MINDO-FORCES Calculation of the Benzyl and Vinyl Radicals and the Reactions ${}^1CH_2+H_2 \rightarrow CH_4$ and $CH_4^{\cdot+} \rightarrow CH_3^{+}+H^{\cdot}$

Salim M. Khalil and Muthana Shanshal

Department of Chemistry, College of Science, University of Baghdad, Adhamiya, Baghdad, Iraq

Z. Naturforsch. **33 a**, 722–730 (1978) ; received February 17, 1978

The MINDO/3-FORCES method is applied for the calculation of the ${}^1CH_2+H_2 \rightarrow CH_4$ reaction. The variation of geometry is carried out in such a manner as to allow for the deviation from the C_{2v} symmetry along the H^7-CH_2 reaction coordinate. The changes in the geometric parameters of the system during the reaction are followed. It is found that the transition state of the reaction corresponds to $R=1.8$ Å and has a geometry closer to the reactants than the products. The calculated activation energy is 13.57 kcal/mol and the calculated reaction enthalpy 106.36 kcal/mol (118.9 kcal/mol exp.). Similar calculations for the $CH_4^{\cdot+}$ yield a D_{2d} structure and a ΔH_f value of 269.68 kcal/mol (274.0 kcal/mol exp.). The activation energy of the decomposition reaction $CH_4^{\cdot+} \rightarrow CH_3^{+}+H^{\cdot}$ is 84.54 kcal/mol, the reaction enthalpy is 42.83 kcal/mol (38.10 kcal/mol exp.).

Using both MINDO/2- and MINDO/3-FORCES a C_{2v} geometry is calculated for the benzyl radical. The ΔH_f values are 48.40 and 67.93 kcal/mol respectively. The latter calculation shows that the rotated perpendicular conformation of the methylene group is by 2 kcal/mol less stable than the planar one. The rotation transition state corresponds to the rotation angle 50°. The change in the geometric parameters during the rotation is followed.

For he vinyl radical the MINDO/3-FORCES calculation yields a CCH angle of 151.1° and a H_f value of 69.8 kcal/mol (65 kcal/mol exp.).

In a recent paper [1] a new method (MINDO-FORCES) for the minimization of molecular energies and the calculation of equilibrium geometries was described. The method was essentially based on the Murtagh-Sargent minimization technique [2], Pulay's FORCE method [3] and the MINDO-SCF MO model. Applied to the treatment of various organic molecules, the MINDO-FORCES yielded energy values and geometries in good agreement with the experimental results. In many cases the calculated MINDO values of Dewar et al. [4] could be improved. We report here MINDO-FORCES calculation results for two reactions of considerable interest to organic and theoretical chemists. First the reaction of single methylene with H_2, then the dissociation reaction of $CH_4^{\cdot+}$ ion into $CH_3^{\cdot}+H^{+}$ are studied. Both reactions were followed along their paths of least energy, starting with the minimized structure of the reactants. Further, the structure of both benzyl and vinyl radicals as well as the rotation barrier of the first radical are studied.

Reaction of singlet methylene with the hydrogen molecule

The type of reaction of methylene with H_2 molecule depends on its electronic configuration (triplet or singlet) [5]. Triplet methylene (${}^3CH_2$) is known to abstract a hydrogen atom from the molecule;

$${}^3CH_2+H_2 \rightarrow CH_3^{\cdot}+H^{\cdot}$$

whereas singlet methylene undergoes an insertion reaction in the H – H bond [5].

$${}^1CH_2+H_2 \rightarrow CH_4$$

Nonempirical quantum mechanical calculations where reported by Schaefer et al. [6]. The insertion reaction was studied theoretically by Kollmar using CNDO method [7], Pedley et al. [8] and by Cremaschi and Simonette [9] using ab initio methods. The CNDO calculation yielded an activation energy 13 kcal/mol while both ab initio calculations yielded activation energies bigger than 50 kcal/mol. Braun et al. [10] studied the kinetics of the singlet and triplet methylene reactions experimentally.

