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 Woodman¹⁰ 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 hydrogens¹¹ 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

(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.

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 suggestion⁵ 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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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 ROB-ERT 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. Schir-MER, JOSEPH H. NOGGLE, JEFFREY P. DAVIS, and PHIL-LIP A. HART, Department of Chemistry and the School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706.

Equation 8 is incorrect and should read

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

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