Use of Semiempirical AM1 Calculations for the Prediction of Proton Electron Spin Resonance Spectra

Stephen F. Nelsen
S. M. McElvain Laboratory of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, WI 53706, U.S.A.

For Me_nX radicals (X = $C^\cdot$, $N^\cdot$, $N^{+\cdot}$, $O^\cdot$, $O^{+\cdot}$, or $S^{+\cdot}$), propanal cation radical, and biacetyl anion radical, quartet-annihilated hydrogen 1*s* spin densities obtained by semiempirical AM1-UHF quantum mechanical calculations are successfully converted into e.s.r. splitting constants for both α- and β-CH by multiplying by 1 177 G. This procedure produces splittings which range from −23 to +135 G, with a correlation coefficient of 0.999 when plotted against the observed splittings, and an average deviation of 1.1 G. The temperature dependence of n-propyl and isobutyl radical β-splittings is well reproduced by these calculations. Allyl, benzyl, and phenoxyl radical calculations have too much spin contamination even after quartet annihilation for successful calculation of their e.s.r. spectra. The spin density calculations are poor for γ- but probably fairly good for δ-hydrogen atoms.

The Dewar group has developed and conveniently packaged an increasingly sophisticated series of programs for performing semiempirical calculations; this has made it easy to carry out geometry optimizations even on rather large open-shell molecules. We consider here the use of the most recent of these semiempirical Hamiltonians, AM1,[1] using the Unrestricted Hartree-Fock option developed by Bischof[2] for MINDO/3. As Dewar and his co-workers have pointed out,[1] AM1 has substantially improved the large non-bonded steric interactions which plagued MINDO/3 and MNDO by causing far too much flattening at easily deformed heavy atoms. For example, both the earlier methods incorrectly obtained planar nitrogen equilibrium geometries for trimethylamine; this is corrected in AM1. Because radical centres are easily pyramidalized, and this motion mixes *s* character into the spin-bearing orbital, the presence of non-bonded interactions which are too large is especially serious for calculation of e.s.r. splitting constants.

Over ten years ago, Bischof[2] presented geometry-optimized MINDO/3-UHF structures for sixteen hydrocarbon and three oxygen-containing radicals, and compared their calculated H(1*s*) spin densities with experimental e.s.r. splitting constants, *a*(H). Because *a*(H) is theoretically proportional to ρ(H), a single proportionality constant *K* to convert calculated ρ[H(1*s*)] spin densities into e.s.r. splitting constants would exist if the calculated spin densities were correct. Best fit to Bischof's data set[2] gave *K* = 394 G, but the correlation of calculated splittings with experimental data was rather disappointingly poor. We believe that it is clear from Bischof's data set that different *K* values would have to be employed for α- and β-hydrogen atoms in MINDO/3-UHF. If we consider only the eleven saturated hydrocarbon radicals, $K(H_\beta)$ = 552 G, but $K(H_\alpha)$ = 369 G. The observed ratio of 1.5 is too large to be caused by various small errors in structure which are undoubtedly present. Because it is well known that the mechanisms for imparting spin to H_α and H_β are quite different, it perhaps was not surprising that MINDO/3 requires different *K* values for different types of hydrogen atom, but this indicates that the spin densities obtained are seriously in error for at least one of the types of hydrogen.

As Bischof noted,[2] the wavefunctions obtained by UHF calculations are spin-contaminated; the UHF wavefunction is an eigenfunction of S_z, but not the spin-squared operator, S^2. The expectation value of S^2, $\langle S^2 \rangle$ for a UHF calculation, is above the value of 0.75 required for a pure doublet state.[3] Bischof implemented the spin annihilation technique of Amos and Snyder,[4] which removes the quartet component of the contamination, usually by far the most important one. Disappointingly, the overall correlation for ρ[H(1*s*)] with observed coupling did not improve, although 'the relative coupling constants for the various hydrogens within a specific radical are much better reproduced by the spin-annihilated correlation'.[2] Using a larger data set with the MNDO-UHF Hamiltonian, Bischof and Friedrich[5] found an even poorer correlation of spin densities with e.s.r. coupling constants, obtaining a correlation coefficient of 0.90 for 88 splittings, and a *K* value of 1 206 (after quartet annihilation). They concluded that the calculation of e.s.r. coupling constants did not seem feasible for assigning experimental data.[5]

