$H^{-}\cdots Fe\cdots P^{+}$ dipole moment at larger θ.

For anions containing the better donor ligands, such as *trans*-$HFe(CO)_3PEt_3^-$, the P–Fe–H system is more electron rich, and the $H\cdots CO$ interaction is expected to be stronger at small θ as compared to the analogous *trans*-$HFe(CO)_3P(OMe)_3^-$. Therefore, more extreme conditions of solvent polarity would be required to generate the angle change, charge separation, and diminution of this interaction for **5** as compared to **3**.

This "direct donation" also appears to be a salient feature of why J_{PH} becomes more positive as θ is increased. The calculations showed that the most prominent molecular orbital responsible for the increase in s overlap density of P and H was the σ(Fe–H) molecular orbital. At low angles (75°) the carbonyl interaction with hydride stabilizes this molecular orbital and the H 1s contribution is only 48%. At high angles (85°) this orbital rises in energy slightly and, more importantly, H 1s retains more electron density and now contributes 60% to this molecular orbital. Interestingly, the percent character of Fe 4s and P 3s also increases in this molecular orbital with increasing angle but in a lesser amount.

We have also examined other classes of anionic transition metal hydride complexes to see if similar behavior could be found. Both PPN^+ and Na^+ salts of the six-coordinate anion, *cis*-$HW(CO)_4P(OMe)_3^-$, in THF displayed *no* change in the J_{PH} value of ca. 31 Hz from +50 to −60 °C. The PPN^+ salt also had no significant changes in the hydride chemical shift (−4.3 ppm) with temperature while the Na^+ salt showed a 0.6-ppm downfield shift at −60° (−4.8 ppm) relative to the +50 °C value (−5.4 ppm). This shift might be attributed to the disruption of the $Na^+\cdots H$—W interaction[24] at lower temperature by the increased dielectric constant of the solvent. As mentioned earlier, the recently isolated *cis*-$HFe(CO)_3P(OPh)_3^-$ (**2**) anion also showed no significant change in J_{PH} over the temperature range +26 to −80 °C. Consistent with this observation ν(CO) IR displayed no structural change in the anion.

Comments and Conclusions

We feel the evidence is convincing that an angular deformation gives rise to changes in J_{PH} for the anions *trans*-$HFe(CO)_3PR_3^-$. Simple motion of the carbonyl groups away from the hydride ligand substantially increases the dipole moment in the anion. The angle changes are mediated by the solvent's ability to stabilize the increased internal dipole moment in the anion. Possibly the reason that the *trans*-$HFe(CO)_3PR_3^-$ hydrides give changes in J_{PH} also accounts for the fact that cis hydrides such as *cis*-$HFe(CO)_3P(OPh)_3^-$ and *cis*-$HW(CO)_4P(OMe)_3^-$ do not. Simple angle deformations in the cis complexes would not be expected to yield significant changes in dipole moment.

Acknowledgment. The authors are grateful to D. J. Darensbourg for reviving the art of infrared intensity interpretations. Grants from the National Science Foundation (CHE8304162 and CHE8603664 to M.Y.D. and CHE8309936 to M.B.H.) primarily supported this work. C. E. Ash held a Gulf Foundation Fellowship. We also are grateful to Viji Danpani and Steve Silber for their expertise and help with the NMR experiments.

---

[24] Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871.

High-Field NMR Determination of Magnetic Susceptibility Tensors and Angular Correlation Factors of Halomethanes

A. A. Bothner-By,* J. Dadok, P. K. Mishra, and P. C. M. Van Zijl*

Contribution from the Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213. *Received December 1, 1986*

Abstract: Quadrupolar splittings in the high-resolution deuteron spectra of deuterated haloforms ($CX_3{}^2H$, X = Cl, Br, I) and methylene halides ($CX_2{}^1H^2H$) have been measured at 14.35 T (93.5 MHz) and used to determine the anisotropy or asymmetry of their molecular magnetic susceptibility tensors. By combination with the known isotropic susceptibilities, the principal susceptibility tensors have been deduced and decomposed into bond susceptibility tensors. Neither the average susceptibilities nor the principal susceptibility tensor elements of the complete halomethane series follow Pascal's additivity rules. The phenomenon is tentatively attributed to a variable paramagnetic contribution perpendicular to the C–X bond. Angular correlation Kirkwood g_2 factors have been determined for $CHCl_3$ and $CHBr_3$ and are compared with available literature data.

It was first demonstrated in 1978 by Lohman and MacLean[1] that high-field high-resolution NMR provides a simple tool to determine magnetic susceptibility anisotropies ($\Delta\chi$) and asymmetries ($\delta\chi$). The basis of the method is that molecules with anisotropic magnetic susceptibilities placed in the strong magnetic field of the spectrometer are subject to orienting torques. In the liquid this orientation is opposed by thermal motions and collisions, but at sufficiently high fields (>10 T for diamagnetic compounds) a net significant alignment results. This induced alignment is manifested in the NMR spectrum in the form of anisotropic nuclear interactions,[1-4] such as direct dipolar or electric quadrupole couplings. The effects which are proportional to the square of the magnetic induction B may be used to investigate magnetic properties and geometries of molecules[1-4] as well as for the determination of nuclear constants (e.g., quadrupole coupling constants).[5]

In this paper electric quadrupole splittings in monodeuterated haloforms and methylene halides have been used to investigate their magnetic susceptibilities. This investigation came about in a serendipitous way. Deuteriochloroform is commonly used as a solvent and heteronuclear lock signal source in high-resolution proton NMR spectroscopy. Difficulties with achieving a satisfactory and stable lock with this solvent at 600 MHz eventually

---

[1] Lohman, J. A. B.; MacLean, C. *Chem. Phys.* **1978**, *35*, 269.

