by about one part in 55,000. Summing the species having the same nominal mass leads to an isotopic distribution in fairly close agreement with that measured at low voltage[21] on a CEC Model 21-103 instrument, and the sum of the d_3 species agrees with that found by low-voltage low-resolution measurement on the benzene prepared from unlabeled maleic anhydride, 4.3%. Thus the analysis shown seems to be reasonably accurate.

Table II shows the observed isotopic distribution of $C_4H_4\cdot^+$ ions and the distribution calculated for cases I, II, and III from benzene with the isotopic composition listed in Table I. Table III shows the corresponding distributions of $C_3H_3^+$. The observed values are all averages of three measurements; the stated uncertainties are average deviations. Two conclusions can be drawn within the uncertainty limits of the experiment.

(1) The presence of $C_4H_4\cdot^+$ and $C_3H_3^+$ ions of nominal mass greater than 56 and 42, respectively, requires contributions from processes corresponding to case II, case III, or both. In view of the recently reported results on $C_4H_4\cdot^+$ ions from benzene-*1,3,5*-$^{13}C_3$[16] case III is preferred over case II.

(2) The yields of $^{12}C_4D_4\cdot^+$, $^{13}C_2{}^{12}CH_2D^+$, $^{13}C^{12}C_2HD_2^+$, and $^{12}C_3D_3^+$ are almost certainly greater and those of $^{12}C_3H_2D^+$, $^{12}C_3HD_2^+$, and $^{13}C^{12}C_2D_3^+$ less than can be accounted for by case II or III and therefore require contributions from processes corresponding to case I as well. The data permit a rough estimate of 30% for the fraction of $C_3H_3^+$ and—though with less confidence—$C_4H_4\cdot^+$ ions that arise by paths in which the carbon atoms are scrambled without breaking the carbon–hydrogen bonds. In the remaining 70%, the hydrogens are scrambled over and beyond whatever carbon scrambling may occur.[23a]

Further work on this system is in progress.

[23a] NOTE ADDED IN PROOF. A mass spectral study of scrambling in benzene-*1*-^{13}*C*-*1*-*d* was reported by D. H. Williams at the Fifth Triennial International Mass Spectrometry Conference, Brussels, Aug 31–Sept 4, 1970 (*J. Chem. Soc.*, in press). He reported that isotopic distributions derived from metastable-peak intensities indicate complete randomization of the carbons and hydrogens independently in the path $C_6H_6\cdot^+ \rightarrow C_4H_4\cdot^+ + C_2H_2$. The difference between our results and those on benzene-*1*-^{13}*C*-*1*-*d* and benzene-*1,3,5*-$^{13}C_3$[16] presumably reflects the difference in the lifetimes of the decomposing ions leading to normal and metastable peaks.

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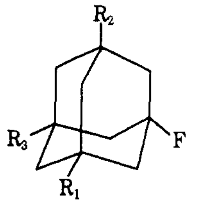
Alkyl Group Substituent Effects in the Adamantane System. Fluorine-19 Chemical Shifts

Sir:

There has been considerable controversy regarding the electronic effect of alkyl groups attached to sp^3-hybridized carbon atoms.[1] For example a methyl group at the 3 position retards the rate of solvolysis of 1-bromoadamantane,[2] thus apparently withdrawing electron density from the adamantane ring. However, Gleicher, *et al.*,[3] have presented data from radical abstraction reactions which indicate that the methyl group may also be electron donating in the adamantane system. In other systems there is additional confusion.[1]

We wish to present the results of our study of the ^{19}F nmr spectra of a variety of alkyl-substituted 1-fluoroadamantanes (I) which bear directly on this question. We chose ^{19}F nmr spectroscopy because the great range of chemical shifts usually encountered often makes possible the discrimination of subtle environmental differences. In this connection, several recent studies are pertinent.[4-6] All compounds[7] were prepared from the corresponding bromides by reaction with silver(I) fluoride in refluxing cyclohexane.[8] Our ^{19}F nmr results are collocated in Table I.



