ALCHEMY program.[14] Xe plus F($P^2{}_u$) can give rise to electronic states of $^2\Sigma^+$ and $^2\Pi$ symmetry, and single-configuration SCF calculations were carried out for both states. The internuclear separations chosen ranged from 3.0 bohrs (1 bohr = 0.5292 Å) to 10.0 bohrs. In addition, a wide variety of configuration interaction (CI) calculations were carried out for the $^2\Sigma^+$ ground state. Of these CI calculations, only results from the first-order wave functions are given. Detailed descriptions of the first-order wave function have been given elsewhere.[9-11] Our wave function included all configurations in which not more than one of the 11 valence electrons occupied an orbital beyond the valence shell. The valence shell consisted of all molecular orbitals which correlated in the separated atom limit with the 2p orbital of F and the 5p orbital of Xe. For $^2\Sigma^+$ XeF using the basis set described earlier, there were 354 configurations in this first-order wave function. The additional CI calculations were performed in order to (a) test the deletion of different types of basis functions and configurations and (b) test the first-order approach by adding a large number of other configurations to the wave function. The most extensive wave function investigated contained 2142 configurations, including in addition all double excitations from the occupied valence σ orbitals. However, the qualitative result was the same as that found with the first-order wave function.

Figure 1 summarizes our results for diatomic XeF. There it is seen that both the $^2\Sigma^+$ and $^2\Pi$ states are repulsive. Note that the configuration interaction treatment of the $^2\Sigma^+$ state yields a significantly less repulsive curve. However, even in the latter case, the $^2\Sigma^+$ ground state is repulsive by ~20 kcal/mol at the experimental XeF_2 bond distance 1.977 Å = 3.737 bohrs. At a somewhat longer bond distance, 2.117 Å = 4.0 bohrs, the potential curve is repulsive by 10 kcal/mol. Thus it is clear that the present theoretical study predicts XeF to be a bound species *only* in the van der Waals sense of our first paragraph. That is, we predict no chemical bond between Xe and F. We have not explicitly calculated the van der Waals attraction, since the dispersion term is not described by the type of wave function used here.[11]

Since the experiments of Falconer and Morton[4] were carried out in the solid state, it is conceivable that there is no conflict between their work and ours. For example, the dissociative XeF radical might somehow be trapped in the XeF_4 crystal long enough to produce an esr spectrum.

It should be noted that preliminary elastic scattering molecular beam experiments by Lee[15] support our contention that XeF is not a chemically bound species. Finally, Klemperer[16] plans to determine the dipole moment of XeF using recently developed methods for studying van der Waals bound molecules. A small dipole moment (~0.1 D) would be consistent with the present theoretical results.

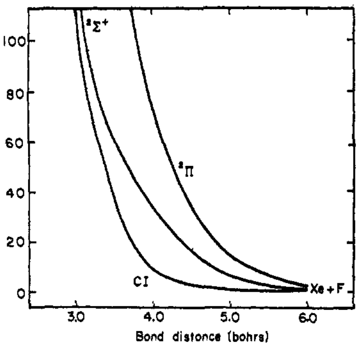

Figure 1. Potential energy curves for xenon monofluoride. The curves labeled $^2\Sigma^+$ and $^2\Pi$ are the results of single-configuration SCF calculations. The curve labeled CI refers to the 354 configuration first-order wave functions. The potential curves have been shifted to yield the same dissociation limit, Xe(^1S) + F(^2P_u).

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[14] A system of programs developed by B. Liu, M. Yoshimine, P. S. Bagus, and A. D. McLean. For a discription see: (a) A. D. McLean in "Proceedings of the Conference on Potential Energy Surfaces in Chemistry," RA18, IBM Research Laboratory, San Jose, Calif., 1971, p 87; (b) P. S. Bagus in "Selected Topics in Molecular Physics," Verlag Chemie, Weinheim/Bergstr., Germany, 1972, p 187.

(15) Y. T. Lee, personal communication.

(16) W. Klemperer, personal communication.

(17) Alfred P. Sloan Fellow.

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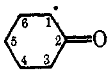
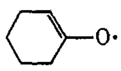
2-Alkanonyl Radicals. Allylic or Not?

Sir:

The 2-cyclohexanonyl radical (I) originally attracted our attention in connection with studies of conformational effects in free radicals containing six-membered rings.[1] However, an assessment of the role of resonance stabilization (*e.g.*, I $\underset{?}{\leftrightarrow}$ II) in 2-alkanonyl radicals



I



II

soon became a problem in itself, particularly in view of several conflicting data and interpretations in the literature[2-10] concerning the properties of this important class of free radicals. We now wish to report the measurement of the ^{13}C and ^{17}O hyperfine splitting constants (hfsc) of the 2-cyclohexanonyl radical by epr spectros-

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(1) D. M. Camaioni and D. W. Pratt, *J. Amer. Chem. Soc.*, **94**, 9258 (1972).

