carborane to the corresponding $R_4C_4B_8H_8$ species, via oxidative fusion of the $H_2Fe(R_2C_2B_4H_4)_2$ complex, was conducted by a previously published procedure.[5,19] Characterization data for $H_2Fe[(CH_3)_2C_2B_4H_4]_2$[5,20] and $H_2Fe[(C_2H_5)_2C_2B_4H_4]_2$[19] have been reported earlier. The compound $H_2Fe[(n\text{-}C_3H_7)_2C_2B_4H_4]_2$ (**4**), an air-sensitive red oil obtained in 68% yield (0.551 g) from the reaction of $(n\text{-}C_3H_7)_2C_2B_4H_5^-$ ion with $FeCl_2$ in THF, exhibits an electron-impact mass spectrum with high-mass cutoff at *m/e* 375, corresponding to that of the $^{56}Fe^{13}C^{12}C_{15}{}^{11}B_8{}^1H_{38}^+$ parent ion, and a parent envelope whose relative intensities correspond to the pattern calculated from natural isotopic abundances. A more intense grouping with local cutoff at *m/e* 317 arises from $(C_3H_7)_4C_4B_8H_8^+$ that forms via loss of FeH_2 from **4**. The ^1H-decoupled 115.5-MHz ^{11}B NMR spectrum in C_6D_6 contains peaks at δ −1.1, −7.9, and −19.5 referenced to $(C_2H_5)_2O\cdot BF_3$ (relative areas 1:2:1).

X-ray Structure Determination on $(C_2H_5)_4C_4B_8H_8$ (2B). A crystal grown from *n*-hexane solution and mounted on a glass fiber was examined by precession photography and found acceptable. Relevant parameters for the data collection and structure determination are given in Table I. The procedures followed in data collection and processing have been described elsewhere.[21] The space group $P2_1/n$ was determined from systematic absences.

The intensities of three standard reflections showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects but not for absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where (F_o^2) was estimated from counting statistics ($p = 0.03$),[22] were used in the final refinement of the structural parameters, after averaging for equivalent reflections.

Solution and Refinement of the Structure. Full-matrix least-squares refinement was based on F, and the function minimized was $w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[23] and those for hydrogen from Stewart et al.[24] The effects of anomalous dispersion for all non-hydrogen atoms were included in F by using the values of Cromer and Ibers[25] for $\Delta F'$ and $\Delta f''$.

The MULTAN 74 program series[26] was used to produce a solution of the phase problem, and an E map gave the positions of the 20 non-hydrogen atoms in the asymmetric unit, allowing an unequivocal assignment of atom types to the peaks. Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of all the nonalkyl, and some alkyl, hydrogen atoms. The remaining alkyl hydrogens were inserted in their calculated positions. The hydrogen atoms were included in the least-squares refinement for several cycles and then held fixed. The model converged to the final R and R_w values given in Table I, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Tables of observed and calculated structure factors and thermal parameters are available as supplementary material. The computing system and programs are described elsewhere.[27]

Acknowledgment. We thank Professor Ekk Sinn for assistance in the X-ray structure determination. This work was supported by the National Science Foundation, Grant No. CHE 81-19936.

Supplementary Material Available: Table IX, measurements of [B]/[A] vs. time for $R_4C_4B_8H_8$ carboranes (R = CH_3, C_2H_5, $n\text{-}C_3H_7$); Table X, measurements of K_{eq} vs. temperature for $R_4C_4B_8H_8$; Table XI, structure factor table for $(C_2H_5)_4C_4B_8H_8$ (12 pages). Ordering information is given on any current masthead page.

