In Support of Anionic Hyperconjugation.
The Versatile Methyl Group

Sir:

The direction of secondary isotope effects on the rates of solvolytic reactions proceeding through carbenionic transition states has been ascribed to hyperconjugation. In the language of perturbation molecular orbital theory, interaction of the highest filled, \( \pi \) symmetry, orbital on a methyl (CD\(_3\)) group with the vacant \( \pi^* \) function at C\(^+\) results not only in net energetic stabilization but also in significant charge reorganization. Specifically, electron density is removed from the methyl CH linkages, resulting in their weakening. The associated reduction in CH stretching force constants leads directly to the observed kinetic and thermodynamic preference for formation of the light cation.

In this communication we present experimental and theoretical evidence in support of the notion that hyperconjugative factors are also operative in the interaction of anionic centers with alkyl substituents. Our data have led us to conclude that a methyl group attached to a center of negative charge may act as an electron acceptor. Furthermore, they indicate that the intrinsic electron-withdrawing ability of a methyl group is comparable with, if not greater than, its ability to donate charge in those instances where it is attached to an electron-deficient center.

We have determined by pulsed ion cyclotron resonance spectroscopy the free energies of the proton transfer equilibria

\[
\text{CD}_3\text{NH}^- + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{CD}_3\text{NH}_2 + \text{CH}_3\text{NH}^- \quad (1)
\]

\[
\Delta G^\circ = -0.37 \pm 0.08 \text{ kcal/mole} \quad (2)
\]

\[
\text{CD}_3\text{O}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{CD}_3\text{OH} + \text{CH}_3\text{O}^- \quad (3)
\]

\[
\Delta G^\circ = -0.50 \pm 0.10 \text{ kcal/mole} \quad (4)
\]

\[
\text{CD}_3\text{S}^- + \text{CH}_3\text{SH} \rightleftharpoons \text{CD}_3\text{SH} + \text{CH}_3\text{S}^- \quad (5)
\]

\[
\Delta G^\circ = -0.30 \pm 0.08 \text{ kcal/mole} \quad (6)
\]

The preferences are also in the same direction, but of far greater magnitude, than secondary effects noted kinetically in solution for reactions leading through what are suspected to be anionic transition states.

The observed isotope effects may be rationalized using the perturbation molecular orbital theory. Interaction of a methyl group with the lone pair on an anionic center to which it is attached through the \( \sigma \) system is describable in terms of stabilizing and destabilizing components (Figure 1). The four-electron term, 1, involving interaction of the methyl \( \pi^* \) orbital and the lone pair at the anion center, results in net energetic destabilization. Both functions are fully occupied, and little if any redistribution of electron density is to be expected. Significant charge reorganization is to be anticipated as a result of the stabilizing two-electron interaction, 2. Specifically, electron density is shifted away from the nonbonded lone pair at the anion center and directed into a CH antibonding orbital on methyl. As a result the CH bonds should weaken giving rise to the observed isotopic preference for formation of the light anion.

Ab initio molecular orbital calculations at the minimal basis STO-3G level concur with the conclusions of the simple
perturbation model. In particular, calculated CH bond lengths for the methylamino, methoxy, and thiomethoxy anions are significantly longer than those in the corresponding neutral precursors. Preliminary calculations using the split-valence-shell 4-31G basis representation\textsuperscript{11} substantiate these conclusions.

\[ 1.100 \text{ Å} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ 1.098 \text{ Å} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ 1.092 \text{ Å} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ 1.086 \text{ Å} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ 1.086 \text{ Å} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

It is, of course, an oversimplification to ascribe the observed secondary $\beta$-determin in the methylamino, methoxy, and thiomethoxy anions indicate the involvement of the corresponding negative hyperconjugative structures involving hydrogen and, therefore, the ability of a methyl group to act as an electron acceptor. This observation, taken together with those on electron-deficient systems, indicates that the methyl substituent is capable of adopting to its immediate environment, serving to donate or to accept electronic charge depending on the needs of the moiety to which it is attached.

### References and Notes

1. For reviews, see (a) V. J. Shiner, ACS Monogr., no. 187, 90 (1970); (b) D. E. Sunko and S. Borico, ibid., no. 187, 160 (1970).


6. Errors quoted correspond to two standard deviations.

7. It should be mentioned that the possibility exists for the deuteron label in the methylamino anion to scramble onto the nitrogen. Although we have no evidence for this at present, rapid scrambling has been noted in a number of instances involving carbocations (e.g., isopropylium). (a) A. Streitwieser, Jr., and D. O. Van Sickle, J. Am. Chem. Soc., 84, 254 (1962), and references therein. For a review, see (b) E. A. Hulevi, Prog. Phys. Org. Chem., 1, 109 (1963).


9. All calculations have been performed using the Gaussian 70 series of computer programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

10. Little is known experimentally about the structures of anions with which to test the predictions of the ab initio calculations regarding their geometries. The small amount of experimental structural data which is available appears to be adequately reproduced by molecular orbital calculations at the minimal basis set STO-3G level, and better so by computations using the split-valence-shell 3-21G method. For a review, see (a) L. Radom, Aust. J. Chem., 28, 1635 (1975). More important, however, is the fact that the theoretical methods employed in the present study have been shown to be capable of reproducing the known geometrical structures for a wide variety of neutral species. (For reviews, see (b) W. A. Latham, W. J. Hehre, L. A. Curtiss, B. Lister, and J. A. Pople, Prog. Phys. Org. Chem., 11, 175 (1974); (c) W. J. Hehre, Acc. Chem. Res., 9, 399 (1976); (d) J. A. Pople in "Modern Theoretical Chemistry", H. F. Schaefer, Ed., Plenum Press, New York, N.Y., in press.) Hence, some degree of confidence may be put in their findings in situations where experimental data are unavailable.


18. A referee has commented that there exists substantial evidence in favor of the notion that CD bonds act as though they were better electron donors than CH linkages. Such an inductive influence would act in the same direction as the proposed hyperconjugative effect (i.e., favor formation of the isotopically light anion), although it would not be likely to account for the large magnitudes of the isotopic preferences noted.

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