[2] van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Acc. Chem. Res.* **1984**, *17*, 172.

[3] Bastiaan, E. W.; van Zijl, P. C. M.; MacLean, C.; Bothner-By, A. A. *Annu. Rep. NMR Spectrosc.* **1987**, *19*, 35.

[4] Bothner-By, A. A.; Gayathri, C.; van Zijl, P. C. M.; MacLean, C.; Lai, J. J.; Smith, K. M. *Magn. Reson. Chem.* **1985**, *23*, 935.

[5] van Zijl, P. C. M.; MacLean, C.; Skoglund, C. M.; Bothner-By, A. A. *J. Magn. Reson.* **1985**, *65*, 316.

0002-7863/87/1509-4180$01.50/0 © 1987 American Chemical Society

Table I. Quadrupole Coupling Constants[27] and Structural Parameters[13-26] for C^2HX_3, $C^2H^1HX_2$, and $C^1H_2{}^2HX$

compd	$(e^2qQ/h)^a$	θ_{XCX}, deg	θ_{XCH}, deg	θ_{HCH}, deg	ref^b
C^2HCl_3	162.7	111.15	107.79		13-16
C^2HBr_3	166.3	111.25	107.69		15, 17, 18
C^2HI_3	167.5	112.0	106.9		18
$C^2H^1HCl_2$	160.2	112.2	108.06	112.1	19
$C^2H^1HBr_2$	160.8	112.64	107.96	112.43	20
$C^2H^1HI_2$	160.9	113.7	107.5	113.3	*c*
$C^2H^1H_2Cl$			108.11	110.75	15, 21
$C^2H^1H_2Br$			108.1	110.8	22, 23
$C^2H^1H_2I$			107.5	111.4	24-26

[a] In kHz; $\eta = 0.00 \pm 0.02$, ref 27. [b] For angles; in case more references are mentioned, data may have been combined, or reviews and original publications are all given. [c] Estimated from combination and extrapolation of the data for all the other compounds in the table.

led us to examine the lock signal itself, which, astonishingly, was a doublet. The measurements reported here were stimulated by the desire to map and understand the pattern of the surprisingly anisotropic magnetic susceptibility tensors of the halomethanes. For chloroform and bromoform a concentration study in the inert solvent cyclohexane was performed in order to assess molecular angular correlation effects.[6]

Two other methods are, in principle, applicable to the determination of the magnetic anisotropy in halomethanes: Zeeman microwave spectroscopy[7,8] and the Cotton–Mouton effect.[8,9] Zeeman microwave spectroscopy[7,8] has been applied to the methyl halides, but not to methylene halides or haloforms, presumably because of the spectral complication arising from the mixture of halogen isotopes. The Cotton–Mouton effect has been observed for chloroform and bromoform.[10,11] However the investigators did not make a variable-temperature study, and this has been found to be important in the numerical interpretation of the results.[12]

Theory

For partially aligned molecules in the liquid phase, the quadrupolar splitting of a deuteron signal is given by the equivalent expressions:[1-3]

$$\Delta\nu = (B^2/10kT)(eQ/h)\sum_i \chi_{ii}V_{ii} \qquad (1A)$$

or

$$\Delta\nu = (B^2/10kT)(eQ/h)\{\Delta\chi V_{zz} + {}^1\!/_2\delta\chi(V_{xx} - V_{yy})\} \qquad (1B)$$

where eQ is the nuclear quadrupole moment, and V_{ii} denotes the electric field gradient at the site of the deuteron defined in the molecular frame ($i = x, y, z$), in which χ is presumed to be diagonal. The field gradients, V_{ii}, are related to the gradients $V_{j''j''}$ defined in the local electric field gradient principal axis frame ($j'' = x'', y'', z''$ with z'' parallel to the C–^{2}H bond) by the equivalent expressions

$$V_{ii} = \sum_{j''}(\cos^2\theta_{ij''})V_{j''j''} \qquad (2A)$$

or

$$V_{ii} = V_{z''z''}\left\{\left(\frac{3}{2}\cos^2\theta_{z''i} - \frac{1}{2}\right) + \frac{\eta}{2}(\cos^2\theta_{x''i} - \cos^2\theta_{y''i})\right\} \qquad (2B)$$

