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NMR Chemical Shifts. 1. The Role of Relative Atomic Orbital Phase in Determining the Sign of the Paramagnetic Terms: ClF, CH_3F, $CH_3NH_3^+$, FNH_3^+, and HC≡CF

Kenneth B. Wiberg,*,† Jack D. Hammer,† Kurt W. Zilm,*,† James R. Cheeseman,‡ and Todd A. Keith†

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107, and Lorentzian, Inc., 140 Washington Avenue, North Haven, Connecticut 06473

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The shielding of several nuclei for molecules in magnetic fields was examined via B3LYP/6-311+G(3df,-3pd) calculations using the MP2/6-31G* geometries. Both the gauge-invariant atomic orbital (GIAO) and individual gauges for atoms in molecules (IGAIM) methods were employed, and the molecules were the isoelectronic series F_2, ClF, CH_3F, $CH_3NH_3^+$, FNH_3^+, and FC≡CH. The main paramagnetic contributions arose from the π and π' molecular orbitals (MOs) interacting with the σ^* MO. The π interaction leads to deshielding in all cases. However, for the π' MO in which the two p atomic orbitals have opposite phase, one nucleus is deshielded but the other is shielded. This appears to be a general phenomenon.

1. Introduction

The ^{19}F of ClF has been found to be shielded relative to F^-, whereas the F_2 is, as expected, strongly deshielded.[1] Fluoride ion should have the largest diamagnetic shift of all fluorine containing compounds because it is spherically symmetric and has completely filled s and p shells. Therefore the greater shielding found for ClF must be due to a shielding "paramagnetic" term that involves the interaction between a filled and an orthogonal virtual orbital in the presence of the magnetic field.

Cornwell presented an analysis of the chemical shift of the fluorine of ClF,[2] and determined that it arises from the interaction of the filled π' orbital that has a node between the p orbitals with the virtual σ^* orbital (Figure 1). The interaction of the lower energy π molecular orbital (MO) (in which the p orbitals have the same phase) with σ^* leads to deshielding at both F and Cl. This feature is found in many molecules including fluorine, and also ethylene, in which the interaction of the π orbital (which is the highest filled orbital) with σ^* leads to deshielding of both carbons. For the π' orbital of ClF, the two p orbitals have opposite phase. The larger coefficient is at chlorine for the π' orbital because in the π MO the larger coefficient is at the more electronegative fluorine. Thus, the chlorine interaction will dominate and lead to deshielding of the chlorine in its interaction with σ^*. Cornwell showed that the consequence of the difference in π-orbital phase at chlorine vs fluorine is that the current density at fluorine will be in the opposite sense to that for chlorine. As a result, fluorine will be shielded, as is observed experimentally.

We carried out a further examination of this system, and of some related isoelectronic molecules in which the same phenomenon should be observed, using modern computational methods. The basic analysis according to Cornwell provides a convenient framework for interpreting the important contributions to the shielding in a variety of circumstances.

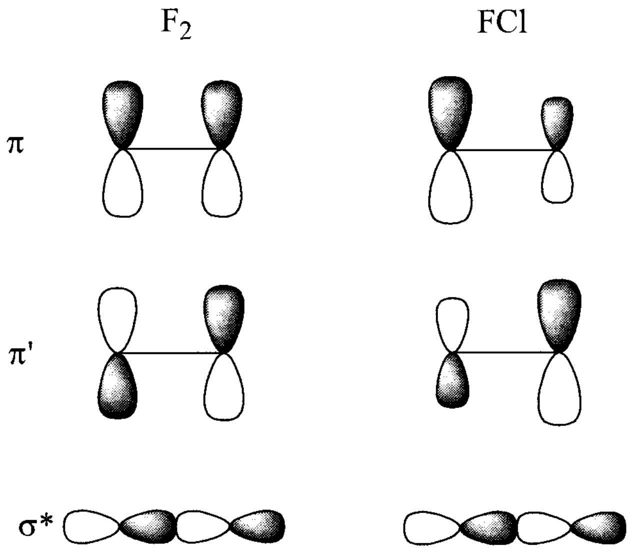

Figure 1. Schematic representation of the π, π' and σ^* MOs of F_2, FCl, and CH_3F.

2. Theory

Calculation of $j^{(1)}$. The nuclear shielding tensor for a given nucleus can be obtained by calculating the first-order magnetically induced electronic current density, $\boldsymbol{j}^{(1)}$, from which the shielding density at a point $\boldsymbol{r}$ may be obtained as[3]

$$\sigma_{\alpha\beta}{}^{N}(\boldsymbol{r}) = -(1/cB)[\boldsymbol{r}_N \times \boldsymbol{j}_\beta{}^{1}(\boldsymbol{r})/r_N{}^{3}]_\alpha \qquad (1)$$

In this expression, $\sigma_{\alpha\beta}{}^{N}$, a tensor quantity, denotes the nuclear shielding for nucleus N along the α-axis when a magnetic field is applied along the β-axis, and $\boldsymbol{r}_N$ is the position vector relative to nucleus N. The total shielding for the nucleus is then derived by integrating the shielding density over all space:

$$\sigma_{\alpha\beta}{}^{N} = \int_r \sigma_{\alpha\beta}{}^{N}(\boldsymbol{r})\, d\boldsymbol{r} \qquad (2)$$

When a closed-shell molecule is placed in a static, homogeneous magnetic field, the first-order induced electronic current

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† Yale University.
‡ Lorentzian, Inc.

