonds. These results suggest a relationship between the $\sigma_\parallel$ component and the strain of the C–C bonds. However, the results in tetrahedrane (**7**) do not follow this relationship and probably suggest caution in the use of such simplifying assumptions.

The degenerate perpendicular component, $\sigma_\perp$, is significantly affected by both the C–H and the C–C bonds, but as the two different contributions follow different patterns along the series of compounds presented here no single effect could be identified as the one responsible for the changes in the perpendicular shielding component.

The shielding tensor changes dramatically along the series bicyclo[1.1.1]pentane (**3**), bicyclo[1.1.1]pentanone (**4**), and norbornadiene (**5**). In all three compounds σ_{22} lies perpendicular to the symmetry plane and changes only 14 ppm along the series. As depicted in Figure 1, σ_{11} and σ_{33} change their orientation from one compound to the other. In order to analyze the behavior of these two components, the calculations on **4** and **5** were repeated in the principal axis system of the methine carbon. In Table III the results of the IGLO bond analysis[4,26] in the principal axis system are summarized. On the basis of the results contained in Table II, only the paramagnetic contributions are listed in Table III.

(26) Schindler, M.; Kutzelnigg, W. *Mol. Phys.* **1983**, *48*, 781.
(27) Ebraheem, K. A. K.; Webb, G. A. *Prog. NMR Spectrosc.* **1977**, *11*, 149.

Table III. Paramagnetic IGLO Bond Contributions to the ^{13}C Methine Chemical Shielding in Bicyclo[1.1.1]pentane, Bicyclo[1.1.1]pentanone, and Norbornadiene[a]

		bicyclo[1.1.1]-pentane (3)	bicyclo[1.1.1]-pentanone (4)	norbornadiene (5)
C_1–C_2	$\sigma_\perp$	−13.9	−44.3	−12.4
	$\sigma_{\perp'}$	−8.1	−16.8	−26.3
	$\sigma_\parallel$	−19.6	2.0	−11.4
C_1–C_3	$\sigma_\perp$	−9.5	−16.7	−8.5
	$\sigma_{\perp'}$	−12.3	−14.0	−9.2
	$\sigma_\parallel$	−19.6	−20.8	−32.2
C_1–C_4	$\sigma_\perp$	−9.5	−16.7	−8.5
	$\sigma_{\perp'}$	−12.3	−14.0	−9.2
	$\sigma_\parallel$	−19.6	−20.8	−32.2
C_1–H	$\sigma_\perp$	−32.8	−28.8	−12.3
	$\sigma_{\perp'}$	−32.8	−43.5	−30.4
	$\sigma_\parallel$	0.0	−12.3	−4.2

[a] Calculations where done with use of basis set II in the principal axes system of the ^{13}C–H shielding tensors. $\sigma_\perp$ lies in the HC_1C_2 plane at 90°, 56°, and 80° from the C–H bond in compounds **3**, **4**, and **5**, respectively. $\sigma_\parallel$ lies perpendicular to $\sigma_\perp$ and to the HC_1C_2 plane. $\sigma_{\perp'}$ lies perpendicular to $\sigma_\perp$ and $\sigma_\parallel$. The numbering is according to Figure 1.
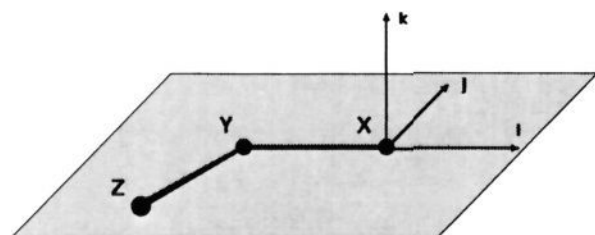
Figure 2. Description of the local bond axes system.

The large increase, relative to bicyclo[1.1.1]pentane (**3**) in the C_1–C_3 and C_1–C_4 paramagnetic contributions to $\sigma_\parallel$ in norbornadiene (**5**), is the cause of the large downfield movement of this component. Note that $\sigma_\parallel$ is the farthest upfield component in **3** but is the farthest downfield in **5**.

