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Relative Abilities of Fluorine and Chlorine to Stabilize Carbenium Ions: Crystal Structures of Two Fluoro-Substituted Carbocations and of $As_2F_{11}^-$

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Abstract: The first crystal structures of fluoro-substituted carbocations and of the $As_2F_{11}^-$ anion are reported. The experimental geometries of the carbenium ions in $[(CH_3)_2CF]^+AsF_6^-$, $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+AsF_6^-$, and $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+As_2F_{11}^-$ and their comparison with that of the $[(o\text{-}ClC_6H_4)(C_6H_5)CCl]^+$ cation show that, in accord with previous theoretical calculations, chlorine stabilizes carbenium ions more efficiently than fluorine. The ^{13}C and ^{19}F NMR spectra of the $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+$ cation were recorded and analyzed with the help of RHF/6-31G(d,p) calculations using the GIAO method. In each of the three fluoro-substituted carbocation crystal structures studied, the carbenium centers are further stabilized by forming two fluorine bridges with the anions, resulting in distorted trigonal bipyramidal environments around the carbenium centers. The $[F_5As{-}F{-}AsF_5]^-$ anion in $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+As_2F_{11}^-$ possesses a symmetric fluorine bridge with an As−F−As angle of 156.5(13)° and staggered AsF_4 groups.

Introduction

Although the nature and structures of carbocations have been studied extensively by electronic structure calculations and spectroscopic techniques,[1] such as NMR or matrix isolation, the number of known crystal structures is quite small.[1,2] Of particular interest in carbocation chemistry is the mechanism and extent to which the highly electron-deficient carbenium center can be stabilized by electron back-donation from its ligands and by bridging to its neighbors.[2] Depending on the nature of the ligand, this stabilization can invoke either p(π) back-donation, if the ligand has a free valence electron pair or involves an aromatic carbon atom, or C−H/C−C hyperconjugation, if the ligand is an alkyl group.[1] If a ligand is highly electronegative, such as fluorine, the inductive electron withdrawing σ-effect is very strong and counteracts the p(π) back-donation, as was demonstrated by natural bond orbital (NBO) analyses for CF_3^+ [3,4] and FCO^+.[4] Unfortunately, the theoretically well-characterized CF_3^+ and FCO^+ cations cannot be stabilized as salts with anions derived from presently known Lewis acids,[4] and only one crystal structure was known for a fluoro-substituted carbocation, that of $[F_2\overline{C{-}S{-}CF{-}S}]^+$,[5] which is stabilized by two sulfur heteroatoms. However, no structure was known for a fluorocarbenium ion without heteroatom stabilization.

The second topic of this study is the $As_2F_{11}^-$ anion. Its existence was first suggested in 1969 on the basis of low-temperature IR[6] and NMR[7] observations. Subsequently, it was positively identified by low-temperature ^{19}F NMR spectroscopy,[8−11] specific conductivity,[9−12] Raman,[12,13] and X-ray powder diffraction data.[14] However, no exact structural data were available for this interesting anion.

Experimental Section

Materials and Apparatus. α,α,α-Trifluorotoluene (Aldrich, Milwaukee, WI), 2,2-difluoropropane (PCR), SO_2 (Matheson), and AsF_5 and SO_2ClF (Ozark Mahoning, Tulsa, OK) were used as received. The HF (Matheson) was dried by storage over BiF_5.[15] Volatile compounds were handled either on a Pyrex glass vacuum line equipped with grease-free Kontes glass−Teflon valves or on a previously described[16] stainless steel−Teflon FEP vacuum line. The NMR spectra were recorded in SO_2 solution at −20 °C on a Bruker AM-360 spectrometer using 5

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mm Teflon tubes (Wilmad Glass Co., Buena, NJ) as sample containers. Single crystals were grown at low temperature by slow cooling of saturated HF solutions, and suitable crystals were selected and mounted with perfluoroether oil in a cold, dry nitrogen flow. The diffraction data were collected at −100 °C, using a Siemens/Nicolet/Syntex $P2_1$ diffractometer with Mo Kα radiation up to a 2θ limit of 55° and the computing packages SHELX-86[17] and SHELX-93[18] for refining the data.

Preparation of $[(CH_3)_2CF]^+AsF_6^-$ (I). In a 0.5 in. o.d. Teflon FEP ampule, which was closed by a steel valve, equimolar amounts of $(CH_3)_2CF_2$ and AsF_5 and a large excess of anhydrous HF (3 mL) were combined at −196 °C. The mixture was warmed to −78 °C, followed by HF removal at −50 °C in a dynamic vacuum, resulting in a white solid that was stable at −50 °C and started to decompose at about −20 °C. It was identified by its crystal structure as $[(CH_3)_2CF]^+AsF_6^-$.

Preparation of $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+AsF_6^-$ (II) and $As_2F_{11}^-$ (III). α,α,α-Trifluorotoluene, when combined as described above for (**I**) with either equimolar amounts or an excess of AsF_5 in HF, SO_2ClF, or SO_2 solution, gave exclusively $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+As_2F_{11}^-$ (vide infra). With a 1-fold or larger excess of α,α,α-trifluorotoluene, the corresponding AsF_6^- salt was obtained. The salts are white solids that are marginally stable at room temperature. (**II**) and (**III**) were characterized by their crystal structures and ^{13}C, ^{19}F, and ^{1}H NMR spectra.