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density in eq 1 can be expressed within the Hartree−Fock framework as:

$$\boldsymbol{j}^{(1)}(\boldsymbol{r}) = \underbrace{-\frac{2e}{m}\sum_{i=1}^{N}[\phi_i^{(0)*}\boldsymbol{p}\phi_i^{(1)} + \phi_i^{(1)*}\boldsymbol{p}\phi_i^{(0)}]}_{\text{paramagnetic}} \underbrace{-(e^2/mc)\sum_{i=1}^{N}\boldsymbol{A}(\boldsymbol{r})\rho_i^{(0)}(\boldsymbol{r})}_{\text{diamagnetic}} \qquad (3)$$

Here, the summation is over the N occupied MOs, $\boldsymbol{p}$ is the linear momentum operator for a single electron, $\phi_i^{(0)}$ are the ground-state MOs, $\phi_i^{(1)}$ are the first-order corrections to $\phi_i^{(0)}$, e is the electronic charge, and m is the electron mass. The vector potential[4]

$$\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B} \times [\boldsymbol{r} - \boldsymbol{r}_0]$$

describes the uniform magnetic field $\boldsymbol{B}$ with gauge origin at $\boldsymbol{r}_o$, and $\rho_i^{(0)}(\boldsymbol{r})$ are the ground state MO electron densities. In this expression, the first term is known as the paramagnetic part, and the second term, which depends only on the ground-state charge density, is known as the diamagnetic part. Note that because $\boldsymbol{j}^{(1)}$ is obtained as a sum over the N occupied MOs, it is possible to calculate the shielding contributions originating from each MO individually. In addition, one can obtain the diamagnetic and paramagnetic contributions separately.

The $\phi_i^{(1)}$ in the paramagnetic term are determined as expansions on the basis of the unperturbed virtual MOs:

$$\phi_i^{(1)} = \sum_{p}^{\text{virtuals}} c_{pi}^{(1)}\phi_p^{(0)} \qquad (4)$$

where the occupied−virtual expansion coefficients $c_{pi}^{(1)}$ are solutions to the coupled-perturbed Hartree−Fock (CPHF) equations[5] (or, if a density functional method is used, they are coupled-perturbed Kohn−Sham (CPKS) equations[6]):

$$c_{pi}^{(1)} = \frac{\sum_{j}^{\text{occ}}\sum_{q}^{\text{virt}}[(ji|pq) - (qi|pj)]c_{qj}^{(1)} - \langle\phi_p^{(0)}|\hat{H}^{(1)}|\phi_i^{(0)}\rangle}{(\epsilon_p^{(0)} - \epsilon_i^{(0)})} \qquad (5)$$

The first-order corrections, $\phi_i^{(1)}$, to the ground-state MOs arise because of the magnetic field perturbation, which in eq 5 is implicit in $\hat{H}^{(1)}$:

$$\hat{H}^{(1)} = (e/2mc)\boldsymbol{B}\cdot[(\boldsymbol{r} - \boldsymbol{r}_0) \times \boldsymbol{p}] \qquad (6a)$$

$$\hat{H}^{(1)} = (e/2mc)\boldsymbol{B}\cdot\boldsymbol{L} \qquad (6b)$$

where $\boldsymbol{L}$ is the angular momentum operator for a single electron with respect to the gauge origin, $\boldsymbol{r}_o$. The sign and magnitude of the expansion coefficients, $c_{pi}^{(1)}$, and therefore the $\phi_i^{(1)}$, are thus determined by the matrix elements

$$\langle\phi_p^{(0)}|\boldsymbol{B}\cdot\boldsymbol{L}|\phi_i^{(0)}\rangle$$

Referring again to eqs 4, 3, and then 1, one can clearly see that within the CPHF procedure, the paramagnetic contribution to the shielding is determined by the extent to which virtual MOs are mixed with occupied MOs via the magnetic field perturbation. This relationship was first derived by Ramsey,[7] and can be expressed as

$$\sigma_{zz}^{\text{para}} = -\frac{e^2\mu_0}{4\pi m_e^2}\sum_n \frac{\langle 0|\boldsymbol{L}_z|n\rangle}{E_0 - E_n}\left\langle n\left|\frac{\boldsymbol{L}_z}{\boldsymbol{r}^3}\right|0\right\rangle \qquad (7)$$

where $|0\rangle$ refers to the electronic ground state, and $|n\rangle$ denotes the electronic excited states.

The Gauge Problem. Because $\boldsymbol{j}^{(1)}$ and the $\sigma_{\alpha\beta}^N$ which are derived from it are physical observables, $\boldsymbol{j}^{(1)}$ must not depend on the choice of gauge origin (i.e., it must be gauge-invariant). Computationally, this condition is met only in the limit of a complete basis set. Because complete basis set calculations are not possible, the calculated values of $\boldsymbol{j}^{(1)}$ will always be dependent upon the gauge origin to some extent. Note, however, that even in the limit of a complete basis set, the way in which $\boldsymbol{j}^{(1)}$ is partitioned into the diamagnetic and paramagnetic terms *does* depend on the choice of $\boldsymbol{r}_o$: The gauge origin dependence in the diamagnetic part is explicit in the vector potential, whereas in the paramagnetic part it is implicit in the $\phi_i^{(1)}$.

In a conventional CPHF calculation, the single gauge origin is usually placed at the molecule's center of nuclear charge, also known as the "common origin". But unless the molecule is small and the basis set is quite large, common-origin calculations do not typically give accurate nuclear shielding results. To minimize the error associated with finite basis set calculations, computational methods have been developed which use multiple-gauge techniques. For example, the gauge-invariant atomic orbital (GIAO) method[8] assigns a gauge origin to each atomic-like basis function used in the expansion of the MOs. In the IGLO method,[9] the canonical molecular orbitals are transformed into a localized set, and an individual gauge origin is placed at the centroid of electronic charge of each orbital. However, the type of gauge transformations used in these methods make it difficult to extract a detailed analysis of the shielding from the calculations.

The individual gauges for atoms in molecules (IGAIM) method[10] is also a multiple-gauge origin method, but it places the gauge origin at each nucleus in the molecule. It is unique in that it uses a multiple set of gauge transformations to determine $\boldsymbol{j}^{(1)}$ within each atomic region accurately. However, rather than calculate the $\phi_i^{(1)}$ separately for every nucleus in the molecule, the gauge origin is placed at the common origin[11] and the $\phi_i^{(1)}$ are calculated once, as described in eqs 4−6. Then, a general expression for $\boldsymbol{j}^{(1)}$, given by Keith and Bader,[12] provides a means for shifting the gauge origin to any nucleus of interest. This type of gauge transformation additionally requires the first-order corrections to the $\phi_i^{(0)}$ because of a linear momentum perturbation.[13] After the gauge origin has been shifted to a given nucleus, $\boldsymbol{j}^{(1)}$ in this atomic region is the same as if the gauge origin had been positioned there originally. In this manner, $\boldsymbol{j}^{(1)}$ is then accurately described within each atomic region, and therefore the $\sigma_{\alpha\beta}^N$ are determined accurately for every nucleus.