On preparing this manuscript we became aware of a recent work of Schaefer et al. [11] reporting an extensive ab initio Cl study of the reaction. Inspecting the structure of the resulting occupied MOs of the reactants and products they came to the conclusion that the reaction should be forbidden according to the Woodward-Hoffman rules. Their calculated activation energy was 26.7 kcal/mol, smaller than the values of the other, single determinant, ab initio calculations [8, 9]. The saddle point of their calculated potential surface corresponds to the values, .74 Å H – H(H_2) and 172.4° HCH bond angle in ${}^1CH_2$.

Choice of the Initial Geometry

The initial geometry of the reaction system corresponds to a C_{2v} arrangement such that the plane containing the H_2 molecule and the C atom bisects the HCH bond angle of the methylene group (Figure 1). The hydrogen molecule approaches $^1CH_2$ along the x-axis in the H^1CH^2 plane (x-y plane). The following initial values of the coordinates are chosen for the calculation of the first point ($R = 3.2$ Å) on the reaction path; 1.5 Å for the H_2 bond, 1.121 Å for th C – H bond and 102° for the HCH bond angle (Φ) of the methylene group. The distance R is kept constant during the minimization procedure as a reaction coordinate. The calculation for other points along the reaction path is initiated by a new choice of the reaction coordinate R and the acceptance of the equilibrium coordinates for the former point. The H^1 and H^2 were allowed to move along the y-axis, the H^3 and H^4 along the x and z axis in order to provide the possibility of deviation from the C_{2v} symmetry. The results of the calculation are listed in Table 1.

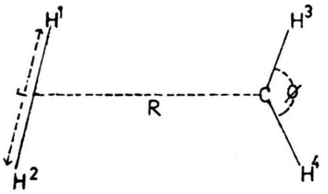


Fig. 1. Initial coordinates for the $^1CH_2 + H_2$ system.

Table 2. MINDO/3-FORCES calculated heats of formation and molecular geometries.

	ΔH_f Calc.	Obsd. [a]	Geometries, Calc. (Obsd.) [b]
H_2	0.16	0.00	H – H, 0.746 (0.742) [f]
CH_4	−6.13	−17.90	C – H, 1.101 (1.106) [c]
$^1CH_2$	100.32	101.00 [e]	C – H, 1.120 (1.110) [d] HCH, 102.0 (102.4) [d]

[a] The observed values are taken from, J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York 1970.

[b] Bond lengths in A and bond angles in deg.

[c] L. S. Bartell, K. Kuchitsu, and R. J. de Neui, J. Chem. Phys. **35**, 1121 (1961).

[d] G. Herzbarg, Proc. Roy. Soc. London, Ser. A **262**, 291 (1961).

[e] W. L. Hase, R. J. Phillips, and J. W. Simons, Chem. Phys. Letters **12**, 161 (1971).

[f] Table of Interatomic Distances, Chem. Soc. Spec. Publ. No. **11** (1958) and No. **18** (1965).

Table 2 includes the calculated heats of formation and geometries of the stable species H_2, $^1CH_2$ and CH_4 compared with the experimental results.

Discussion of the Reaction Path

In agreement with the recent results of Schaefer et al. [11] the MINDO/3-FORCES calculation results show that the electronic configurations of the $H_2 + {}^1CH_2$ and CH_4 systems differ by two electrons. The obtained noncorrelation is due to the crossing

Table 1. MINDO/3-FORCES calculated heats of formation ΔH_f (kcal/mol) and geometries (bond lengths are in Å and angles in degrees) of $^1CH_2 + H_2$ reaction system.