Theoretical Calculations

Various ab initio calculations were carried out on the free $[(CH_3)_2CF]^+$, $[m\text{-}(CF_3C_6H_4)(C_6H_5)CF]^+$, and $[As_2F_{11}]^-$ ions using the Gaussian 98[19] and ACES II[20] program systems on IBM RS/6000 work stations. The highest level of theory employed for each system was the restricted Hartree−Fock (RHF) method[21] for $[m\text{-}(CF_3C_6H_4)(C_6H_5)CF]^+$, the B3LYP[22] density functional approach for $[As_2F_{11}]^-$, and the single- and double-excitation coupled-cluster method[23] with a noniterative treatment of connected triple excitations,[24] denoted CCSD(T), for $[(CH_3)_2CF]^+$. Several atomic basis sets were employed, including the 6-31G(d,p)[25] set for $[m\text{-}(CF_3C_6H_4)(C_6H_5)CF]^+$, the 6-311+G(d)[26,27] set for $[As_2F_{11}]^-$, and the 6-311++G(2d,2p)[28] and TZ2P[29] (triple-ζ, double-polarization) sets for $[(CH_3)_2CF]^+$. Optimized geometries and vibrational spectra were obtained in every case, and for $[(CH_3)_2CF]^+$, a study was made of the effects of rotating the methyl groups with respect to each other. Additionally, isotropic NMR shieldings for $[m\text{-}(CF_3C_6H_4)(C_6H_5)CF]^+$ were calculated at the RHF/6-31G(d,p) level using the gauge-including atomic orbital (GIAO) solution to the gauge-invariance problem.[30] Chemical shifts were obtained by referring these shieldings to those of the standard reference compounds tetramethylsilane and fluorotrichloromethane, which were computed at the same level of theory.

Results and Discussion

Reliable bond length determinations are uniquely suited for evaluating the relative stabilization of carbenium ions by different ligands. The highly electron-deficient carbenium centers formally possess only six valence electrons and must be stabilized by the formation of partial multiple bonds. Therefore, the observed bond shortenings in carbenium ions, compared to normal single bonds, reveal the relative contributions from different ligands to the stabilization of a carbenium ion. Whereas methods, such as ^{13}C NMR shielding measurements, permit evaluation of only the total contribution from all ligands, structure determinations by single-crystal X-ray diffraction give the individual contributions from each ligand.

$[(CH_3)_2CF]^+AsF_6^-$(I). The dimethylfluorocarbenium cation was first observed in 1967 by Olah, Chambers, and Comisarow by low-temperature ^1H and ^{19}F NMR spectroscopy of solutions of either 2,2-difluoropropane in SbF_5/SO_2 or 2-fluoropropene in FSO_3H/SbF_5.[31,32] Its ^{13}C NMR spectrum was reported in 1972.[33] On the basis of the observed ^{13}C shift differences between the cations, $(CH_3)_2CX^+$ and CX_3^+, and the related halocarbons, CH_3CHXCH_3 and $CH_3CX{=}CH_2$, and a fortuitous correlation of ^{13}C NMR shifts with Pauling's electonegativities, it was concluded[33,34] that fluorine is a better back-donor than chlorine. This view was recently challenged, however, in two theoretical studies, one by Frenking and co-workers[3] and another by some of us.[4]

Single crystals of (**I**) were obtained by slowly cooling equimolar amounts of $(CH_3)_2CF_2$ and AsF_5 in anhydrous HF solution (1).

$$(CH_3)_2CF_2 + AsF_5 \xrightarrow{HF} [(CH_3)_2CF]^+AsF_6^- \qquad (1)$$

The crystal and structure refinement data and selected bond lengths and angles of (**I**) are given in Tables 1 and 2. Full details of the structural results are available as Supporting Information. The structure of an individual $[(CH_3)_2CF]^+$ cation, connected by two fluorine bridges to neighboring AsF_6^- anions, is shown in Figure 1.

The structure of (**I**) is ionic, containing discrete $[(CH_3)_2CF]^+$ cations and AsF_6^- anions. The C_2CF skeleton of the cation is

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Table 1. Crystal Data and Structure Refinement for $[(CH_3)_2CF]^+[AsF_6]^-$(**I**), $[m\text{-}(CF_3C_6H_4)(C_6H_5)CF]^+ [AsF_6]^-$ (**II**) and $[m\text{-}(CF_3C_6H_4)(C_6H_5)CF]^+ [As_2F_{11}]^-$ (**III**)

	I	II	III
empirical formula	$C_3H_6AsF_7$	$C_{14}H_9AsF_{10}$	$C_{14}H_9As_2F_{15}$
formula weight	250.00	442.13	612.05
temperature	173(2) K	193(2) K	193(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
crystal System	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell dimensions			
a, Å	8.854(3)	7.8612(14)	15.101(5)
b, Å	9.544(3)	8.2778(15)	8.649(2)
c, Å	8.856(3)	13.1942(20)	15.190(7)
α, deg	90	83.157(9)	90
β, deg	108.77(2)	85.342(10)	99.09(4)
γ,deg	90	62.915(10)	90
volume, Å^3	708.6(4)	758.6(2)	1959.0(12)
Z	4	2	4
density (calcd)	2.344 g/cm^3	1.936 g/cm^3	2.075 g/cm^3
absorption coefficient	4.866 mm^{-1}	2.347 mm^{-1}	3.549 mm^{-1}
F(000)	480	432	1176
goodness-of-fit on F^2	1.178	1.036	1.019
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0713$ $wR_2 = 0.1744$	$R_1 = 0.0635$ $wR_2 = 0.1502$	$R_1 = 0.1076$ $wR_2 = 0.2777$
R indices (all data)	$R_1 = 0.0800$ $wR_2 = 0.1959$	$R_1 = 0.0831$ $wR_2 = 0.1650$	$R_1 = 0.1617$ $wR_2 = 0.3431$

