rinsed with 50 ml of hexane. The mixture obtained was washed with saturated aqueous Na_2CO_3 solution and with water and was dried on $MgSO_4$. Enone **8c** (12.5 g) (98% pure, 61% yield) was obtained, bp 57° (40 mm); nmr 1.12 (s, 9 H), 2.24 (s, 3 H), 5.66 (s, 1 H), 5.75 (s, 1 H).

3,4,4-Trimethylpentan-2-one (8b) was obtained by catalytic (Raney Ni) hydrogenation of **8c** in absolute EtOH at about 30° under atmospheric pressure (80% yield).

Preparation of Cis Enones (10–18). All cis enones were prepared by fractionation of the acidified trans enones; the following synthesis is typical. Enone **7** (9.5 g) and 0.1 g of paratoluenesulfonic acid were distilled (15 mm) with a reflux ratio of 100:1 on a 25 theoretical plate spinning band column (see Table VII).

Table VII

Fraction no.	Bp, °C	Weight, g	% trans enone	% cis enone
1	58–63	1.0	69	28
2	63–60	1.6	42	57
3	60–58	1.2	26	73
4	58	1.5	41	58
Residue		4.5		

It was impossible to obtain pure cis enone directly; fractions 2–4 of this example were purified by preparative vpc.

Purification of Enones. All enones were purified on Aerograph Autoprep vpc apparatus with a 10 ft, 15% SE30 on 100–120 Chromosorb W column. With one exception (see Table II) products were purer than 99%, as checked using a Aerograph Model 1200 chromatograph, just before and after obtaining spectra. This precaution was very important, above all for cis enones which isomerize quickly (giving trans enones and other unidentified products) under the influence of light.

Product Identification. In addition to uv (observed n → π^* bands have not been noted in this paper) and ir spectra (see Tables II and III) which are very typical of the -COC=C framework, nmr spectra were recorded (about 10% in CCl_4) on a Varian Model DP60 and a JEOL Model JNM C60 HL (see Table VIII).

Table VIII. Nmr Spectra for Trans and Cis Enones[a]

Enone no.	δ_R	δ_{Me}[b]	Enone no.	δ_R	δ_{Me}[b]
2t	2.42 (2 H)m 1.05 (3 H)t	2.10	**2c**	2.45 (2 H)m 1.05 (3 H)t	1.80
3t	. . .[c]	2.07	**3c**	. . .[c]	1.84
4t	. . .[c]	2.06	**4c**	. . .[c]	1.86
5t	2.84 (1 H)m 1.07 (6 H)d	2.08	**5c**	2.70 (1 H)m 1.06 (6 H)d	1.90
6t	1.12 (9 H)s	2.06	**6c**	1.12 (9 H)s	1.88
7t	1.00 (9 H)s 2.26 (2 H)s	2.08	**7c**	1.00 (9 H)s 2.30 (2 H)s	1.87
8t	0.91 (9 H)s 0.98 (3 H)d 2.50 (1 H)m	2.10	**8c**	0.91 (9 H)s 0.98 (3 H)d 2.50 (1 H)m	1.89
9t	0.90 (9 H)s 1.08 (6 H)s	2.03	**9c**	0.90 (9 H)s 1.09 (6 H)s	1.87

[a] δ for ethylenic protons are not given since this portion of the spectrum was not analyzed. For trans enones, ten peaks corresponding to an ABX_3 spectrum with J = 15–17 Hz, between about 6 and 7 ppm, were observed. For cis enones, it seems that the δ of the two ethylenic protons are very similar. For enones **1t** and **c** see E. S. Waight and R. L. Erskine in "Steric Effects in Conjugated Systems," Butterworths, London, 1958. [b] δ of the center of the doublet. [c] Multiplets.

The value of δ_{Me} in cis and trans enones is in agreement with Baldwin's results[9] for 3-penten-2-one.

Acknowledgment. We wish to acknowledge our indebtedness to Professor J. E. Dubois for helpful discussions, to Professor J. P. Matthieu who allowed us access to his "curve resolver" and to Mrs. B. Duchatellier for invaluable help with the synthesis.

Substituent Effects. XI.[1] Polar and π-Electron Substituent Effects by ^{19}F Nuclear Magnetic Resonance

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Abstract: A number of substituted aryl fluorides have been synthesized and their ^{19}F chemical shifts measured. The results provide conclusive experimental proof that polar effects play a major role in determining ^{19}F chemical shifts in aryl fluorides. Furthermore, the ^{19}F chemical shifts provide definitive experimental evidence for hyperconjugative electron withdrawal by substituted methyl groups in the ground state of neutral molecules.

The large response of ^{19}F chemical shifts to substituent-produced perturbations has made fluorine nuclear magnetic resonance spectroscopy an attractive tool for the study of substituent effects.

