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Theoretical Analysis of Dipole Moment Derivatives in Fluoromethanes. (I) Fluoroform

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The analysis of the integrated infrared intensities of a variety of hydrocarbons and fluorocarbons revealed that the effective charge of hydrogen atom (χ_H) fell within the range of value¹, $\chi_H/e = 0.088 \pm 0.015$. For example, the effective charge for the hydrogen atom in methane was observed to be² $\chi_H/e = 0.092$. However, it was found in our previous report³ that the effective hydrogen atom charge in fluoroform is $\chi_H/e = 0.049 \pm 0.006$. Although this value is somewhat close to that in most hydrocarbons, the value is, strictly speaking, outside of the range of values common to other fluorocarbons.⁴ Consequently, it should be worthwhile to perform a theoretical analysis on the dipole moment derivatives and IR intensities of fluoroform. In this work, the quantum mechanical results are analyzed for the charge-charge flux-overlap (CCFO) electronic contributions to the dipole derivatives^{5,6}.

The equilibrium structural data, and the definition of the internal and symmetry coordinates are taken from the previous report³. The normal coordinates were calculated by using the harmonic force field reported by Kirk and Wilt⁷. The transformation matrix between the internal coordinates and the Cartesian displacement coordinates was evaluated by using Wilson's method⁸. To calculate the elements of the "Atomic Polar Tensors" (APT)^{9,10}, the numerical difference approximation $\partial P/\partial \sigma \approx \Delta P/\Delta \sigma$ is employed, with $\Delta \sigma = 0.02 \text{ \AA}$. Experimental values are used both for the molecular geometry and for the force field. The C→H bond was defined as the positive Z-axis.

The absolute intensities calculated by the CNDO¹¹ and *ab initio* methods are presented in Table 1. The *ab initio* calculations were carried out with the GAUSSIAN-70 program¹² using a 6-31G basis set.

With regard to the intensities, we see that the *ab initio* results are somewhat in better agreement with the experimental values. Major discrepancy concerns the CF₂ bending modes (ν_3 and ν_6). The CNDO calculated intensity of the ν_3 band in CDF₃ is too small. In general, the agreement between prediction and experimental data is better than a factor of two. It is not possible to separate experimentally the two intense and strongly overlapping CF stretching modes ν_2 and ν_5 of CHF₃, so Table 1 lists the sum of these two intensities. The CNDO and *ab initio* calculations have resulted in the 28 and 23% contributions of the ν_2 mode, respectively, to the intensity of the overlapping $\nu_2 + \nu_5$ band. On the other hand it was found that the directions (signs) of the dipole moment derivatives with respect

to the normal coordinates of fluoroform, $\partial P/\partial Q_i$, calculated by both methods were in good agreement.

The effective charge (χ)¹³, mean dipole derivative (\bar{P})¹³, and atom anisotropy (β)¹³ of the hydrogen atom are summarized in Table 2. The *ab initio* effective charge of the hydrogen atom in fluoroform is in good agreement with the experimental value. The CNDO calculated value is about two times larger than the experimental value. On the other hand, in methane the CNDO calculated value is 20% smaller than the experimental value while the *ab initio* value is about 35% larger than the observed one.

It can be seen from Table 2 that the atom anisotropy is nearly twice larger than the effective charge in both molecules, fluoroform and methane. Nevertheless, the CNDO calculations predicted the relative value of atom anisotropy in fluoroform too small rendering the mean dipole derivative to be relatively large.

According to the "charge-charge flux-overlap" (CCFO) model^{5,6}, the atomic polar tensor of the hydrogen atom, P_{x^H} , obtained from a MO calculation may be written as a sum of three contributions

$$P_{x^H} = P_{x^H}(\text{charge}) + P_{x^H}(\text{charge flux}) + P_{x^H}(\text{overlap}) \quad (1)$$

The first two terms on the right-hand side may be associated with the classical charge-charge flux model,^{14,15} whereas the third term represents a quantum-mechanical "interference" term,⁵ which is not amenable to a classical visualization. Considering a specific APT element of the hydrogen atom we may write eq. (1) as

$$\partial P_{x^H}/\partial x_H = q_H + \sum_{\alpha} (\partial q_{\alpha}/\partial x_H) x_{\alpha} + (\partial p_{x^H}/\partial x_H) \quad (2)$$

where q_H is the equilibrium net charge on the hydrogen atom, the summation represents the intramolecular charge transfer and $(\partial p_{x^H}/\partial x_H)$ denotes the non-classical contribution.