Table 2. Bond Lengths [Å] and Angles [deg] for $[(CH_3)_2CF]^+[AsF_6]^-$

Bond Distances	
As(1)−F(6)	1.710(5)
As(1)−F(5)	1.712(5)
As(1)−F(1)	1.713(6)
As(1)−F(4)	1.718(5)
As(1)−F(3)	1.718(5)
As(1)−F(2)	1.728(5)
F−C(1)	1.285(11)
C(1)−C(3)	1.413(13)
C(1)−C(2)	1.450(13)
Bond Angles	
F(1)−As(1)−F(4)	179.0(3)
F(6)−As(1)−F(3)	179.2(3)
F(1)−As(1)−F(3)	89.0(3)
F(4)−As(1)−F(3)	90.0(3)
F(6)−As(1)−F(2)	90.0(3)
F(5)−As(1)−F(2)	179.3(3)
F(1)−As(1)−F(2)	90.1(3)
F(4)−As(1)−F(2)	89.6(3)
F(3)−As(1)−F(2)	89.3(3)
F−C(1)−C(3)	117.3(8)
F−C(1)−C(2)	116.5(8)
C(3)−C(1)−C(2)	126.1(8)
Bridge Bonds	
C(1)−F(2′)	2.66(1)
C(1)−F(6)	2.78(1)
F(2′)···C(1)−F	78.9(8)
F(6)···C(1)−F	76.3(8)
F(2′)···C(1)−C(2)	89.5(8)
F(2′)···C(1)−C(3)	100.8(8)
F(6)···C(1)−C(2)	85.5(8)
F(6)···C(1)−C(3)	106.8(8)

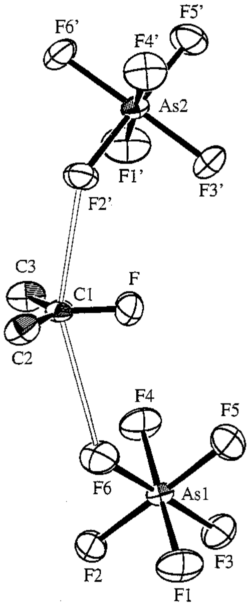

Figure 1. Structure, numbering scheme, and fluorine bridging of the $[(CH_3)_2CF]^+$ cation in (**I**). The displacement ellipsoids are drawn at the 50% probability level.

planar, and its central C(1) atom completes its coordination with two longer, approximately perpendicular fluorine contacts of 2.66 and 2.78 Å, which are significantly shorter than the sum of the C−F van der Waals radii (3.17 Å)[2,35] and involve the F(6) and (F2′) atoms of two different AsF_6^- anions (see Figure 1). These fluorine bridges help to populate the empty p_z orbital of the carbenium center, thereby enhancing its stabilization. They also cause a slight distortion of the AsF_6^- anions from octahedral symmetry. The C−F bond length in $[(CH_3)_2CF]^+$ is 1.285(11) Å and is significantly shorter than the average length of 1.333 ± 0.005 Å found for olefinic C−F bonds,[36] indicating substantial electron back-donation from fluorine to the carbenium center. The C(1)−C(2) and C(1)−C(3) bonds of $[(CH_3)_2CF]^+$ were found to be 1.450(13) and 1.413(13) Å, respectively; the apparent difference in their lengths is less than 3σ and is believed to be insignificant. This conclusion is supported by an ab initio calculation in which we froze the positions of the two methyl groups such that one C−H bond of one CH_3 group was coplanar with the unoccupied p_z orbital on the carbenium carbon and the other CH_3 group was rotated by 90°. Even at the highly correlated CCSD(T)/TZ2P level, the maximum differences in the calculated C−C bond lengths were only about 0.001 Å, suggesting that one-sided methyl hyperconjugation,[37] which is strongly angle-dependent,[1,38] is very unlikely to cause a difference as large as 0.037 Å in the C−C bond lengths. A similar theoretical analysis was carried out by Schleyer and co-workers for the 2-propyl cation, $[(CH_3)_2CH]^+$, which showed that at the MP2/6-31G* level the C−C bond lengths change only by about 0.01 Å for its different rotational isomers.[38] It should be noted that the observed average C−C bond length in $[(CH_3)_2CF]^+$ of 1.432 Å is significantly shorter than the average length of 1.510(5) Å found for the C−C bond in C−C═C type molecules,[36] indicating significant C−C bond-shortening due to methyl hyperconjugation.[37]

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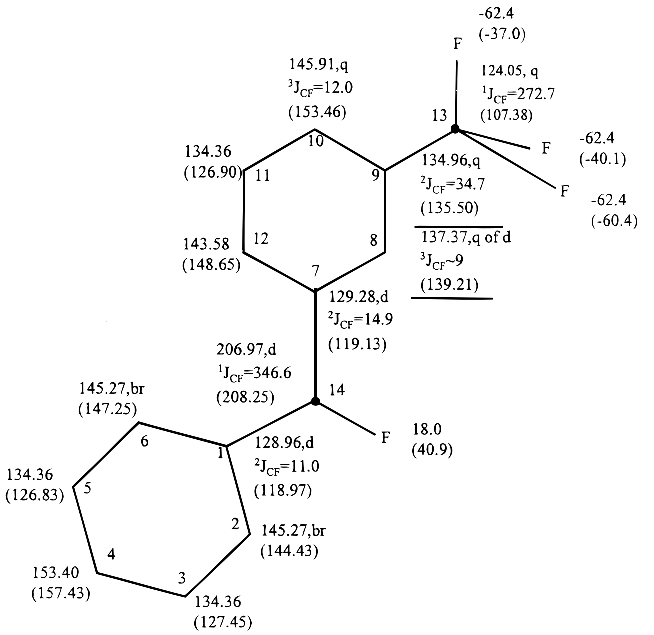
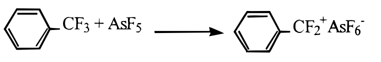
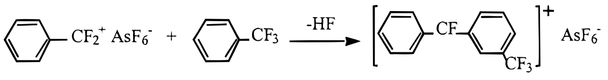


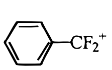
Figure 2. Observed (calculated) ^{13}C and ^{19}F chemical shifts (ppm), multiplicity, and coupling constants (Hz) of the [(*m*-$CF_3C_6H_4$)(C_6H_5)-$CF]^+$ cation.