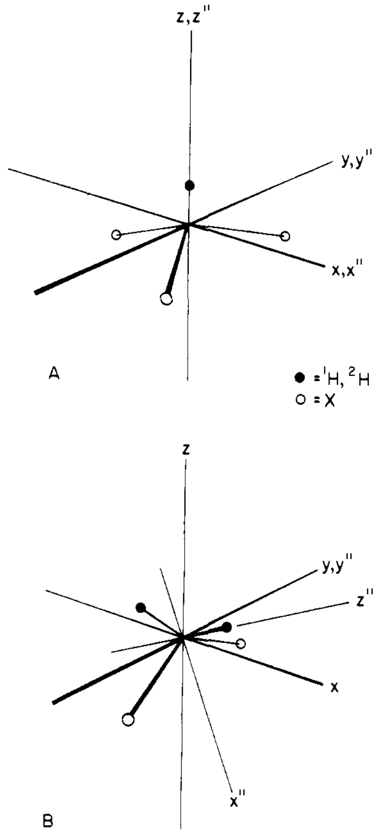

Figure 1. Molecular and local frames for haloforms (A) and methylene halides (B). For the haloforms both frames are identical; for the methylene halides the frames are connected by a rotation around the y,y'' axis (note that in our definition the X–X axis is in the yz plane; the H–H axis is in the xz plane).

where η, the asymmetry parameter, is defined as $(V_{x''x''} - V_{y''y''})/V_{z''z''}$, and the double primes refer to the local frame. The molecular and local frames are shown in Figure 1. Bond angles for all compounds investigated are gathered from the literature[13-26] in Table I.

For the molecules under study, the deuteron quadrupole coupling constants, $eQV_{z''z''}/h$ or e^2qQ/h, have recently been measured by solid-state NMR,[27] as well as by NMR of molecules partially oriented in liquid-crystal solvents.[28] The interpretation of the liquid-crystal studies is complicated by solvent effects, while solid-state values are known to be close to liquid-state values. We

---

(6) van Zijl, P. C. M.; MacLean, C.; Bothner-By, A. A. *J. Chem. Phys.* **1985**, *83*, 4978.

(7) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653.

(8) Appleman, B. R.; Dailey, B. P. *Adv. Magn. Reson.* **1974**, *7*, 231.

(9) Beans, J. W. *Rev. Mod. Phys.* **1932**, *4*, 133.

(10) Le Fevre, R. J. W.; Murthy, D. S. M.; Ritchie, G. L. D. *Aust. J. Chem.* **1971**, *24*, 1177.

(11) Vul'fson, S. G.; Dianora, O. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1984**, *10*, 2269; *Chem. Abstr. 102*, 45459n.

(12) Geschka, H.; Pferrer, S.; Häussler, H.; Hüttner, W. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 790.

(13) Yamamoto, K.; Konaka, S.; Kimura, M. *J. Mol. Struct.* (*THEOCHEM*) **1985**, *133*, 169.

(14) Suzuki, K.; Kunimi, H.; Kimura, M., unpublished results, mentioned in ref 13.

(15) Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. In Landolt-Bernstein, New Series, *Structure Data of Free Polyatomic Molecules*; Hellwege, K. H., Ed.; Springer Verlag, Berlin, Heidelberg, New York, 1976; Vol. II/7.

(16) Jen, M.; Lide, D. R. *J. Chem. Phys.* **1962**, *36*, 2525.

(17) Williams, Q.; Cox, T.; Gordy, W. *J. Chem. Phys.* **1952**, *20*, 1524.

(18) Tamagawa, K.; Masao, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2747.

(19) Harmony, M. D.; Mathur, S. N.; Merdian, S. *J. Mol. Spectrosc.* **1979**, *75*, 144.

(20) Wellington Davis, R.; Gerry, M. C. C. *J. Mol. Spectrosc.* **1985**, *109*, 269.

(21) Duncan, J. L.; McKean, D. C.; Mullinson, P. D.; McCulloch, R. D. *J. Mol. Spectrosc.* **1973**, *46*, 232.

(22) Tamagawa, K.; D. Sc. *Thesis*, Hokkaido University, 1981; mentioned in ref 13.

(23) Miller, S. L.; Aamodt, L. C.; Dousmanis, G.; Townes, C. H.; Kraithman, J. *J. Chem. Phys.* **1952**, *20*, 1112.

(24) Mallinson, P. D. *J. Mol. Spectrosc.* **1975**, *55*, 94.

(25) Duncan, J. L. *J. Mol. Struct.* **1974**, *22*, 225.

(26) Matsuura, H.; Overend, J. *J. Chem. Phys.* **1972**, *56*, 5725.

(27) Kunwar, A. C.; Gutowsky, H. S.; Oldfield, E. *J. Magn. Reson.* **1985**, *62*, 521.

(28) Jokisaari, J.; Hiltunen, Y. *J. Magn. Reson.* **1986**, *67*, 319 and references therein.

have therefore used the values of Kunwar et al.[27] which are also listed in Table I. In these measurements the field gradient asymmetry parameter, η, was taken to be zero, and the question arises how much this assumption will influence the interpretation of our data. For the haloforms, which possess C_{3v} symmetry, with the C–^{2}H bond lying along the threefold axis, it follows that both η and $\delta\chi$ are identically zero. The z and z'' axes coincide, and eq 1 reduces to the simple form