Table 3 shows the atomic polar tensor of the hydrogen atom in fluoroform. According to the *ab initio* calculation, the charge and overlap contributions are dominant. The charge-flux contribution is about one half of the other two terms. Nevertheless, it can be seen that all three of the constituent parts of the polar tensor defined in equation (1) are significant. On the other hand, the CNDO calculations represent that the

Table 1. Comparison between the Experimental Infrared Intensities, A , of Fluoroform with Values from CNDO and *ab initio* Calculated Polar Tensors (Units are Km mol^{-1})

	Band(cm^{-1})	Expt'l ^a	CNDO	6-31G
CHF ₃	ν_1 (3077)	23.9	64.8	38.7
	ν_2 (1154.7) + ν_3 (1187.5)	626.8	423	731
	ν_3 (709.7)	12.1	28.7	29.7
	ν_4 (1397.5)	82.0	170	137
	ν_6 (518.9)	4.17	15.2	16.7
	ΣA_i	749	702	953
CDF ₃	ν_1 (2268)	29.5	71.2	56.5
	ν_2 (1123.3)	75.7	99.3	145
	ν_3 (704.4)	12.8	29.6	31.1
	ν_4 (1235.5)	577	467	676
	ν_5 (989)	47.3	1.50	26.1
	ν_6 (513.7)	4.48	14.0	16.1
ΣA_i	747	683	951	

^a Experimental values taken from Kim and King, Ref. 3.

Table 2. Effective Atomic Charges(χ), Mean Dipole Derivatives (\bar{P}), and Atom Anisotropies (β) of Hydrogen Atoms in Fluoroform and Methane^a

		χ_H/e	\bar{P}_H/e	β_H/e
Fluoroform	Expt'l ^b	0.049	-0.003	0.104
	CNDO	0.115	-0.111	0.064
	6-31G	0.046	-0.031	0.072
Methane ^c	Expt'l	0.092	-0.003	0.195
	CNDO	0.074	-0.008	0.156
	6-31G	0.124	-0.003	0.263

^a For the detailed definition of these parameters, see Ref. 13. ^b Taken from Ref. 3. ^c Calculated by using the data reported in Ref. 2.

charge flux contribution is dominant while the net charge contribution is relatively less significant. The most safest conclusion which can be drawn from the results made by both methods is that the quantum-mechanical interference term should not be neglected in the interpretation of integrated infrared intensities. Similar conclusion have been made for methane.²

The CNDO method seems, however, not to provide a reliable result, in the light of the CCFO model, for fluoroform. Particularly the CNDO results disagree with the *ab initio* results most on the signs of the three contributions of equation (1). It can be seen from Table 3 that the CNDO calculations are not very successful in describing the APT of the hydrogen atom of fluoroform.

According to the *ab initio* calculations, the net charge of the hydrogen atom in fluoroform is larger than that in methane. This may be accused to the difference in the electronegativities between the fluorine and hydrogen atoms. It is interesting to notice the large discrepancy of the charge flux contributions in both molecules. As the CH bond stretches, the dipole moment due to the electronic rearrangement increases in fluoroform while that in methane decreases. Particularly noteworthy in fluoroform is the decrease of the

Table 3. Comparison of Hydrogen Atom Polar Tensors of Fluoroform and Methane in Natural Units(e^{a,b})

		$\partial P_x / \partial X_H (= \partial P_y / \partial Y_H)^c$	$\partial P_z / \partial Z_H^c$	
Fluoroform	charge	CNDO	-0.018	-0.018
		6-31G	0.195	0.195
	charge-flux	CNDO	-0.085	-0.064
		6-31G	-0.106	0.038
	overlap	CNDO	0.012	-0.069
		6-31G	-0.096	-0.312
APT	CNDO	-0.091	-0.151	
	6-31G	-0.007	-0.079	
	Expt'l ^d	0.036	-0.067	
Methane ^e	charge	CNDO	0.013	0.013
		6-31G	0.155	0.155
	charge-flux	CNDO	-0.046	-0.093
	6-31G	-0.033	-0.185	
overlap	CNDO	0.077	-0.033	
	6-31G	-0.037	-0.148	
	APT	CNDO	0.044	-0.113
	6-31G	0.085	-0.178	
	Expt'l	0.062	-0.134	

^a For more detailed definition of APT, see Ref. 10. ^b The C→H bond was defined as the positive Z-axis. ^c P_x, P_y, P_z are the components of the total dipole moment on the space-fixed axes. X_H, Y_H, Z_H are the space-fixed Cartesian displacement coordinates of the H-atom.