[(*m*-$CF_3C_6H_4$)(C_6H_5)CF]$^+$$AsF_6^-$(II) and [(*m*-$CF_3C_6H_4$)-($C_6H_5$)CF]$^+$$As_2F_{11}^-$(III). Our original intent was to prepare $C_6H_5CF_2^+AsF_6^-$ from $C_6H_5CF_3$ by fluoride abstraction with AsF_5 in HF solution, because the formation of the $C_6H_5CF_2^+$ cation from $C_6H_5CF_2Cl$ in SO_2/SbF_5 solutions at −75 °C had previously been established by ^{1}H and ^{19}F NMR spectroscopy.[39] Surprisingly, it was found that under our conditions, that is, $C_6H_5CF_3$ and AsF_5 in HF, SO_2, or SO_2ClF solutions at −20 °C, the only observed products were either (**II**) or (**III**), obtained when using an excess of trifluorotoluene or AsF_5, respectively. The formation of dimeric cations in (**II**) and (**III**) can be explained by a coupling reaction of an intermediate $C_6H_5CF_2^+$ cation (2) with a second $C_6H_5CF_3$ molecule (3), a typical Friedel−Crafts benzylation.

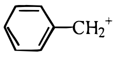
 (2)

 (3)

This pronounced tendency of

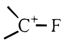


to dimerize resembles that of



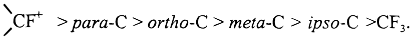
to polymerize.[39] Compounds (**II**) and (**III**) are white solids that are marginally stable at room temperature.

The structure of the cation in (**II**) and (**III**) was established by ^{13}C and ^{19}F NMR spectroscopy, single-crystal X-ray diffraction, and electronic structure calculations. The ^{13}C NMR assignments, summarized in Figure 2, are based on the observed ^{13}C−^{19}F coupling constants and the chemical shifts from an RHF/6-31G(d,p) calculation[21] at the optimized geometry, which closely resembled the observed one. The calculated ^{19}F shifts appear to be uniformly about 20 ppm more positive than the observed ones at this level of calculation. The observed shift



of 18.0 ppm for (**II**) is in good agreement with that of 11.5 ppm, previously reported for $[(C_6H_5)_2CF]^+$.[39] The observed chemical shifts for the three fluorines of the CF_3 group are, as expected, rotationally averaged.

The agreement between the calculated and observed ^{13}C shifts (Figure 2) is generally quite good, and in the cases of somewhat larger deviations, even the overall shift sequences are retained, that is, the ^{13}C shifts decrease in the expected[41] order (shown below). The line width of the C2/C6 resonance was found to



be larger than the others and to be strongly temperature dependent, possibly due to incipient rotational averaging of C2 and C6 in the given temperature range. The chemical shift of 207 ppm for the carbenium center in (**II**) agrees well with those of 209 and 212 ppm found for $[(C_6H_5)_2C(OH)]^+$ and $[(C_6H_5)_3C]^+$, respectively,[41] indicating comparable shielding and stabilization by the aryl groups through *ortho*- and *para*-quinoidal resonance structures.

Crystal and refinement data of compounds (**II**) and (**III**) are given in Table 1, and their bond lengths and angles are given in Tables 3 and 4, respectively. Full details of the structural results are available as Supporting Information. The structures of the individual [(*m*-$CF_3C_6H_4$)(C_6H_5)CF]$^+$ cations, including their bridging to two neighboring AsF_6^- or $As_2F_{11}^-$ anions, are shown in Figures 3−5.

The structures of (**II**) and (**III**) are ionic, containing discrete [(*m*-$CF_3C_6H_4$)(C_6H_5)CF]$^+$ cations and AsF_6^- and $As_2F_{11}^-$ anions, respectively. Although the R factor of (**III**) is considerably higher than that of (**II**), the identity of the cations in (**II**) and (**III**) and the presence and structure of the $As_2F_{11}^-$ anion are well established. In the cations, the C_2CF^+ skeleton is again perfectly planar. The CF_3-substituted and the unsubstituted phenyl groups in (**II**) and (**III**) are twisted by 39.3° and 47.5°, respectively, with respect to each other. This twisting is not caused by crystal packing effects, as the minimum energy structure calculated for the free gaseous cation exhibits a comparable twist angle. The plane of the C_2CF^+ skeleton approximately halves the dihedral angle formed by the two phenyl groups. As in compound (**I**), the carbenium centers in (**II**) and (**III**) form along their p_z axes two close fluorine bridges of about 2.78 and 3.04 Å, respectively, with fluorine atoms from two different anions. Whereas the two bridging fluorine atoms of AsF_6^- in (**II**) are cis to each other, those of $As_2F_{11}^-$ in (**III**) are trans to each other. The C−F bond lengths in (**II**) and (**III**) are about 1.31 Å and are only slightly shorter than the average C−F bond lengths of 1.333 ± 0.005 and 1.33 Å found for olefinic C−F bonds[35] and the CF_3 group of this cation, respectively, indicating only weak back-donation from fluorine

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[39] Olah, G. A.; Cupas, C. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1966**, *88*, 362.

[40] (a) Gomes de Mesquita, A. H.; MacGillavry, C. H.; Ericks, K. *Acta Crystallogr.* **1965**, *18*, 437. (b) Krebs, B.; Paulat, V. *Z. Naturforsch.* **1979**, *34B*, 900. (c) Calderazzo, F.; Pallavicini, P.; Pampaloni, G.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1990**, 2743. (d) Krausse, J.; Heublein, G.; Rudakoff, G.; Leibnitz, P.; Reck, G. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 45.