Calculations of CH *Splittings using AM1-UHF.*—We show AM1-UHF-calculated* spin densities for saturated radicals $CH_n(CH_3)_{3-n}$ in Table 1. Our reason for choosing only these four out of the dozens of saturated radicals for which e.s.r. splittings have been measured for calibration of AM1 spin densities is the sensitivity of $a(H_\beta)$ to geometry. Observed e.s.r. splittings are a time average over internal motions of the radical, and rotational barriers for most dissymmetric alkyl groups are sufficiently low that just using the equilibrium geometry, even if it were known to be correct, cannot give the observed splittings. Although averaging over a calculated energy surface for a dissymmetric alkyl substituent can be achieved, it seems impossible to know whether differences between calculation and experiment arise from errors in the relative energies of conformations or in the spin densities calculated for given conformations. We have elected to use symmetric methyl substituents, for which the splittings calculated for the three hydrogen atoms in a given methyl group rotation calculation may be simply averaged to predict the e.s.r. splitting constant. Properly, one should also average the entries in Table 1 over all internal motion of the radicals. We have looked at the effects of averaging over bending at the spin-bearing carbon atoms, and find only a slight decrease in average ρ[H(1*s*)] values of 0.6 to 1.2%; including such a correction would not significantly change the *K* value obtained. We note that as for MINDO/3 and MNDO, the AM1-UHF single-determinant spin densities require different *K* values for α- and β-hydrogen atoms

---

* We thank Timothy Clark (Universität Erlangen-Nürnberg) for providing the AMPAC 1.00 package (QCPE no. 506, *QCPE Bull.*, 1986, **6**, 24a) with Bischof's spin-projection subroutine (from QCPE no. 383, *QCPE Bull.*, 1979), which was installed in AMPAC by B. Reindl, used for these calculations, as well as for discussion of this problem.

Table 1. AM1-UHF hydrogen atom spin densities for methyl, ethyl, isopropyl, and t-butyl radicals

Species	Type	Single determinant	Quartet-annihilated
$^{\bullet}CH_3$	α	−0.060 11	−0.020 04
$^{\bullet}CH_2CH_3$	α	−0.057 70	−0.019 22
	β	+0.034 47	+0.022 77
$^{\bullet}CH(CH_3)_2$	α	−0.056 31	−0.018 74
	β	+0.031 34	+0.020 72
$^{\bullet}C(CH_3)_3$	β	+0.028 90	+0.018 99

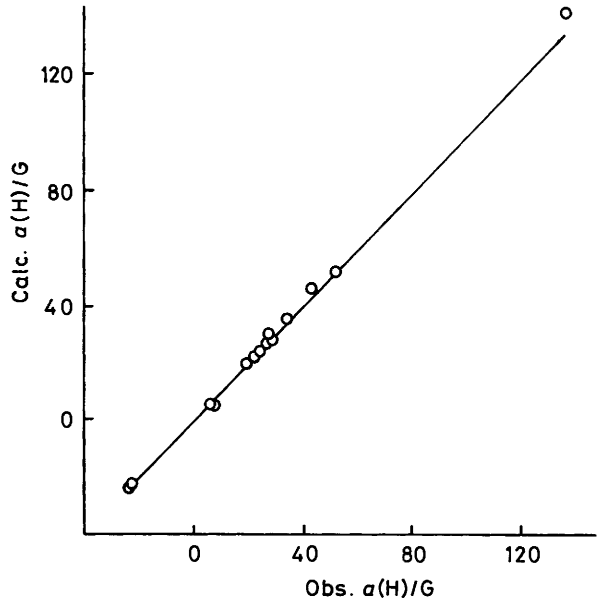


Figure 1. Plot of calculated (AM1-UHFQ) *vs.* observed α and β for the species of Table 2. The line drawn has unit slope, and is not a fit to the data

Table 2. Observed and calculated hydrogen splittings (G)

