nuclei in the set ("a_H" = $a_{Hg}/\alpha_H{}^{Hg}$). Previously this has involved exhaustive computer application or endor techniques.

Experimental Section

The electrochemical studies were performed as previously described.[1] Electron spin resonance spectra were simulated using a program similar to SESR described by Stone and Maki,[16] with suitable modifications to permit use on the Virginia Polytechnic Institute's Computing Center IBM 360/40-50 with associated Calcomp plotter.

All three isomers of the bis(nitrophenyl)mercury and bis(4-nitronaphthyl)mercury were prepared through symmetrizing of the corresponding RHgCl compound according to the method of Hein.[17] The RHgCl compounds were prepared from the corresponding anilines *via* the mercury diazonium double salt according to Nesmeyanov.[18] The nitrophenylphenylmercury isomers and 4-nitronaphthylphenylmercury were obtained by phenylating the appropriate RHgCl compound with $(C_6H_5)_2SnCl_2$, again according to Nesmeyanov.[19] All of the compounds analyzed correctly for C, H, N.

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(16) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(17) F. Hein and K. Wagler, *Ber.*, **58**, 1499 (1925).

(18) A. N. Nesmeyanov, N. F. Glushnev, P. F. Epifanskii, and A. I. Flegontov in "Selected Works in Organic Chemistry," A. N. Nesmeyanov, Ed., MacMillan Co., New York, N. Y., p 21.

(19) A. N. Nesmeyanov, *et al.*, in ref 18, p 191.

Chemical Shifts for Bicyclic Fluorides[1]

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Abstract: The ^{19}F chemical shifts of four series of bicyclic molecules have been determined. There are major differences in the ^{19}F chemical shifts of fluorine atoms bonded to the bridgehead carbon atoms of different bicyclic molecules. These chemical-shift differences may be related to the change in p character of the endocyclic bonding orbitals of the bridgehead carbon atom. The SCS[2] for 4-substituted-1-fluorobicyclo[2.2.2]octanes are anomalous in the sense that electron-withdrawing groups produce large upfield shifts. These results suggest that substituent-induced structural changes modify the shielding environment of the fluorine nucleus thereby altering the chemical shift importantly. The magnitude of dipolar substituent effects (σ induction, electric field effects, and van der Waals interactions) on the ^{19}F substituent chemical shifts for several other quite rigid bridged anthracene derivatives, II–IV, were determined. The SCS for these molecules are small and negative in accord with the view that structural variations are responsible for the upfield shifts in the octane series. The data for the bridged anthracenes reveal that, for ^{19}F magnetic resonance, substituent effects propagated through σ bonds and through the dielectric medium are much less important than substituent effects propagated through π bonds.

Fluorine nuclear magnetic resonance spectroscopy has been used to study substituent-induced chemical shift (SCS),[2] to assay the substituent's influence on the distribution of electron density, and to unravel the mechanisms by which the substituent alters the distribution of electron density. Studies of this kind are appropriate because, although the theory for the chemical shift is complex,[3] the fluorine chemical shifts are dominated by the paramagnetic term of the Ramsey equation[4] and, as such, are interpretable within the framework of the conventional localized bond model.[5] Several theoretical treatments have been presented for the interpretation of SCS for complex molecules.[5–7] The changes in shielding have been related principally to substituent-induced changes in the ionic character and π bond order of the carbon–fluorine bond and to changes in the hybridization of the bonding oribtal of the fluorine atom.[5] In addition, changes in the π electron density on the carbon atom[6] of the carbon–fluorine bond and on more remote carbon atoms[7] have been reasoned to influence the chemical shift. The Prosser–Goodman treatment for π electron density variations has been coupled with an electric field theory[8a] considering both dipolar electric field and van der Waals contributions to account for SCS in aliphatic and aromatic fluorocarbons.[8b–g]

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(1) Chemistry of the Bicyclo[2.2.2]octanes. IX. . This research was supported by the National Science Foundation, GP-7448. A preliminary report has appeared: G. L. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, **90**, 212 (1968).

