Comments on the Geometry of CH_2

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Although the vast majority of the theoretical determinations [1−10] of the geometry of the ground state of CH_2 had favored a bent structure [11], it is only very recently that the controversy about its nonlinearity has ended [12].

Prompted by WASSERMAN's E.S.R. results [13], HERZBERG, upon reexamination of the UV spectrum of CH_2, has recently proposed [12] 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 earlie 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, elsewhere [14] and shall not be repeated here.

Figure 1 gives the angular dependence of the modified extended Hückel energy (E_{MEH}) of CH_2 as a function of the internuclear distance. Our results indicate that $r_0(\mathrm{CH}) \cong 1.10$ Å and $\sphericalangle \mathrm{HCH} \cong 135.8°$ 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 CH_2 not only does the modified extended Hückel approximation seem to be superior to the regular one, a doctored version [7] 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 BENDER and SCHAEFER [9] 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 $^3B_1$ 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.

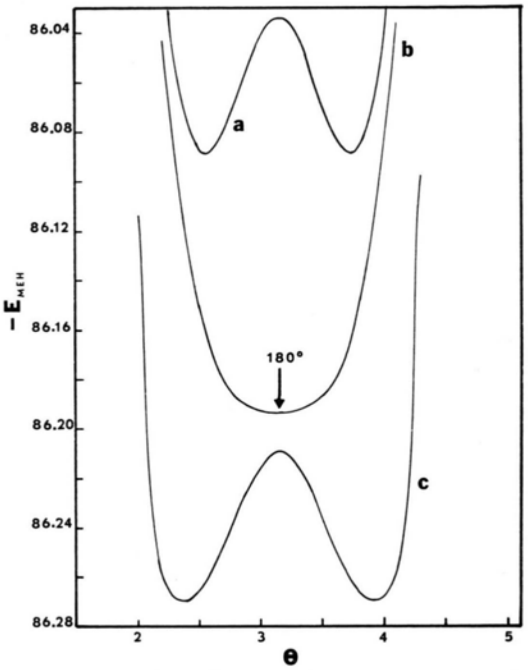

Fig. 1. Angular * dependence of E_{MEH} ** (CH_2) as a function of r(CH).

* 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.

Table 1. Theoretical and experimental geometric parameters of methylene.

Author (s)	Type of Calculation or experiment	$r_{\min}$(CH)	< CHC
HARRISON and ALLEN [8]	*Ab initio* Valence Bond	1.058 Å	138°
BENDER and SCHAEFER III [9]	*Ab initio* M.O.	1.096	135.1
LATHAN, HEHRE and POPLE [10]	*Ab initio* 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

* This value is actually for r_0(CH).

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