I

The most striking feature of the data is the large *shielding* effect exhibited by the methyl group. The value of +2.8 ppm should be compared with +3.6 and +5.0 ppm found for –CO$_2$R and –F as substituents in the same system.[9] This methyl effect is additive as

Table I. Fluorine-19 Nmr Chemical Shifts of Alkyl-Substituted 1-Fluoroadamantanes (I)

R_1	R_2	R_3	Chemical shift[a]	SCS[b]
H	H	H	130.0	0.0
CH_3	H	H	132.79	2.79 (2.79/CH_3)
CH_3	CH_3	H	135.29	5.29 (2.65/CH_3)
CH_3	CH_3	CH_3	137.78	7.78 (2.60/CH_3)
C_2H_5	H	H	132.29	2.29
i-C_3H_7	H	H	131.25	1.25
tert-C_4H_9	H	H	130.15	0.15

[a] Chemical shifts are in parts per million upfield from internal $CFCl_3$ in dilute CCl_4 solution measured at 56.4 or 94.3 MHz using the side-band modulation technique and reading shifts directly from an H–P 5212-A frequency counter. Precision was always better than ±0.05 ppm. Separate experiments showed that concentration variation had virtually no effect on the observed shift. [b] Substituent chemical shift = (chemical shift of compound) − (chemical shift of 1-fluoroadamantane).

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(1) An excellent discussion of the problem may be found in: C. W. Woodworth, Ph.D. Thesis, Princeton University, Princeton, N. J., 1969.

(2) R. C. Fort, Jr., and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 4194 (1964); P. von R. Schleyer and C. W. Woodworth, *ibid.*, **90**, 6528 (1968).

(3) P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *ibid.*, **90**, 4122 (1968).

(4) M. J. S. Dewar and T. G. Squires, *ibid.*, **90**, 210 (1968).

(5) G. L. Anderson and L. M. Stock, *ibid.*, **90**, 212 (1968); **91**, 6804 (1969).

(6) J. B. Dence and J. D. Roberts, *ibid.*, **91**, 1542 (1969).

(7) All new compounds gave satisfactory analytical data.

(8) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

(9) P. von R. Schleyer and R. W. Taft, Jr., unpublished results.

seen from the data for the di- and trimethyl derivatives. This large shift produced by distant methyl groups is all the more remarkable in light of the report of Hooper, Sheppard, and Woodman[10] that the fluorine chemical shift of the 1-fluoroalkanes from 1-fluoropropane through 1-fluoroheptane varies by less than ±0.4 ppm.

Another unusual feature of our data is the continuous *decrease* in shielding exhibited by the alkyl group as the hydrogens of the methyl group in the 3 position are successively replaced by other methyl groups. A plot of the shielding effect observed *vs.* the number of δ-methyl hydrogens[11] is linear and exhibits a correlation coefficient of 0.9977. Thus, hyperconjugation as a possible explanation of this *ground-state phenomenon* is implicated, contrary to the results of the solvolysis studies.[2] Furthermore, the order of apparent electron release observed (*i.e.*, Me > Et > *i*-Pr > *tert*-Bu) is exactly the reverse of that observed by Schleyer.

That our data may be explained *simply* by electron release of the alkyl group *via* hyperconjugation is however unlikely since the alkyl-group effect has the same sign as that of the "classical" electron-withdrawing fluoro and alkoxycarbonyl groups.[9] Stock's suggestion[5] of "substituent-induced structural changes" which modify the shielding environment of the fluorine nucleus is therefore the most likely explanation, albeit the least informative.

We are continuing our investigation of this and the related bicyclo[2.2.2]octyl system and defer a more complete discussion to the full paper.

Acknowledgment. We are grateful to Professor Paul von R. Schleyer for generously supplying starting materials. Valuable communications with Professors P. von R. Schleyer, L. M. Stock, J. D. Roberts, and R. W. Taft, Jr., are acknowledged with pleasure.