Ramsey Formalism. The IGAIM method provides a natural choice of gauge. When the origin coincides with the nucleus, the diamagnetic term is dominated by core electrons, whereas the paramagnetic term is largely comprised of contributions from the valence electrons. This choice of gauge, and the resulting partitioning of diamagnetic and paramagnetic shielding, is the one best suited for discussing shielding in terms of the type of perturbation theory expressed in the Ramsey equation. When an occupied MO is identified which contributes substantial paramagnetic shielding, IGAIM facilitates the use of the Ramsey formalism to examine the nature of the virtual MOs to which it is coupled.

TABLE 1: Calculated B3LYP/6-311+G(3df,3pd) Energies and Nuclear Shielding

A. Shielding

compound	energy	atom	$\sigma_{x,y}$	σ_z	σ_{iso}	σ_{exp}
F^-	−99.891 46	F	480	480	480	
F_2	−199.586 28	F	−647	488	−269	−233
FCl	−560.031 74	F	723	492	646	637
		Cl	−1717	1152	−761	
MeF	−139.803 34	F	473	427	458	471
		C	67	180	105	
$MeNH_3^+$	−96.257 62	C	130	185	148	
		N	217	223	219	
FNH_3^+	−156.086 33	F	143	449	245	
		N	64	220	116	
HC≡CF	−176.614 91	F	343	489	392	
		C	−17	285	84	
		C(H)	114	281	170	

B. ^{19}F Relative to F^-

compound	$\delta_{x,y}$	δ_z	δ_{iso}	δ_{iso}(obs)
F_2	1127	−8	749	~720
FCl	−243	−12	−166	~−160
CH_3 F	7	53	22	~20
FNH_3^+	338	31	235	

C. ^{13}C Shifts Relative to TMS

	calculated			observed		
compound	$\delta_{x,y}$	δ_z	δ_{iso}	$\delta_{x,y}$	δ_z	δ_{iso}
MeF	116	3	78	105	15	75
$MeNH_3^+$	53	−2	35			

For clarity, we should emphasize that the diamagnetic term always leads to a positive shielding contribution, whereas the paramagnetic term can lead either to a negative shielding contribution *or* a positive shielding contribution. To avoid ambiguity in the following discussion, the sign of the paramagnetic shielding will be made clear using either a table or a bar graph.

3. Calculations

The structures of F_2, ClF, CH_3F, CH_3NH_3+, FNH_3+, and FC≡CH were calculated at the MP2/6-31G* level of theory. Calculation of the total nuclear shieldings was done using both GIAO and IGAIM. At the B3LYP/6-311+G(3df,3pd) density functional level (using Cartesian 6D and 10F basis functions), the two methods give essentially the same result. In this work, however, only the IGAIM shielding values will be described.[14] IGAIM was used to calculate the occupied MO contributions, as well as the occupied−virtual contributions to paramagnetic shielding. All calculations were done using Gaussian 95.[15]

The results of the shielding calculations are summarized in Table 1. The observed fluorine absolute shielding[16] of F_2, FCl, and CH_3F are fairly well reproduced. Correspondingly, the chemical shifts of F_2 and ClF relative to F^- are reasonably well reproduced, considering that there is some uncertainty in the shift for fluoride ion. Methyl fluoride is the only compound for which the tensor components are known, and the calculated values are in satisfactory agreement with the experiment.[18]

4. ClF and F_2

Figure 2 gives the shielding for F_2 on an MO basis in graphical form. A table of the shielding values is available as Supporting Information. The 1s orbital at fluorine (MO 1 and 2) gives the major component of the nuclear shielding. The effect of the electrons on the diamagnetic shielding goes as $1/r^3$, and therefore the 1s electrons are the most effective in shielding the nuclei. MOs 3 and 4 correspond to the 2s electrons, and they give a smaller diamagnetic contribution.

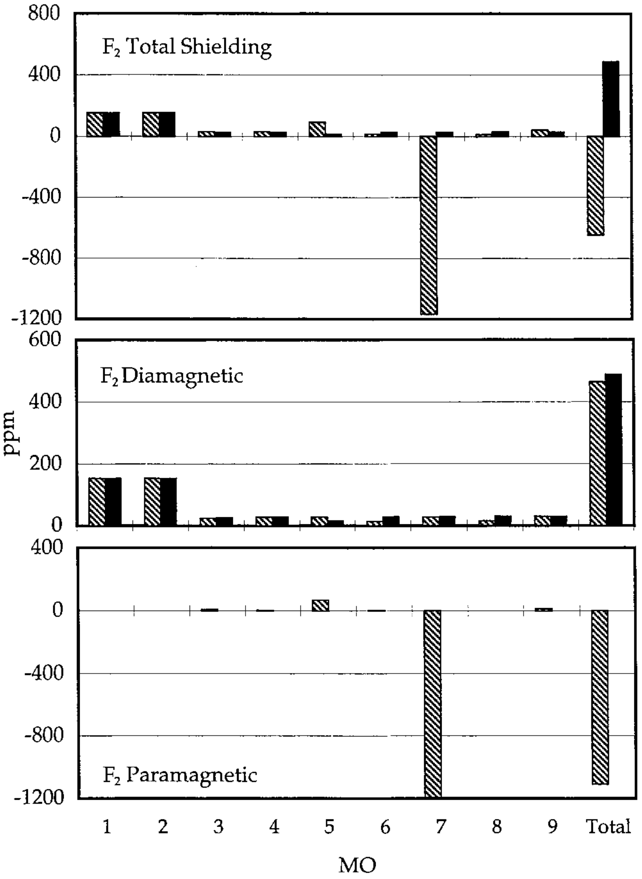

Figure 2. Shielding of F_2 on an MO-by-MO basis. The solid bars refer to the *z* (long axis) components, and the shaded bars refer to the *xx* and *yy* components.