(2) The ^{19}F substituent chemical shift (SCS) is defined as the difference between the resonance frequency of a ^{19}F nucleus in a substituted molecule and that of the same nucleus in a molecule in which a hydrogen atom replaces the substituent. Positive values mean that the resonance signal for the substituted compound is upfield of the signal for the hydrogen-bearing reference compound.

(3) (a) W. N. Lipscomb, *Advan. Mag. Resonance*, 2, 137 (1966); (b) J. I. Musher, *ibid.*, 2, 177 (1966).

(4) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 172, 317; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Ltd., Oxford, 1965, Chapters 4 and 11.

(5) M. Karplus and T. Das, *J. Chem. Phys.*, **34**, 1683 (1962).

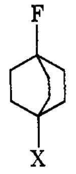
(6) F. Prosser and L. Goodman, *ibid.*, **38**, 374 (1963); (b) R. W. Taft, F. Prosser, L. Goodman, and G. T. David, *ibid.*, **38**, 380 (1963).

(7) M. J. S. Dewar and J. Kelemen, *ibid.*, **49**, 499 (1968).

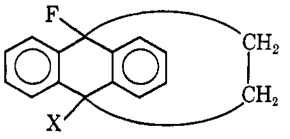
(8) (a) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960); (b) N.

Several empirical relationships have been considered for the correlation of the influence of sterically remote substituents on the ^{19}F chemical shift.[9-11] Taft and Dewar and their associates have concluded that a four-parameter treatment involving separate terms for inductive or dipolar field effects and π electron interactions is necessary.

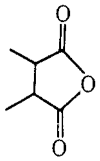
Several different proposals have been advanced to account for the SCS. Often, the net chemical shift has been partitioned into a polar contribution operating through σ bond induction, an electric field effect, or a van der Waals interaction, and into a π electron contribution operating through π induction and resonance effects. Taft has suggested that the polar contribution has an inductive origin, that field effects are responsible for only a small portion of the SCS, and that π electron influences are dominant in the aromatic compounds. Dewar, on the other hand, has proposed that the polar contribution has a field effect origin, that σ induction is negligible, and that polar and π electron contributions are often of comparable magnitude. Emsley and Feeney and their associates, as noted previously, have advocated a theoretical treatment based on combined field and π electron contributions. In their model, the field contribution is assigned a less important role than in the treatment suggested by Dewar and his students. These divergent views concerning the relative magnitude of the contributions from polar and π electron effects exist because data for satisfactory model compounds are unavailable. The studies of halogen-substituted cyclic perfluorocarbons, *e.g.*, perfluorcyclohexene, provide the most pertinent prior information concerning the magnitude of the polar contribution to the ^{19}F SCS.[8b-g,12] This work suggests that, by contrast with π electron contributions, the polar contribution is modest. To establish this point with more confidence for hydrocarbons, we adopted the approach used in earlier studies of the propagation of substituent effects in this laboratory[13] and determined the SCS for 4-substituted 1-fluorobicyclo[2.2.2]octane, I, and three series of bridged anthracenes, II–IV. The geometric relationship between the fluorine atom and the sterically remote, unconjugated substituent in the bridged compounds is very similar to the relationship between these groups in 1,4-disubstituted benzenes. Accordingly, comparisons of the SCS for the aromatic and bicyclic compounds provide an experimental estimate of the relative efficiency of conjugated and unconjugated structures for the propagation of substituent effects important in magnetic resonance.



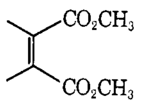
I



II



III



IV

Results

1-Fluorobicyclo[2.2.2]octane and 1,4-difluorobicyclo-[2.2.2] octane were kindly provided by K. Morita and J. C. Kauer, respectively.[14] The methods adopted for the synthesis of the other fluorides will be reported elsewhere.

The ^{19}F chemical shifts were measured as described in the Experimental Section. The results are presented in Tables I–IV.

Table I. ^{19}F SCS for 4-Substituted 1-Fluorobicyclo[2.2.2]octanes[a]

Substituent	SCS, ppm
H	0.00
$CO_2C_2H_5$	+4.47
F	+9.23

[a] In carbon tetrachloride solutions at probe temperature.