Since the fluorine chemical shifts are dominated by the paramagnetic term of the Ramsey equation,[3] certain approximations are usually unavoidable if they are to be discussed in the terms that have proved useful in the case of chemical reactivity.[4] A number of theo-

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(1) Part X: M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, **93**, 4187 (1971).

(2) To whom correspondence should be addressed at The University of Texas at Austin.

(3) (a) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954); (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, Chapter 4.

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Table I. Relative ^{19}F Chemical Shifts (ppm) in Dimethylformamide and Benzene[a]

Substituent, X	Compound					
	1[b]	**2**[b]	**3**[c]	**4**[c]	**3**[d]	**4**[d]
CO	−1.49 (−1.64)[e]	−1.40 (−1.68)[e]	−1.78 (−2.18)[e]	−0.26 (−0.84)[e]	−1.31 (−1.85)	+0.09 (−0.49)
O	−1.50 (−1.50)	−1.50 (−1.59)	−3.10 (−3.08)	−0.55 (−0.68)	−2.63 (−2.75)	−0.20 (−0.33)
NCH_3	−0.98 (−0.85)	−0.46 (−0.46)	−2.26 (−2.31)	−0.23 (−0.41)	−1.79 (−1.98)	+0.12 (−0.06)
$N^+(CH_3)_2$	−4.49	−3.04	−7.91	−2.16	−7.44	−1.81
S	−1.83 (−1.83)	−1.19 (−1.35)	−2.34 (−2.45)	−0.61 (−0.83)	−1.87 (−2.12)	−0.26 (−0.48)
SO_2	−3.78 (−4.18)	−2.06 (−2.69)	−4.76 (−5.47)	−1.00 (−1.87)	−4.29 (−5.14)	−0.65 (−1.52)
S^+CH_3	−6.17	−3.56	−6.81	−2.49	−6.34	−2.14

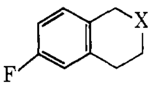
[a] In parentheses. [b] The chemical shifts of **1** and **2** relative to 6-fluorotetralin. [c] The chemical shifts of **3** and **4** relative to *p*- and *m*-fluorotoluene, respectively. [d] The chemical shifts of **3** and **4** relative to *p*- and *m*-ethylfluorobenzene, respectively. [e] Taken from ref 18a.

retical treatments have appeared relating changes in shielding to substituent-induced changes in the π charge density on the fluorine atom, in the carbon–fluorine π bond order, and in the charge distribution in the remainder of the molecule,[3b,4–8] and attempts to correlate observed ^{19}F chemical shifts with substituent-induced perturbations have met with varying measures of success.[9–14]

Various opinions have been expressed in this connection concerning the contribution of polar effects to the observed ^{19}F substituent chemical shifts (SCS). Taft[11] has suggested that polar effects are propagated by a σ-bond inductive mechanism, that electric field effects account for only a small portion of the SCS, and that π-electron influences are the major factors responsible for SCS in aryl fluorides. Dewar, *et al.*,[13] have assigned little or no importance to σ induction, suggesting rather that the electric field model gives a much more satisfactory description of polar effects in such systems and that polar and π-electron contributions are of the same order of magnitude for aryl fluorides. Finally, Emsley and Feeney[7] combine both field and π-electron contributions but assign the field effect a considerably lesser role than that proposed by Dewar and his associates.

This latter view has gained considerable support in the past few years with the demonstration that polar contributions to ^{19}F SCS in saturated molecules are in fact quite small.[15–17]

The difficulty of separating polar and π-electron effects in unsaturated systems, as well as a lack of suitable model compounds, has, however, prevented an examination of pure polar contributions to ^{19}F chemical shifts in aryl fluorides. Recently, ^{19}F nmr studies[18] of bicyclic systems **1** and **2** in which the C–X σ bond is constrained to a varying degree to the nodal plane of the aromatic ring, together with their monocyclic analogs **3** and **4**, suggest that this may be possible. Furthermore, an added feature of these systems is the possibility of being able to assess the relative importance of the π-inductive and hyperconjugative mechanisms of substituted methyl groups. Although compelling experimental evidence now exists for hyperconjugative electron release from carbon–metal σ bonds in the ground states of neutral molecules,[18b] electron withdrawal by such a mechanism has so far escaped unequivocal experimental detection.[19]



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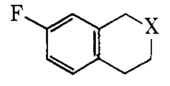

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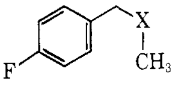

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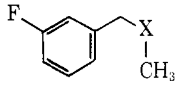

4

The purpose of the present research is twofold: first, to provide unambiguous experimental proof that ^{19}F chemical shifts in substituted aryl fluorides are determined in part by polar effects; second, to present unequivocal experimental evidence that substituted methyl groups (CH_2X, where X is more electronegative than C) affect electron withdrawal, in part, by a hyperconjugative mechanism. We have accordingly extended the ^{19}F nmr study of the bicyclic systems **1** and **2**, together with their monocyclic analogs **3** and **4**, to compounds where X = NCH_3, $N^+(CH_3)_2$, O, S, S^+CH_3, and SO_2. In this paper we report their synthesis and a study of their ^{19}F spectra.