^d Taken from Ref. 3. ^e Taken from Ref. 2.

electronic charge density of the hydrogen atom during the CH bond stretching. In methane the corresponding value increases.

The experimental fact that the effective hydrogen atom charge in fluoroform is about one half of that in methane can not be ascribed as due to one particular term in equation (1). All three terms seem to be correlated with one another. Nevertheless, the dominant cause may be accused to the difference in the charge flux contribution influenced by the neighbor H-F or H-H interactions.

The observations made in this work suggest that the effective charge as well as the APT elements are sensitive to the neighbor (H-F in fluoroform and H-H in methane) interactions. To establish possible correlations between intensity data and the classical parameters of chemical systematization would require more information than that provided here. It is hoped that this is borne out by calculations on other species of interest.

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Cleavage of Acid-Labile Protective Groups by Tris (*p*-bromophenyl) aminium Hexachloroantimonate

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Selective cleavage of protective groups in polyhydroxy compounds are very useful in organic synthesis, especially in the field of carbohydrate and nucleoside chemistry. Recently we reported new methods for the selective cleavage of acetals and ketals.^{1,2}

In this paper, we report the cleavage of acid-labile protective groups by a stable cation radical, namely tris (*p*-bromophenyl)aminium hexachloroantimonate,³ (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻. This cation radical has been used for the cleavage of the *p*-methoxybenzyl ether in moist acetonitrile^{4,5}. It has been suggested that *p*-methoxybenzyl ether radical is involved as an essential intermediate in that cleavage reaction. We initially hoped that (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ might selectively cleave acetals but not ketals. Since acetal has a acetal proton, a transformation shown in Scheme 1 might be possible whereas the ketal does not have a that kind of hydrogen. However, (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ in this work nonselectively cleaved not only acetals and ketals but also other acid-labile protective groups.

Table 1 shows the results of the cleavage. A benzylidene acetal **1** (0.041g, 0.20 mmol) was treated with (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ (0.092g, 0.20 mmol) in acetonitrile (10ml) at room temperature. The reaction was monitored by gas chromatography. After 30 min, the reaction was quenched by saturated aqueous sodium bicarbonate (2ml). Cyclohexanediol and benzaldehyde were produced in 95% yield. Ketals were also cleaved under the same condition as that for the acetal to give rise to ketones and diols. This result indicates that cyclic carboxonium ion as shown in Scheme 1 is not the intermediate of this cleavage reaction. In dried DME, CH₂Cl₂, or CH₃CN, the cleavage was very slow but the products were also carbonyl compounds and diols which are the usual hydrolysis products of acetals and ketals.

We, therefore, examined the possibility of the involvement of protic acid which might be produced from the radical cation. At first, we hoped to neutralize the protic acid by addition of a base such as pyridine, 2,6-lutidine, triethylamine, or solid sodium bicarbonate. However, those bases readily

destroyed the cation radical. Then, we prepared other hexachloroantimonate salts, namely benzyltriethylammonium hexachloroantimonate(PhCH₂Et₃N⁺ SbCl₆⁻) and tetraethylammonium hexachloroantimonate(Et₄N⁺ SbCl₆⁻).⁶ Neither of them could cleave acetals and ketals in acetonitrile or in methylene chloride. When two or three equivalents of water were added to the reaction mixture, acetals and ketals were hydrolyzed to give carbonyl compounds and diols in poor yields (see Table 2).

Other acid-labile protective groups such as trityl, tetrahydropyranyl, and *tert*-butyldimethylsilyl groups were also cleaved by (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ in acetonitrile at room temperature as shown in Table 1.

A few further experiments were performed in order to gain more insight into these cleavage reactions. Less than one equivalents of (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ could cleave the protective groups although a larger amount of the reagent enhanced the reaction rate. Dried solvents substantially decreased the reaction rates but in the usual distilled solvents, the reaction proceeded rapidly.

Based on these results, we could speculate that the reaction would be initiated by the cation radical but the cleavage should be the result of the hydrolysis catalyzed by the proton produced in the initial reaction. A very small amount of water contained in the solvents might be enough for this hydrolysis. Thus, as shown in Scheme 1 and Scheme 2, (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ generate the cation radical of acetal or ketal at first and then a proton is eliminated from the cation radical of the acetal or the ketal. The next step is the protonation of the acetal or the ketal by the proton eliminated in the earlier step. In the presence of water, then a usual hydrolysis occurs.

Although (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻ did not show selectivities, it efficiently and cleanly cleaved acid-labile protective groups in the organic solvents. The suggested reason for the cleavage would promote further systematic studies on this interesting hydrolysis induced by cation radical.

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