Table II. ^{19}F SCS for Ethylene Adducts (II)

4-Substituent	SCS,[a] ppm
H	0.00
Br	−2.00
CN[b]	−0.50
COOH[b]	−2.05

[a] In carbon tetrachloride solution at probe temperature. [b] These compounds were available from a previous study.[13c]

Table III. ^{19}F SCS for Maleic Anhydride Adducts (III)

	SCS, ppm			
4-Substituent	1,4-Dioxane	DMF	Acetone	Methanol
H	0.00	0.00	0.00	0.00
Br	−0.87	−0.94	−1.00	−0.91
Cl	−0.52	−0.57	−0.57	−0.54
$COOCH_3$	−0.91	−1.01	−1.03	−0.98
CN	−0.41	−0.43	−0.48	−0.41
NO_2	−0.65	−0.80	−0.86	Ins[a]
$NHCOCH_3$	−0.50	−0.58	−0.60	Ins
$OCOCH_3$	+0.03	−0.18	−0.11	Ins
F	+0.58	+0.58	+0.55	Ins
OCH_3	+0.26	+0.28	+0.28	Ins

[a] Ins = Insoluble.

Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Mol. Phys.*, **8**, 133 (1964); (c) N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *ibid.*, **8**, 467 (1964); (d) J. W. Emsley, *ibid.*, **9**, 381 (1965); (e) J. Feeney, L. H. Sutcliffe, and S. M. Walker, *ibid.*, **11**, 117, 129, 137, 145 (1966); (f) J. W. Emsley and L. Phillips, *ibid.*, **11**, 437 (1966); (g) K. L. Williamson and B. A. Braman, *J. Amer. Chem. Soc.*, **89**, 6183 (1967).

(9) (a) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951); (b) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, 74, 4809 (1952); (c) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(10) (a) R. W. Taft, *J. Amer. Chem. Soc.*, **79**, 1045 (1957); (b) R. W. Taft, E. Price, I. R. Fox, I. E. Lewis, K. K. Anderson, and G. T. David, *ibid.*, **85**, 709 (1963); (c) *ibid.*, **85**, 3146 (1963); (d) R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2489 (1965); (e) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, 6, 147 (1968); (f) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 5236 (1968).

(11) (a) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966); (b) M. J. S. Dewar and W. Adcock, *ibid.*, **89**, 379 (1967); (c) M. J. S. Dewar and Y. Takeuchi, *ibid.*, **89**, 390 (1967); (d) M. J. S. Dewar and T. Squires, *ibid.*, **90**, 200 (1968); (e) Y. Takeuchi, *Sci. Papers Coll. Gen. Educ. Univ. Tokyo*, **16**, 231 (1966); (f) *ibid.*, **17**, 53 (1967).

(12) Contemporary contributions are treated in the discussion.

(13) (a) H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86**, 5188 (1964); (b) R. Golden and L. M. Stock, *ibid.*, **88**, 5928 (1966); (c) F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967).

(14) (a) Z. Suzuki and K. Morita, *J. Org. Chem.*, **32**, 31 (1967); (b) J. C. Kauer, Central Research Department, du Pont Company.

Table IV. ^{19}F SCS for Dimethyl Acetylenedicarboxylate Adducts (IV)

4-Substituent	SCS, ppm 1,4-Dioxane	DMF	Acetone	Methanol
H	0.00	0.00	0.00	0.00
Br	−0.71	−0.69	−0.72	−0.88
NO_2	−1.62	−1.68	−1.55	−1.83
CN	−0.49	−0.88	−0.70	−0.89
$OCOCH_3$	−0.36	−0.29	−0.18	−0.42
OCH_3	−0.14	−0.09	−0.09	Ins[a]

[a] Ins = Insoluble.

Discussion

Bridgehead ^{19}F Chemical Shifts. The bicyclic fluorides, as discussed, were studied to assess the influence of sterically remote, unconjugated substituents on the chemical shift. Because the results for the bicyclo[2.2.2]octyl fluorides are quite unusual, the equally remarkable chemical shifts for unsubstituted bicyclic *tertiary* fluorides, Table V, will be discussed first.