Results and Discussion

Before considering the relative ^{19}F chemical shifts for **1–4** listed in Table I, it is instructive to examine

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(16) G. W. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, **90**, 212 (1968); **91**, 6804 (1969), and references therein.

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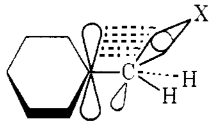
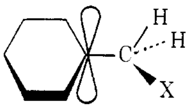
molecular models of these systems. A number of important features immediately become apparent. First it is readily seen that the geometries of the bicyclic systems **1** and **2** are more constrained than those of their monocyclic analogs **3** and **4**. Whereas the substituted methyl groups in the latter systems can be assumed to undergo free rotation,[20] the constraint in the alicyclic rings of **1** or **2** ensures a relatively precise definition of the spatial relationship of the CH_2X group with respect to the C–F bond. Although the time-averaged location of the CH_2X dipole can be assumed to be similar in the symmetrically substituted system **3** and in **1**, the situation is quite different for the unsymmetrical system **4**. An electric field model would therefore predict the electronic effect of the C–X λ bond to be significantly different in **2** and **4**, whereas no difference would be predicted on the basis of a through-bond model (σ-inductive effect).

Second, it can be seen that whereas the C–X σ bond in **3** and **4** can exist in the conformation corresponding to maximum σ–π conjugation or hyperconjugation (see I and II),[21,22] the C–X σ bond in **1** or **2** is more or less constrained to lie in the nodal plane of the adjacent π system.[23] If then the hyperconjugative mechanism is significant and the π-inductive effect relatively unimportant, the electron-withdrawing ability of the C–X σ bond should be significantly less in the bicyclic system **1** than in the monocyclic analog **3**. The effect should be most pronounced where the dihedral angle in **1** is fairly small.[23] Furthermore, since the spatial relationship between the C–X dipole or pole and the C–F bond is similar for **1** and **2**, the electronic effect of the C–X σ bond in **1** should approach that in **2** when the dihedral angle is small.[23]



I

Hyperconjugative interaction between phenyl and CX bond in the favored conformation



II

Conformation in which the interaction vanishes

If on the other hand the π-inductive effect is more important than hyperconjugation, then the electrical effect of the C–X bond should be similar in **1** and **3** but significantly different between **1** and **2** for *all* groups.

Comparison of the relative ^{19}F chemical shifts for **1–4** (Table I) provides a fairly definite answer to our problems. It can be seen that the electron-withdrawing ability of the C–X σ bond,[24] as indicated by the degree of deshielding of the fluorine nucleus, varies markedly with conformation. Since σ- and π-inductive effects are expected to be insensitive to angular effects of this type, the results clearly support a model based on the electric field effect and hyperconjugation. The marked difference between the electron withdrawal by the substituted methyl groups in **2** and **4**, where the relative chemical shifts are presumably dominated by polar effects, strongly suggests that the field effect makes a substantial contribution to ^{19}F substituent chemical shifts in aryl fluorides.

The relatively large effects in **2** due to CO, O, NCH_3, or $N^+(CH_3)_2$ are in contrast to the much smaller effects of these substituents in saturated fluorides.[15] The differences must be due to a greater effective polarizability of the CF bond when the fluorine is attached to a conjugated system. In saturated fluorides polarization must involve the CF σ bond which is very strong and stiff. In a conjugated fluoride, however, there is the additional possibility of polarization by increased donation of fluorine p electrons into the adjacent π system. This argument can be put in another way. In the usual perturbation treatment of chemical shifts, there is a mixing of excited states with the ground state under the influence of an applied electric field, leading to a change in the paramagnetic term. This effect should in general be greater, the smaller the effective excitation energy. In the case of unsaturated or aromatic fluorides there will be relatively low-lying exicted states involving the fluorine electrons, whereas in saturated fluorides the corresponding excitation energies must be much larger.

Since the relative chemical shifts in **2** depend essentially on polar effects, we plotted them against σ^{SF} values calculated by the FMMF method.[1] This empirical treatment uses a simplified model in which the dipole moment of the bond CX between a substituent and an adjacent carbon *i* is represented by equal and opposite point charges on carbon and at a point *j* one standard bond length (1.40 Å) from carbon along the CX bond. The interaction with a fluorine atom attached at atom *m* is given by the general equation[1]

$$\sigma_{im}{}^{SF} = F^S R_{im}{}^2 + M^S q_{im} + M^S \sum_{k \neq m} \frac{q_{ik} \cos \theta_{kn}}{r_{kn}{}^2} \qquad (1)$$

where

$$R_{im}{}^2 = \frac{\cos \theta_{in}}{r_{in}{}^2} - \frac{\cos \theta_{jn}}{r_{jn}{}^2} \qquad (2)$$

Here θ_{in} is the angle between the CF bond vector and a line of length r_{im} drawn from atom *i* to the midpoint (*n*) of the CF bond, while q_{im} is the charge produced at

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[20] The direction and magnitude of the resultant dipole depend upon the various rotamer populations in an unknown way.

