

ref 9) fails to reproduce the degeneracy of the S_0 and S_1 states in linear CH_2 . This difficulty can be removed by including CI with the lowest doubly excited configuration as is shown by the corresponding plot in the figure. Inclusion of such CI lowers the energy of normal molecules (e.g., the S_0 state of CH_2 , at equilibrium) by ~ 3 kcal/mol. Since MINDO/3 is parameterized for single-determinant wave functions, CI should not be included except in cases when the HOMO and LUMO are degenerate or nearly degenerate. The S_0 - T_1 separation should therefore be found from the single-determinant values, as in Table I.

We have also used MINDO/3 to study the $^3\Sigma$ and $^1\Delta$ states of O_2 . The results are compared with experiment in Table II. Here again the agreement is good for both states.

Table II. Calculated and Observed Properties of $^3\Sigma$ and $^1\Delta$ O_2

State	ΔH_f , kcal/mol		Bond length, Å	
	Calcd	Obsd	Calcd	Obsd
$^3\Sigma$	-3.9	0	1.206	1.207 ^a
$^1\Delta$	22.8	22.6 ^a	1.206	1.216 ^a

^a G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1965.

These results suggest that the superiority of MINDO/3 over MINDO/2 may extend to triplet states and so provide a simple and convenient way to calculate their properties.

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MINDO/3 Study of the Multiplicity of Cyclopentadienate Cations¹

Sir:

We recently reported² MINDO/3^{3,4} calculations for various possible geometries of the $(CH)_5^+$ cation (1). The singlet state of lowest energy was found to be a distorted nonplanar form (2) of the cyclopentadienate cation. The MINDO/3 method has now been extended to triplet states, using the "half-electron" approximation,⁷ and has been shown to give good results for the electronic states of methylene.⁶ We have therefore carried out calculations for the triplet state of 1 and for the singlet and triplet states of the pentachloro derivative (3), $(CCl)_5^+$, of 1.

(1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126.

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(3) MINDO/3⁴ is an improved version of the MINDO/2 semiempirical SCF treatment.⁵ For a brief summary of the changes, see Dewar, Haddon, and Weiner.⁶

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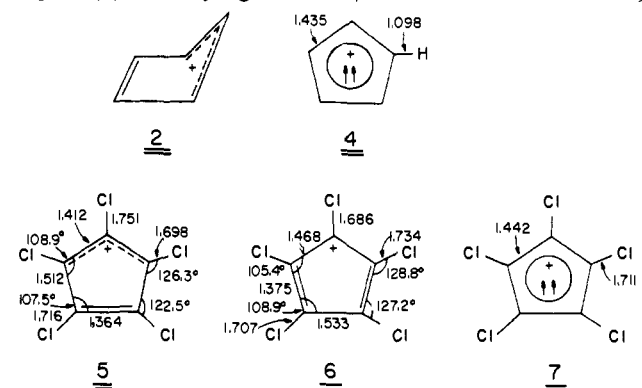
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We find 4 to be more stable than 2 by 1.6 kcal/mol. This is in agreement with recent epr work⁸ which has shown that the cyclopentadienate cation has a triplet ground state. As one would expect, 4 is predicted to have a symmetrical pentagonal structure with the indicated bond lengths (Å).

The lowest singlet state of 3 is predicted to be planar, unlike that (2) of 1. The ring does, however, undergo Jahn-Teller distortion to two isomers 5 and 6, the latter being the more stable by 0.4 kcal/mol. The predicted bond lengths, shown (Å) in 5 and 6, conform in an entertaining way to the indicated "localized" structures. Thus the CC bond lengths in 5 are close to the values for single, double, and allylic CC bonds while those in 6 alternate analogously. Likewise the CCl bonds at the end of the "allylic" system in 5 are short, as would be expected for such bonds in the 1,3 positions of an allyl cation, while the CCl bond adjacent to the "localized" positive charge in 6 is still shorter. The fact that the CCl bond at the "2-allylic" position in 5 is long can also be understood on this basis since the SCF method predicts a high electron density at the 2 position of an allyl cation.

The lowest energy state of 3 is again predicted to be a triplet (7), this lying 1.6 kcal/mol below 6. Breslow,



Hill, and Wasserman⁹ showed that the pentachlorocyclopentadienate cation almost certainly has a triplet ground state.

The prediction that the singlet and triplet states of these ions are very close together in energy also seems likely to be correct, given that in the case of the pentaphenylcyclopentadienate cation the singlet is lower than the triplet by 0.5 kcal/mol.¹⁰

We have also calculated the zero field splitting parameter $D^{11,12}$ for 4 and 7. In the ZDO approximation (such as INDO) and neglecting spin-orbit interactions

$$D = \sum_i \sum_k \{ a_{\mu i}^2 a_{\nu k}^2 - a_{\mu i} a_{\nu i} a_{\mu k} a_{\nu k} \} \langle ii | (3g^2 \beta_0^2 / 4) \times (r_{12}^2 - 3z_{12}^2) r_{12}^{-5} | kk \rangle$$

where $a_{\mu i}$ is the coefficient of the AO ϕ_i in the MO ψ_{μ} , r_{12} is the distance between electron 1 occupying ψ_{μ} and electron 2 occupying ψ_{ν} and z_{12} the corresponding differ-

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(12) For symmetrical planar polygonal π systems such as 4 and 7 the parameter E vanishes.¹¹

ence between their z coordinates, and ψ_μ and ψ_ν are the singly occupied MOs. The values for the integrals, calculated using Slater AOs, were taken from the literature.^{13,14} The values (cm^{-1}) obtained were as follows: (CH_5^+ calcd 0.153, obsd⁸ 0.1868 ± 0.0005 ; (CCl_5^+ calcd 0.111, obsd⁹ 0.1495). The agreement is gratifying, particularly since we did not include the spin-orbit contribution¹⁵ which may be quite large in the case of 7.