Table V. ^{19}F Chemical Shifts for Some Tertiary Fluorides

Tertiary fluoride	Chemical shift, ppm[a]
t-Butyl[b]	132
1-Adamantyl[c]	132
1-Bicyclo[2.2.2]octyl[d]	148
1-(4-Carboethoxybicyclo[2.2.2]octyl)[d]	152
1-(4-Carboethoxybicyclo[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 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] This compound was generously provided by P. Beak.

Important changes in the ^{19}F chemical shifts in this set of *tertiary* fluorides result from apparently modest differences in structure. The proton chemical shifts for the bridghead hydrogen atoms in the corresponding bicyclic hydrocarbons are considerably smaller and, when comparable, in the opposite order.[15] The difference in the proton chemical shift between bicyclo[2.2.2]octane and bicyclo[2.2.1]heptane has been related, in part, to the altered electron distribution in the carbon–hydrogen bond resulting from the increased s character of the exocyclic bonding orbital of the bridgehead carbon atom of the heptane.[16] The large increase in ^{19}F chemical shift from *t*-butyl fluoride to apocamphyl fluoride has, we believe, a similar origin. The enhanced s character of the exocyclic bonding orbital should, just as for hydrogen, cause a downfield shift in the fluorine resonance. However, the p character of the endocyclic bonding orbitals of the bridgehead carbon atoms increases proportionately and the ^{19}F chemical shift depends in a most important way on the π bond order.[5–7,17,18] Consequently, the observed chemical shifts for the fluorides may quite reasonably be ascribed to a change in bond order resulting from the interaction between the nonbonding orbitals of the fluorine atom and the endocyclic carbon–carbon bond orbitals with enhanced p character.[19]

SCS for Bicyclo[2.2.2]octanes. The most unusual SCS for 4-substituted 1-fluorobicyclo[2.2.2]octanes are presented in Table I. Similar large upfield chemical shifts induced by electron-withdrawing substituents have been detected by other investigators. The SCS for 1-fluoro-3-carbomethoxy- and 1,3-difluoroadamantane are 3.6 and 5.0 ppm, respectively.[22] Some hydroxy derivatives of *n*-alkyl fluorides and their esters also exhibit positive SCS in fluorotrichloromethane that are enhanced in trifluoroacetic acid solution.[23] Observations of this kind are incompatible with the expectations of traditional theories concerning the influence of electron-withdrawing substituents on the chemical shift. These theories predict that such substituents should deshield the test nucleus and cause a downfield shift.[24] Accordingly, the large positive SCS are probably not the consequence of a simple dipolar substituent effect. Rather, the important structural dependence of the chemical shifts of the unsubstituted bicyclic fluorides, discussed in the previous section, and the finding that substituents do measurably alter the structure of bicyclo[2.2.1]heptane[16,25] suggest that the large positive SCS are more reasonably assigned to a substituent-induced structural change that alters the shielding environment of the fluorine nucleus, perhaps through the enhancement of the carbon–fluorine bond order. To illustrate, if the distance between C_1 and C_4 in difluorobicyclo[2.2.2]octane were greater than the distance between these nuclei in 1-fluorobicyclo[2.2.2]octane, then the p character in the endocyclic bonding orbitals of the bridgehead carbon atom would increase with an attendant increase in bond order and an unfield shift. Similar interpretations can be advanced for the other upfield SCS.[23] Should this idea prove correct then ^{19}F SCS

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(15) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and T. Tanida, *Can. J. Chem.*, 42, 926 (1964).

(16) Precise structural work (electron diffraction) indicates that the sum of the three internal skeletal angles for bicyclo[2.2.1]heptane ($C_6C_1C_2$, $C_6C_1C_7$, $C_7C_1C_2$) is 308° compared to 328.5° for a tetrahedral arrangement. This result is in accord with the view that the exocyclic bonding orbital of the bridgehead carbon atom has more s character than that of a tetrahedral array: J. F. Chaing, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, 90, 3149 (1968).

(17) The chemical shift for fluoroacetylene, 261 ppm relative to $CFCl_3$, illustrates this dependence; ref 4b, p 916.