[21] In resonance terminology, this σ–π interaction would be represented in terms of a contribution by the ionic structure ($PhCH_2{}^+X^-$) to the resonance hybrid describing the ground state.

[22] σ–π conjugation should be most favored when the CCX plane is orthogonal to the ring and vanishes when the C–X bond lies in the plane of the ring; see, *e.g.*, (a) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, **63**, 41 (1941); (b) M. J. S. Dewar, *ibid.*, **74**, 3345 (1952). The resonance integral β^θ is given approximately by $\beta^\theta \simeq \beta^0 \cos \theta$, where θ is the angle of twist. (c) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

[23] In **1** and **2** the alicyclic ring is conformationally mobile, there being two freely interconvertible conformations. However, whereas the interconversion is between two half-chair conformations where X = CH_2, CO, NCH_3, $N^+(CH_3)_2$, or O, the systems seem to favor half-boat forms where X = S, S^+CH_3, or SO_2. In fact, the models for the large sulfur groups cannot be maintained in a half-chair conformation. The dihedral angle between the CCX plane and the aromatic ring in the half-boat arrangement is approximately 50–55°, while the dihedral angle in the half-chair conformation is approximately 25–30°.

[24] It is assumed, as a first approximation, that the differences between the relative chemical shifts reflect the electronic behavior of the C–X σ bond. This postulate is based on two reasonable assumptions: (i) that the effects of CH and CC hyperconjugation are indistinguishable in the ground states of neutral molecules;[22c] and (ii) that the extent to which CH_2 can undergo hyperconjugative electron release from its CH bonds is the same for similar groups (X). We believe that the best reference system for estimating relative chemical shifts in monocyclic systems is somewhere between the extremes, namely methyl- and ethyl-substituted fluorobenzene. We have therefore listed relative chemical shifts for both systems in Table I.

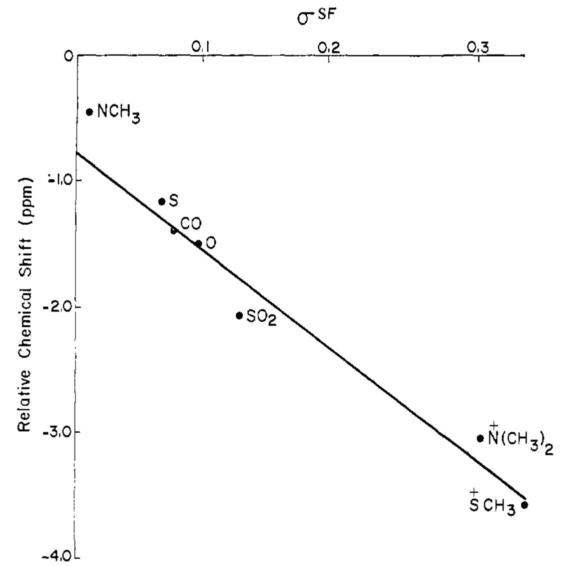


Figure 1. Experimental relative ^{19}F chemical shifts of **2** plotted against σ^{SF} values calculated by the FMMF method.

atom m by an amino substituent attached at atom i and is calculated by an SCF π MO procedure.[25]

The σ^{SF} values for **2** were calculated from eq 1 by assuming that the last two terms in this equation can be neglected so that a plot of the relative chemical shifts against the field effect term F^S/R_{im}^2 is linear.[26] The substituent parameters F^S, calculated from the ionization of 4-substituted bicyclooctane-1-carboxylic acids (50% (w/w) aqueous ethanol), are listed in Table II.[27]

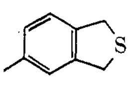
Table II. Values of F Parameters

Substituent	F	Substituent	F
CH$_3$	−0.086	CO$_2$H	3.10
F^a	4.68	CO$_2$C$_2$H$_5$	3.13
Cl	4.89	NH$_2$^{a}	0.245
Br	4.87	NHAc^a	3.10
I^a	4.45	COCH$_3$^{a}	3.53
OH	2.45	SCH$_3$^{a}	2.19
OCH$_3$	3.12	SO$_2$CH$_3$^{a}	5.95
CN^a	5.60	N$^+$(CH$_3$)$_3$^{a}	9.66
NO$_2$	7.00	S$^+$(CH$_3$)$_2$^{a}	11.10

^{a} Data for the corresponding bicyclooctanecarboxylic acids are not available for the given solvent; F^5 values calculated from log (K_X/K_H) values estimated by Swain and Lupton.[28]

Although the correlation (Figure 1) is not good, this is probably due to the uncertainty in specifying the spatial factor.[29]