These results, together with those for methylene,⁶ seem to suggest that MINDO/3 may prove useful for the study of triplet states.

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High Resolution Deuterium Magnetic Resonance. The Stereochemical Dependence of Relaxation Times

Sir:

We have measured deuterium spin-lattice relaxation times (T_1) for the series of compounds shown in Table I, by the inversion recovery method.¹ Magnetic relaxation of deuterium is induced entirely by an intramolecular quadrupole mechanism,² and the interpretation of ^2H relaxation times is consequently much simpler than for ^1H or ^{13}C . For the compounds in Table I, ^2H relaxation may be controlled by two kinds of molecular motion—anisotropic molecular tumbling and intramolecular rotation. The magnitude of T_1 can change by a factor of 10, depending on the rate of internal rotation.³ We should like to emphasize in this communication the general utility and simplicity of interpretation of ^2H relaxation data in exploration of stereochemistry, intramolecular rotation, and anisotropic motion.

Compounds 1 and 2 (group I) are considered to allow free rotation of the deuteriomethyl group, which should result in relatively long relaxation times. This rotation can be hindered by substitution of chlorine or bromine into the methyl group, resulting in shorter values of T_1 for compounds 3–6.⁴ Group II in Table I shows the deuterium relaxation times for various aromatic compounds. For benzene and pyridine symmetry considerations dictate equal (or almost equal) relaxation times for all deuterons. From the geometry of compounds 9–14 the molecular motion in solution is expected to be anisotropic. Rotations about the axes through the substituent and in the aromatic plane are expected to be the most rapid, leading to a lengthening of relaxation times for those deuterons whose position relative to the applied magnetic field is altered. There-

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(4) The molecular weight dependence of the overall rotation should be of second order and it is ignored. A lack of significant contribution to the deuterium relaxation by quadrupolar nuclei such as chlorine and bromine is implied by the absence of line broadening of the neighboring deuterium resonance.

fore the shortest relaxation time is realized for the C–D group of 14. Similarly, the relaxation times of deuterium in the para position of substituted benzenes 10, 12, and 13 are shorter than those of the meta and ortho positions. In 9 and 11 the accidentally degenerate deuterium resonances do not permit measurement of individual relaxation times. Similar conclusions regarding the influence of anisotropic motion on ^{13}C relaxation times have been reached by Levy, *et al.*⁵ Although relaxation by rapid ring inversion in 15 tends to diminish the difference in the relaxation times at different positions, the small differences may still be interpreted in terms of favored rotation about an axis through the C=O bond. The large difference in T_1 for 16 and 17 is greater than expected from the increase in overall correlation time due to increased molecular size of 17. This is attributable to preferred rotation of 17 about the C_3 axis which is less effective in averaging out the quadrupolar contribution than motion about the C_2 axis of 16. In the substituted naphthalenes it is clear from the T_1 values that steric hindrance for CD_3 rotation decreases in the order 18 (α) > 19 > 18 (β) > 20. Comparison of the data for 21 and 22 demonstrates the relative efficacies of rotations about the two indicated axes at averaging out the quadrupole contribution to ^2H relaxation.

For *N,N*-dimethylformamide (23), correct resonance assignments can be made by ^2H nmr by simply taking into account preferential rotational axes. Both hydrogen and ^{13}C spectra show two peaks, arising from the methyl groups cis and trans to the carbonyl group. Assignment of these two peaks was made by use of the nuclear Overhauser enhancement between the methyl and formyl protons in ^1H nmr,⁶ while the ^{13}C resonances were assigned on the basis of a steric upfield shift.⁷ The different relaxation times for the CD_3 groups in 23 can be best explained in terms of anisotropic rotation. It has already been shown that for 23, the rotational correlation time about an $\text{N}\cdots\text{O}$ axis (Table I) is approximately 50 times shorter than the rotation perpendicular to this axis.⁸ Therefore we may expect the cis CD_3 group, located perpendicular to this axis, to experience a very efficient averaging of quadrupole effects (*i.e.*, long relaxation times), while the trans CD_3 group, located on the axis, should have shorter T_1 's. Since deuterium and ^{13}C relaxation times can be correlated very well⁹ we feel that even the different ^{13}C relaxation times for 23 and those for the syn and anti methyl groups in acetoxime⁷ have to be explained in terms of anisotropic rotation, instead of the initially proposed steric hindrance.

It is clear from the foregoing that high resolution ^2H nmr provides a powerful indicator of stereochemistry and anisotropic motion. It is thus complementary to the earlier technique developed by Lehn and coworkers¹⁰ where the influence of a ^2H coupled to ^1H was measured

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