(18) Karplus and Das[5] conclude that a unit increase in π bond order would contribute an upfield shift of 770 ppm.

(19) Datum for a *tertiary* fluorine atom of a cyclopropane, *e.g.*, 1-fluoro-1-methylcyclopropane, is unavailable. However, the approximate chemical shifts, relative to fluorotrichloromethane for the *secondary* fluorine atoms of *exo* and *endo*-7-fluoronorcarane, are 217 and 238 ppm, respectively,[20] compared to about 170 ppm for cyclohexyl fluoride.[21]

(20) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, *J. Amer. Chem. Soc.*, **89**, 5719 (1967).

(21) K. Ito, K. Inukai, and T. Isobe, *Bull. Chem. Soc. Jap.*, **33**, 315 (1960).

(22) R. W. Taft, private communication.

(23) P. E. Peterson, R. J. Bopp, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **91**, 1251 (1969).

(24) The more recent charge alternation theory for the σ inductive effect (J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967)) also fails to accommodate the data. This theory, qualitatively, suggests that the signals for the difluorooctane and fluorocarboethoxyoctane should appear, respectively, at higher and lower field than the signal for the unsubstituted fluorooctane. The opposite order should obtain for the adamantanes. Further, the observed SCS appear far greater than could be accommodated by the σ bond induction model with its large attenuation factor.

(25) Although it is well established that the structures of small carbon compounds depend importantly on the nature of the ligands, *e.g.*, fluoromethane compared to difluoromethane,[26] long-range substituent-induced structural perturbations have not yet been systematically studied.

(26) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 1.

may be a very valuable probe for the detection of even very modest changes in structure.

SCS for Bridged Anthracenes. The data for the ethylene (II), maleic anhydride (III), and dimethyl acetylenedicarboxylate (IV) adducts are summarized in Tables II–IV.[27]

The approach adopted for the experimental definition of the polar contribution to the SCS centered on the study of a fluoride with a fixed structure, geometrically similar to fluorobenzene. The bicyclo[2.2.2]octanes yield anomalous results indicating that caution is necessary in the selection of a model compound and in the interpretation of the results. The anthracene adducts with bridging benzene nuclei should, in principle, be much less subject to substituent-induced structural perturbations because the positions of many nuclei linked by strong bonds must be altered to effect a change in geometry.[28] This consideration and the observations obtained in this study and other recent studies suggest that the SCS for the acetylene adducts do portray the polar interactions that would be realized in a rigid molecule, such as benzene.

Several lines of evidence support this conclusion. First, there is a major decrease in the magnitude of the SCS for all the anthracene adducts compared to the SCS for the bicyclo[2.2.2]octanes. Second, the SCS show a small dependence on the nature of the adduct with more negative values detected for the dimethyl acetylenedicarboxylate adducts than for the anhydrides. This sensitivity is most apparent for the nitro group with SCS about -0.7 ppm for the anhydride and about -1.7 ppm for the acetylene adduct. For the methoxy group, the SCS is positive (0.28 ppm) in the anhydride series and negative (-0.1 ppm) in the acetylene series. Thus, in the least easily deformed acetylene series, the dipolar contribution of the methoxy group is apparently realized. Third, the data for the acetylene derivatives are in the order predicted by the conventional polar substituent constants for aliphatic molecules, *e.g.*, σ_I[10] and F.[11] Fourth, other investigators have also found small SCS in compounds with the test nucleus and the substituent in an unconjugated configuration. Dewar and Squires observed that substituents in the 6 position of *trans*-decalin had only a minor influence on the chemical shift of axial and equatorial fluorine nuclei in the 1 position.[11d] Della reported that the SCS for *cis*-3-substituted 1-trifluoromethylcyclohexanes are small and negative for several electron-withdrawing substituents.[29] Gale and Krespan similarly reported that the SCS for *meta*- and *para*-substituted α,α-ditrifluoromethylbenzylamines, alcohols, and fluorides were small and in a conventional order.[30] These facts suggest that the SCS for the acetylene-bridged anthracenes accurately portray the influence of remote unconjugated dipolar groups.