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Carbon-13 Chemical Shift Tensors of Halobenzenes

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Abstract: The carbon-13 chemical shift tensor of each carbon atom in fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene has been determined. The system used was liquid crystal solutions of the halobenzenes. The anisotropic carbon-13 chemical shifts of the solute in each liquid crystal solution were measured. The ordering factors of the solute molecule were determined from a computer analysis of the proton (and fluorine-19 for fluorobenzene) spectrum. The data of six liquid crystal solutions of each halobenzene were used to calculate the chemical shift tensors. A striking observation is that the tensor component along the C–X axis for the ipso carbon does not change substantially with the substituent in the halobenzenes and in some other mono- and disubstituted benzenes. It was also found that, with the exception of iodobenzene, the tensor component perpendicular to the ring decreases (becomes more shielded) with the separation of the carbon atom from the substituent. This is in contrast to the isotropic shifts, which do not show regular changes with the position of the carbon atom in the ring.

Carbon-13 chemical shifts are very sensitive to the nature of the directly and indirectly bonded atoms and functional groups in a molecule. They have been extensively used in the determination of molecular structures and conformations. A substituent on a benzene ring has a profound effect on the σ- and π-electron densities of all carbon atoms on the ring and can cause substantial changes in chemical properties and reactivities of the compound. An extensive effort has been made to correlate carbon-13 chemical shifts and electron densities and reactivities of substituted benzenes.[1-3] The electronic distributions of aromatic compounds are very anisotropic. Consequently, the chemical shift tensors of aromatic compounds show large anisotropies.[4-10] Obviously the study of the components of the chemical shift tensors would yield more information on molecular structure than the study of the

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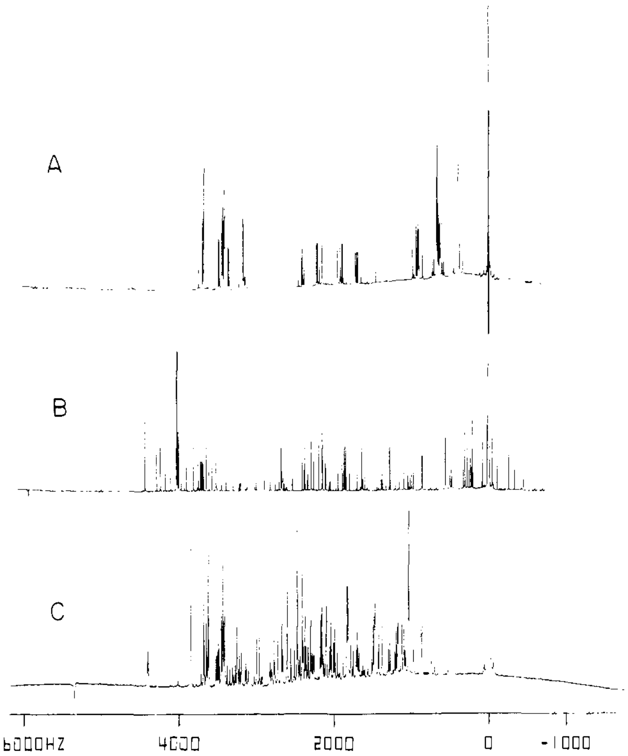

Figure 1. ^{1}H NMR spectra of fluorobenzene in liquid crystal solutions at 300 MHz and 298 K: (A) in EBBA, (B) in NP 1565 TNC, (C) in ZLI 1167. The peak at 0 Hz is due to Me$_4$Si.

traces alone, which are the values observed in isotropic liquids. Hopefully, a knowledge in the three-dimensional chemical shift data would contribute to a better understanding of structurally selective chemical properties and reactivities.

Although chemical shift tensors of a number of aromatic compounds have been reported,[4-10] there has been no systematic effort to study the effect of the substituent in monosubstituted benzenes. We have recently studied the ^{13}C chemical shift tensors of benzonitrile[11] and will report the results of halobenzenes in this paper.