[41] *Carbon-13 NMR Spectroscopy*; Kalinowski, H. O.; Berger, S.; Braun, S.; John Wiley & Sons: Chichester, 1986.

Table 3. Bond Lengths [Å] and Angles [deg] for $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+[AsF_6]^-$

Bond Distances			
As(1)−F(4)	1.789(3)	C(11)−C(16)	1.406(7)
As(1)−F(3)	1.710(3)	C(11)−C(12)	1.410(7)
As(1)−F(5)	1.717(3)	C(12)−C(13)	1.366(7)
As(1)−F(2)	1.720(3)	C(13)−C(14)	1.393(8)
As(1)−F(6)	1.725(3)	C(14)−C(15)	1.399(8)
As(1)−F(1)	1.734(3)	C(15)−C(16)	1.369(8)
F(11)−C(1)	1.316(5)	C(21)−C(22)	1.402(7)
F(12)−C(2)	1.331(7)	C(21)−C(26)	1.408(7)
F(13)−C(2)	1.326(6)	C(22)−C(23)	1.376(7)
F(14)−C(2)	1.349(6)	C(23)−C(24)	1.398(7)
C(1)−C(11)	1.420(7)	C(24)−C(25)	1.390(7)
C(1)−C(21)	1.431(7)	C(25)−C(26)	1.379(7)
C(2)−C(23)	1.502(7)		

Bond Angles			
F(4)−As(1)−F(3)	89.8(2)	F(12)−C(2)−C(23)	113.0(5)
F(4)−As(1)−F(5)	90.4(2)	F(14)−C(2)−C(23)	110.9(5)
F(3)−As(1)−F(5)	179.7(2)	C(16)−C(11)−C(12)	120.0(5)
F(4)−As(1−F(2)	90.4(2)	C(16)−C(11)−C(1)	118.9(5)
F(3)−As(1)−F(2)	91.0(2)	C(12)−C(11)−C(1)	121.1(5)
F(5)−As(1)−F(2)	89.3(2)	C(13)−C(12)−C(11)	119.9(5)
F(4)−As(1)−F(6)	179.5(2)	C(12)−C(13)−C(14)	119.9(5)
F(3)−As(1)−F(6)	90.0(2)	C(13)−C(14)−C(15)	120.6(5)
F(5)−As(1)−F(6)	89.8(2)	C(16)−C(15)−C(14)	120.0(5)
F(2)−As(1)−F(6)	90.0(2)	C(15)−C(16)−C(11)	119.6(5)
F(4)−As(1)−F(1)	89.7(2)	C(22)−C(21)−C(26)	119.6(5)
F(5)−As(1)−F(1)	90.0(2)	C(22)−C(21)−C(1)	119.4(5)
F(2)−As(1)−F(1)	178.8(2)	C(26)−C(21)−C(1)	120.9(5)
F(6)−As(1)−F(1)	88.9(2)	C(23)−C(22)−C(21)	119.7(4)
F(11)−C(1)−C(11)	115.4(4)	C(22)−C(23)−C(24)	120.4(5)
F(11)−C(1)−C(21)	114.1(4)	C(22)−C(23)−C(2)	120.8(5)
C(11)−C(1)−C(21)	130.5(4)	C(24)−C(23)−C(2)	118.8(5)
F(13)−C(2)−F(12)	108.2(5)	C(25)−C(24)−C(23)	120.2(5)
F(13)−C(2)−F(14)	105.9(5)	C(26)−C(25)−C(24)	119.9(5)
F(12)−C(2)−F(14)	105.6(4)	C(25)−C(26)−C(21)	120.1(5)
F(13)−C(2)−C(23)	112.8(4)		

Bridge Bonds			
C(1)···F(6)	2.79(1)	F(1)···C(1)···C(11)	97.1(4)
C(1)···F(1)	2.78(1)	F(1)···C(1)···C(21)	91.1(4)
F(1)···C(1)···F(6)	164.8(4)	F(6)···C(1)···C(11)	93.1(4)
F(1)···C(1)···F(11)	81.1(4)	F(6)···C(1)···C(21)	90.8(4)
F(6)···C(1)···F(11)	84.4(4)	Dihedral angle between phenyl groups 39.3	

to the carbenium center. By contrast, the average $C^+{-}C_{ipso}$ bond length of 1.43 Å between the carbenium center and the carbon atoms of the phenyl groups is significantly shorter than that of 1.502(7) Å found for the $C_6H_4{-}CF_3$ bond in (**II**) and the average of 1.47 ± 0.02 Å found for $C_6H_5{-}CO_2H$ and salicylic acid,[36] but is similar to those of 1.449(2) and 1.425(10) Å, found for the trityl[40] and $(o\text{-}ClC_6H_4)(C_6H_5)CCl^+$ [42] cations, respectively. This $C^+{-}C_{ipso}$ bond shortening demonstrates that the aromatic substituents play the dominant role in stabilizing the carbenium center in (**II**) and (**III**). The average C−C bond distances ($C_{ipso}{-}C_{ortho}$ = 1.407(7), $C_{ortho}{-}C_{meta}$ = 1.373(7), $C_{meta}{-}C_{para}$ = 1.395(7) Å) in the two phenyl rings are also similar to those found for the trityl[40] and $(o\text{-}ClC_6H_4)(C_6H_5)CCl^+$ [42] cations.