The importance of polar effects in determining the magnitude of ^{19}F chemical shifts in aryl fluorides is strikingly illustrated by the large difference between the chemical shifts of 5-fluoro-1,3-dihydrobenzo[*c*]thiophene (**5**) and 5-fluoro-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**6**).[30] The signal for **6** was downfield from that of **5** by 4.56 ppm in DMF and 4.98 ppm in benzene. Since the C–S σ bonds lie in the plane of the ring, σ–π conjugation should play no role in determining the relative ^{19}F chemical shifts. The predominant electronic factor must therefore be the strong inductive field effect of the very polar S$^{\delta+}$=O$^{\delta-}$ bonds. The fact that the downfield shift is significantly *smaller* in the polar solvent DMF than in benzene is particularly relevant in view of a recent paper by Taft and coworkers.[31] Note that similar solvent effects are also observed for SO$_2$ in **1**–**4** (Table I). The smaller but similar effect for the tetralones (X = CO) was pointed out earlier.[18a]



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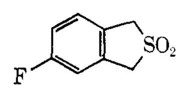

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It is known that polar solvents normally enhance the downfield shifts of strongly electron-withdrawing neutral substituents when they are directly attached to aromatic systems.[31] Changing the solvent from benzene to DMF leads for example to an increase in the electron-withdrawing power of the acetyl and sulfonyl substituents. Taft, *et al.*,[31] have concluded on the basis of an empirical analysis of model systems that this effect is not due to π-electron delocalization between the substituent and the ring. They therefore attributed it to the polar effect of the substituent. Their arguments would lead one to expect the π-inductive effect to be enhanced in aprotic solvents.[32] However, in our systems the π-inductive effect should[13] have been effectively eliminated by the interposition of a methylene group between the aromatic ring and the substituent. We believe that our observations can be rationalized only in terms of a direct electrostatic interaction which is attenuated by polar solvents, as a result of their greater effective dielectric constants.

Finally, it may be seen that the electron-withdrawing ability of the C–X σ bond is usually less in **1** than in **3**, the reduction being most pronounced when the dihedral angle in **1** is small (X = O, NCH$_3$, or N$^+$(CH$_3$)$_2$).[23] Furthermore, the electron-withdrawing ability of the C–X σ bonds in **1** and **2** differs considerably when the dihedral angle is substantial (X = S, SO$_2$, or S$^+$CH$_3$).[23] We believe that only the stereoelectronic requirements of a hyperconjugative mechanism can account for these observations. Further support for significant hyperconjugation by the C–S bond comes from the chemical shift of 5-fluoro-1,3-dihydrobenzo[*c*]thiophene (5), where the C–S σ bond is clearly in the nodal plane of the adjacent aromatic system. The chemical shifts (relative to 5-fluoroindan) in DMF (−0.64 ppm) and in benzene (−0.55 ppm) are clearly much smaller than those observed for S in **1** or **3** (Table I).

The suggestion that the net electronic effect of CH$_2$X (X being more electronegative than C) on the ground states of neutral molecules is partly determined by hyperconjugative electron withdrawal is not without prec-

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(26) F^S values for NH$_2$ and OCH$_3$ were used for the N and O systems, while F^S values for COCH$_3$, SCH$_3$, SO$_2$CH$_3$, N$^+$(CH$_3$)$_3$, and S$^+$(CH$_3$)$_2$ were employed for the other systems when X = CO, S, SO$_2$, N$^+$(CH$_3$)$_2$, and S$^+$CH$_3$, respectively.

(27) The values reported here are revised values which differ slightly from those previously reported.

(28) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90** 4328 (1968).

(29) In **1**: R_{im}^2 = 0.0247 (X = N, N$^+$(CH$_3$)$_2$, O, S, and S$^+$CH$_3$) and 0.0201 (X = CO and SO$_2$). In **2**: R_{im}^2 = 0.0313 (X = N, N$^+$-(CH$_3$)$_2$, O, S, and S$^+$CH$_3$) and 0.0219 (X = CO and SO$_2$).

(30) Available from another project: W. Adcock and M. J. S. Dewar, to be published.

(31) R. T. C. Brownlee, S. K. Dayal, J. L. Lyle, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 7208 (1972), and references therein.

(32) G. L. Anderson, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **93**, 6984 (1971).