There are several methods of measuring ^{13}C chemical shift tensors. The most accurate way is to study the proton-decoupled NMR spectra of single crystals oriented at various angles.[5-7] Another way of determining the tensor components is to perform a line-shape analysis of the spectrum of a polycrystalline solid.[4] When there are overlapping signals, they can be resolved by using magic-angle spinning, and the anisotropic patterns of individual signals can be reconstructed from the spinning sidebands[12-14] or by using pulses synchronized with the rotation of the spinner.[9,15,16] It is also possible to resolve the overlapping pattern by using a two-dimensional study with rapid flipping of the spinning axis.[17] An alternative approach is to study the ^{13}C NMR spectra of solute molecules in liquid crystal solutions.[18,19] This kind of study in natural abundance is now possible with use of a technique developed in this laboratory.[11,20] An advantage of this method is

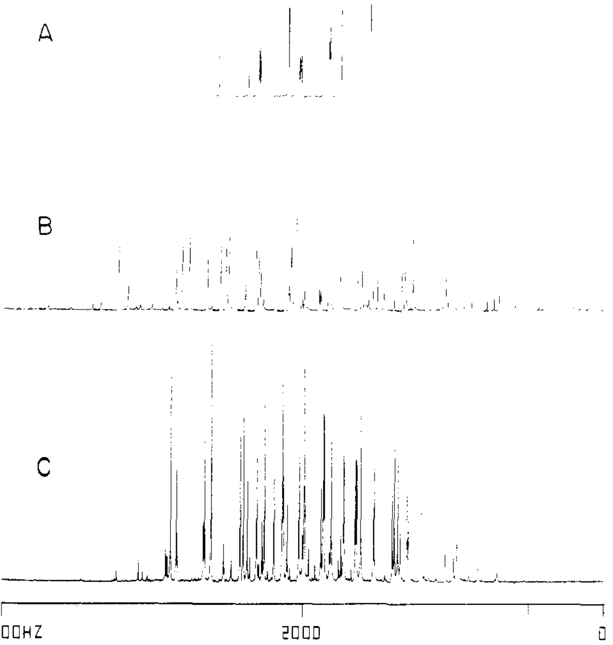

Figure 2. ^{19}F NMR spectra of fluorobenzene in liquid crystal solutions at 282.23 MHz and 298 K: (A) in EBBA, (B) in NP 1565 TNC, (C) in ZLI 1167. The center of each spectrum has a different chemical shift.

that low-melting compounds can be readily studied at room temerature in the liquid crystal solutions.

Experimental Section

p-Ethoxybenzilidene-*p*-*n*-butylaniline (EBBA) was obtained from American Liquid Crystal Co., Kent, OH. NP 1565 TNC and ZLI 1167 were obtained from EM Chemicals, Hawthorne, NY.

All the NMR spectra were taken with a Varian XL-300 NMR spectrometer at 298 K. The solvent peaks are reduced by using a spin-echo sequence, and the efficiency of proton decoupling was increased by using phased-alternated broad-band decoupling.[11,20] The MLEV-16[21] or MLEV-64[22] sequences were used in these experiments. More efficient sequences specially developed for the application in liquid crystal solutions are now available.[23]

Results

The proton and fluorine-19 NMR spectra of fluorobenzene in three liquid cyrstal solvents (EBBA, NP 1565 TNC, and ZLI 1167) are shown in Figures 1 and 2, respectively. A comparison of these spectra with those first published in 1965[24] and later in 1972[25] demonstrates the significant improvement of NMR spectrometers and liquid crystal solvents over the past 20 years. In addition to these spectra, the spectra of fluorobenzene in three mixed solvents (EBBA–NP 1565 TNC, EBBA–ZLI 1167, and ZLI 1167–NP 1565 TNC, all ca. 8:2 by weight) were also measured. These spectra were analyzed by using the PANIC program in an IBM NR/80 spectrometer to obtain the ordering factors of fluorobenzene in all six solvents. The proton spectra of chlorobenzene, bromobenzene, and iodobenzene in the six solvents were also measured and analyzed.

