

if the appropriate force constants from the valence force field for methanol reported by Margottin-Maclou¹¹ are transferred, then the qualitative results of our calculations are retained. Finally, the conformational dependence of R provides a ready explanation for the observed discrepancy of 20 cm^{-1} between the CD and absorption maxima, namely, that the CD band is a population weighted sum of conformer contributions.

The calculations for II were done twice with two different force fields. For both fields the diagonal force constants for the *tert*-butyl groups were transferred from the alkane force field of Schachtschneider and Snyder¹² (S-S). However, the diagonal and off-diagonal force constants for the CHCl end of the molecule were taken in the first instance from the alkyl chloride field of (S-S)¹³ and in the second instance from the ethyl chloride field of Dempster and Zerbi¹⁴ (D-Z). The resultant two fields will be denoted, respectively, as the (S-S)-(S-S) field and the (S-S)-(D-Z) field.

As shown in Table II, the two fields give somewhat

Table II. Rotational and Dipole Strengths for (R)-(-)-Neopentyl-1-d-Chloride

Force field	$\bar{\nu}$ (cm^{-1})	R (esu cm^2)	D (esu cm^2) ²
Obsd	2204	-2×10^{-45}	1.0×10^{-39}
Calcd (S-S)-(S-S)	2202	-4.0×10^{-46}	1.2×10^{-39}
Calcd (S-S)-(D-Z)	2204	-1.0×10^{-45}	1.2×10^{-39}

different results, with the (S-S)-(D-Z) field predicting an R value more nearly in accord with experiment. This, despite the fact that the two fields predict frequencies for the C*-D stretching mode that differ by only 2 cm^{-1} . The superiority of the (D-Z) ethyl chloride field for the present purposes is probably related to the fact that it was fit to several *deuterated* isomers of ethyl chloride, while the (S-S) alkyl chloride field was fit to a series of *undeuterated* *n*-alkyl chlorides. However, the important inferences to be drawn are: (1) the sensitivity of the calculated R values to the precise choice of force constants when dealing with relatively small rotational strengths (*cf.* the R values for I and II) and (2) the potential utility of vibrational optical activity data as additional criteria in the selection and determination of vibrational force constants.

Some further conclusions can be tentatively drawn from the above results. First, within limits, the point charge model can probably be used in a semiempirical way to make reasonable estimates of vibrational electric dipole transition moments. However, as the calculated R values are low, by an order of magnitude in the case of I, it seems that the model may fail as regards magnetic dipole transition moments. This is in accord with the discussion of Schellman,² who anticipated possible underestimation of magnetic dipole transition moments by the point charge model.

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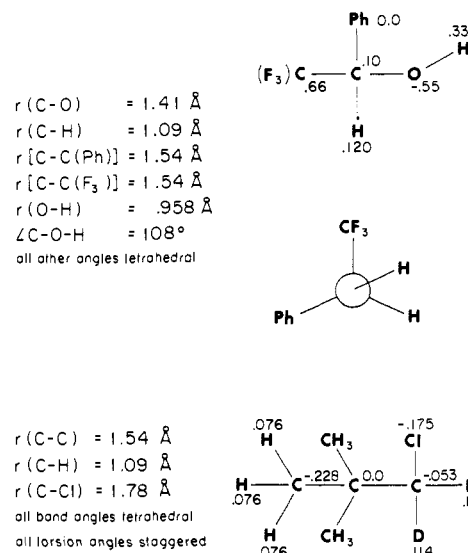


Figure 1. Molecular geometries and atomic charges (units of $e = 4.80 \times 10^{-10}$ esu).

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MINDO/3 Study of the Electronic States of Methylene¹

Sir:

While the ground state of methylene is known² to be a triplet, the separation of this from the lowest singlet has been a matter of controversy. Earlier calculations³⁻⁹ had led to values in the range 25-40 kcal/mol, in agreement with an admittedly uncertain estimate (38 kcal/mol) from electron impact work.¹⁰ On the

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Table I. Calculated and Observed Properties of CH₂ in Various States

State	Property	Experiment	MINDO/3	MINDO/2 ^a	<i>Ab initio</i> SCF	"Best" correlated <i>ab initio</i> SCF ^b
S ₀	ΔH_f^c	101 ^d	100.2	95.8		
	$r_{CH}, \text{\AA}$	1.12 ^e	1.12	1.097 ^f	1.100, ^g 1.133 ^h	1.125
	HCH angle, deg	103.2 ^e	100.2	107	105.4, ^g 104.4, ^h 108, ⁱ 105, ^j 100, ^k 105 ^l	101.0
T ₁	ΔH_f^c	93.9 ± 0.7, ^m 91.9 ± 1, ⁿ ≤ 95.5 ^o	91.5	67.5		
	$r_{CH}, \text{\AA}$	1.078 ^p	1.078	1.062 ^f	1.069, ^g 1.095, ^h 1.096 ^q	
	HCH angle, deg	136 ^{p,r}	134.1	142	132, ^g 133.3, ^h 138, ⁱ 132.5, ^j 130, ^k 135 ^l	134
S ₁	ΔH_f^c		125.0	97.0		
	$r_{CH}, \text{\AA}$	1.05 ^p	1.078	1.050 ^f	1.092 ^h	
	HCH angle, deg	140 ± 15 ^p	141.7	180	143.8, ^h 148, ⁱ 180, ^j 135 ^l	
S ₀ , T ₁	S ₀ -T ₁ ^s	8, ^t 9 ^d	8.7	28.3	37, ^g 22, ^h 33, ⁱ 25, ^j 20.3, ^k 11.5 ^l	11.0 ± 2