Several interactions including magnetic anisotropy, σ inductive effects of both the traditional and alternate form, dipolar field effects, and van der Waals contributions deserve consideration in the interpretation of the data for series IV. Cogent arguments against a significant long-range σ inductive contribution to the SCS have been made by Dewar and his students.[11] These convincing arguments need not be repeated. Magnetic anisotropy contributions should not differ appreciably for hydrogen and fluorine nuclei. Any important contribution from this source may be confidently excluded on the basis of the extremely small proton SCS observed for the bridgehead hydrogen atoms of 4-substituted dibenzobicyclo[2.2.2]octa-2,5-dienes, Table VI.

Table VI. Proton SCS for Some 4-Substituted Dibenzobicyclo[2.2.2]octa-2,5-dienes[a]

4-Substituent	SCS, ppm[b]
H	0.00
$COCH_3$	-0.022
Br	-0.037
CN	-0.072
NO_2	-0.063

[a] R. C. Parish, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1965. [b] In carbon tetrachloride with tetramethylsilane as internal reference.

A quantitative theory has been advanced for the influence of sterically remote substituents based on dipolar electric field effects and van der Waals interactions.[8] The viewpoint of this theory is expressed in eq 1 where A and B are parameters defined, in part, by

$$\text{SCS} = A\Delta E_Z - B(\Delta E^2 + \Delta\langle E^2\rangle) \qquad (1)$$

experiment, E_Z is the component of the field acting along the carbon–fluorine bond direction, E^2 is the square of the total electric field at the fluorine nucleus arising from point dipoles placed at the center of any polar bonds in the molecule, and $\langle E^2\rangle$ is estimated by eq 2

$$\langle E^2\rangle = \sum_i 3P_iI_i/r_i^6 \qquad (2)$$

where P_i is the polarizability of the electron group, I_i is the first ionization potential, and r_i is the distance between the bond moment and the fluorine nucleus. The theory has enjoyed good success in the interpretation of the data for fluorocarbons.[8] The calculated[31] SCS for the halogen derivatives of the bridged anthracene are between -0.2 and -0.4 ppm, somewhat less, in magnitude, than the experimental results which are between -0.5 and -1.0 ppm.

In summary, the SCS for the bridged anthracenes, in particular the acetylene adducts, offer a close estimate of the influence of remote groups on the ^{19}F chemical shift in the absence of π electron interactions and substituent-induced structural changes. The magnitude of the SCS is quite small, smaller than estimated by the empirical field model developed by Dewar and his students[11] but larger than estimated by the combined field effect–van der Waals effect model based on Buckingham's theory.[8] If the Pople formulation for the inductive effect is qualitatively correct,[4a] then induction can be excluded from consideration. However, if the traditional formulation for this effect is correct, then a contribution from this source, although unlikely,[11] is not excluded by the

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(27) The SCS for the anhydrides, Table III, are virtually solvent independent. The small, irregular solvent effects observed for the acetylenes, Table IV, will not be discussed.

(28) The problem is discussed by G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967). These authors note that the bending-force constant for CCH is greater for aryl carbon atoms and least for tetrahedral carbon atoms. The bending force constants for three-carbon fragments, *e.g.*, $CCCH_3$, are not yet established with confidence.

(29) E. W. Della, *Chem. Commun.*, 1558 (1968).

(30) D. M. Gale and C. G. Krespan, *J. Org. Chem.*, 33, 1002 (1968).

(31) Calculated from eq 1 and 2 using the parameters adopted in previous applications;[8] see also ref 4b, p 139. For the purpose of this calculation, it was assumed that the key component oft he bridged anthracene, $F–C_1\cdots C_4–X$, was colinear with a C_1C_4 distance of 2.5 Å; see ref 13c.

data. Most important, however, is the establishment of the modest magnitude of ^{19}F SCS in the absence of a conjugated π electron system.[11d,29]

Experimental Section

^{19}F Chemical Shift Measurements. Reagent grade solvents were used without further purification. 1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB), obtained from Peninsular Chemresearch, Inc., Gainsville, Fla., was used without further purification. Hexafluorobenzene (HFB) was purified by distillation.