Carbon-13 NMR spectra of the halobenzenes in the same samples were measured at the same temperature as for the proton study. The spectra of fluorobenzene in three liquid crystal solvents are shown in Figure 3. Each type of carbon shows two peaks due to carbon–fluorine dipolar and scalar couplings. The center

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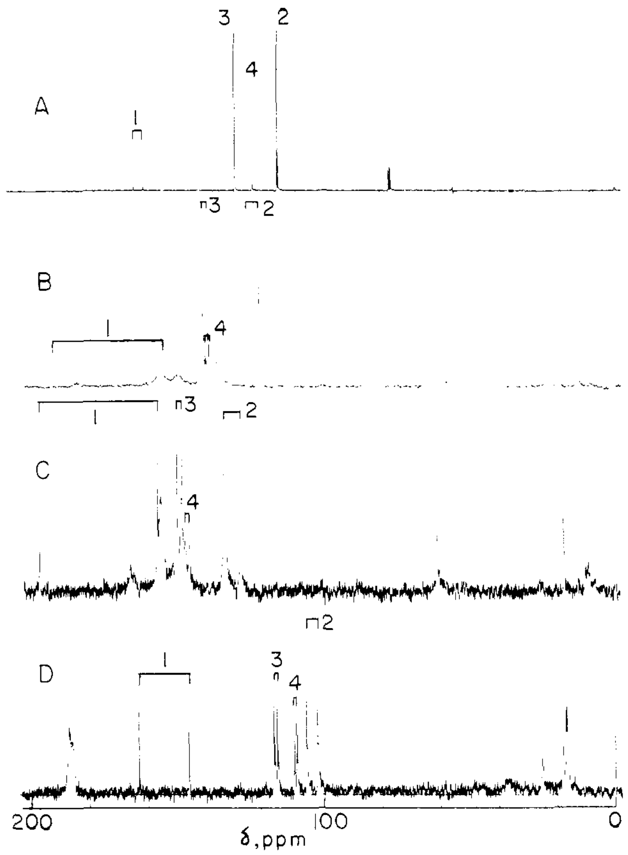

Figure 3. ^{13}C NMR spectra of fluorobenzene in liquid and liquid crystal solutions at 75.45 MHz and 298 K: (A) in $CDCl_3$, (B) in EBBA, (C) in NP 1565 TNC, (D) in ZLI 1167. The peak at 0 ppm is due to Me_4Si, and other unmarked peaks are residual solvent peaks.

of each pair determines the anisotropic chemical shift of each type of carbon. The anisotropic carbon-13 chemical shifts and the ordering factors calculated from the proton (and fluorine-19 for fluorobenzene) spectra were used to calculate the carbon-13 chemical shift tensor of each type of carbon in the halobenzenes. The method was discussed previously[11] and is briefly outlined in the following for the sake of clarity in discussion.

For a solute molecule with C_2, D_2, or D_{2h} symmetry, the observed chemical shift in a liquid crystal solution is[18]

$$\delta_{\text{aniso}} = \delta_{\text{iso}} + \tfrac{2}{3}S_{zz}[\delta_{zz} - \tfrac{1}{2}(\delta_{xx} + \delta_{yy})] + \tfrac{1}{3}(S_{xx} - S_{yy})(\delta_{xx} - \delta_{yy}) \quad (1)$$

where the δ_{ii}'s are the major components of the chemical shift tensor and S_{zz} and $S_{xx} - S_{yy}$ are the ordering factors. In this notation, the z axis is the C_2 axis and the y axis is perpendicular to the plane of symmetry. δ_{iso} is the trace of the chemical shift tensor:

$$\delta_{\text{iso}} = \tfrac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz}) \quad (2)$$

Data of δ_{aniso} and ordering factors obtained from six liquid crystal solutions of each compound were fitted to eq 1 and 2 to calculate δ_{xx}, δ_{yy}, and δ_{zz} for each type of carbon atom. For a more extensive set of experimental data to be obtained, 20% of $CDCl_3$ was added to each liquid crystal solution to make it isotropic; the chemical shifts of the isotropic solutions were measured and the data were also used in the least-squares fitting with the ordering factors being zero.