(2) W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 3625 (1964).

(3) O. H. Griffith, *J. Chem. Phys.*, **42**, 2644 (1965).

(4) H. Fischer, *Z. Naturforsch. A*, **20**, 428 (1965).

(5) H. Zeldes and R. Livingston, *J. Chem. Phys.*, **45**, 1946 (1966).

(6) G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967).

(7) G. Golde, K. Möbius, and W. Kaminski, *Z. Naturforsch. A*, **24**, 1214 (1969).

(8) K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **92**, 5541 (1970).

(9) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

(10) P. H. Kasai and D. McLeod, *J. Amer. Chem. Soc.*, **94**, 7975 (1972).

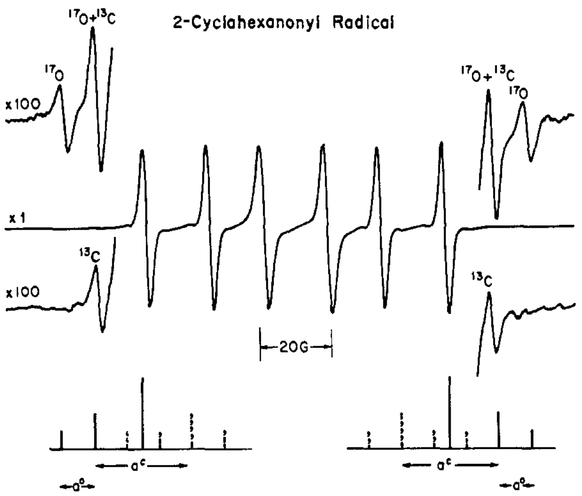

Figure 1. First-derivative epr spectra of the 2-cyclohexanonyl radical in adamantane-h_{16} at 273 °K showing the main (^{1}H, ^{12}C, ^{16}O) spectrum, one of the three pairs of ^{13}C satellites observed in natural abundance at high gain (below the main spectrum), and the ^{17}O and ^{13}C satellites observed in a ^{17}O-enriched sample of cyclohexanone at high gain (above). The stick diagram illustrates the splitting of each of the wing lines of the main spectrum by the ^{17}O and one of the ^{13}C nuclei ($a^C \sim 3a^O$); the dotted lines represent peaks which are not clearly resolved.

copy which has made possible a determination of the complete π-orbital spin density distribution in this radical and a quantitative evaluation of the relative importance of structures analogous to I and II in radicals of this type.

X-Irradiation of a solid pellet of adamantane containing a small amount of unlabeled cyclohexanone leads to formation of the 2-cyclohexanonyl radical which has a_α^H = 18.1 G (one proton), a_β^H = 33.0 G (two protons), and g = 2.0048 at 273°K. Under high gain conditions, each of the six epr lines of the radical shows three pairs of ^{13}C satellites which are most clearly resolved on the wings of the spectrum; one line of the pair with the largest ^{13}C hfsc is illustrated in Figure 1 below the main spectrum. When a sample containing ^{17}O-enriched cyclohexanone[11] is irradiated, the additional lines shown above the main spectrum are observed at high gain; these can be assigned as ^{17}O satellites which have approximately the same intensity as the ^{13}C lines in natural abundance. The splitting of each of the wing lines by the ^{17}O ($I = {}^5/_2$) and the largest ^{13}C ($I = {}^1/_2$) hyperfine coupling is summarized in the stick diagram below the spectra in Figure 1. A careful computer fit of the wings of the main spectrum yields the hfsc a^C = 26.6, $a^{C'}$ = 14.0, $a^{C''}$ = 10.7, and a^O = 9.3 G.

