Thirdly, the effects in decalin cannot be due to simple electrostatic polarization, for, if they were, one would expect the SCS of the hydroxy- and aminodecalins to change very greatly on passing to the corresponding salts (RO$^-$ and RNH$_3^+$) where a neutral dipole has been replaced by a group with a full formal charge. These changes in fact were small, less than that due to replacement of methylene by carbonyl.

These observations seem to suggest that in this system the effects of substituents on the chemical shifts of fluorine are stereochemical rather than electronic, being due to conformational distortion of the decalin skeleton. This would also account for the large SCS of the axial fluorine in the octalone system. Here the ring containing the fluorine is distorted considerably from a normal chair conformation so that the axial fluorine is forced into rather severe steric interaction with protons in the 8 and 10 positions.

In the work[2] on aryl fluorides, it was shown that substituents apparently exercise two different effects, one involving π polarization, the other a direct electrostatic interaction across space on the C–F bond. The results reported here show, however, that this second effect does *not* involve polarization of the C–F σ bond as was previously[2] assumed. The solution of this apparent dilemma lies in the incorrect assumption that has commonly been made, that the effect of a substituent on an adjacent π system depends on localized interactions (π-inductive or mesomeric) *via* the adjacent atom in the ring. In fact, the electrostatic effects of a charged or polar substituent will extend over the whole of an adjacent conjugated system. When a fluorine atom is attached to a conjugated system, the p electrons of the strongly electronegative fluorine will not normally be delocalized into the π system to any great extent, *i.e.*, the C–F bond will have a π bond order of almost zero and the fluorine atom will have a π charge density close to two. Any polarization of the C–F π bond will therefore involve orbitals that are largely concentrated on fluorine. Consequently, if such a polarization is to be brought about by the direct electrostatic (field) effect of a distant polar group, the dominant factor will be the electrostatic field it sets up at the fluorine atom. The field effect of the earlier paper therefore refers to π polarization, not σ polarization, so no corresponding effect is observed in the case of saturated fluorides.

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Chemical Shifts for Bicyclic Fluorides[1,2]

Sir:

Fluorine chemical shifts may be quite reasonably interpreted within the framework of conventional bond property theory because the paramagnetic term of the Ramsey equation is dominant.[3] This notion and the utility of the magnetic resonance method underlie investigations of substituent effects on ^{19}F resonance.[4] The focus of this work is, quite naturally, directed toward the interpretation of substituent chemical shifts (SCS) for aryl fluorides. Somewhat conflicting views have been expressed concerning the importance of electric field effects on ^{19}F resonance. Thus, Taft[4d–g] has suggested that these effects are small. Dewar, on the other hand, recently proposed that the field effect plays a relatively important role in the determination of the SCS.[4h–j] Emsley, *et al.*,[4k–n] report that the SCS for substituted fluorocarbons are compatible with the electric field theory advanced by Buckingham.[5] Our interest in the origin and transmission of the polar effect[6] prompted this investigation of the influence of sterically remote, unconjugated substituents on the chemical shifts of substituted and unsubstituted bicyclic fluorides.[7] An important feature of the magnetic resonance of bridgehead fluorine atoms is discussed first as a prelude to the interpretation of the substituent effects that were also examined.[8] The results for some *tertiary* fluorides are presented in Table I.

Table I. Chemical Shifts for Some Tertiary Fluorides

Compound	^{19}F chemical shift, ppm[a]
t-Butyl[b]	132
1-Adamantyl[c]	132
1-Bicyclo[2.2.2]octyl[d]	148
1-(4-Carbethoxybicyclo[2.2.2]octyl)[d]	152
1-(4-Carbethoxybicyclo[2.2.2]oct-2-enyl)[d]	164
1-Dibenzobicyclo[2.2.2]octa-2,5-dienyl[d]	191
1-Apocamphyl[d,e]	194

[a] The chemical shifts are reported for the compound in carbon tetrachloride solution relative to fluorotrichloromethane as an external reference. [b] N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963). [c] R. W. Taft, private communication. [d] This study. [e] A sample of this compound was generously provided by P. Beak.

Table II. Chemical Shifts for Derivatives of 1-Fluorobicyclo[2.2.2]octane

4-Substituent	Substituent chemical shift, ppm[a]
H	0.00
CO$_2$C$_2$H$_5$	+4.47
F	+9.23

[a] For carbon tetrachloride.

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(1) Chemistry of the Bicyclo[2.2.2]octanes. VIII. This research was supported by a grant from the National Science Foundation.

(2) We are indebted to M. J. S. Dewar and T. Squires, *J. Am. Chem. Soc.*, **90**, 200 (1968), for delaying publication of their work in order that the results of these parallel studies could appear simultaneously.

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(7) The new compounds were identified and characterized by the mode of preparation, by spectroscopic study, and by microanalysis.