For the substituent effect on the chemical shift anisotropy of individual carbon atoms to be compared, the tensor components in the molecular axes are transformed to a bond-axis system.[11] In the latter system, the a axis is the CH or CX axis and the c axis is perpendicular to the ring. The axes a, b, and c do not necessarily coincide with the principal axes of the chemical shift tensors for carbons 2 and 3 because of the lack of symmetry about the corresponding C–H bonds. However, the respective angles between the two sets of axes may be quite small,[5-7] and the bond axes do form a reasonable axis system for the purpose of comparing the data of all carbons. The results of the present work are listed in Table I.

Discussion

In this section, we will first access the accuracy of the data and then discuss the significance of the results.

In the measurement of the anisotropic chemical shifts, Me_4Si is used as internal reference. An implicit assumption in this choice is that the anisotropic chemical shift of Me_4Si is negligible. The validity of this assumption has been recently examined,[26] and it has been found that the error is very small and does not contribute significantly to the overall uncertainty of the results.

The second assumption is that δ_{iso} and the tensor components δ_{xx}, δ_{yy}, and δ_{zz} remain the same in various liquid crystal solutions. In a previous study, we used the value of δ_{iso} obtained in $CDCl_3$ for the least-squares fit to eq 1 and 2.[11] It is well-known that δ_{iso} has a small dependence on the solvent used ($\lesssim 0.5$ ppm except when hydrogen bonding is involved).[1-3] This appears to be small compared to the uncertainties in the tensor components (several ppm) obtained from studies in either liquid crystals or in solids. However, if an incorrect value of δ_{iso} is used in the least-squares fitting of the liquid crystal data, possible errors would be amplified several times because the ordering factors are about 0.1 to 0.2 in our studies. Therefore, we did not use any fixed values of δ_{iso} in the fitting procedure of the present data. We found that the chemical shifts in the isotropic solutions formed by adding 20% $CDCl_3$ to the liquid crystal solutions are very close to each other and to that in $CDCl_3$ (all within 0.1 ppm). The calculated values of δ_{iso} agree well with the averaged experimental values in these isotropic solutions (Table I). This is an indication that the tensor components calculated from the liquid crystal solutions are reliable and that the assumption of δ_{iso} being constant in various liquid crystal solutions is a reasonable one. A possible way of directly determining δ_{iso} for each solution is to study the liquid crystal solutions with magic-angle spinning. The accuracy of the data would depend upon the exact alignment of the spinning axis with respect to the magnetic field and the extent of solvent interference, because even with magic-angle spinning the peaks in the liquid crystal solutions are considerably broader than those in isotropic liquids. In the case of EBBA, NP 1565 TNC, and mixed solvents, the aromatic peaks of the solvent may interfere with the solute peaks.

The calculation of the chemical shift tensors according to eq 1 and 2 requires the knowledge of the ordering factors S_{zz} and $S_{xx} - S_{yy}$ for each solution. They were obtained from computer analyses of the proton (and fluorine-19) spectra of the liquid crystal solutions with the PANIC program in an Aspect 2000 computer in an IBM NR/80 spectrometer. The dipolar coupling constants obtained are then used to calculate the ordering parameters and coordinates of the hydrogen atoms. In the calculation, r_{35} was taken as 4.301×10^{-10} m. This is the distance in benzene without vibrational correction and is regarded as least influenced by solvent effect.[27] Vibrational corrections of the dipolar coupling constants were not used because they usually affect the values of coordinates to less than 1% and the values of the ordering factors even less. The strong orientation of the C_2 axis of chlorobenzene, bromobenzene, and iodobenzene makes the spectra deceptively simple, which reduces the accuracy of the computed dispolar coupling constants of the 2,6 and the 3,5 proton pairs.[28] This makes the vibrational correction unwarranted. Fortunately, uncertainties in the S values of the order of 1% or less do not appreciably affect the calculated values of the tensor components.