^a See ref 9. ^b See ref 15. ^c Heat of formation (kcal/mol). ^d W. L. Hase, R. J. Phillips, and J. W. Simons, *Chem. Phys. Lett.*, **12**, 161 (1971). ^e G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961). ^f Corrected value; see ref 9. ^g See ref 5. ^h See ref 8. ⁱ See ref 3. ^j See ref 6. ^k See ref 13. ^l See ref 14. ^m V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harlee, *J. Chem. Phys.*, **42**, 3791 (1965). ⁿ W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968). ^o W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *J. Chem. Phys.*, **50**, 1938 (1969). ^p G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971); *Proc. Roy. Soc., Ser. A*, **295**, 107 (1966); G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, pp 491, 584. ^q See ref 4. ^r See ref 2. ^s Singlet-triplet separation (kcal/mol). ^t H. M. Frey, *J. Chem. Soc., Chem. Commun.*, 1024 (1972).

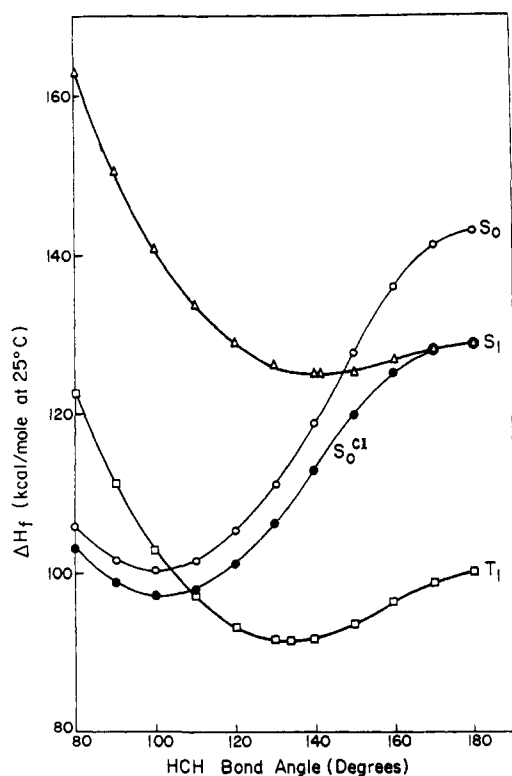


Figure 1. Plot of calculated (MINDO/3) heat of formation (ΔH_f) vs. HCH bond angle for the S₀ (O), S₁ (Δ), and T₁ (□) states of CH₂. Values (●) are also given for S₁ including CI with the lowest doubly excited configuration.

other hand recent photochemical studies have implied a very small singlet-triplet separation (1–2¹¹ and 2.5¹² kcal/mol) and three very recent and very detailed *ab initio* SCF calculations^{13–15} have led to intermediate

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values (20,¹³ 11.5,¹⁴ and 11.0 ± 2¹⁵ kcal/mol). Recent experimental work has given estimates of the heats of formation of singlet and triplet methylene (Table I) which lead to a singlet-triplet separation (8–9 kcal/mol) in reasonable agreement with the results of the latest^{14,15} and apparently most reliable of the *ab initio* calculations.

An improved version of the MINDO method (MINDO/3^{16,17}) has now been developed in these laboratories. This appears to avoid the systematic errors present in MINDO/2. We have used this to study methylene, partly to check to the ability of MINDO/3 to deal with an unusual singlet species (*i.e.*, carbene) and partly to see if it would give a better estimate of the energy of the triplet than MINDO/2.⁹ Calculations for the triplet were carried out as before by the "half-electron" method.^{21,22}

The MINDO/3 results are compared with experiment and with the results of *ab initio* calculations in Table I. It will be seen that they agree well with experiment and with the results of the most recent and most detailed¹⁵ *ab initio* calculation.

Figure 1 shows MINDO/3 estimates of the variation in the energies of the various states of CH₂ with the bond angle. The results agree qualitatively with those from *ab initio* calculations; MINDO/3 naturally (*cf.*

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(17) MINDO/3 follows the original version^{18,19} of MINDO/2, with two exceptions. First, the one-center integrals are estimated by Oleari's method; see Dewar and Lo.²⁰ Secondly, the Slater exponents for valence shell AOs are treated as parameters, different values being used for 2s and 2p AOs. These exponents appear only in the calculation of overlap integrals, used in the Mulliken approximation for the one-electron resonance integrals.^{18,19}

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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 Cyclopentadienyl 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 cyclopentadienyl 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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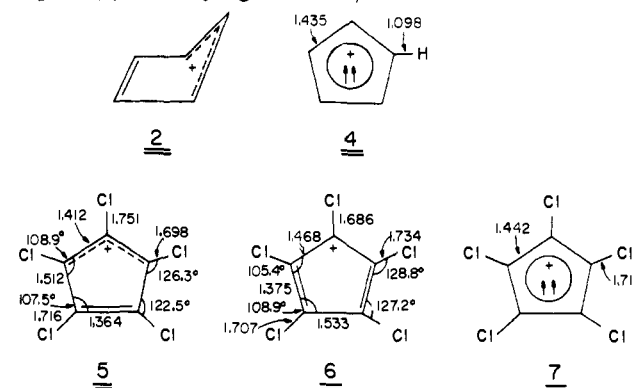
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We find **4** to be more stable than **2** by 1.6 kcal/mol. This is in agreement with recent epr work⁸ which has shown that the cyclopentadienyl cation has a triplet ground state. As one would expect, **4** is predicted to have a symmetrical pentagonal 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 pentachlorocyclopentadienyl 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 pentaphenylcyclopentadienyl 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