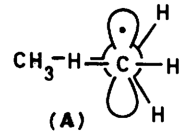
Species	Ref.	Type	Obs. a(H)	Calc. a(H)[a]
$^{\bullet}CH_3$	*b*	α	23.04	−23.58
$^{\bullet}CH_2CH_3$	*b*	α	22.38	−22.62
		β	26.86	+26.80
$^{\bullet}CH(CH_3)_2$	*b*	α	22.11	−22.05
		β	24.68	+24.38
$^{\bullet}C(CH_3)_3$	*b*	β	22.72	+22.35
$^{\bullet}N_2$	*c*	β	27.36	+30.26
$^{\bullet}NH_2{}^{+}$	*d*	β	34.27	+35.63
$^{\bullet}N_3{}^{+}$	*e*	β	28.56	+28.33
$^{\bullet}O$	*f*	β	52	+51.96
$^{\bullet}O_2{}^{+}$	*g*	β	43	+46.06
$^{\bullet}S_2{}^{+}$	*h*	β	20	+20.05
$EtCH{=}O^{+\bullet}$	*j*	β	135.1	+142.4
		δ	4.4(3H)	+3.90
		δ	12.5	+10.89
(E)-$(CH_3CO)_2{}^{-\bullet}$	*k*	β	5.67	+5.65
(Z)-$(CH_3CO)_2{}^{-\bullet}$	*k*	β	6.75	+5.27

[a] Calculated using $a(H) = 1\,177\rho[H(1s)]$, AM1-UHFQ. [b] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147. [c] W. C. Danen and T. T. Kensler, *J. Am. Chem. Soc.*, 1970, **92**, 5235. [d] W. C. Danen and R. C. Rickard, *J. Am. Chem. Soc.*, 1972, **94**, 3254. [e] R. W. Fessenden and P. Neta, *J. Phys. Chem.*, 1972, **76**, 2857. [f] M. Iwasaki and K. Turiyama, *J. Am. Chem. Soc.*, 1978, **100**, 1964. [g] J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, 1981, **103**, 6994. [h] J. T. Wang and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 1184. [j] L. D. Snow and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 1090; see also P. J. Boon, M. C. R. Symons, K. Ushida, and T. Shida, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1213. [k] G. A. Russell and C. E. Osuch, *J. Am. Chem. Soc.*, 1982, **104**, 3353.

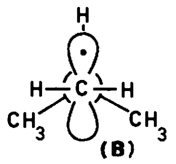
[$K(H_\beta) = 784.3(51)$, $K(H_\alpha) = 387.9(47)$; ratio 2.0], and that there is significant spin contamination, $\langle S^2 \rangle$, rising from 0.7613 to 0.7622 as the number of methyl groups on the carbon increases. Use of Bischof's quartet-annihilation subroutine (which we will refer to for convenience as UHFQ) lowers $\langle S^2 \rangle$ to under 0.7501 for all four radicals. As shown in Table 1, quartet contamination raising $\langle S^2 \rangle$ under 2% increases $\rho[H(1s)]$ as much as a factor of three for α-hydrogen atoms, but much less for β-hydrogen atoms. We believe it is noteworthy that, despite the difference in spin mechanisms, α- and β-hydrogen atoms give essentially the same K value after quartet annihilation, 1 177(27), and find it very encouraging that AM1 CH $\rho[H(1s)]$ values pass this test for internal consistency. Equality of K_β and K_α is an unexpected result of using the AM1 Hamiltonian, which was certainly not parameterized to cause this. For UHFQ calculations on ethyl radical, MINDO/3 gives $K_\beta/K_\alpha = 0.783$, MNDO 1.293, and AM1 1.013. We note that K is far from the observed coupling of the hydrogen atom, 506 G. The K value definitely depends on the atom to which a hydrogen is attached, and only CH splittings are considered here.

Table 2 compares observed a(H) values and those calculated by AM1-UHFQ for some *O*-, *N*-, and *S*-centred radicals, radical cations, and radical anions with methyl substituents, and these calculated *versus* observed values are plotted in Figure 1. We believe it is noteworthy to find good agreement over such a diverse series of spin-bearing atom and charge types; the correlation coefficient of a plot of the three CH_α and twelve CH_β splittings of Table 2 is 0.999, and the average deviation 1.1 G. There is a slight rise in calculated splitting relative to that observed for the cation radicals. Propanal cation was included in Table 2 despite its dissymmetric substituent because it has one of the largest β-splittings known, and also has had both its averaged and frozen δ-methyl group splitting determined, so that the geometry sensitivity of this δ-splitting could be considered. The experimental ratio of the aligned CH splitting to the averaging one is 2.84, far from the McConnell value of 2.00 for a methyl group interacting with a pure *p* orbital. Use of the standard K value gives an 11% low a(3H) value, and AM1 obtains the experimental frozen/averaging splitting ratio as 2.79. To have an anion radical for comparison with the cation-radical-rich data set presented, the dimethyl semidiones were included; agreement is excellent for the *s-trans* conformation, but rather poor for *s-cis*.