To summarize the above discussion, we feel that the basic assumption of δ_{iso}, δ_{xx}, δ_{yy}, and δ_{zz} being invariant in different liquid crystal solutions may be the largest source of error in the results

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Table I. Carbon-13 Chemical Shift Tensors (ppm)[a]

		δ_{iso}	δ_{aa}	δ_{bb}	δ_{cc}
benzene[b]		128.4	234 ± 3	146 ± 3	6.2 ± 0.2
fluorobenzene	C1	162.8 (162.82 ± 0.02)	238 ± 2	157 ± 4	94 ± 1
	C2	115.2 (115.24 ± 0.02)	175 ± 2	157 ± 2	14 ± 1
	C3	129.9 (129.98 ± 0.03)	203 ± 3	179 ± 2	7 ± 1
	C4	123.9 (124.02 ± 0.04)	216 ± 3	155 ± 5	0 ± 2
chlorobenzene	C1	134.1 (134.18 ± 0.05)	237 ± 3	111 ± 6	54 ± 3
	C2	128.4 (128.4 ± 0.1)	184 ± 4	171 ± 2	29 ± 2
	C3	129.7 (129.71 ± 0.05)	192 ± 4	182 ± 3	15 ± 2
	C4	126.3 (126.41 ± 0.06)	239 ± 3	130 ± 6	10 ± 3
bromobenzene	C1	122.3 (122.44 ± 0.03)	233 ± 3	82 ± 7	52 ± 4
	C2	131.4 (131.43 ± 0.04)	183 ± 4	170 ± 2	40 ± 2
	C3	130.0 (130.00 ± 0.06)	182 ± 4	180 ± 3	28 ± 3
	C4	126.7 (126.82 ± 0.06)	240 ± 3	116 ± 7	24 ± 4
iodobenzene	C1	94.4 (94.34 ± 0.01)	230 ± 2	41 ± 6	12 ± 3
	C2	137.3 (137.31 ± 0.05)	188 ± 4	173 ± 2	51 ± 3
	C3	130.2 (130.13 ± 0.07)	178 ± 5	179 ± 3	33 ± 3
	C4	127.4 (127.32 ± 0.08)	242 ± 3	113 ± 8	26 ± 5

[a] The values in parentheses are averages of experimental values. [b] References 10 and 26.

of the chemical shift tensors. The uncertainties of the data are a few ppm, which are comparable to those in polycrystalline solid-state studies but larger than those in single crystal work. Even though the relative errors in δ_{cc} seem to be quite large (Table I), we must note that the percentage errors in $(\delta_{ii} - \delta_{iso})/\delta_{iso}$ are in general about the same for all three components.

We now turn to an examination of the results of the data in Table I and their significance.

The most striking result in Table I is that δ_{aa}'s for the ipso carbon (C_1) of the halobenzenes do not differ substantially from δ_{aa} in benzene and do not change a great deal with the substituent. This component is the chemical shift along the C–X axis. Intuitively one would expect that it would change significantly with the electronegativity of the substituent. However, its change with the substituent is much smaller than that of δ_{bb}, δ_{cc}, and δ_{iso}. We note that the absence of substantial changes in δ_{cc} for the directly substituted carbon in the benzene ring has also been observed in benzonitrile,[11] *p*-dimethoxybenzene,[13,16,17] *p*-xylene,[7] and 1,2,4,5-tetramethylbenzene,[5] but not in hexamethylbenzene.[6] Whether this trend is general for other mono- and disubstituted benzenes remains to be determined. The significance of this intriguing result as related to the effect of the substituents on the electronic structures of these compounds should be an interesting topic for theoretical study.

