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.

George H. Wahl, Jr.,* Max R. Peterson, Jr.
Department of Chemistry, North Carolina State University
Raleigh, North Carolina 27607

Received August 15, 197

---

[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.

* Address correspondence to this author.

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.

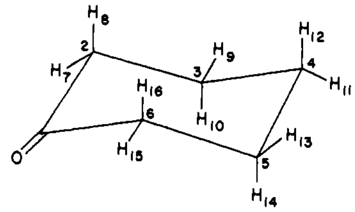
In Table IV, the fourth column under *p*-xylene, the decimal point was displaced and the four values should be 4.3, 3.4, 3.1, and 2.9, respectively.

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.

Table II. Comparisons of Internuclear Distances in Models with Calculated Results

	$\theta = 0°$ [a]		$\theta = 35°$ [a]		
Distance	Measured on model, Å	Calcd from exptl ratios, Å	Measured on model, Å	Calcd from exptl ratios, Å	Calcd from exptl ratios, Å
$r_{1'2'}$	2.8	. . .	2.9	3.2	. . .
$r_{1'8}$	2.5	2.3	2.6	. . .	2.4
$r_{2'8}$	3.7	3.4	4.6	3.8	3.5

[a] θ is the angle between the glycosidic bond and its projection on the plane of the base. In the second case, the plane of the base is tilted away from the ribose.

The left-hand side of eq A4 should read f_i^d, and the fourth line following eq A4 should read: and $f_i^j = (\langle I_{zj}\rangle - I_{0j})/I_{0j}, \ldots$

A Classical 7-Norbornenyl Cation. Competition between Aryl and Alkenyl Functions in Stabilizing 7-Aryl-7-norbornenyl Cations [*J. Amer. Chem. Soc.*, **92**, 3783 (1970)]. By Herman G. Richey, Jr., James D. Nichols, Paul G. Gassman, Allison F. Fentiman, Jr., S. Winstein, M. Brookhart, and R. K. Lustgarten, Department of Chemistry, University of California, Los Angeles, California 90024.

Footnote *f* of Table I should read: Resembles a triplet, spacing between absorptions ~2 Hz.

Nuclear Magnetic Resonance Contact Shifts of Some Binuclear Iron(III) Phenanthroline Complexes [*J. Amer. Chem. Soc.*, **92**, 4141 (1970)]. By Mark Wicholas, Department of Chemistry, Western Washington State College, Bellingham, Washington 98225.

The sentence immediately following Table I should read: Here, save for the 2,9-proton resonance, the half-widths in $[Fe_2(phen)_4O]Cl_4$ are between 50 and 200 Hz.[9]

Book Reviews

A Handbook of Alkaloids and Alkaloid-Containing Plants. By Robert F. Raffauf, College of Pharmacy, Northeastern University, Boston, Mass., in association with Smith Kline and French Laboratories, Philadelphia, Pa. Wiley-Interscience, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1970. 16 × 23.5 cm. $50.00.

The explosive growth of knowledge in the area of alkaloid chemistry during the last twenty years has been attended by many reviews, monographs, and treatises, by which the needs of inquirers wishing to learn the chemistry of most groups of alkaloids are well served. It has been less easy to explore the relationships between alkaloids and the plants they occur in, or to document the known occurrences of alkaloids throughout the plant kingdom. This book has been compiled to fill this gap and should be a valuable reference text for alkaloid chemists, phytochemists, and others in the field.

The first section of the book is a listing of alkaloids in alphabetical order of the plant families in which they occur. In this section the molecular formula, molecular weight, melting point, optical rotation, and literature reference are given for each alkaloid. Here the net has been cast widely, and "alkaloids" include peptide-like compounds and simple nitrogenous natural products; moreover, the occurrence of compounds like bufotenine in both plants and animals is shown. Then follows an alphabetical listing of the alkaloids with synonyms, referred back to the first section. An alphabetical listing of plant genera and the alkaloids produced within each genus is given next, followed by lists arranged by molecular formula and molecular weight. Two sections then follow in which the alkaloids are listed, again by genera in which they are found, and structures are given for them. The great variety of structures has been organized by referring each alkaloid to a basic skeletal formula in the second of these sections, and indicating with each reference in the first the variations to be made on that skeleton to give the structural formula of the alkaloid. The structures do not include stereochemical information. Some errors have crept in; for example, in the *Alstonia* alkaloid section the structure for macralstonidine is incorrect and that for macralstonine is missing; but a very great deal of information has been arranged and made readily accessible. The bibliography of 2076 references, in which the standard texts by Henry, Manske and Holmes, Boit, and Willaman and Schubert are all encompassed in reference 1, is the last section. The literature is covered through mid-1968.

This book clearly meets a real need, and should be found in every library reference section on natural products. It will also be valuable to specialists in the field.

P. W. Le Quesne
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104