To test the utility of AM1-UHFQ calculations in consideration of conformational effects on radicals we have examined the results for the β-splitting of n-propyl and isobutyl radicals, which have been discussed in detail by Fessenden[6] (referred to for convenience as F) and later by Krusic, Meakin, and Jesson[7] (KMJ). Fessenden inferred the minimum-energy conformations (**A**) for propyl radical and (**B**) for isobutyl radical



(A)



(B)

from the sizes of the β-splittings, and treated their temperature dependence by calculating the energy levels for a cosine dependence of the energy, and performing Boltzmann averaging

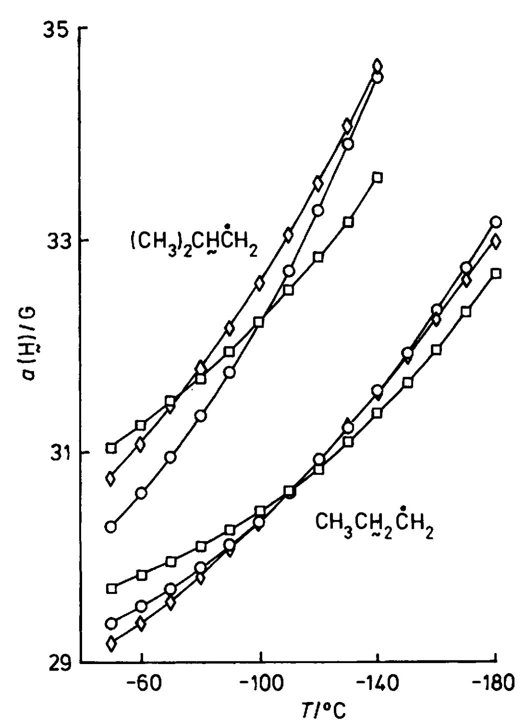
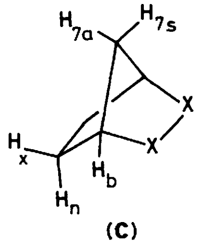


Figure 2. Plot of β splitting *versus* temperature for isobutyl and n-propyl radicals: circles, observed (ref. 7); squares calculated using idealized energy and splitting curves (ref. 7); diamonds, AM1-UHFQ (this work)

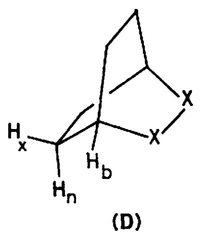
on these energy levels using a $\cos^2\theta$ dependence for $a(H_\beta)$. KMJ did a similar treatment, and also noted that the levels are spaced so closely that the far simpler Boltzmann weighting over the potential energy curve gives virtually the same answer. The two groups obtained almost identical best fit rotational barriers: n-propyl 0.412 (F) and 0.407 (KMJ); isobutyl 0.295 (F) and 0.303 kcal mol^{-1} (KMJ).* Both F and KMJ discuss the fact that $\cos^2\theta$ dependence of $a(H_\beta)$ does not fit the experimental data in detail; the decreases in $a(H_\beta)$ calculated as the temperature is increased are too small. We optimized the energies of these radicals by AM1-UHF at 15° increments over a full 180° span of θ, allowing the trivalent carbon to be non-planar, but keeping the angles of the C_α–H bonds with the plane bisecting them the same, so that the rotations could be accomplished. The degree of non-planarity calculated was negligible, and the shapes of the curves were only trivially different between 0 and 90 and 90 and 180°. Conformations (**A**) and (**B**) were calculated as the optimum-energy conformations, and barriers of 0.83 and 0.77 kcal mol^{-1} were obtained for n-propyl and isobutyl radicals, respectively. KMJ noted that the barrier to rotation for n-propyl radical must be greater than the 0.4 kcal mol^{-1} obtained using idealized curves, because they were able to detect the dissymmetry of (**A**) in the linewidths of the $M_I(H_\alpha) = 0$ lines at very low temperatures. We carried out Boltzmann averaging over smooth curves through the $E(\theta)$ and UHFQ $\rho_\beta(\theta)$ points at a 2° resolution in θ.† In Figure 2 we compare our results, obtained by using $K = 1\,118$ which gave best fit to n-propyl radical, with the experimental values and Fessenden's calculated values using idealized $E(\theta)$ and $a(H_\beta)$ curves. We note that the temperature dependence is far better represented by AM1-UHFQ than by using idealized curves, suggesting that the rotational barriers estimated by F and KMJ might well be far off. As both F and KMJ note, however, experimental data are not very sensitive to barrier, and we do not believe that the better fit obtained is real evidence that the AM1-UHF barriers are correct.