$$\Delta\nu = (B^2/10kT)(eQ/h)\Delta\chi V_{z''z''} \tag{3}$$

For the methylene halides, the situation is more complicated since η need not be exactly zero, and three independent principal susceptibilities should in principle be evaluated. However, it can be shown that both $\Delta\chi$ and V_{zz} in eq 1B are expected to be small, so that the term $\Delta\chi V_{zz}$ is negligible compared to $(^1/_2)\delta\chi(V_{xx} - V_{yy})$ in the formula for the splitting. First consider V_{zz}: in the tetrahedral case eq 2 yields $V_{zz} = 0$ and only the $\delta\chi$ part remains; for nontetrahedral angles it will be illustrative to calculate the field gradients for the extreme case, namely, $C^2H^1HI_2$. Equation 2 gives $V_{zz} = (-0.047 + 0.349\eta)V_{z''z''}$ and $V_{xx} - V_{yy} = (1.047 + 0.651\eta)V_{z''z''}$. The asymmetry parameter is generally less than 0.05, so that it can be concluded that V_{zz} is not more than 5% of $V_{xx} - V_{yy}$. Second, consider $\Delta\chi$: to estimate the ratio of $\Delta\chi$ and $\delta\chi$ we assume that the molecular susceptibility tensor may be decomposed into contributions from each of the C–H and C–X bonds and that the bond susceptibility tensors are axial (χ_{cc} parallel to bond axis; $\chi_{aa} = \chi_{bb}$ perpendicular to bond axis; $\Delta\chi_n = \chi_{cc} - \chi_{bb}$ for the nth bond). The bond anisotropies then add to give the molecular anisotropies according to the rule

$$\Delta\chi_i = \sum_n \Delta\chi_n(^3\!/_2 \cos^2 \theta_{in} - {}^1\!/_2) \tag{4}$$

with $\Delta\chi_i = \chi_{ii} - {}^1/_2(\chi_{jj} + \chi_{kk})$ and the molecular axes i, j, k are cyclically permutable.[6] Our $\Delta\chi = \Delta\chi_z$ and $\delta\chi = {}^2/_3(\Delta\chi_x - \Delta\chi_y)$; for the methylene halides this leads to

$$\Delta\chi = (3 \cos^2 (^1\!/_2\theta_{XCX}) - 1)\Delta\chi_{CX} + (3 \cos^2 (^1\!/_2\theta_{HCH}) - 1)\Delta\chi_{CH} \tag{5}$$

$$\delta\chi = -2 \sin^2 (^1\!/_2\theta_{XCX})\Delta\chi_{CX} + 2 \sin^2(^1\!/_2\theta_{HCH})\Delta\chi_{CH} \tag{6}$$

where θ is the bond angle given in Table I and $\Delta\chi_{CH}$ and $\Delta\chi_{CX}$ are the susceptibility anisotropies for the C–H and C–X bonds, respectively. For $C^2H^1HI_2$ one finds $\Delta\chi = -0.103\Delta\chi_{CX} - 0.093\Delta\chi_{CH}$ and $\delta\chi = -1.402\Delta\chi_{CX} + 1.396\Delta\chi_{CH}$. It is known from the literature[7] that $\Delta\chi_{CX}$ is at least three times as large as $\Delta\chi_{CH}$, which is confirmed by the data for CH_3I and CHI_3 in Table IV. So $\Delta\chi$ will be at most about 5–10% of $\delta\chi$. Combined with the small V_{zz} relative to $V_{xx} - V_{yy}$, it can be concluded that the splitting for the methylene halides can be interpreted in terms of the single parameter $\delta\chi$:

$$\Delta\nu = (B^2/20kT)(eQ/h)\delta\chi(V_{xx} - V_{yy}) \tag{7}$$

The theory outlined above applies to isolated molecules. In liquids the susceptibility is an effective quantity, and angular correlation with neighboring molecules has to be accounted for. The molecular $\Delta\chi$ can be obtained from gas-phase studies or from solutes at sufficiently low concentration in an inert solvent. For this purpose cyclohexane and ether have proved to be suitable.[29] At higher concentrations a Kirkwood[30] g_2 factor is commonly introduced, defining an effective susceptibility

$$(\Delta\chi)_{\text{eff}} = g_2(\Delta\chi)_{\text{mol}} \tag{8}$$

If $\delta\chi$ comes into the equations more g_2 factors can be introduced; the theory has been described elsewhere.[6,29] However, only $CHBr_3$ and $CHCl_3$ ($\delta\chi = 0$) have been investigated for angular correlation effects in this work. For all other compounds a solution of 1–5 mol % in cyclohexane or diethyl ether was measured to determine the molecular $\Delta\chi$ values.

Table II. Quadrupolar Deuteron Splittings at 14.35 T As Well As Some Scalar ^{1}H–^{2}H Couplings for the Halomethanes.

compd	solvent	concn (mol %)	$\Delta\nu$ (Hz)	$\lvert J_{^2H^1H}\rvert$ (Hz)
C^2HCl_3		100	0.223 ± 0.003	
	C_6H_{12}[a]	50	0.217 ± 0.005	
	C_6H_{12}	5	0.208 ± 0.005	
	C_6H_6[b]	66	0.14 ± 0.02	
	C_6H_6	33	0.11 ± 0.02	
$C^2H^1HCl_2$	$(C_2H_5)_2O$[c]	1–2	0.093 ± 0.003	1.103 ± 0.003
C^2HBr_3		100	0.361 ± 0.015	
	C_6H_{12}	50	0.342 ± 0.010	
	C_6H_{12}	5	0.320 ± 0.005	
$C^2H^1HBr_2$	C_6H_{12}	2	0.125 ± 0.003	0.984 ± 0.003
C^2HI_3	C_6H_{12}	0.5	0.564 ± 0.010	
$C^2H^1HI_2$	C_6H_{12}	5	0.199 ± 0.003	0.942 ± 0.003

[a] Cyclohexane. [b] Benzene. [c] Ether.