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[10] D. L. Hooper, N. Sheppard, and C. M. Woodman, *J. Mol. Spectrosc.*, 24, 277 (1967).

[11] *E.g.*, 3-methyl-1-fluoroadamantane has 3; 3-ethyl has 2; and, 3-*tert*-butyl has none.

Additions and Corrections

Vibrational Effects in the Xylenes [*J. Amer. Chem. Soc.*, **91,** 7585 (1969)]. By W. Albert Noyes, Jr., and D. A. Harter, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

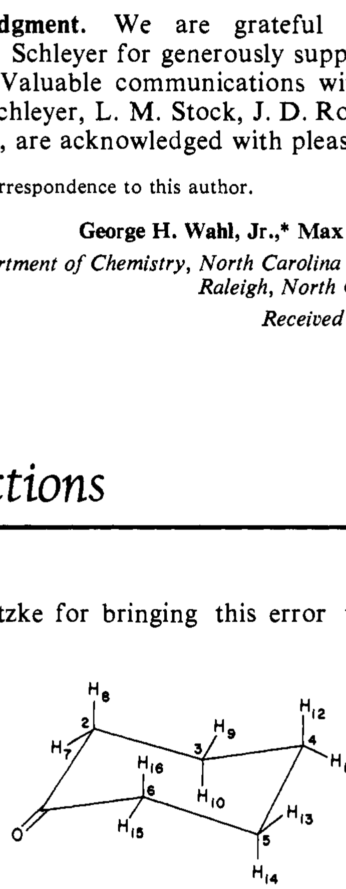
In Table IV, the fourth column under *p*-xylene, the decimal point was displaced and the four values should be 4.3, 3.4, 3.1, and 2.9, respectively.

Formation and Spectrum of Tetracyanoethylene Dimer Anion $(TCNE)_2^-$ [*J. Amer. Chem. Soc.*, **92,** 886 (1970)]. By M. Itoh, Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago, Illinois 60637.

Interpretation of the formation of the dimer anion is unfortunately incorrect, and the anion dimer, $(TCNE^-)_2$, may be formed in that experimental condition, because further investigations of epr and absorption spectra of $TCNE^-,M^+$ (Na, K, and Cs) both in the solution and in the solid state show the formation of the anion dimer of which detail will be submitted to the journal in the near future. Concentration dependence of the visible absorption spectra on pages 887–888 can be also interpretated in the monomer–dimer equilibrium (see ref 7 on page 886).

The Direct Calculation of Optical Rotatory Strengths [*J. Amer. Chem. Soc.*, **92,** 1813 (1970)]. By Roy R. Gould and Roald Hoffmann, Department of Chemistry, Cornell University, Ithaca, New York 14850.

The cyclohexane figure on page 1815 is incorrect. The correct figure, the one to which the calculations in the text refer, is shown below. We are grateful to Dr. G. Snatzke for bringing this error to our attention.



Activation Volumes for Combination and Diffusion of Geminate *t*-Butoxy Radicals [*J. Amer. Chem. Soc.*, **92,** 2440 (1970)]. By Robert C. Neuman, Jr., and Robert J. Bussey, Department of Chemistry, University of California, Riverside, California 92502.

In Table IV, the rate constant ratios k_c/k_d should read k_d/k_c in both the title and column heading.

Determination of Molecular Geometry by Quantitative Application of the Nuclear Overhauser Effect [*J. Amer. Chem. Soc.*, **92,** 3266 (1970)]. By Roger E. Schirmer, Joseph H. Noggle, Jeffrey P. Davis, and Phillip A. Hart, Department of Chemistry and the School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706.

Equation 8 is incorrect and should read

$$0.36a_8 + 0.41\langle r_{2'8}{}^{-6}\rangle - 0.14\langle r_{1'8}{}^{-6}\rangle = 0 \qquad (8)$$

Due to an arithmetic error, Table II is incorrect and should read as shown below.