Table III. ^{19}F Chemical Shifts (ppm) in DMF for Para-Substituted Fluorobenzenes

Substituent	Chemical shift[a]
$-CH_2N^+(CH_3)_3$[b]	−7.70
$-CH_2P^+(CH_3)_3$[b]	−4.16
$-CH_2Br$[c]	−5.07

[a] Relative to *p*-fluorotoluene. [b] Counterion, Br^-. [c] See ref 36.

edent. It has been known for some time, but generally overlooked, that the nqr frequencies of ^{35}Cl in benzyl chloride (33.6 MHz) and in chloromethyl methyl ether (30.181 MHz) are lower than in methyl chloride (34.2 MHz). This result is consistent with a hyperconjugative transfer of charge from the π system or p orbitals to the C–Cl σ bond.[22c,33]

Similar hyperconjugative interactions are probably also important in several other connections. Thus they are probably responsible for the fact that the "inductive effect" of a CH_2X substituent on the acid dissociation constant of benzoic acid is greater when it is in the para position than when it is in the meta position. Exner[34] had attributed this difference to a π-inductive mechanism. Another example seems to be provided by the different effects of the groups $-CH_2N^+(CH_3)_3$, $-CH_2P^+(CH_3)_3$, and $-CH_2As^+(CH_3)_3$ on electrophilic substitution in benzene.[35] Whereas $-CH_2N^+(CH_3)_3$ is meta-directing, $-CH_2P^+(CH_3)_3$ favors substitution in the para position. Table III compares the relative ^{19}F chemical shifts for these substituents together with that for CH_2Br.[36]

It can be seen that there is a considerable difference in electronic behavior between the two positively charged species. Recently, Symons[37] has suggested that the electronic effect of the $-CH_2P^+(CH_3)_3$ group may be explained in terms of hyperconjugative electron release from the C–P σ bond, despite the positive charge. He has also attributed the ortho,para-directing effect of halomethyl substituents to a similar phenomenon, *i.e.*, electron release from the carbon–halogen σ bond. On the basis of our observations, together with the nqr data previously mentioned, we find this proposal unacceptable.

It seems clear that the electronic effect of substituted methyl groups (CH_2X, where X is more electronegative than C) can be partitioned into three components: (i) electron withdrawal by an inductive field effect; (ii) hyperconjugative electron withdrawal by the C–X σ bond; and (iii) hyperconjugative electron release from the C–H σ bonds. Since the electron-withdrawing effect of positive poles is expected to decrease with increasing size of the atom bearing the formal positive charge, the relative importance of i, ii, and iii will be markedly different for $-CH_2N^+(CH_3)_3$ and $-CH_2P^+(CH_3)_3$. Obviously no *a priori* assessment of the relative importance of these components can be made. Apparently iii plays a greater relative role for $-CH_2P^+(CH_3)_3$ than for $-CH_2N^+(CH_3)_3$. It is of interest to note that recent work by Ridd, *et al.*,[33] indicates that the electronic effect of the $-CH_2N^+R_3$ group on electrophilic aromatic substitution is sensitive to the conformation of the group with respect to the aromatic ring. This would be consistent with our conclusion that ii is significant in the case of the $-CH_2N^+R_3$ substituent.

It is unfortunately impossible at present to estimate the relative magnitudes of the various effects from experiments such as those described here for lack of the necessary structural information. We were forced to base our arguments on geometries deduced from examination of molecular models. While this does not affect their validity in a qualitative sense, it does make it impossible to estimate the inherent hyperconjugative ability of the various CX bonds, *i.e.*, the effects that would be observed if they were constrained to lie in the optimum orientation relative to an adjacent conjugated system. Thus our assumption of free rotation about the C–CH_2 bond in the monocyclic species $ArCH_2X$ must lead to an underestimate of the average ArCX dihedral angle, for if CX hyperconjugation is important, it must tend to increase this angle in order to maximize the resulting stabilization.

Experimental Section

Although most of the compounds described in this paper are new, the methods of synthesis followed well established procedures. The quaternary ammonium and sulfonium salts were readily prepared by treating ether solutions of the appropriate amines and sulfides with methyl fluorosulfonate. The salts were collected, washed with ether, and dried prior to measuring their nmr spectra. *p*-Fluorobenzyltrimethylammonium bromide and *p*-fluorobenzyltrimethylphosphonium bromide were prepared by treating ether solutions of *p*-fluorobenzyl bromide with trimethylamine and trimethylphosphine, respectively. 5-Fluoroindan and 6-fluorotetralin were available from a previous investigation.[18b]

The elemental analyses agreed well with those calculated (C, ±0.2; H, ±0.1; in 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline, C, 0.4) except for the two fluoroisochromans where the carbon analyses were too low by over 1%. Since it is known that isochromans autoxidize very easily, it seems likely that some hydroperoxide had formed before the analyses were carried out. The proton nmr spectra were clearly in accord with the assigned structures.

Melting points are uncorrected. The pmr spectra were recorded for chloroform-*d* solutions with a Varian A-60 spectrometer, while the fluorine nmr spectra were measured with a Varian DP-60 spectrometer and a Perkin-Elmer R12A operating at 56.4 MHz, using solutions containing 15% (w/w) of the fluoro compound together with 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as internal standard.

5-Fluoro-1-indanone. *m*-Fluorobenzaldehyde was converted to β-(*m*-fluorophenyl)propionic acid according to the method outlined by Vogel[39] for dihydrocinnamic acid. The β-(*m*-fluorophenyl)propionic acid, mp 40–41°, was treated with thionyl chloride to obtain the acid chloride, bp 74–78° (0.5 mm). The acid chloride (34.5 g) was cyclized[40] to 5-fluoro-1-indanone, which crystallized from *n*-pentane in white crystals, mp 32–33° (lit.[41] bp 113–114° (10 mm); n^{25}D 1.5499).