Table 4. Bond Lengths [Å] and Angles [deg] for $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+[As_2F_{11}]^-$

Bond Distances			
As(1)−F(2)	1.623(13)	C(1)−C(21)	1.42(2)
As(1)−F(5)	1.636(13)	C(1)−C(11)	1.44(2)
As(1)−F(7)	1.655(14)	C(2)−C(23)	1.46(3)
As(1)−F(6)	1.663(11)	C(11)−C(12)	1.35(2)
As(1)−F(4)	1.673(14)	C(11)−C(16)	1.43(2)
As(1)−F(1)	1.881(13)	C(12)−C(13)	1.37(2)
As(2)−F(10)	1.612(13)	C(13)−C(14)	1.34(3)
As(2)−F(3)	1.652(10)	C(14)−C(15)	1.42(3)
As(2)−F(11)	1.663(11)	C(15)−C(16)	1.43(2)
As(2)−F(8)	1.687(12)	C(21)−C(26)	1.36(2)
As(2)−F(9)	1.695(13)	C(21)−C(22)	1.40(2)
As(2)−F(1)	1.874(14)	C(22)−C(23)	1.39(2)
F(21)−C(1)	1.31(2)	C(23)−C(24)	1.39(2)
F(22)−C(2)	1.33(2)	C(24)−C(25)	1.39(2)
F(23)−C(2)	1.32(2)	C(25)−C(26)	1.38(2)
F(24)−C(2)	1.34(2)		

Bond Angles			
F(2)−As(1)−F(5)	94.2(10)	F(9)−As(2)−F(1)	87.4(8)
F(2)−As(1)−F(7)	94.5(11)	F(8)−As(2)−F(1)	82.2(9)
F(5)−As(1)−F(7)	171.3(8)	As(2)−F(1)−As(1)	156.5(13)
F(2)−As(1)−F(6)	92.0(9)	F(21)−C(1)−C(21)	115.1(13)
F(5)−As(1)−F(6)	90.9(6)	F(21)−C(1)−C(11)	115.5(13)
F(7)−As(1)−F(6)	88.8(7)	C(21)−C(1)−C(11)	129.3(13)
F(2)−As(1)−F(4)	95.4(11)	F(23)−C(2)−F(24)	105(2)
F(5)−As(1)−F(4)	89.8(9)	F(23)−C(2)−F(22)	104(2)
F(7)−As(1)−F(4)	89.4(10)	F(24)−C(2)−F(22)	105(2)
F(6)−As(1)−F(4)	172.5(10)	F(23)−C(2)−C(23)	113(2)
F(2)−As(1)−F(1)	175.0(10)	F(24)−C(2)−C(23)	115(2)
F(5)−As(1)−F(1)	87.9(8)	F(22)−C(2)−C(23)	113(2)
F(7)−As(1)−F(1)	83.4(9)	C(12)−C(11)−C(16)	123(2)
F(6)−As(1)−F(1)	92.5(9)	C(12)−C(11)−C(1)	121.2(14)
F(4)−As(1)−F(1)	80.1(10)	C(16)−C(11)−C(1)	115(2)
F(10)−As(2)−F(3)	97.0(8)	C(11)−C(12)−C(13)	119(2)
F(10)−As(2)−F(11)	91.8(8)	C(14)−C(13)−C(12)	122(2)
F(3)−As(2)−F(11)	94.0(7)	C(13)−C(14)−C(15)	122(2)
F(10)−As(2)−F(8)	169.2(8)	C(14)−C(15)−C(16)	118(2)
F(3)−As(2)−F(8)	93.7(7)	C(15)−C(16)−C(11)	116(2)
F(11)−As(2)−F(8)	88.6(7)	C(26)−C(21)−C(22)	120.5(14)
F(10)−As(2)−F(9)	89.7(8)	C(26)−C(21)−C(1)	121.1(14)
F(3)−As(2)−F(9)	95.2(8)	C(22)−C(21)−C(1)	118.3(13)
F(11)−As(2)−F(9)	170.4(7)	C(23)−C(22)−C(21)	118.8(14)
F(8)−As(2)−F(9)	88.1(7)	C(24)−C(23)−C(22)	119(2)
F(10)−As(2)−F(1)	87.2(9)	C(24)−C(23)−C(2)	119(2)
F(3)−As(2)−F(1)	175.0(9)	C(22)−C(23)−C(2)	122(2)
F(11)−As(2)−F(1)	83.2(8)	C(23)−C(24)−C(25)	123(2)
C(26)−C(25)−C(24)	116(2)	C(21)−C(26)−C(25)	122(2)

Bridge Bonds		Dihedral Angles
C(1)···F(4)	3.01(2)	between: phenyl groups 47.46(43)
C(1)···F(6)	3.07(2)	[As(1)F(1,2,5,7)] and [As(2)F(1,3,9,11)] 45.0(6)
F(4)···C(1)···F(6)	155.7(13)	[As(1)F(1,2,4,6)] and [As(2)F(1,3,9,11)] 49.4(5)
F(4)···C(1)···F(12)	79.1(13)	[As(1)F(1,2,4,6)] and [As(2)F(1,3,8,10)] 40.2(7)
F(6)···C(1)···F(12)	102.0(13)	[As(1)F(1,2,5,7)] and [As(2)F(1,3,8,10)] 51.6(4)
F(4)···C(1)···C(3)	117.8(13)	[As(1)F(4,5,6,7)] and [As(2)F(8,9,10,11)] 14.2(4)
F(6)···C(1)···C(3)	84.1(13)	
F(4)···C(1)···C(9)	74.6(13)	
F(6)···C(1)···C(9)	83.3(13)	

Relative Ability of Fluorine and Chlorine to Stabilize Carbenium Ions. A comparison of the bond lengths of (**II**) and (**III**) with that of the closely related $[(o\text{-}ClC_6H_4)(C_6H_5)CCl]^+$ cation[42] and those of the corresponding $CH_3CX{=}CH_2$ haloolefins demonstrates that chlorine, [R(C−Cl)−R(C^+−Cl) = 0.07 Å], is a better electron back-donor than fluorine, [R(C−F)−R(C^+−F) = 0.02 Å]. This finding confirms the results of the recent theoretical calculations[3,4] and prompted us to analyze the following assumptions which led to the previous postulate[33,34] of an opposite stabilization effect.

