

Comments on the Geometry of CH₂

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(Z. Naturforsch. 26 a, 1245 [1971]; received 5 May 1971)

Although the vast majority of the theoretical determinations¹⁻¹⁰ of the geometry of the ground state of CH₂ had favored a bent structure¹¹, it is only very recently that the controversy about its nonlinearity has ended¹².

Prompted by WASSERMAN's E.S.R. results¹³, HERZBERG, upon reexamination of the UV spectrum of CH₂, has recently proposed¹² that an *alternate* interpretation of the observed data suggests that the latter be bent with a CH equilibrium distance of 1.078 Å and an HCH angle of 136°, in contradistinction to his earlier values of 1.029 Å and 180°.

We, in this laboratory, have considered the geometry of this radical within the framework of the modified extended Hückel approximation, the methodology of which is given, in detail, elsewhere¹⁴ and shall not be repeated here.

Figure 1 gives the angular dependence of the modified extended Hückel energy (E_{MEH}) of CH₂ as a function of the internuclear distance. Our results indicate that $r_0(\text{CH}) \cong 1.10$ Å and $\angle \text{HCH} \cong 135.8^\circ$ with an approximate potential barrier of 1.4 kcal/mole. It is indeed interesting to note that at the earlier reported internuclear distance of 1.029 Å our calculations suggest a linear structure.

Perhaps, the most important outcome of the present study, however, was the fact that in the case of CH₂ not only does the modified extended Hückel approximation seem to be superior to the regular one, a doctored version⁷ of which gives a shallow minimum at 155°, but that it also compares favorably well with the most elaborate of *ab initio* calculations (s. Table 1). It is indeed extremely gratifying to find that our simple methodology gives as good results as the most sophisticated and "high-accuracy" calculations of BEN-

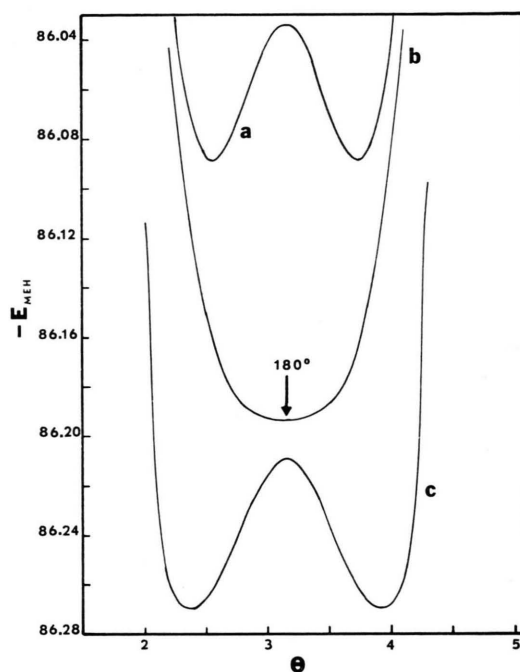


Fig. 1. Angular * dependence of E_{MEH} ** (CH₂) as a function of $r(\text{CH})$.

* θ (in radians) represents the HCH angle. E_{MEH} is given in eV.
** E_{MEH} does not include the constant contribution of the electron in the out-of-plane 2p_z orbital of carbon.

† The internuclear distances considered are (a) 1.18 Å; (b) 1.029 Å and (c) 1.10 Å.

DER and SCHAEFER⁹ whose "wave functions were of the configuration-interaction variety, including the SCF function plus all singly and doubly excited configurations arising from a 'double- ξ ' gaussian basis set", and which, all in all, included 408 ³B₁ configurations!

Although similar accuracy cannot be expected for all the hydrocarbons, it is perhaps, not very difficult to see why our methodology^{14,15} seems promising for the practicing organic chemist.

Author(s)	Type of Calculation or experiment	$r_{\min}(\text{CH})$	$\angle \text{HCH}$
HARRISON and ALLEN ⁸	<i>Ab initio</i> Valence Bond	1.058 Å	138°
BENDER and SCHAEFER III ⁹	<i>Ab initio</i> M.O.	1.096	135.1
LATHAN, HEHRE and POPL ¹⁰	<i>Ab initio</i> M.O. (4-31 G)	1.069	132.0
This work	Semi-empirical M.O.	1.10	135.8
Experimental ¹²	UV Spectroscopy	1.078 *	136

Table 1. Theoretical and experimental geometric parameters of methylene.

* This value is actually for $r_0(\text{CH})$.

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