It should be noted that eq 8 is only valid if angular correlation does not influence the direction of the main susceptibility axis in the molecule. This will, for instance, not be the case in the situation of molecular complex formation. In formula 8 it is assumed that neighboring molecules influence only the orientation, not the principal axes in the molecule.

Experimental Section

Materials. Deuteriochloroform (99.8% ^{2}H) was obtained from Aldrich, deuteriobromoform from Merck Sharp and Dohme. Deuterioiodoform was obtained by hydroxide-catalyzed exchange of iodoform with ^2H_2O (Aldrich) and purified by vacuum sublimation. Deuterated methylene bromide and iodide were prepared from bromoform and iodoform according to Hartmann and Dreger[31] and Adams and Marvel[31] with substitution of 50% $^2H_2O/^1H_2O$ for H_2O. This results in a mixture of $C^1H_2X_2$, $C^1H^2HX_2$, and $C^2H_2X_2$ in the ratio 1:2:1. The deuterium signals of $C^1H^2HX_2$ and $C^2H_2X_2$ are, however, resolved at 93.75 MHz as a consequence of the isotope effect (see Figure 2b). Purification was by vacuum distillation. [$^2H_1$]methylene chloride was produced by reduction of $CHCl_3$ with Zn and deuterioacetic acid, according to Greene.[32] After the reaction about 6 mol % $C^2H^1HCl_2$ was left in the $CHCl_3$ as estimated from proton NMR. This was dissolved in cyclohexane at a 1:4 ratio.

NMR. Samples were prepared by weight, using cyclohexane or ether as an inert solvent, degassed and sealed in 5-mm NMR tubes (Wilmad, 528-PP). All deuteron spectra were recorded at the NMR Facility for Biomedical Studies, Carnegie Mellon University, Pittsburgh. Spectra were recorded at 14.35 T (93.75 MHz) or 14.57 T (95.18 MHz). Digital resolution after zero filling the F.I.D. was typically 0.001–0.004 Hz/pt. Resolution enhancement was applied to obtain the splittings. The precision of the quadrupolar couplings varies between 1 and 4%.

Results

The measured quadrupolar splittings as well as some scalar couplings for the $C^2H^1HX_2$ compounds are listed in Table II. Examples of some spectra are given in Figure 2 for C^2HCl_3 and $C^1H^2HBr_2/C^2H_2Br_2$. From Figure 2b it is clear that monodeuterated compounds must be used to obtain the quadrupolar splittings. If more deuterons are present, quadrupolar and scalar couplings, which are of the same order of magntiude, will interfere and the splitting pattern is complicated or obscured.[33]

The interpretation of the couplings in terms of molecular susceptibilities is not completely unambiguous. This is because the sign of the coupling is not obtained from the experiment. However, the assignment can be made on physical grounds. For the haloforms the sign can be deduced from the changes observed in the splitting when benzene is used as a solvent. It is known[34] that chloroform and benzene associate to form 1:1 charge-transfer complexes with the threefold and sixfold axes parallel. The effective $\Delta\chi$ of such a complex will be the algebraic sum of the $\Delta\chi$'s of the individual molecules. Since the C^2HCl_3 splitting and thus

---

(29) van Zijl, P. C. M.; MacLean, C.; Bothner-By, A. A. *J. Chem. Phys.* **1985**, *83*, 4410.

(30) Kirkwood, J. G. *J. Chem. Phys.* **1939**, *7*, 911.

(31) Hartman, W. W.; Dreger, E. E. *Organic Syntheses*; Wiley: New York, 1932; Collect. Vol. I, p 349. Adams, R.; Marvel, C. S. *Ibid*, p 350.

(32) Greene, W. H. *Jahresber. Fortschr. Chem.* **1879**, 490.

(33) Bothner-By, A. A.; Gayathri, C.; van Zijl, P. C. M.; MacLean, C. *J. Magn. Reson.* **1984**, *56*, 456.

(34) Forster, R. In *Organic Charge Transfer Complexes*; Academic Press: London, New York, 1969.

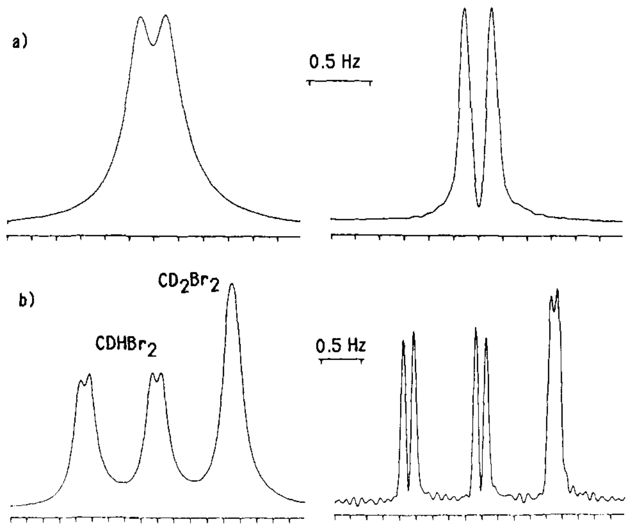

Figure 2. Normal and resolution-enhanced spectra (14.35 T, 296 K) of pure $CDCl_3$ (a) and a mixture of $CHDBr_2$ and CD_2Br_2 at 5 mol % in cyclohexane (b). The obscurity of the quadrupolar splitting in CD_2Br_2 as a consequence of interference of the scalar deuteron-deuteron coupling is clearly visible. (This figure is also used in a recent review (ref 3) and is reproduced, with permission from this reference.)