(i) The stabilizing effect of a halogen ligand is governed by p(π) back-donation from the free valence electron pairs on the halogen and an opposing electron withdrawing inductive σ effect.

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[42] Laube, T.; Bannwart, E.; Hollenstein, S. *J. Am. Chem. Soc*. **1993**, *115*, 1731.

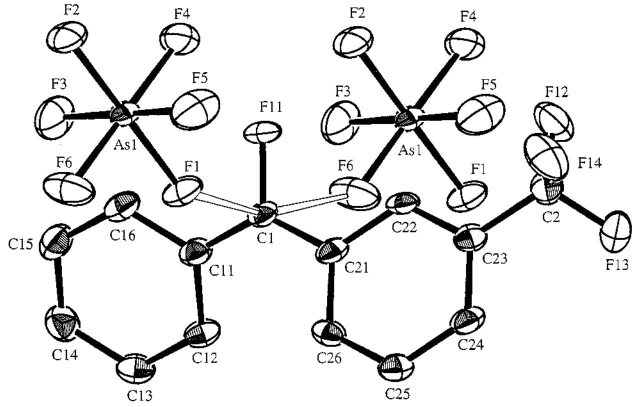


Figure 3. Structure, numbering scheme, and fluorine bridging of the $[(m\mathrm{CF_3C_6H_4})(\mathrm{C_6H_5})\mathrm{CF}]^+$ cation in (**II**).

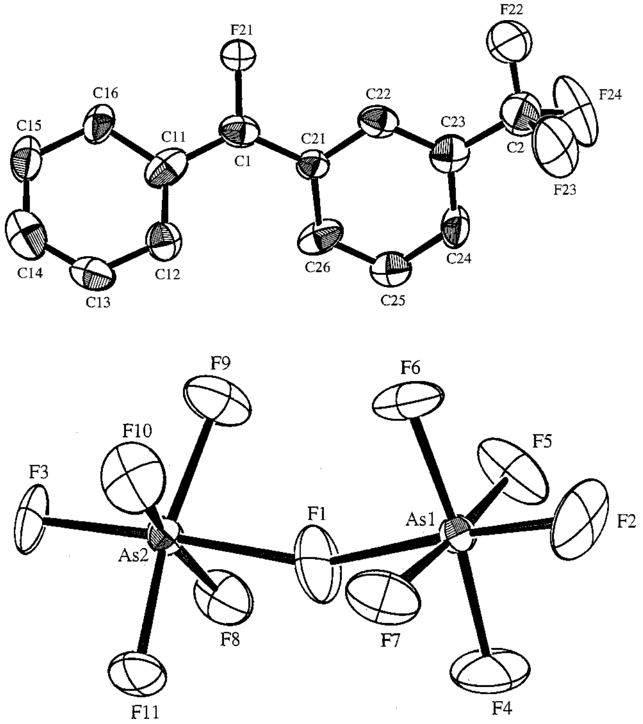


Figure 4. Structures and numbering schemes for the ions in (**III**) with the displacement ellipsoids drawn at the 50% probability level.

(ii) The changes in the σ effect on going from fluorine to the heavier halogens were assumed to be identical for neutral $\mathrm{CH_3CHXCH_3}$ and $\mathrm{CH_3CX{=}CH_2}$ halocarbons and carbenium ions,

$$>\mathrm{CX}^+$$

that is, the slopes of the plots of their ^{13}C NMR shifts against the electronegativity of the halogens were assumed to be identical.

(iii) The deviations from parallelism, observed for the carbenium ions, were attributed exclusively to p(π) back-donation and taken as a measure of the stabilizing power of the corresponding halogen.

The weak point of this postulate is assumption (ii). As was shown by previous theoretical calculations,[3,4] C^+ is highly electron-deficient and is more electronegative than chlorine. Therefore, in the carbenium cations chlorine becomes both a π *and* a σ donor, while the more electronegative fluorine is only a π donor and strongly withdraws electron density from the carbon through the σ effect, as previously shown for $\mathrm{CF_3}^+$ and $\mathrm{CCl_3}^+$.

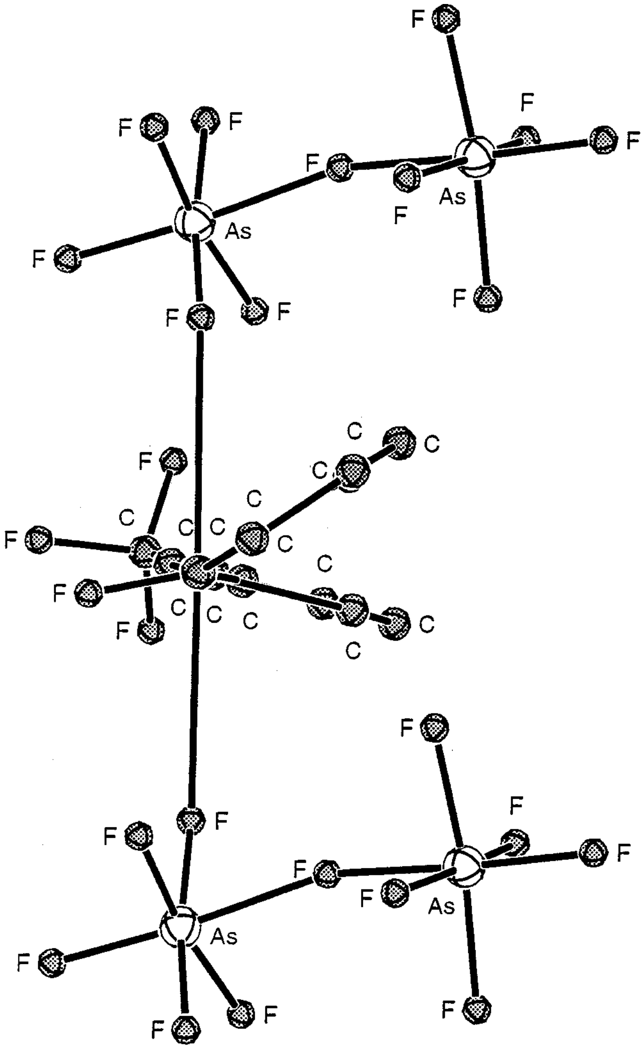
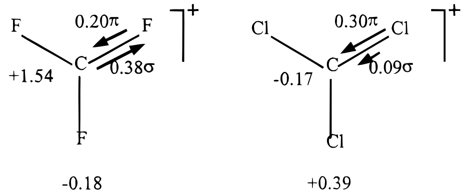


Figure 5. Fluorine bridges between C1 of the cation and F4 and F6 of the anions in (**III**).