2-Carboxy-5-fluorophenylacetic Acid or 4-Fluorohomophthalic Acid. 5-Fluoro-1-indanone (8.4 g) was oxidized by the method employed for converting indene to homophthalic acid.[42] The 4-

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fluorohomophthalic acid crystallized from benzene and then hot water in microcrystals, mp 172°.

4-Fluoro-*o*-2-hydroxyethylbenzyl Alcohol. 4-Fluorohomophthalic acid (17.42 g, 0.088 mol), converted with ethanolic hydrochloric acid to the diester, after recrystallization from *n*-pentane, had mp 31°. This was reduced with lithium aluminum hydride to 4-fluoro-*o*-2-hydroxyethylbenzyl alcohol by the method used by Anderson and Holliman[43] for *o*-2-hydroxyethylbenzyl alcohol. A sample after sublimation had mp 40–42°.

4-Fluoro-*o*-2-bromoethylbenzyl Bromide. A solution of crude 4-fluoro-*o*-2-hydroxyethylbenzyl alcohol (6.0 g, 0.035 mol) in acetic acid saturated with hydrogen bromide (45%, w/v) was heated in a sealed tube according to the method outlined by Anderson and Holliman.[43] After 10 hr the solution was diluted with cold water and the separated oil extracted with ether. Removal of the ether gave an oil which solidified on standing (8.2 g) and when crystallized from *n*-pentane had mp 35–36°.

6-Fluoroisochroman. 4-Fluoro-*o*-2-hydroxyethylbenzyl alcohol (3.0 g) was mixed with fused potassium hydrogen sulfate (1.0 g) and heated at 60–70° for approximately 20 min.[44] Distillation under a nitrogen atmosphere afforded a colorless oil (0.6 g): bp 54° (6 mm); n^{22}D 1.5204; nmr (60 MHz) triplet centered at δ 2.83 (2 H), triplet centered at δ 3.93 (2 H), broad singlet centered at δ 4.72 (2 H), and complex multiplet centered at δ 6.84 (3 H).

The compound was stored under nitrogen as recommended by Siegel and Coburn[44] for isochroman.

6-Fluorothioisochroman. 4-Fluoro-*o*-2-bromoethylbenzyl bromide (2.25 g, 0.02 mol) was converted to 6-fluorothioisochroman in the same manner as described by Holliman and Mann[45] for thioisochroman. Distillation afforded a colorless oil (1.46 g): bp 76° (0.4 mm); n^{20}D 1.5782; nmr (60 MHz) broad singlet centered at δ 2.92 (4 H), singlet centered at δ 3.70 (2 H), and complex multiplet centered at δ 6.95 (3 H).

6-Fluoro-1,2,3,4-tetrahydro-2-thionaphthalene 2,2-Dioxide. 6-Fluorothioisochroman (0.6 g) was treated with 38% peracetic acid at 0° according to the method outlined by Cava and Deana[46] for 1,3-dihydrobenzo[*c*]thiophene. The acetic acid solution was poured onto ice and the white precipitate collected, dried, and recrystallized from methanol, giving 6-fluoro-1,2,3,4-tetrahydro-2-thionaphthalene 2,3-dioxide (0.48 g): mp 120–121°; nmr (60 MHz) broad singlet centered at δ 3.32 (4 H), broad singlet centered at δ 4.24 (2 H), and complex multiplet centered at δ 7.02 (3 H).

6-Fluoro-2-methyl-1,2,3,4-tetrahydroisoquinoline. An ethanolic solution of 4-fluoro-*o*-2-bromoethylbenzyl bromide (3 g, 0.01 mol) was treated with methylamine according to the method outlined by Holliman and Mann[45] for 2-methyl-1,2,3,4-tetrahydroisoquinoline. Distillation of the crude product afforded a colorless oil (0.2 g): bp 60° (0.8 mm); n^{23}D 1.5183; nmr (60 MHz) singlet centered at δ 2.43 (3 H), complex multiplet centered at δ 2.75 (4 H), broad singlet centered at δ 3.53 (2 H), and complex multiplet centered at δ 6.90 (3 H).

6-Fluoro-1-indanone. *p*-Fluorobenzaldehyde was converted to β-(*p*-fluorophenyl)propionic acid according to the method outlined by Vogel[39] for dihydrocinnamic acid. The acid, mp 87–88°, was treated with thionyl chloride to obtain the acid chloride, bp 54–56° (0.1 mm). The acid chloride (34.5 g) was cyclized[37] to 6-fluoro-1-indanone, which crystallized from *n*-pentane in white crystals, mp 52°.