Table III. Magnetic Susceptibilities (cm^3/molecule) of the Halomethanes

compd	$10^{28}\chi_{xx}$	$10^{28}\chi_{yy}$	$10^{28}\chi_{zz}$	$10^{28}\Delta\chi$	$10^{28}\delta\chi$	$10^{28}\chi_{av}$[a]
CHI_3	-2.17	-2.17	-1.50	0.668	0	-1.944
CH_2I_2	-1.31	-1.78	-1.54	0	0.469	-1.545
CH_3I[b]	-0.89	-0.89	-1.07	-0.183	0	-0.949
$CHBr_3$	-1.50	-1.50	-1.12	0.382	0	-1.371
CH_2Br_2	-0.93	-1.23	-1.08	0	0.298	-1.081
CH_3Br[b]	-0.66	-0.66	-0.81	-0.141	0	-0.710
$CHCl_3$	-1.07	-1.07	-0.81	0.254	0	-0.984
CH_2Cl_2	-0.66	-0.88	-0.77	0	0.224	-0.773
CH_3Cl[b]	-0.49	-0.49	-0.62	-0.131	0	-0.531

[a] Reference 35. [b] Reference 36.

$\Delta\chi_{eff}$ are decreased by this association, the signs of $\Delta\chi$ of C^2HCl_3 and benzene must be opposite. Benzene is well known to have a negative $\Delta\chi$ (large diamagnetic susceptibility parallel to the sixfold axis), so $\Delta\chi$ of chloroform is positive. The splittings of the haloforms also show a small decrease on changing concentration in cyclohexane, a noncomplexing, virtually inert solvent. This is ascribed to an angular correlation effect between chloroform molecules.

The sign of the susceptibility asymmetry of the methylene halides can be derived assuming that the C-X bond tensors change only moderately on going from CHX_3 to CH_2X_2. From eq 4 one obtains for haloforms

$$\Delta\chi = +3(\tfrac{3}{2}\cos^2\theta_{HCX} - \tfrac{1}{2})\Delta\chi_{CX} + \Delta\chi_{CH} \qquad (9)$$

while for methylene halides

$$\delta\chi = -2\sin^2(\tfrac{1}{2}\theta_{XCX})\Delta\chi_{CX} + 2\sin^2(\tfrac{1}{2}\theta_{HCH})\Delta\chi_{CH} \qquad (10)$$

For the haloforms $\Delta\chi$ is positive, and since $|\Delta\chi_{CX}| > |\Delta\chi_{CH}|$, it follows that $\Delta\chi_{CX}$ is negative. By the same reasoning $\delta\chi$ for the methylene halides is positive. Finally for methyl halides:

$$\Delta\chi = 3(\tfrac{3}{2}\cos^2\theta_{HCX} - \tfrac{1}{2})\Delta\chi_{CH} + \Delta\chi_{CX} \qquad (11)$$

and $\Delta\chi$ is negative, as confirmed by the literature data in Table III.

The accuracies of the determined susceptibilities can be deduced from the quantities in eq 1 and 2. For the haloforms it is only determined by the value of e^2qQ/h, and the splitting. So the maximum estimated error will be in the range of 3-7%. For the methylene halides this may be a few percent larger in view of the neglect of η, the possible error in the bond angle and perhaps an extra 1% for deleting the $\Delta\chi V_{zz}$ contribution.

Table IV. C-X Bond Susceptibilities (cm^3)[a] Calculated for the Bonds in Each Molecule of the Series CHX_3, CH_2X_2, CH_3X Using Table III and Eq 4 and 12[b]

bond	compound	$10^{28}\chi_{cc}$[a]	$10^{28}\chi_{bb}$[a]	$10^{28}\Delta\chi$	$10^{28}\chi_{bond,av}$[c]
C-I	CHI_3	-1.05	-0.42	-0.63	-0.63
	CH_2I_2	-0.95	-0.57	-0.38	-0.70
	CH_3I	-0.91	-0.68	-0.23	-0.76
C-Br	$CHBr_3$	-0.69	-0.31	-0.38	-0.44
	CH_2Br_2	-0.65	-0.38	-0.27	-0.47
	CH_3Br	-0.64	-0.45	-0.19	-0.51
C-Cl	$CHCl_3$	-0.50	-0.21	-0.29	-0.31
	CH_2Cl_2	-0.45	-0.25	-0.20	-0.32
	CH_3Cl	-0.45	-0.28	-0.17	-0.34

[a] χ_{cc} along the bond; χ_{bb} perpendicular. [b] χ_{cc}(C-H) = -0.093×10^{-28} cm^3 and χ_{bb} (C-H) = -0.051×10^{-28} cm^3 are used (ref 43). [c] $\chi_{bond,av} = {}^1/_3(\chi_{cc} + 2\chi_{bb})$.