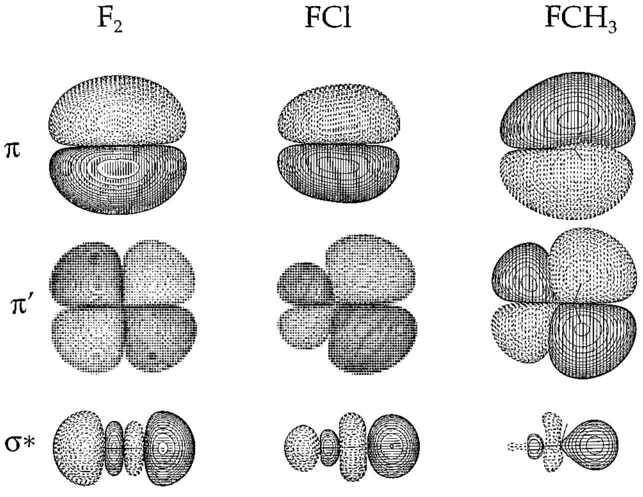

Figure 3. The π, π', and σ* MOs of F_2, FCl, and CH_3F. The contour levels are 0.01 for the π MOs and 0.05 for the σ* MO.

The deshielding is due to the interaction of the π MOs with the virtual orbitals. Here, MO 6 and 7 are the π orbitals and MO 8 and 9 are the π' orbitals (Figure 3). The interaction of the π-MO with the lowest energy unoccupied orbital (σ*) is the source of the deshielding of the fluorine nucleus, and there are no significant contributions from the other virtual orbitals. On the other hand, symmetry considerations show that for F_2 the interaction of π' with σ* can give only a small contribution to the total shielding.

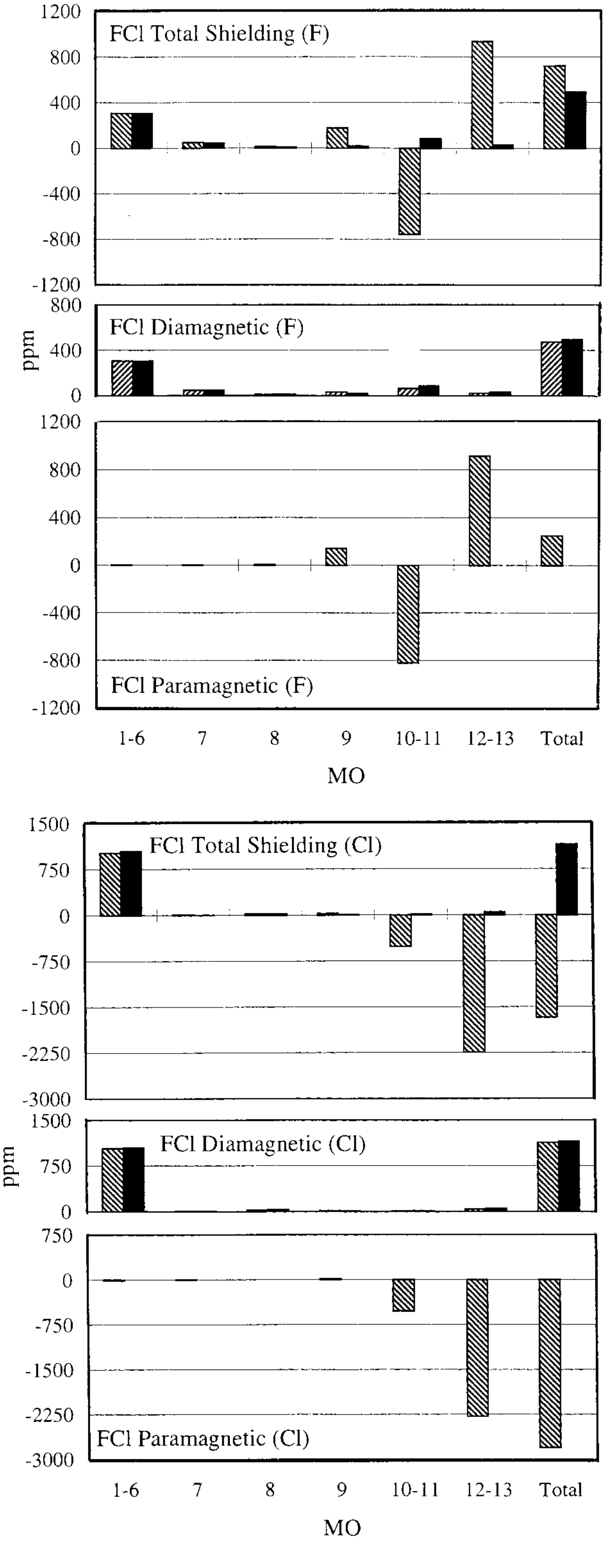

Figure 4. Shielding of FCl on an MO-by-MO basis. The solid bars refer to the *z* (long axis) components, and the shaded bars refer to the *xx* and *yy* components.