R [a]	r [a]	Φ [b]	ΔH_f	I [A]	F [B]	Geometries
3.2	0.748	101.1	100.96	2	10^{-3}	CH^3, 1.122; CH^1, 3.222; H^1CH^3, 129.1; H^1CH^2, 13.3.
3.0	0.750	101.3	101.26	8	2×10^{-3}	CH^3, 1.122; CH^1, 3.023; H^1CH^3, 129.0; H^1CH^2, 14.2.
2.5	0.753	101.5	102.87	10	10^{-3}	CH^3, 1.122; CH^1, 2.528; H^1CH^3, 128.8; H^1CH^2, 17.0.
2.0	0.753	101.5	108.50	5	3×10^{-3}	CH^3, 1.125; CH^1, 2.035; H^1CH^3, 128.5; H^1CH^2, 21.3.
1.8	0.751	101.2	113.89	2	2×10^{-3}	CH^3, 1.126; CH^1, 1.839; H^1CH^3, 128.5; H^1CH^2, 21.3.
1.6	0.772	104.0	105.01	15	4×10^{-3}	CH^3, 1.123; CH^1, 1.780; H^1CH^3, 120.0; H^1CH^2, 30.0.
1.2	1.158	118.2	62.84	22	4×10^{-3}	CH^3, 1.084; CH^1, 1.332; H^1CH^3, 117.6; H^1CH^2, 51.52.
1.0	1.346	118.2	22.10	11	2×10^{-3}	CH^3, 1.089; CH^1, 1.205; H^1CH^3, 115.2; H^1CH^2, 67.9.
0.8	1.598	115.7	−0.84	11	2×10^{-3}	CH^3, 1.095; CH^1, 1.131; H^1CH^3, 112.1; H^1CH^2, 89.9.
0.633	1.804	109.5	−6.15	10	2×10^{-3}	CH^3, 1.102; CH^1, 1.102; H^1CH^3, 108.9; H^1CH^2, 109.8.
0.6	1.836	111.6	−5.72	10	2×10^{-3}	CH^3, 1.103; CH^1, 1.097; H^1CH^3, 107.7; H^1CH^2, 112.6.

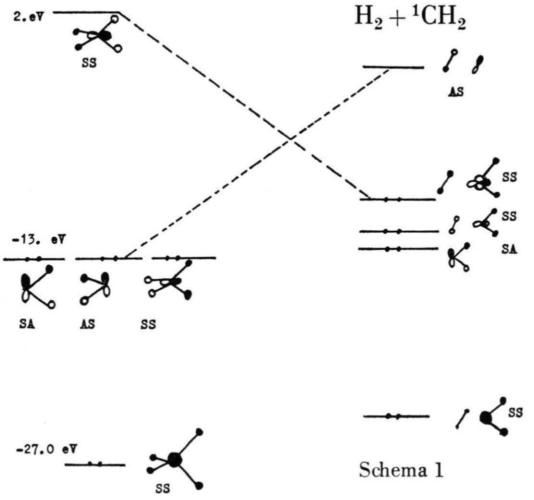
[A] Number of geometric iterations.

[B] Maximum forces (a. u.).

[a] Distance in Å.

[b] Angle in deg.

of an antibonding AS MO of the reactants with a bonding SS MO of CH_4 during the reaction (Scheme 1). The path of the reaction is obtained by plotting the values for the heat of formation against R (reaction coordinate) as shown in Figure 2. It goes through a transition state at $R = 1.8$ Å and proceeds towards the product ($R = 0.633$ Å). The geometry of the transition state is closer to the reactants than the products, in agreement with the ab initio-CI results [11] and with Hammonds suggestion [12] that, in the highly exothermic reaction the transition state should resemble the reactants. Inspection of the geometric parameters indicates that the transition state maintains the C_{2v} symmetry. The HCH angle of methylene remains constant (101°) up to the transition state and increases after that to 118.2° ($R = 1.0$ Å). It decreases then to 109.5° at $R = 0.633$. Figure 3 shows the variation of this angle along the reaction coordinate. Also the C – H bond distance of $^1CH_2$ remains constant (1.122 Å) up to $R = 2.5$ Å and is 1.12 Å at the transition state. After that it decreases and then increases as shown in Figure 4. The H^1CH^2 angle undergoes a continuous increase (13.3° to 112.6°) along the reaction path.