2-Carboxy-4-fluorophenylacetic Acid or 5-Fluorohomophthalic Acid. 6-Fluoro-1-indanone (8.4 g) was oxidized by the method employed for coverting indene to homophthalic acid.[42] The 5-fluorohomophthalic acid crystallized from benzene and then hot water in microcrystals, mp 175–176°.

5-Fluoro-*o*-2-hydroxyethylbenzyl Alcohol. 5-Fluorohomophthalic acid (17.42 g, 0.088 mol) was converted with ethanolic hydrochloric acid to the diester after recrystallization from *n*-pentane, mp 23–24°. This was reduced with lithium aluminum hydride to 5-fluoro-*o*-2-hydroxyethylbenzyl alcohol in the same way as described above for the 4-fluoro isomer. A sample after sublimation had mp 31–32°.

5-Fluoro-*o*-2-bromoethylbenzyl bromide was prepared from the corresponding diol in the same way as described above for the 4-fluoro isomer. Crystallized from *n*-pentane, it had mp 27–29°.

7-Fluoroisochroman was prepared from the corresponding diol in the same way as described above for the 6-fluoro isomer. Distillation under a nitrogen atmosphere afforded a colorless oil: bp 110° (6 mm); n^{22}D 1.5212; nmr (60 MHz) triplet centered at δ 2.85 (2 H), triplet centered at δ 3.91 (2 H), broad singlet centered at δ 4.70 (2 H), and complex multiplet centered at δ 6.90 (3 H). The compound was stored under nitrogen.

7-Fluorothioisochroman was prepared from 5-fluoro-*o*-2-bromoethylbenzyl bromide in the same manner as described above for the 6 isomer. Distillation afforded a colorless oil (1.4 g): bp 70–74° (0.3 mm); n^{20}D 1.5780; nmr (60 MHz) broad singlet centered at δ 2.90 (4 H), singlet centered at δ 3.70 (2 H), and complex multiplet centered at δ 6.95 (3 H).

7-Fluoro-1,2,3,4-tetrahydro-2-thionaphthalene 2,2-dioxide was prepared from 7-fluorothioisochroman (0.6 g) in the same manner as described above for the 6 isomer. When it was crystallized from methanol (0.4 g), it had: mp 85°; nmr (60 MHz) broad singlet centered at δ 3.28 (4 H), broad singlet centered at δ 4.22 (2 H), and complex multiplet centered at δ 7.02 (3 H).

7-Fluoro-2-methyl-1,2,3,4-tetrahydroisoquinoline was prepared from 5-fluoro-*o*-2-bromoethylbenzyl bromide (3 g, 0.01 mol) in the same manner as described above for the 6-fluoro isomer. Because the yield of crude product was poor (0.1 g), no attempt was made to purify it. Nmr analysis indicated that the desired compound represented approximately 85% of the crude product: nmr (60 MHz) singlet centered at δ 2.40 (3 H), complex multiplet centered at δ 2.75 (4 H), broad singlet centered at δ 3.50 (2 H), and complex multiplet centered at δ 6.90.

***p*-Fluorobenzyldimethylamine.** *p*-Fluorobenzyl bromide (5.4 g) was converted to *p*-fluorobenzyldimethylamine according to the method outlined by Eliel and coworkers[47] for *p*-methylbenzyldimethylamine. Distillation afforded a colorless oil: bp 60° (17 mm); n^{19}D 1.4832.

***p*-Fluorobenzyl Methyl Sulfide.** *p*-Fluorobenzyl bromide (21.3 g) was treated with thiourea, as outlined by Vogel,[39] to obtain *p*-fluorobenzylmercaptan. Distillation under a nitrogen atmosphere afforded a colorless oil (7.5 g): bp 86° (18 mm). The mercaptan (7.0 g) was converted to the sulfide according to the method outlined by Thomson and Stevens[48] for benzyl methyl sulfide. Distillation afforded a colorless oil (3.5 g), bp 98° (18 mm); n^{22}D 1.5362.

***p*-Fluorobenzyl Methyl Sulfone.** *p*-Fluorobenzyl methyl sulfide (1.13 g, 0.007 mol) was oxidized according to the method described above for 6-fluoro-1,2,3,4-tetrahydro-2-thionaphthalene 2,2-dioxide. Crystallization from methanol afforded the desired sulfone (0.6 g), mp 105°.

***m*-Fluorobenzyldimethylamine** was prepared from *m*-fluorobenzyl bromide (5.48 g) in the same way as the para isomer. The amino formed a colorless oil (1.5 g): bp 80° (25 mm); n^{22}D 1.4828.

***m*-Fluorobenzyl methyl sulfide** was prepared from *m*-fluorobenzyl bromide in the same way as the para isomer. The sulfide was distilled as a colorless oil: bp 86° (17 mm); n^{22}D 1.5378.

***m*-Fluorobenzyl Methyl Sulfone.** *m*-Fluorobenzyl methyl sulfide was converted to the sulfone in the same way as the para isomer. Crystallization from methanol gave mp 98°.

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