The reversal of direction of the σ effect from fluorine to the heavier halogen atoms occurs only in the carbenium ions but not in the neutral halocarbons in which the halogen ligands are always more electronegative than carbon and carry a negative charge. Consequently, assumption (ii) is deemed invalid.

Since the stabilization of a carbenium center should depend on the *total* electron density supplied by a given ligand to C^+, i.e., the sum of the π and the σ effects, and because the ^{13}C NMR shielding of C^+ is governed by its electron density, the direct ^{13}C NMR shifts, and not the shift differences between carbenium ions and neutral hydrocarbons, should be used to evaluate the stabilizing effect of ligands on a carbenium center. Inspection of published ^{13}C NMR shift tables[41] for numerous carbenium ions strongly supports this conclusion.

The $\mathrm{As_2F_{11}}^-$ Anion. The $\mathrm{As_2F_{11}}^-$ anion had previously been identified by spectroscopic[6−13] and conductometric[9,12] studies and X-ray powder diffraction data;[14] the present study is the first crystal structure determination of this anion. The structure of $As_2F_{11}^-$ (Figure 4) resembles in most aspects those found for $Sb_2F_{11}^-$,[43] with two somewhat distorted AsF_6 octahedra sharing one corner and a symmetric As−F−As bridge forming an angle of 156.5(13)°. The two AsF_6 octahedra in $As_2F_{11}^-$ are staggered with respect to each other, forming dihedral angles of about 46° to minimize the F···F repulsions. This staggered arrangement is analogous to that previously found for the isoelectronic $[AsF_5{-}O{-}AsF_5]^{2-}$ anion,[44] which possesses a symmetric As−O−As bridge with an angle of 136°. The slight tilt of the fluorines of the equatorial AsF_4 planes toward the bridge can be explained by the longer As−F bridge bond being less repulsive than the shorter terminal $As{-}F_{ax}$ bonds. Only one AsF_6 group of $As_2F_{11}^-$ is involved in the formation of two fluorine bridges to two cations, causing slight elongations of the As(2)−F(8) and As(2)−F(9) bonds.

After completion of this study, we learned that Minkwitz and Neikes have also obtained a crystal structure of a salt containing an $As_2F_{11}^-$ anion,[45] and that the geometry of their $As_2F_{11}^-$ anion closely resembles that found by us for (III). Although the structures of the $As_2F_{11}^-$ anions in both studies and that of isoelectronic $[AsF_5OAsF_5]^{2-}$ are very similar, it should be kept in mind that in $Sb_2F_{11}^-$ both the Sb−F−Sb bridge angle and the dihedral angle between the two SbF_6 octahedra are very soft and can vary over a wide range.[43c] A similar behavior cannot be excluded for $As_2F_{11}^-$, and additional crystal structures containing this anion will be needed to judge if similarly wide variations are possible for $As_2F_{11}^-$.

Conclusions

(i) The first crystal structures of fluoro-substituted carbocations without heteroatom stabilization and of $As_2F_{11}^-$ were determined.

(ii) It is shown that in the absence of a better donor a fluoroligand can significantly stabilize a carbenium center through back-donation, as evidenced by a shortening of the $C^+{-}F$ bond in $(CH_3)_2CF^+$ by about 0.05 Å.

(iii) If aromatic carbon atoms or heteroatoms, which are better back-donors than fluorine, are also present, the back-donation from fluorine is strongly diminished, as evidenced by a shortening of the $C^+{-}F$ bond in (**II**) by only 0.02 Å.

(iv) Chlorine is a better back-donor than fluorine, as shown by a comparison of the analogous structures of $[(m\text{-}CF_3C_6H_4)(C_6H_5)CF]^+$ ($\Delta C^+{-}F \approx 0.02$ Å and $\Delta C^+{-}C_{ipso} \approx 0.07$ Å) and $[(o\text{-}ClC_6H_4)(C_6H_5)CCl]^+$ ($\Delta C^+{-}Cl \approx 0.07$ Å and $\Delta\, C^+{-}C_{ipso} \approx 0.07$ Å).

(v) The crystal structure of $(CH_3)_2CF^+$ also shows strong evidence for stabilization of the carbenium center by methyl-hyperconjugation ($\Delta C^+{-}CH_3 \approx 0.08$ Å).

(vi)All three fluoro-substituted carbocation structures of this study are further stabilized by fluorine bridging with the counterions. These fluorine bridges are approximately perpendicular to the planar C_2CF^+ skeleton and are along the axis of the unoccupied p_z orbital of C^+.

(vii)The structure of the $As_2F_{11}^-$ anion closely resembles that of isoelectronic $[AsF_5OAsF_5]^{2-}$ with a bent symmetric As−F−As bridge and dihedral angles of about 46° (staggered AsF_4 groups).

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Supporting Information Available: Tables of structure determination summaries, anisotropic displacement parameters, calculated hydrogen coordinates, and isotropic displacement parameters of (**I**), (**II**), and (**III**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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