Discussion

In Table III the susceptibility anisotropies, asymmetries, and averages are listed. The averages and the values for the methyl halides are obtained from the literature.[8,35,36]

For the haloforms and methylene halides, to our knowledge, there are no microwave data for comparison. Two compounds have been studied by the Cotton-Mouton effect, namely, $CHCl_3$[10,11,37] and $CHBr_3$.[11] The values found are $\Delta\chi(CHCl_3) = 0.30 \times 10^{-28}$ cm^3 (ref 37) and 0.19×10^{-28} cm^3 (ref 11) and $\Delta\chi(CHBr_3) = 0.26 \times 10^{-28}$ cm^3 (ref 11). These values deviate beyond the error limits of our measurements. Even the two literature values for $\Delta\chi(CHCl_3)$ differ markedly. In our view this can be explained by the complexity of the Cotton-Mouton measurements, where more than one unknown quantity (molecular polarizabilities, local field contributions, etc.) have to be evaluated. Also this method is a bulk measurement, which makes it more complicated to do measurements in mixtures. Ritchie et al.[38,39] pointed out that the errors in the infinite dilution $\Delta\chi$ values from the old Cotton-Mouton measurements may be as large as 20-60%. On the other hand, the NMR method is simple, molecular properties are studied, and the constants in the formulas are in general well known (Table I).

The values in Table III can be used to evaluate the bond susceptibilities for the C-X bonds in each compound to see whether they vary in the series CH_3X, CH_2X_2, CHX_3, or if they follow a Pascal additivity relationship.[40] This is of interest, since it has long been known that the isotropic magnetic susceptibilities of halomethanes do not follow Pascal's rules. French and Trew[41] and Lacher[42] have drawn particular attention to the trends in the susceptibilities of the halomethanes, and point out that the diamagnetic susceptibilities of the haloforms and tetrahalomethanes are much less than would be predicted on the basis of a Pascal scheme. Lacher proposes that the susceptibilities may be calculated based on consideration of pairwise interactions of C-X bonds: each additional substitution by X decreases the diamagnetic contribution from each C-X bond, or atom. Now that the main susceptibility components are available for the whole series of compounds, perhaps a more detailed understanding of this deviation can be obtained. The values for the bond susceptibilities are listed in Table IV.

They have been evaluated using eq 4 and the Pascal relation

$$\chi_{av} = \sum \chi_{bond,av} \qquad (12)$$

where χ_{av} is the isotropic susceptibility, $(^1/_3)(\chi_{xx} + \chi_{yy} + \chi_{zz})$. The anisotropic and isotropic susceptibilities of the C-H bond were

---

(35) *Handbook of Chemistry and Physics*; The Chemical Rubber Co.: Cleveland, Ohio, 1978; Vol. 58.

(36) Vanderhart, D. L.; Flygare, W. H. *Mol. Phys.* **1970**, *18*, 77.

(37) Battaglia, M. R.; Ritchie, G. L. D. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 209.

(38) Ritchie, G. L. D.; Vrbancich, J. *Aust. J. Chem.* **1982**, *35*, 869.

(39) Battaglia, M. R.; Ritchie, G. L. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 901.

(40) Pascal, P. *Chimie Generale*; Masson et Le: Paris, 1949.

(41) French, C. M.; Trew, V. C. G. *Trans. Faraday Soc.* **1945**, *41*, 439.

(42) Lacher, J. R. *J. Am. Chem. Soc.* **1947**, *69*, 2067.

assumed constant, and the values given by Schmaltz et al.[43] were used (see Table IV).

The present measurements do indeed show a new and surprising aspect of this topic: the anisotropies in the bond susceptibilities increase sharply (in absolute value) with increased halogen substitution. Another trend can be seen from the Table IV: the diamagnetic susceptibilities parallel to the C–X bond (χ_{cc}) appear to become slightly larger with increasing halogen substitution, while the perpendicular diamagnetic susceptibilities (χ_{bb}) decrease sharply; it is the latter which cause the large paramagnetic terms in the susceptibilties of the polyhalogenated methanes. A ready explanation for this is not apparent in terms of electron circulations. One possible rationale is that the perpendicular susceptibility depends on paramagnetic circulation of electrons around the chlorine nucleus via the p_x or p_y valence orbitals and the antibonding σ orbital to carbon. Additional halogen substitution could change the electron distribution and hybridization of the σ and σ^* orbitals, enhancing this circulation.

Angular Correlation. From the concentration series of chloroform and bromoform, the Kirkwood g_2 factor of the pure compounds can be calculated (eq 8). This gives $g_2(CDCl_3) = 1.07$ and $g_2(CDBr_3) = 1.13$. Battaglia and Ritchie performed an analogous concentration-dependent Cotton–Mouton study[37] in cyclohexane. Their lowest concentration is about 20 mol %. Our extrapolation of their curve leads to $g_2 = 1.20$. They themselves extrapolate differently obtaining $g_2 = 1.25$. Angular correlation has also been studied for chloroform by Alms et al.[44] using Rayleigh scattering, and for chloroform and bromoform by Patterson and Griffiths[45] from Rayleigh and Raman line-width data. Both groups report values leading to a g_2 of about 1.6 for chloroform, and the latter group finds a value of about 2.3 for bromoform, all at room temperature. These values differ substantially from those found by the NMR method or the Cotton–Mouton method. We can see two possible reasons for this discrepancy.