Table III. Substituent Chemical Shifts for Some Anthracene Adducts

	Substituent chemical shift, ppm[a]						
Solvent	OCOCH$_3$	Cl	Br	CO$_2$CH$_3$	CN	NHCOCH$_3$	NO$_2$
			Maleic Anhydride Adducts				
1,4-Dioxane	+0.03	−0.52	−0.87	−0.91	−0.41	−0.50	−0.65
Dimethylformamide	−0.18	−0.57	−0.94	−1.01	−0.43	−0.58	−0.80
Acetone	−0.11	−0.57	−1.00	−1.03	−0.48	−0.66	−0.86
Methanol	*b*	−0.54	−0.91	−0.98	−0.41	*b*	*b*
			Ethylene Adducts				
Carbon tetrachloride	*c*	*c*	−2.00	−2.05[d]	−0.50	*c*	*c*

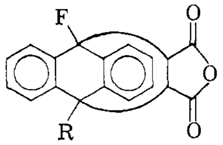
[a] Measured as noted in ref 8. [b] Not sufficiently soluble for measurement. [c] Not examined. [d] The carboxylic acid rather than the ester was examined.

The ^{19}F chemical shifts of these fluorides exhibit a large dependence on the character of the *tertiary* carbon atom. The upfield shifts observed for the more strained compounds are not in accord with the prediction that an increase in the s character of the exocyclic bonding orbital should produce a downfield shift.[9] These upfield shifts are, however, compatible with the idea that the bond order is larger[3] in these strained molecules because there is an important interaction between the nonbonding electrons of the fluorine atom and the endocyclic carbon–carbon bonds with enhanced p character.

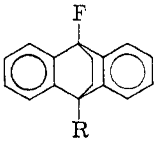
The substituent effects that were observed for the 4-substituted bicyclo[2.2.2]octyl fluorides (I)[10] are presented in Table II.

These data are incompatible with both empirical and theoretical predictions for the polar effect of electron-withdrawing substituents on the chemical shift.[4] However, the positive SCS may be rationalized on the basis of the idea that there is an important repulsive interaction between the more electropositive bridgehead carbon atoms of the disubstituted bicyclic molecules leading to an elongation of the structure and an increase in the p character of the endocyclic carbon–carbon bonds. If future work verifies this suggestion it is evident that ^{19}F resonance may prove valuable for the detection of even modest changes in structure.

The SCS values for the maleic anhydride (II) and ethylene (III) adducts of anthracene were also measured. The results are summarized in Table III.



II



III

Inasmuch as the dibenzobicyclo[2.2.2]octa-2,5-diene skeleton is not easily deformed, we believe that the SCS values presented in Table III reflect the correct sign and magnitude of the polar effects of substituents in this environment. The small shifts are compatible with Buckingham's theory[5] which predicts, for example, that SCS for the 4-chloro and 4-bromo derivatives should be about −0.4 ppm. Although it is evident that other factors must influence the SCS values in these molecules, it seems safe to conclude that polar effects (whether inductive or electric field in origin) have a modest influence on the chemical shifts of the bicyclic compounds.

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The Role of Second Triplet States in Solution Photochemistry. I. Reactions of Rigid Systems Sensitized by Anthracene and Substituted Anthracenes

Sir:

We wish to report here a case of triplet–triplet energy transfer involving the T$_2$ state of the donor molecule.

The donors used in our studies are anthracene and substituted anthracenes. The energy diagram of anthracene[1] is shown in Figure 1. The acceptors used are several rigid systems, **1–4**, which have well-identified unimolecular triplet-state reactions.[2–4] Because of geometric restrictions, it is obvious that "nonvertical" excitations[5,6] involving distortion of the double bonds

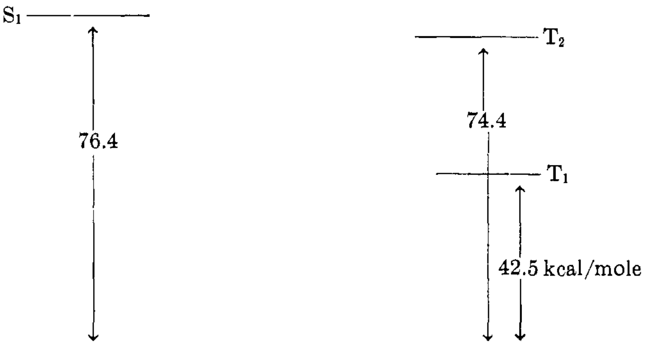
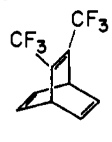
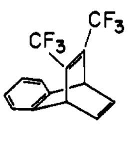


Figure 1. Energy diagram of anthracene.



1



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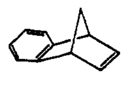

4

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(8) The chemical shifts were determined by the side-band technique with either tetrachlorotetrafluorocyclobutane or hexafluorobenzene as internal references using Varian HR 56 or HA 56-60 equipment.

(9) The smaller chemical shifts for the bridgehead hydrogen atoms in comparable hydrocarbons are in the opposite order: K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and T. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(10) We are indebted to K. Morita and J. C. Kauer for samples of the unsubstituted and 4-fluoro derivatives, respectively.

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