The substitution of one of the methylene groups in bicyclo-[1.1.1]pentane (**3**) by a carbonyl affects only modestly the component perpendicular to the OC_2C_1H plane relative to the values in the corresponding parent hydrocarbon. The carbonyl substitution has a dramatic effect on $\sigma_\parallel$, moving it downfield by 59 ppm.

It is possible to understand this unusually low field component in bicyclo[1.1.1]pentanone (**4**) from the analysis of the canonical molecular orbitals (MOs). In **4** the MO which contains the C_1–C_2 bond has the proper symmetry to be mixed by the angular momentum operator with the lowest unoccupied MO (LUMO), a somewhat delocalized carbonyl π^* orbital, giving rise to a large paramagnetic contribution perpendicular to both of them, i.e., the direction along $\sigma_\parallel$. The carbonyl substitution also leads to a large antisymmetric contribution of 27 ppm mainly originating in the C_1–C_2 bond, according to the analysis of the IGLO bond contributions.

The tensor IGLO bond contributions[26] from an X–Y bond, $\sigma_{\mu\nu}^{XY}$, calculated in the molecular frame can be rotated to the local bond frame to obtain better insights into the origin of the chemical shift. The local bond frame is defined (Figure 2) by one axis, $\hat{i}$, along the internuclear axis of the bond under consideration and two axes, $\hat{j}$ and $\hat{k}$, in the plane perpendicular to it. In general the choice of these two perpendicular axes is arbitrary, but in the cases given in Table II the choice is dictated by the molecular symmetry. $\hat{j}$ is chosen in the symmetry plane and $\hat{k}$ is perpendicular to the symmetry plane. The results of this kind of analysis in a large number of molecules as well as a detailed description of the method will be reported elsewhere.[28]

(28) Facelli, J. C.; Grant, D. M.; Michl, J., submitted for publication.

Table IV. C—C Bond Contributions, $\sigma_{\mu\nu}^{CC}$, in the Local Bond Frame[a] to the Shielding Tensors

isobutane (1)	$\begin{bmatrix} 0.01 & 0.76 & 0 \\ 0.76 & -14.05 & 0 \\ 0 & 0 & -18.18 \end{bmatrix}$
bicyclo[1.1.1]pentane (3)	$\begin{bmatrix} -2.26 & 9.50 & 0 \\ 9.50 & -25.40 & 0 \\ 0 & 0 & -13.87 \end{bmatrix}$
cubane (6)	$\begin{bmatrix} -4.97 & 12.73 & 0 \\ 12.73 & -28.18 & 0 \\ 0 & 0 & -12.38 \end{bmatrix}$
tetrahedrane (7)	$\begin{bmatrix} -1.66 & 7.01 & 0 \\ 7.01 & -32.57 & 0 \\ 0 & 0 & -11.55 \end{bmatrix}$

[a] All values in ppm. Paramagnetic contributions calculated with basis set II. $\hat{i}$: along the bond. $\hat{j}$: perpendicular to the bond, in the symmetry plane containing the bond. $\hat{k}$: perpendicular to the symmetry plane.

The local bond frame for the C–H contributions coincides with the principal axes system of the methine shielding tensor in compounds **1**, **3**, **4**, and **7**. For these bond contributions the C_3 symmetry axis demands the degeneracy of the components in the plane perpendicular to the C–H bond (see Table II). The situation is different for the C–C bonds which do not lie along the symmetry axis of the molecule. In Table IV the IGLO bond contributions to the shielding tensors in the local bond frame are given for the C–C bond in compounds, **1**, **3**, **6**, and **7**. In isobutane (**1**), for all practical purposes, the two components perpendicular to the C–C bond are degenerate and the contributions along the bond as well as the nondiagonal elements are negligible. The component along the bond and the off-diagonal elements become larger as the strain increases. σ_{jj}^{CC} varies monotonically from −14.05 to −32.57 ppm as the CCC angle is decreased.