Comparison of the observed ^{13}C hfsc with those measured for ethyl radical [a_α^C = (+)39.07, a_β^C = (−)13.57 G][12] suggests that the largest ^{13}C splitting in 2-cyclohexanonyl [a^C = (+)26.6] should be assigned to C-1 and the smallest [$a^{C''}$ = (−)10.7] to C-6.[13] With this assignment and the appropriate[15] spin polarization constants for ^{13}C, we calculate a value of (+)0.75 for the π-orbital spin density at the radical site (ρ^{C_1}) which is in substantial agreement with the indirect estimates of Griffith[3] and Russell, *et al.*,[6] based on the proton hfsc of other 2-alkanonyl radicals. If we then assume that the π-orbital spin density at the carbonyl carbon (ρ^{C_2}) is zero,[16] the π-orbital spin density on oxygen can be calculated from the relationship $\rho^O = a^O/Q_{OC}{}^O$. Taking a^O = (−)9.3 and $Q_{OC}{}^O$ = −44.5 G,[17] we find ρ^O = (+)0.21. The assumption $\rho^{C_2} = 0$ can be tested by comparing the intermediate ^{13}C hfsc [$a^{C'}$ = (−)14.0] with that calculated for the carbonyl carbon on the basis of spin polarization effects alone. Using the values $Q_{C_1C_2}{}^{C_2}$ = −13.9[15] and $Q_{OC_2}{}^{C_2}$ = −25.1 G,[17] the contributions to $a^{C'}$ from the spin density on C-1 and O are (−)10 and (−)5.3 G, respectively. Since the sum of these is in reasonable agreement with the experimental value of $a^{C'}$, we conclude that ρ^{C_2} is near zero and that ρ^{C_1} = (+)0.75 and ρ^O = (+)0.21.

The values of ρ^{C_1} and ρ^O determined in this work can be used to estimate the relative contributions of structures I and II in the 2-cyclohexanonyl radical. The fact that $\rho^{C_1} > \rho^O$ indicates that the singly occupied "nonbonding" π orbital in this radical is located primarily on C-1 while the doubly occupied bonding π orbital is located primarily on C-2 and O. This is in accord with the difference in first ionization potentials of carbon and oxygen and indicates that the radical is essentially alkyl in character. However, the value of ρ^{C_1} (0.75) lies between those expected for a secondary alkyl radical (0.84)[18,19] and a 1-methylallyl radical (0.54)[18,20] which suggests a small but significant contribution of II to the structure of the 2-cyclohexanonyl radical. In agreement with this, the value of ρ^O (0.21) is smaller than expected for an "allylic" oxygen (0.59)[18] but larger than expected for an oxygen which is γ to the radical site of an alkyl radical and in the nodal plane of the π orbital containing the unpaired electron (~0).[21] A comparison of the observed spin densities with those calculated for the two limiting cases described above leads to the conclusion that the 2-cyclohexanonyl radical is approximately 30% allylic in character, *i.e.*, that the contribution of structure II is about 15%.

Delocalization effects of this magnitude are entirely consistent with the proton hfsc,[2–6,14] g values,[3,5,14] and optical spectra[14] of a wide variety of radicals of this type and explain the unusually high barriers to rotation about the C-1–C-2 bond which have been observed in the acetonyl and 1,1-dimethylacetonyl radicals (9.4 and >10 kcal/mol, respectively).[7,14] Therefore, we believe that resonance stabilization of the type observed for allylic systems contributes in a small but chemically significant way to the structure of 2-alkanonyl radicals.

Acknowledgments. This work was supported in

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(11) Prepared by exchange with normalized H$_2$O containing approximately 4 atom % ^{17}O. Analysis of the ketone by mass spectrometry showed an enrichment of about 2.5 atom % ^{17}O which is in agreement with the epr results.

(12) R. W. Fessenden, *J. Phys. Chem.*, 71, 74 (1967).

(13) This assignment has been verified by INDO.[14]

(14) D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, submitted for publication.

(15) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

(16) A value $|\rho^{C_2}|$ = 0.04 has been estimated from epr measurements on other 2-alkanonyl radicals.[14]

(17) P. D. Sullivan, J. R. Bolton, and W. E. Geiger, *J. Amer. Chem. Soc.*, **92**, 4176 (1970).

(18) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972.

(19) In view of the fact that the π orbital at the radical site can hyperconjugate with only one "methyl" group, this estimate is probably low.

(20) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

(21) G. P. Laroff and R. W. Fessenden, *J. Chem. Phys.*, **55**, 5000 (1971).

part by Atomic Energy Commission Contract No. AT(11-1)-3435 and by grants from the National Science Foundation (GU-3184) and the Merck Foundation. We wish to thank T. Cohen for suggesting the ^{17}O experiment, D. Wood for assistance with the INDO calculations, and P. Meakin for a copy of his epr program.

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Acetylcholine, Gauche or Trans? A Standard *ab Initio* Self-Consistent Field Investigation

Sir:

In the hope of clarifying a confused situation we feel justified in adding one more theoretical calculation to the already extensive series performed on acetylcholine (Figure 1).

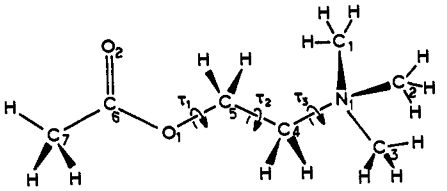

Figure 1. Atom numbering and torsion angles of interest in acetylcholine.