The consistency in the chemical shift of the halobenzenes and benzonitrile is also observed for δ_{iso} and δ_{bb} of the meta carbon (C3; Table I and ref 11). The reason for this is not clear.

Another interesting observation is that, in the same molecule, δ_{iso} for each halobenzene and for benzonitrile does not change regularly with the position of the carbon atom, but δ_{cc} decreases regularly with the separation from the substituent, except for iodobenzene. Thus, δ_{cc} may be a better parameter to correlate with the electron density than δ_{iso} is.

Finally, we made an investigation to see whether the chemical shift tensor components can be related to the Hammett σ constants, as in the case of isotropic shifts.[1-3] It is known that the ^{13}C isotropic shifts at the para position of monosubstituted benzenes (δ_p) can be related to the reactivity constants by

$$\delta_p - \delta_o = \rho_I\sigma_I + \rho_R\sigma_R{}^0 \qquad (3)$$

where δ_o is the chemical shift of benzene, σ_I is the Hammett inductive parameter which measures the effect of polarization of the π electrons by a substituent, $\sigma_R{}^0$ is the Hammett resonance parameter which measures the ability of a substituent to delocalize π electrons to or from the benzene ring, and ρ_I and ρ_R are constants measuring the effects of these two terms. The values of σ_I and $\sigma_R{}^0$ for a number of compounds have been tabulated,[1] and the values of ρ_I and ρ_R determined from 15 compounds in several solvents are given.[1]

Table II. Results of Dual Parameter Fit for the ^{13}C Chemical Shifts of Halobenzenes[a]

	aa	bb	cc	av	iso[b]
ρ_I	89	−176	100	4.3	4.64
$\rho_R{}^0$	198	−320	185	21	21.46
RMSD, ppm	0.6	7	8	5	0.2

[a] The values of σ_I and $\sigma_R{}^0$ for fluorobenzene, chlorobenzene, and iodobenzene are given in ref 1; the corresponding values of iodobenzene used in this calculation are $\sigma_I = 0.39$ and $\sigma_R{}^0 = -0.13$. [b] In $CDCl_3$; ref 1.

The results of fitting the chemical shift tensor components of the para carbons of halobenzenes to the dual parameter equation (eq 3) are given in Table II. Even though the RMSD's of the tensor components appear to be quite large, their values are comparable to the experimental errors and their ratios to $(\delta_p - \delta_o)$ are comparable to those of the isotropic data. It is of interest to note that the average values of ρ_I and ρ_R for the three components are amazingly close to the corresponding values in $CDCl_3$. This seems to affirm the validity of fitting the tensor data to the commonly used equation for isotropic chemical shifts (eq 3). Another interesting result from the fitting is that the ratio of ρ_R/ρ_I, which is often interpreted as the relative importance of the σ electron density vs. the σ electron density, are quite different for the isotropic and the anisotropic data. The ratio ρ_R/ρ_I is 4.6 for the isotropic data, but is 2.2 (for δ_{aa}) or less (for δ_{bb} and δ_{cc}) for the anisotropic data. The significance of these results remains to be further studied.

It was found that a general relation similar to eq 3 cannot be established for the ipso, ortho, and meta carbons of monosubstituted benzenes.[2] If we consider the halobenzenes only, such a relation can be found for these carbon atoms for either the isotropic shifts or the tensor components. However, it is known that, as far as ^{13}C chemical shifts are concerned, the halogens are a special group of substituents[1,29] which cannot be categorized as either electron withdrawing or electron donating.[29] Therefore, we are reluctant to correlate the chemical shift tensors of the ipso, ortho, and meta carbons with the Hammett σ constants without the availability of more data for other compounds. When such data are available, it will be of interest to examine whether or not the relations established for the tensor components of the para carbon can be generalized and relations for the tensor components of other carbon atoms in the benzene ring can be found.

Registry No. Fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; iodobenzene, 591-50-4.

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