The bond contributions in the local bond frame (Figure 2) are related to the methine carbon shielding tensor by

$$\sigma_\parallel = 3[\sigma_{ii}^{CC}\cos^2\theta + 2\sigma_{ij}^{CC}\cos\theta\sin\theta + \sigma_{jj}^{CC}\sin^2\theta] \quad (1)$$

$$\sigma_\perp = {}^3\!/_2[\sigma_{jj}^{CC}\cos^2\theta - 2\sigma_{ij}^{CC}\cos\theta\sin\theta + \sigma_{ii}^{CC}\sin^2\theta + \sigma_{kk}^{CC}] + \sigma_\perp^{CH} \quad (2)$$

where θ is the angle between the C–C bond and the C_3 symmetry axis. The contribution from non-adjacent bonds is neglected in eq 1 and 2.

It is clear from eq 1 and 2 that the shielding components of the methine carbons have an explicit angular dependence on the angle θ, between the C–C bond and the C_3 axis. Furthermore, as discussed above, the bond contributions $\sigma_{\mu\nu}^{CC}$ themselves also depend on θ. Unfortunately, the components of the bond contributions, which are intimately related to the electronic structure of the bond, cannot be extracted from the experimental components of the shielding tensor with eq 1 and 2. Their determination rests on the validity of the computational methods.

IV. Conclusions

This study shows how sensitive the methine ^{13}C shielding tensors are to the electronic structure of the molecule. This high sensitivity of methine shielding tensors is characteristic of the aliphatic ^{13}C shielding tensors, in contrast with olefinic ^{13}C shielding tensors, which exhibit far larger anisotropies[2,3,29,30] but less variation with structure changes.

Quantum chemical calculations have been proven to be very useful not only in making tentative assignments of the tensor components but also in the analysis of the relationship between shielding tensors and molecular structure.

The overall agreement between experiment and theory provides a certain level of confidence in the calculated localized bond contributions. The nearly cylindrical symmetry of localized bonds

(29) Beeler, A. J. Ph.D. Dissertation, University of Utah, 1984.
(30) Veeman, W. S. *Prog. NMR Spectrosc.* **1984**, *16* 193.

is manifested by a very small σ_{ii}^{CC} term and modest off-diagonal elements encountered in this study. Even bonds associated with considerable strain still exhibit a relative modest σ_{ii}^{CC} along the internuclear axis.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE 83-10109. The authors

are grateful to Drs. W. Kutzelnigg and M. Schindler for the copy of their IGLO program and to Drs. D. A. Dougherty, P. E. Eaton, and K. B. Wiberg for providing some of the compounds used in this study.

Magnetic Interaction among Diphenylmethylene Molecules Generated in Crystals of Some Diazodiphenylmethanes

Tadashi Sugawara, Hideyuki Tukada,[†] **Akira Izuoka, Shigeru Murata, and Hiizu Iwamura***

Contribution from the Division of Applied Molecular Science, Institute for Molecular Science, Okazaki 444, Japan. Received December 12, 1985

Abstract: When polycrystalline solid samples of *p*-methoxy- and *p,p'*-dimethoxydiphenyldiazomethanes (**3** and **4**, respectively) were photolyzed in an ESR cavity at 10 K, fine structures due to triplet (T), quintet (Q), and higher multiplet species (M) were observed. The Q signals, e.g., $|D| = 0.136$ and $|E| = 0.015$ cm^{-1} from **4**, were always most conspicuous and interpreted as arising from the pairwise interaction of the triplet *p,p'*-dimethoxydiphenylmethylene (**2**) formed in the host crystals of **4**. The Curie plot of the ESR signal intensities and $1/\chi_p$ vs. *T* plot have shown that Q is the ground state for the pair of T carbenes. From the light intensity dependence, the formation of the Q pair in polycrystalline **4** was found to be one-photonic especially at shorter wavelength. In sharp contrast with the case of **3** and **4**, photolysis of *p,p'*-dichlorodiphenyldiazomethane (**6**) gave predominantly an ESR spectrum of a triplet *p,p'*-dichlorodiphenylmethylene (**5**), accompanied by a weak signal of a thermally populated quintet species. The magnetic susceptibility measurement also showed a presence of very weak magnetic interaction among triplet species **5**. The average spin multiplicity determined by the magnetic field dependence on the magnetization was $S = (3.8 \pm 0.4)/2$ for **2** and $S = (1.9 \pm 0.2)/2$ for **5**, respectively. The pairwise ferromagnetic interaction between the T carbenes generated in the crystals of **4** was explained in reference to their crystal packing estimated from that of the corresponding *p,p'*-dimethoxybenzophenone. The magnetic model for **5** is also discussed based on the crystal packing of **6** determined by an X-ray analysis.