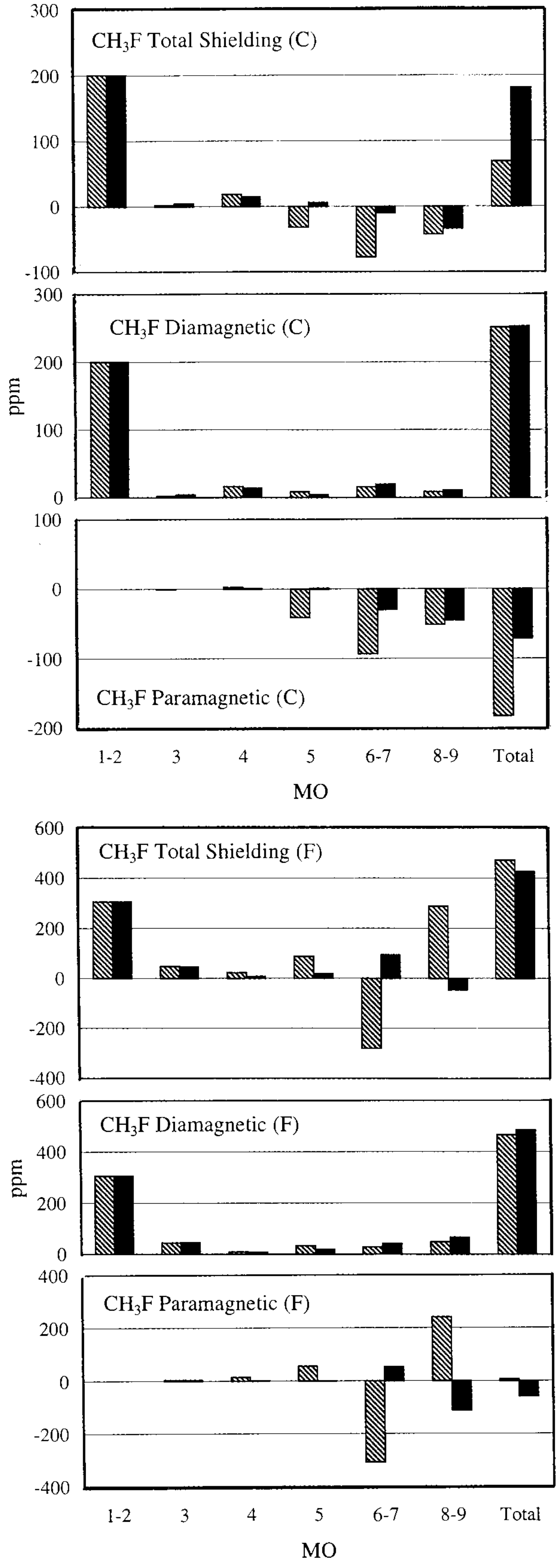

Figure 5. Shielding of CH_3F on an MO-by-MO basis.

In ClF, the interaction of the π MO with σ^* gives a large deshielding for both Cl and F (Figure 4). At the chlorine, the interaction of π' with σ^* also gives a large deshielding, but at fluorine, the interaction of π' with σ^* gives a large shielding contribution. Both arise from the paramagnetic term. This is clearly due to the difference in relative phase of the p atomic orbitals at Cl and F in the π' molecular orbital (Figure 3). With F_2, the difference in phase between the π' p-orbitals at the two fluorine atoms leads to no significant paramagnetic terms because the effect at one atom would be canceled by the other.

5. Methyl Fluoride

Methyl fluoride is isoelectronic with fluorine, and its molecular orbitals resemble those of ClF (Figure 3). The methyl

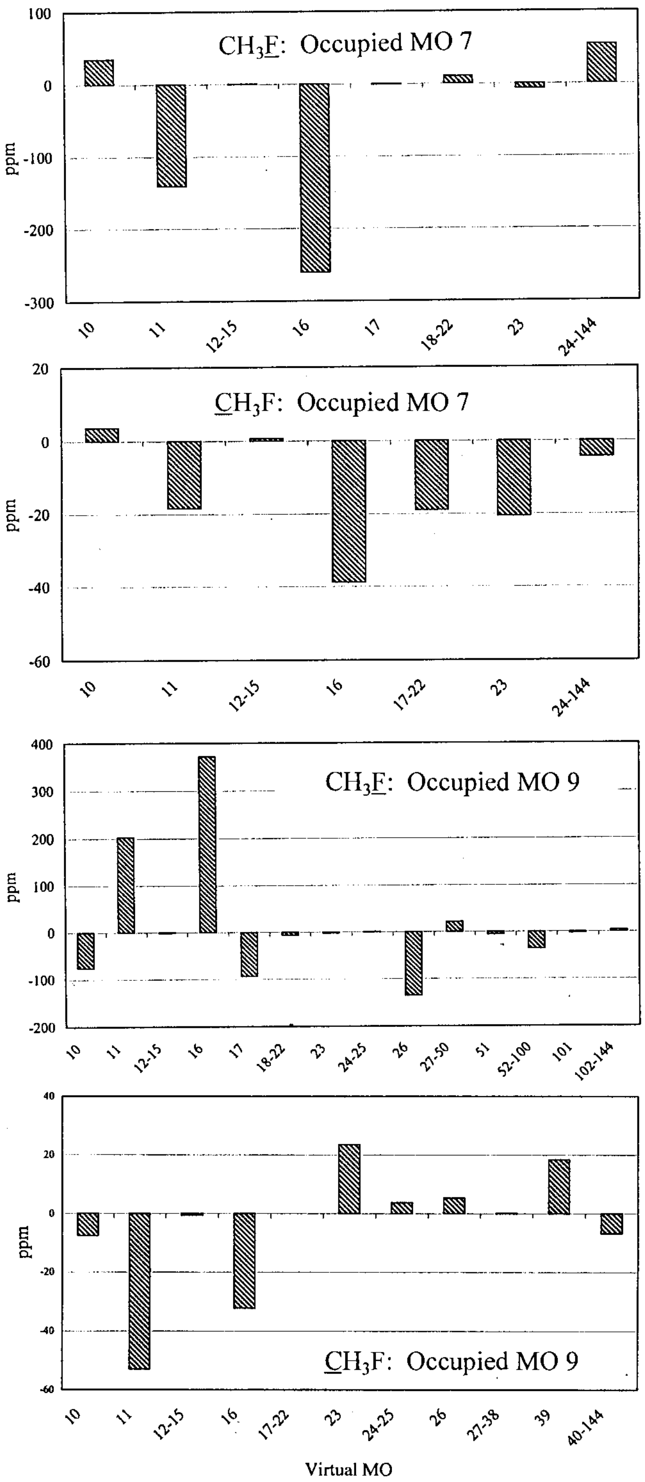

Figure 6. Principal occupied−virtual MO interactions for CH_3F.

group contributes a pair of degenerate p orbitals that combine with the p orbitals at fluorine to give the π and π' molecular orbitals. MO 11 is one of the σ^* orbitals that interacts with π and π', and MO 16, which is similar but with a larger coefficient at F, also contributes. Thus, the interactions should be quite similar for methyl fluoride and ClF. Table 1 shows that the calculated chemical shifts including their tensor components are calculated satisfactorily, and therefore it is useful to examine the shielding components on an MO basis (Figure 5).