Measurements were made with Varian HR 56 and A56-60 instruments at 56.4 Mc on dilute solutions of the compound at probe temperature. Since most compounds are only slightly soluble in the solvents used, the chemical shift represents the intramolecular SCS at infinite dilution.

A side band on the internal reference was placed less than 200 cps from the desired signal. The frequency of the output signal was monitored electronically. The spectrum was swept in both upfield and downfield directions. The chemical shift, measured from the side band to the center of the signal plus the frequency of the side band, was taken as the average of the several upfield and downfield measurements.

The chemical shifts of the substituted compounds were referenced to the parent compounds in each series to define the SCS ($SCS_X = CS_X - CS_H$), where X represents the substituent, and CS_X and CS_H represent the chemical shift in ppm of the substituted and unsubstituted compounds relative to the internal reference (TCTFCB or HFB). In actual measurements TCTFCB and HFB were used as internal references for the 10-substituted 9-fluoroanthracenes and the bridged anthracenes, respectively. The maximum estimated error is 0.03 ppm and actual error is probably much less. It was demonstrated that the SCS agreed within less than 0.03 ppm when the parent compound was used as an additional internal reference.

Mass Spectrometry in Structural and Stereochemical Problems. CLXXIX.[1] The Electron Impact Induced Rearrangements of 1-Phenylheptenes. Further Evidence for Double Bond Lability[2]

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Abstract: The mass spectra of a series of isomeric 1-phenylheptenes have been measured. Evidence for extensive hydrogen and even phenyl rearrangement ions has been uncovered through the use of deuterium and ^{13}C-labeled analogs. Mass spectrometry is not a very useful tool for differentiating between such double bond isomers due to the ease of double bond migration after ionization.

During the course of our investigation into the electron impact induced rearrangements of organic compounds we observed that the mass spectra of a series of isomeric 1-phenylheptenes (I–V) exhibited many similar features (Figures 1–5).

This type of behavior seems typical of isomeric monoolefins in general, and there have been several reports attesting to similarities in the mass spectral fragmentation pattern of esters of unsaturated fatty acids,[4] isomeric menthenes,[5] phenylpropylenes,[6] and pentenes.[7] The phenomenon has been attributed to hydrogen rearrangements which result in a common mixture of molecular ions.[8] The mode of these rearrangement processes is not entirely clear and mechanisms involving 1,2-hydrogen,[9] 1,3-hydrogen,[10] and even more distant hydrogen shifts[11] have been invoked to explain the mass spectrometric behavior of simple olefins. In view of this diversity of mechanistic pathways, we have synthesized several isotopically labeled analogs of I and II (Table I) and examined their behavior upon electron

Table I. Comparison of Mass Shifts Encountered in the Isotopically Labeled Compounds for the *m/e* 117 Peak

Compd no.	Compound	% *m/e* 117 which shifts to[a] 117	118	119	120
VI	2,4,6-d_3-$C_6H_5CH{=}CHC_5H_{11}$			6	94
VII	$C_6H_5CH{=}CHCH_2CD_2C_3H_7$	95	5		
VIII	2,4,6-d_3-$C_6H_5CH_2CH{=}CHC_4H_9$			6	94
IX	$C_6H_5CD_2CH{=}CHC_4H_9$		12	88	
X	$C_6H_5CH_2CH{=}CHCD_2C_3H_7$	91	9		
XI	$C_6H_5CH_2CD{=}CDC_4H_9$		17	83	
XII	$C_6H_5{}^{13}CH_2CH{=}CHC_4H_9$	2	98		

[a] All the compounds have been corrected to 100% isotopic purity and the mass shifts calculated, after correcting for natural ^{13}C abundance, utilizing both the labeled and unlabeled mass spectra. Because of the errors in the mathematical procedure the results in the tables are considered to be only accurate to within 6% (J. Trudell Ph.D. Thesis, Stanford University, 1969).

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[1] For paper CLXXVIII, see K. Strong, P. Brown, and C. Djerassi, submitted for publication.

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[3] Postdoctoral Research Fellow, 1968–1969.

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