Firstly, it is not clear that the definition of the phenomena measured in the two kinds of studies is the same. For example, we note that a neat liquid consisting of long-lived rigid dimers with parallel major axes would yield a g_2 value of 1.0 by comparison of Rayleigh light scattering and Raman line-shape analysis, but 2.0 by the NMR method or the Cotton–Mouton effect.

The second explanation is that collision-induced changes in the effective polarizability of the small molecules studied here may perhaps not be neglected anymore. This has recently been discussed by Ladanyi et al.[46,47] who calculate that this effect will lead to an effective polarizability in Raman and Rayleigh scattering, which is lower than the molecular value. The change in α is based on a dipole–induced–dipole interaction and may be quite large in strong dipoles like the haloforms under study here. For larger polyatomic molecules these effects will become negligible,[47] so that g_2 factors of, for instance, substituted benzenes may be expected to agree better with the NMR data. Finally, in the calculation of g_2 from the ratio of Rayleigh and Raman correlation times, it is assumed that there is negligible dynamic correlation between neighbors. However, small dipolar molecules may well have a significant rotational anticorrelation, which would bring the static g_2 value into closer agreement.

The concentration-dependent study of scattering by only one technique (Rayleigh scattering) should in principle give a correct g_2 value if the viscosity of the different solutions is kept constant. Therefore the deviation between our value for $CDCl_3$ and the one obtained by Alms et al.[44] is not quite clear. Measurements on substituted benzenes performed in this way give comparable g_2 factors with the NMR technique as well as with the Cotton–Mouton effect.[6,29]

Finally it should be noted that the NMR orientation method is a clean simple technique, which provides reasonably accurate quantities to be used in a straightforward interpretable theory, where the quantities in the formulas are well known, while the optical techniques are experimentally complex and contain quantities in the formulas which are sometimes hard to obtain (local field factors, hyperpolarizability); also line-shape analyses may for many compounds be quite complex.

Scalar ^1H–^2H Couplings in the Methylene Halides. Measurements of the scalar $J_{^1H^2H}$ couplings in methylene halides were made at an early date.[48] Our measurements are more precise and lead to J_{HH} geminal coupling constants of −7.19 Hz for CH_2Cl_2, −6.41 Hz for CH_2Br_2, and −6.14 Hz for CH_2I_2.

Acknowledgment. The authors thank Professors B. M. Ladanyi, G. D. Patterson, and J. I. Brauman for discussions concerning the comparison of NMR data with Rayleigh and Raman scattering experiments. This work was performed with support from the National Science Foundation. NMR spectra were recorded using the 620-MHz instrument at the NMR Facility for Biomedical Studies, Pittsburgh, supported by National Institutes of Health Grant RR00292.

Registry No. C^2HCl_3, 865-49-6; C^2HBr_3, 2909-52-6; C^2HI_3, 2787-27-1; $C^2H^1HCl_2$, 1665-01-6; $C^2H^1HBr_2$, 2253-83-0; $C^2H^1HI_2$, 2253-85-2; $C^2H^1H_2Cl$, 4960-86-5; $C^2H^1H_2Br$, 1861-05-8; $C^2H^1H_2I$, 992-96-1.

---

(43) Schmaltz, T. G.; Norris, C. L.; Flygare, W. H. *J. Chem. Phys.* **1973**, *59*, 7961.
(44) Alms, G. R.; Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Chem. Phys.* **1973**, *59*, 5304; **1973**, *59*, 5310.
(45) Patterson, G. D.; Griffiths, J. E. *J. Chem. Phys.* **1975**, *63*, 2406.
(46) Ladanyi, B. M. *Chem. Phys. Lett.* **1985**, *121*, 351.
(47) Ladanyi, B. M.; Levingen, N. E. *J. Chem. Phys.* **1984**, *81*, 2620.
(48) Bernstein, H. J.; Sheppard, N. *J. Chem. Phys.* **1962**, *37*, 3012.

Semipolar P–O and P–C Bonds. A Theoretical Study of Hypophosphite and Related Methylenephosphoranes

Andrew Streitwieser, Jr.,* Andrzej Rajca,[1a] Robert S. McDowell,[1b] and Rainer Glaser[1c]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720.
Received August 25, 1986

Abstract: Structures, energies, and electronic structures as derived from integrated projected densities are presented from ab initio MO calculations of H_3PO (**1**), H_3PCH_2 (**2**), $H_2PO_2^-$ (**3**), $OPH_2CH_2^-$ (**4**), and $H_2P(CH_2)_2^-$ (**5**). The results show that allylic conjugation is not important in **3**, **4**, and **5** and that the PO and PC bonds in these compounds are best represented as dipolar bonds with little double-bond character. Simple electrostatic considerations suffice to interpret many of the results obtained concerning structure and energy.

The nature of the phosphorus–oxygen bond in phosphine oxides[2–6] and of the phosphorus–carbon bond in ylides[7–10] has received much recent theoretical attention. Hartree–Fock calculations together with structural effects, population analyses, and analyses

0002-7863/87/1509-4184$01.50/0 © 1987 American Chemical Society