At both carbon and fluorine, the main shielding is due to a diamagnetic term involving the 1s orbitals (MO 1 at F and MO 2 at C). These shielding terms are almost independent of the groups attached to the atom in question. The MOs formed from the 2s orbitals give a smaller diamagnetic contribution. The interaction of the π MO with σ^* again leads to deshielding at both carbon and fluorine. On the other hand, the interaction of π' with σ^* leads to deshielding at carbon and shielding at the more electronegative fluorine. Thus, the interactions in methyl fluoride parallel those in ClF. The shielding of fluorine derived

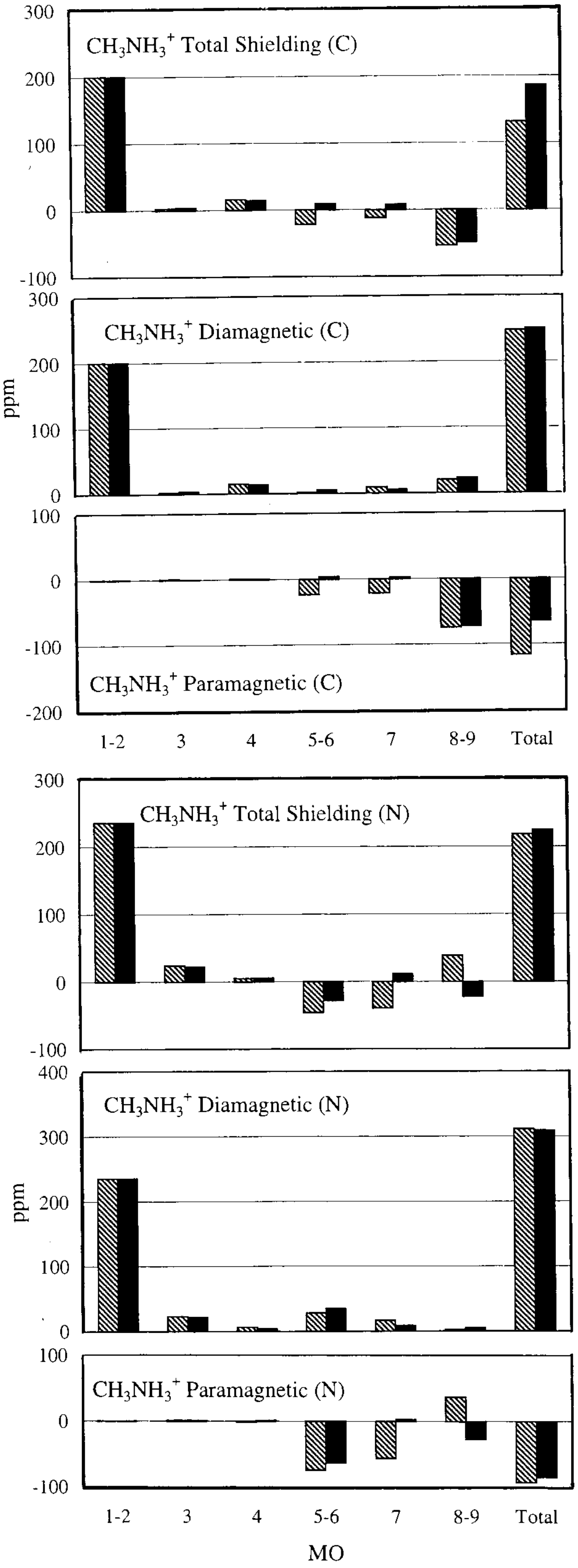

Figure 7. Shielding of methylammonium ion on an MO-by-MO basis.

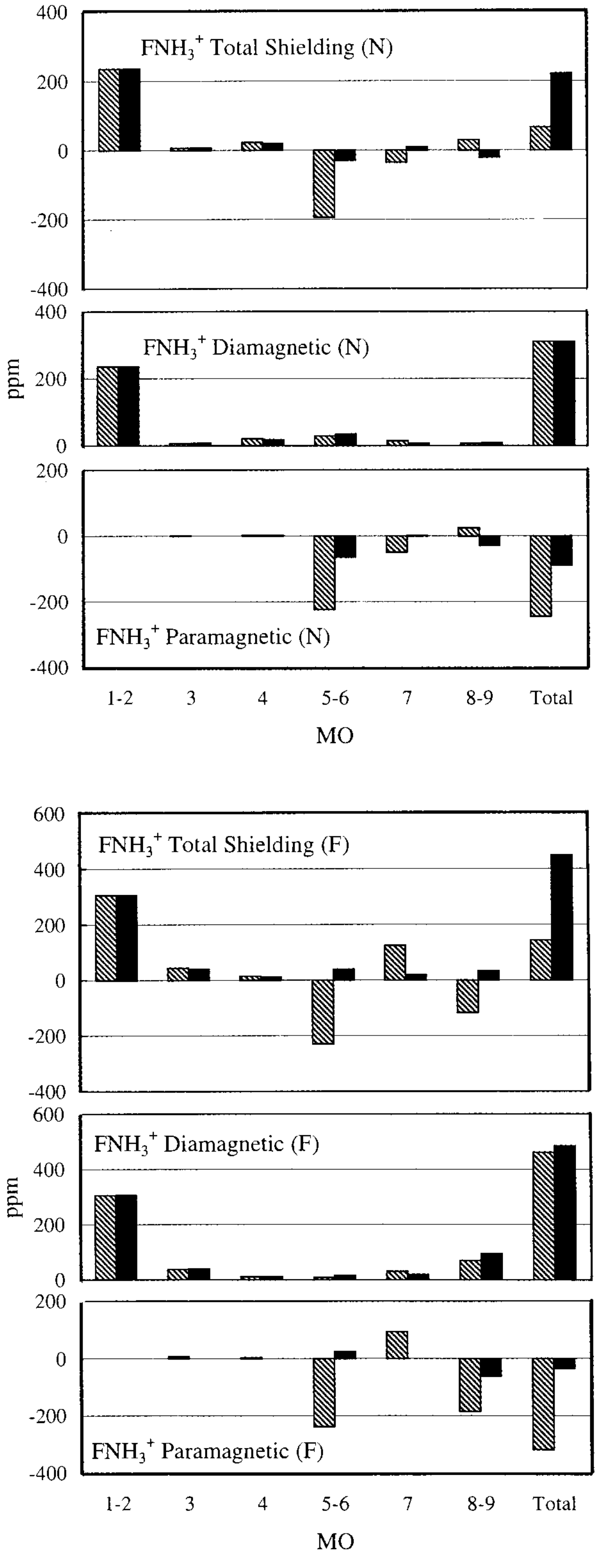

Figure 8. Shielding of fluoroammonium ion on an MO-by-MO basis.

from π' is just enough to compensate for the deshielding from π, leading to a net shielding for F close to that for F$^-$. The key occupied–virtual MO interactions and their associated contributions to paramagnetic shielding are shown graphically in Figure 6.