Since the advent of dicarbenes in the ground quintet state,[1] the possibility fo constructing organic ferromagnets has been discussed from a theoretical point of view.[2] However, it is only of recent date that experimental approaches to organic ferromagnets have been started by investigators in various fields.[3] In order to simulate macroscopic ferromagnets by organic molecular assemblies, it is imperative to introduce ferromagnetic intermolecular interaction among open-shell organic molecules and connect them magnetically to form domain structures.[4] High spin hydrocarbons,[5] such as *m*-phenylenebis(phenylmethylene) and its homologues, seem to be the most efficient building blocks to constitute magnetic domains. We have already shown the "superparamagnetic" behavior of the ground state nonet carbene, *m*-phenylenebis((diphenylmethylen-3-yl)methylene).[6] Its intermolecular interaction however turned out to be weak and antiferromagnetic in fortuitously formed aggregates and neat polycrystals.

McConnell's theory serves as a guiding principle to design intermolecular magnetic interaction of π-spin-containing hydrocarbons.[7] According to the theory, the intermolecular magnetic interaction is governed both by the intermolecular exchange integral, J_{ij}^{AB}, between the most interacting sites *i* and *j* on molecules A and B, respectively, and by the product of spin densities $\rho_i^A \rho_j^B$ at *i* and *j* where S^A, S^B are the total spin operator of molecules A and B, respectively. Since J_{ij}^{AB} is usually negative in sign, the sign of $\rho_i^A \rho_j^B$ is crucial to determine the character of magnetic interaction (eq 1).

$$\mathcal{H}^{AB} = -S^A \cdot S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B \qquad (1)$$

Let us consider the interaction between two superimposable benzene rings one from each diphenylcarbene molecule. There are four modes of overlap in reference to the relative orientation of phenylmethylenyl substituents as depicted below. The sign of ρ_i is established to alternate on the benzene rings of the diphenylcarbene molecules.[8] The ferromagnetic interaction is predicted for pseudo-ortho or -para orientation, since spin densities have opposite signs at the most interacting sites. The interaction becomes antiferromagnetic in pseudo-geminal or -meta orientation.

By taking advantage of the [2.2]paracyclophane skeleton we have recently shown that the spin multiplicity of two interacting

[†] IMS fellow 1982–1984. Current address: Department of Chemistry, College of Arts and Sciences, University of Tokyo, Komaba, Tokyo 153.

(1) (a) Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. (b) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. (c) Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

(2) (a) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. (b) Ovchinnikov, A. A. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 928. (c) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (d) Buchachenko, A. L. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1146. (e) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* **1982**, *77*, 3101. (f) Tyutyulkov, N.; Schuster, P.; Polansky, O. *Theor. Chim. Acta* **1983**, *63*, 291.

(3) (a) Breslow, R.; Juan, B.; Kluttz, R. Q.; Xia, C. Z. *Tetrahedron* **1982**, *38*, 863. (b) Iwamura, H.; Sugawara, T.; Itoh, K.; Takui, T. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 251. (c) Breslow, R. *Ibid.* **1985**, *125*, 261.

(4) Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293.

(5) (a) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722. (b) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *Ibid.* **1986**, *108*, 2147.

(6) (a) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. (b) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *Ibid.* **1986**, *108*, 368. (c) Kimura, K.; Bandow, S. *Solid State Phys.* **1984**, *20*, 467.

(7) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(8) (a) Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327. (b) Anderson, R. J.; Kohler, B. E. *J. Chem. Phys.* **1978**, *65*, 2451.