We also briefly investigated the results of AM1-UHF calculations on the tertiary radicals discussed by KMJ, which we note gave significantly poorer fit than the primary radicals to the experimental data. The AM1-UHF $E(\theta)$ curve for t-pentyl radical is far shallower than those for the primary radicals (KMJ found it steeper). More seriously, the tertiary radicals are calculated to be significantly non-planar at carbon. The energy curve over which averaging would be needed to obtain a picture of what AM1-UHF predicts may no longer be adequately considered as one-dimensional in rotational angle, greatly increasing the complexity of the problem. We shall not consider the question further here, except to note that the rotational barriers quoted by KMJ for t-pentyl and 1,1,2-trimethylpropyl radicals should not be considered to be at all accurate.

Limitations of AM1-UHFQ *Calculations of Spin Density*.— In contrast to α-, β-, and probably δ-splittings, γ-splittings are not properly handled by AM1-UHFQ (or other semiempirical) calculations. γ-Splittings are especially sensitive to orbital alignments,[8] so we have chosen to employ bicyclo[2.2.1]heptyl (**C**) and bicyclo[2.2.2]octyl (**D**) peroxide cation radicals (X = O) and semidione radical anions (X = CO) to document this statement. The rigid frameworks force the H_γ–C bonds to be in close to proper alignment relative to the bicyclic framework, and the formal spin-bearing system is essentially pure *p*-hybridized, avoiding the complexities of rehybridization effects. Nevertheless, the calculated splittings of Table 3 indicate that the ρ[H(1*s*)] values obtained are too negative. Like earlier semiempirical calculations,[8] the response of AM1-UHF calculations to **W**-plan alignment of H_γ is qualitatively appropriate. Increasing the bend at nitrogen in hydrazine cations containing (**C**) and (**D**) units is calculated to increase ρ[H(1*s*)] for **W**-plan-aligned hydrogen atoms, as occurs experimentally.[9] Nevertheless, γ-hydrogen atoms which are not in **W**-plan alignment are calculated with negative spin densities, which is experimentally not true.[9] We suggest that improperly treating the 1,3 overlaps, as in semiempirical calculations, will cause improper calculated results for any splittings in which 1,3 interactions are important, including the bridgehead β-hydrogen atoms of (**C**) and (**D**) (these are γ to one spin-bearing centre and β to another).



(**C**)



(**D**)

Delocalized radicals also remain a problem, as indicated in Table 4. The states obtained by AM1-UHF (as with earlier methods) are very spin-contaminated for allyl and even more contaminated for benzyl and phenoxyl. The quartet annihilation subroutine fails to give effectively a nearly pure doublet, as it does for the species in Table 2, for which the calculated CH spin densities do fit the experimental spectra well. Significantly, too

---

* 1 kcal = 4.184 kJ.

† In agreement with ref. 8, which considered rotational barriers, calculations by J. M. Standard and P. R. Certain using quantum mechanical energy levels obtained for a variety of nitrogen inversion barriers gave the same spin density results as simple Boltzmann averaging over the potential surface. There seems to be no reason to employ the at least hundred-fold increase in calculation time required to use the quantum mechanical treatment for these purposes.

Table 3. Observed and calculated hdyrogen splittings (G) for bicyclic compounds

Species	H(type)	Obs. a(H)	Calc. a(H)[a]
(**A**)(XX = $OO^{+\bullet}$)[b]	7a(γ)	2.20	−0.35
	7s(γ)	1.10	−1.13
	x(γ)	9.95	+1.51
	n(γ)	0.36	−0.40
	b(β)	1.20	+0.62
(**A**)(XX = $OCCO^{-\bullet}$)[c]	7a(γ)	6.48	+1.81
	7s(γ)	0.36	−0.21
	x(γ)	2.49	+0.35
	n(γ)	<0.1	−0.13
	b(β)	2.49	+1.42
(**B**)(XX = $OO^{+\bullet}$)[b]	x(γ)	4.70	+1.14
	n(γ)	0.27	+0.12
	b(β)	1.18	0.00
(**B**)(XX = $OCCO^{-\bullet}$)[d]	x(γ)	2.09	+0.22
	n(γ)	unres.	−0.07
	b(β)	unres.	+0.26

[a] Calculated using a(H) = 1 177ρ[H(1s)], AM1-UHFQ. [b] S. F. Nelsen, M. F. Teasley, A. J. Bloodworth, and H. Eggelte, *J. Org. Chem.*, 1985, **50**, 3299. [c] G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mallox, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespor, and Y. Kosgi, *J. Am. Chem. Soc.*, 1974, **96**, 7237. [d] G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Am. Chem. Soc.*, 1967, **89**, 6629.