In addition to the interactions described above, there is also a small upfield paramagnetic term at fluorine derived from MO 5 (Figure 5). This occupied MO couples with many of the virtual orbitals, making it difficult to obtain a simple description of the interaction.

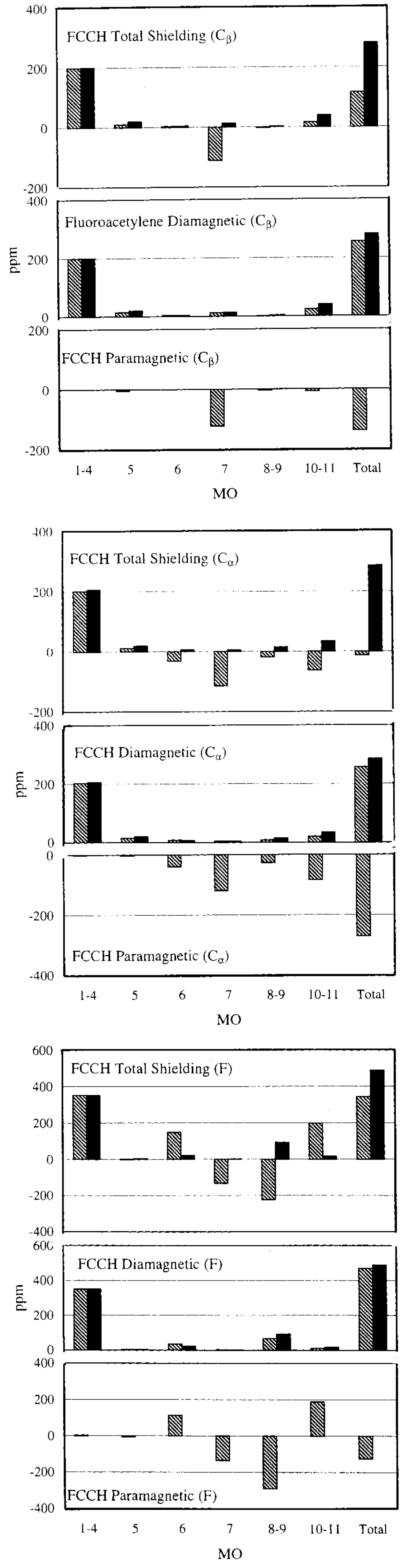

Figure 9. Shielding of fluoroacetylene on an MO-by-MO basis.

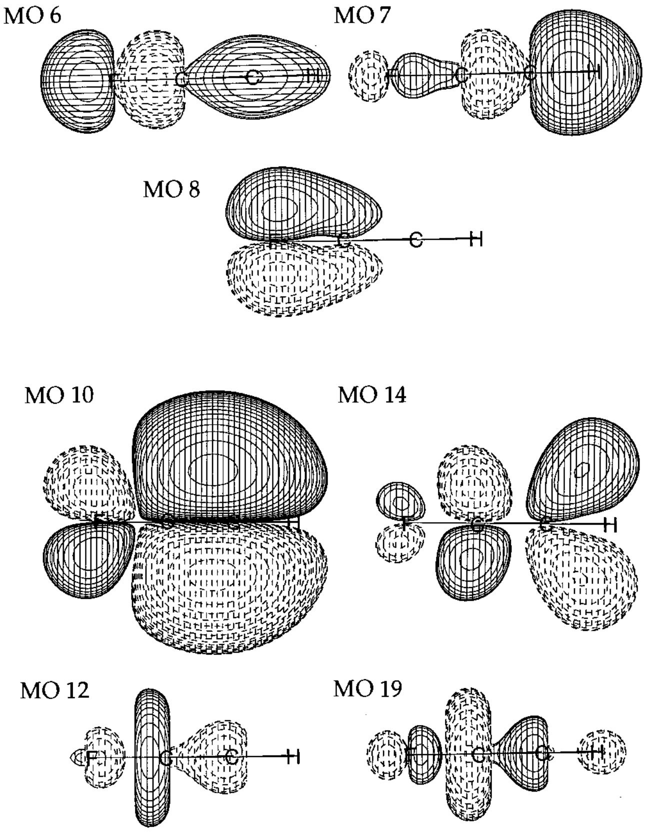

Figure 10. Some MOs of fluoroacetylene. MOs 6−10 are occupied, and MOs 12−19 are virtual MOs.

6. Methylammonium Ion and Fluoroammonium Ion

Methylammonium ion is isoelectronic with F_2 and methyl fluoride, and it was examined in the same fashion (Figure 7). MOs 5 and 6 are the degenerate pair of π MOs and MOs 8 and 9 form π'. With carbon, there are deshielding terms derived from the interaction of π and π' with σ^*. However, at nitrogen, there is a deshielding term derived from the π MO, and a shielding term derived from π'. Again, the less electronegative atom is deshielded by both the π and π' interactions, whereas the more electronegative nitrogen is deshielded by the π interaction and shielded by the π' interaction.

The fluoroammonium ion follows the same pattern (Figure 8). In this case, it appears that the ammonium group is more electronegative than fluorine. Fluorine is deshielded by the interaction of both π and π' with σ^*, whereas nitrogen is deshielded by the π interaction and shielded by the π' interaction.