The majority of recent theoretical papers using a large variety of methods[1] agree on the preference of the molecule for a gauche orientation of the N^+ and the esteric O atoms, this conformation being also that observed in the crystal structure and in solution for acetylcholine itself and for the majority of its derivatives.[2]

Surprisingly, a recent "*ab initio*" study of the problem[3] obtains the trans (extended) form as the most stable one for acetylcholine with, moreover, a relatively high energy (10–18 kcal/mol) with respect to the gauche forms.

These results were obtained, however, by a particular *ab initio* procedure recently developed[4] for the treatment of large molecules, where the molecular orbitals are built as linear combinations of predetermined gaussian orbitals of simple molecular fragments. Another feature of this computation is the use of average bond lengths and idealized hybridization for bond angles in the input geometries. A recent study[2b] has shown, however, that the geometrical input data have, in the particular case of acetylcholine, a rather strong influence on the results.

We have therefore considered it appropriate to perform a reinvestigation of the problem of the preferential conformation of this important molecule using a standard *ab initio* SCF procedure and a more precise geometry. The program GAUSSIAN 70[5] was used with an STO 3G basis[6] which has proven useful in a number of conformational studies.[7] As geometrical input data, we have used, in a first step, the X-ray results obtained for the crystal of acetylcholine chloride.[8] Computations have been performed for the all trans conformation ($\tau_1 = \tau_2 = 180°$) and for two folded forms, the gauche ($\tau_1 = 180°$, $\tau_2 = 60°$) and the near-gauche ($\tau_1 = 180°$, $\tau_2 = 80°$) which is the form found in the crystal of acetylcholine chloride. The results (Table I) indicate a clear preference for the gauche forms which both lie about 3 kcal/mol below the trans conformer, in agreement with the majority of the previous computations.

Table I. Energies of Conformers of Acetylcholine (SCF *ab Initio* Method and Chloride Geometry)

Form	Deg			ΔE, kcal/mol
	τ_1	τ_2	τ_3	
Trans	180	180	180	0
Near-gauche	180	80	180	−3.1
Gauche	180	60	180	−3.2

In view of this result and in an attempt to elucidate the reasons for the disagreement with the results obtained by Genson and Christoffersen, we have repeated the STO 3G computations for the same three conformations, this time using the input geometry of these authors. The results are given in Table II; it is seen that even with these authors' geometry the near-gauche form is, within the standard *ab initio* procedure, the most stable one. Moreover the energy differences between the trans, gauche, and near-gauche forms appear much smaller than in ref 3 and more in line with other theoretical predictions.

Table II. Energies of Conformers of Acetylcholine Using the Geometry of Ref 3

Form	Deg			ΔE, kcal/mol	
	τ_1	τ_2	τ_3	SCF[a]	Ref 3[b]
Trans	180	180	180	0	0
Near-gauche	180	80	180	−0.8	+10
Gauche	180	60	180	+3.4	+19
Gauche	180	60	160	−0.8	

[a] SCF *ab initio* results. [b] Results of ref 3 (molecular fragments).

A close examination of scale models corresponding to the various forms as obtained by using Genson and Christoffersen's geometry indicates that it leads in the gauche conformation to a very close approach of a methyl group of the onium head to the ester oxygen (the contact being, in this case, much closer than when the chloride geometry is being used). It seems very

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(1) For recent reviews see: (a) B. Pullman, Ph. Courrière, and J. L. Coubeils, *Mol. Pharmacol.*, 7, 391 (1971); (b) B. Pullman and Ph. Courrière, *ibid.*, 9, 612 (1972).

(2) For recent reviews see: (a) E. Shefter in "Cholinergic Ligand Interactions," D. J. Triggle, J. F. Moran, and E. D. Barnard, Ed., Academic Press, New York, N. Y., 1971, p 83; (b) P. Pauling in "Conformation of Biological Molecules and Polymers," E. D. Bergmann and B. Pullman, Ed., Proceedings of the Vth Jerusalem Symposium, Academic Press, New York, N. Y., 1973, p 505.

(3) D. W. Genson and R. F. Christoffersen, *J. Amer. Chem. Soc.*, **95**, 362 (1973).

(4) R. E. Christoffersen, *Advan. Quantum Chem.*, **6**, 333 (1972).

(5) W. G. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, submitted for publication.

(6) W. G. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(7) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970); L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971); L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971).

(8) J. K. Herdklotz and R. L. Sass, *Biochem. Biophys. Res. Commun.*, **40**, 523 (1970).