Table 4. Comparison of observed and calculated hydrogen splittings (G) for allyl, benzyl, and phenoxyl radicals

Species	$\langle S^2\rangle$[a]	$\langle S^2\rangle$[b]	Hydrogen	Obs. a(H)	Calc. a(H)[c]
Allyl[d]	0.930	0.756	H(1) (inner)	14.84	−15.67
			H(1) (outer)	13.90	−15.30
			H(2)	4.06	+9.86
Benzyl[e]	1.218	0.942	H(α)	16.35	−12.12
			H(*ortho*)	5.14	−7.77
			H(*meta*)	1.75	+6.43
			H(*para*)	6.14	−7.45
Phenoxyl[f]	1.138	0.866	H(*ortho*)	6.60	−9.64
			H(*meta*)	1.96	+7.44
			H(*para*)	10.4	−10.13

[a] Single determinate (AM1-UHF). [b] Quartet-annihilated (AM1-UHFQ). [c] Calculated using a(H) = 1 177ρ[H(1s)], AM1-UHFQ. [d] J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, 1968, **90**, 7157. [e] A. Carrington and I. C. P. Smith, *Mol. Phys.*, 1965, **9**, 137. [f] T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 1962, 253.

high a negative spin is still obtained at Hückel nodes even after quartet annihilation, so it is not surprising that the proton splittings estimated are poor.

Conclusions.—In summary, for formally localized radicals like those of Table 2, carbon-bound α- and β-hydrogen atoms are converted into predicted e.s.r. splitting constants (in G) by multiplying the UHFQ spin densities by 1 177. Even modest amounts of spin contamination greatly alter calculated spin densities. These calculations successfully predict β-splittings for *N*-, *O*-, and *S*-centred cation radicals as well as for neutral radicals. We emphasize that it is important to separate the question of whether the splittings calculated are correct for a given conformation (which we believe is adequately established from Table 2) from that of whether the energy profile as geometry is changed is given correctly by AM1-UHF. In species with considerable conformational flexibility, averaging predicted spin densities over an energy surface is required, and AM1-UHF calculations appear to do a good job on the conformations of n-propyl and isobutyl radical. These calculations have recently been applied to the questions of twisting in olefin cation radicals[10] and to CO twisting in epoxide cation radicals[11].

Acknowledgements

We thank the National Science Foundation and the National Institutes of Health for financial support of this work (under grants CHE-8415077 and GM-29549, respectively). We especially thank Timothy Clark for valuable discussions of these problems.

References

1 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
2 P. Bischof, *J. Am. Chem. Soc.*, 1976, **98**, 6844.
3 T. Clark, 'A Handbook of Computational Chemistry,' Wiley-Interscience, New York, 1985, p. 98.
4 A. T. Amos and L. C. Snyder, *J. Chem. Phys.*, 1964, **41**, 1773.
5 P. Bischof and G. Friedrich, *J. Comput. Chem.*, 1982, **3**, 486.
6 R. W. Fessenden, *J. Chim. Phys.*, 1964, **61**, 1570.
7 P. J. Krusic, P. Meaken, and J. P. Jesson, *J. Phys. Chem.*, 1971, **75**, 3438.
8 For a review see F. W. King, *Chem. Rev.*, 1976, **76**, 157.
9 S. F. Nelsen, T. B. Frigo, Y. Kim, J. A. Thompson-Colon, and S. C. Blackstock, *J. Am. Chem. Soc.*, 1986, **108**, 7926.
10 T. Clark and S. F. Nelsen, *J. Am. Chem. Soc.*, 1988, **110**, 868.
11 F. Williams, S. Dai, L. D. Snow, X.-Z. Qun, T. Bally, S. Nitsche, E. Haselbach, S. F. Nelsen, and M. F. Teasley, *J. Am. Chem. Soc.*, 1987, **109**, 7526.

Received 14*th July* 1987; *Paper* 7/1255