7. Fluoroacetylene

The effect of relative phase is not restricted to compounds having just two non-hydrogen atoms. One example is fluoroacetylene. The shielding data on an MO basis are shown in Figure 9 and the relevant MOs are depicted in Figure 10. The distribution of paramagnetic shielding among the 11 MOs is a bit different from that in the compounds discussed so far. For example, the occupied σ' orbital (MO 7) couples strongly with the virtual π^* orbitals (MOs 14 and 15) to give large paramagnetic shifts at each of the three heavy atoms (Table 2). However, the relative phase phenomenon observed in the compounds above is also in evidence at the fluorine and the internal acetylene carbon (C_α). MOs 8 and 9 are the degenerate pair of π orbitals and MOs 10 and 11 form the π'. At both fluorine and C_α, there are deshielding terms derived from the interaction of π with the virtual σ^* (MO 12). Although the $\pi'-\sigma^*$ interaction is also deshielding at C_α, because π' has opposite phase at fluorine, a large shielding term is produced at the fluorine atom. In this case, again, the less electronegative atom is deshielded by the π' paramagnetic interaction, whereas the more electronegative fluorine is shielded by the π' interaction. The important occupied−virtual coupling contributions are given in Figure 11.

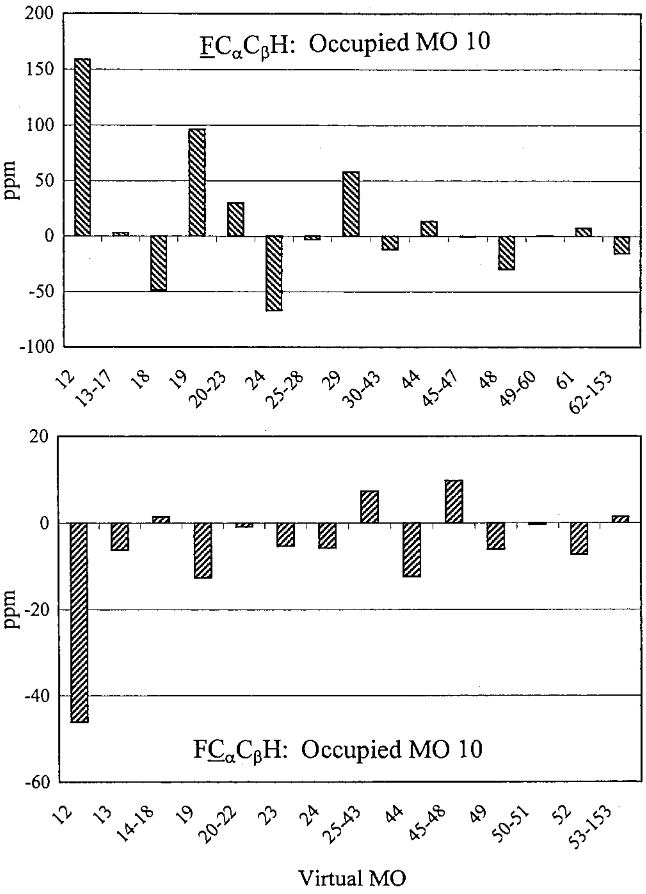

Figure 11. Principal occupied−virtual MO interactions for MO 10 in fluoroacetylene.

TABLE 2: $FC_\alpha{\equiv}C_\beta H$: Occupied−Virtual MO Paramagnetic Contributions

	Occupied	Virtual	σ_x
C_α	7	14	−117
C_β	7	14	−86
	7	20	−45
F	7	14	−170
C_α	8	30	−14
F	8	12	−88
F	8	19	−125
F	8	22	−11
F	8	23	−34

This type of analysis also enables one to examine the origin of an interesting difference in shielding between acetylene and fluoroacetylene. Relative to unsubstituted acetylene, the C_α resonance in fluoroacetylene is deshielded by 38 ppm. This seems reasonable, because the highly electronegative fluorine withdraws electron density from the directly bonded carbon and leads to deshielding. However, the resonance of C_β is *shielded* with respect to acetylene by 88 ppm. This curious substituent effect has been observed for some time in many systems, but is poorly understood.

Referring again to Figure 9, the diamagnetic contributions to shielding on an MO basis in fluoroacetylene are roughly the same for both carbons. Because no paramagnetic current is induced when a magnetic field is applied along the bonding axis of a linear molecule, the difference in the shielding between the two carbons must originate from the perpendicular components of the paramagnetic shielding. Examination of these components indicates that, although C_α derives significant paramagnetic deshielding from the occupied π and π' orbitals, these interactions are effectively "turned off" at C_β. Thus, it appears that when a fluorine atom is substituted for one of the hydrogen atoms in acetylene, the fluorine atom changes the character and the nodal distribution of the MOs such that the paramagnetic deshielding is enhanced at the directly bonded carbon, whereas at the terminal carbon it is substantially diminished.

8. Summary

The principal diamagnetic terms arise from the 1s and 2s orbitals, and they are relatively insensitive to their environment. The paramagnetic terms arise from the interaction of occupied orbitals with virtual orbitals that are rotated by 90° and may lead to either deshielding or shielding. The normal interaction leads to deshielding. However, when two p orbitals in an occupied MO have opposite phases, the dominant interaction will lead to deshielding, but the other atom will be shielded. This should be a general phenomenon, and should be found in other systems.

In this and other related studies, we found that the contributions of the individual molecular orbitals to the total shielding of a given atom are usually easily understood. It appears that NMR spectroscopy is intimately concerned with the details of the MOs that form the given molecule.

Calculations. The geometry optimizations and shielding calculations were carried out using Gaussian-95.[15]

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Supporting Information Available: Tables of calculated shielding for F_2, FCl, CH_3F, CH_3NH_3+, FNH_3+, and $HC{\equiv}CF$ (7 pp). Ordering and access information is given on any current masthead page.

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(13) These are calculated using eqs 4 and 5, replacing $\hat{H}^{(1)}$ in eq 6 with $\hat{H}^{(1)} = (e/2mc)\boldsymbol{B}\cdot\hat{p}$.

(14) The GIAO results are available in the Supporting Information.

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