Schema 1

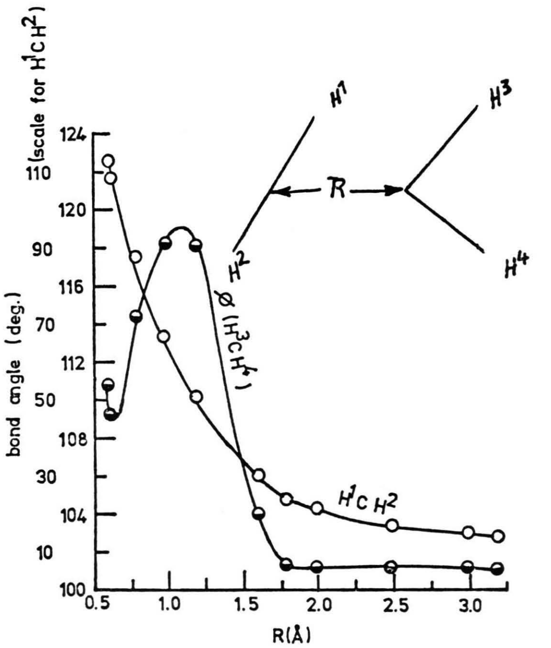


Fig. 3. Variations of the angle (Φ) and the H^1CH^2 angle along the reaction path of the $^1CH_2 + H_2 \rightarrow CH_4$ reaction.

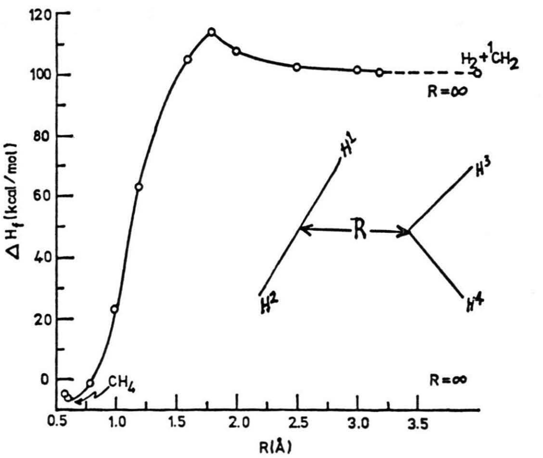


Fig. 2. MINDO/3-FORCES calculated reaction path for the $^1CH_2 + H_2 \rightarrow CH_4$ reaction.

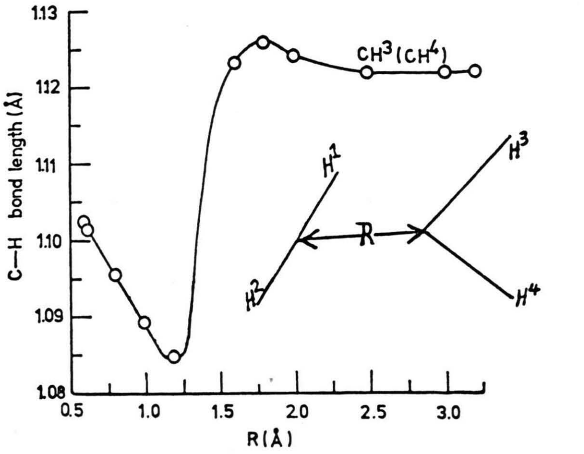


Fig. 4. Variation of the CH bond length of $^1CH_2$ along the reaction path of the $^1CH_2 + H_2 \rightarrow CH_4$ reaction.

The change in energy corresponds to an activation energy of 13.57 kcal/mol. The calculated reaction enthalpy is 106.36 kcal/mol. This value is greater than the speculated value of Pedley et al. [8] (47.85 kcal/mol) based on ab initio calculation and closer to the experimental value (118.9 kcal/mol) obtained from the summation of the heats of formation.

Calculation of the Equilibrium Geometry of $CH_4^{\cdot+}$ and the Path of its Decomposition Reaction $CH_4^{\cdot+} \rightarrow CH_3^+ + H^\cdot$

The structure of the methane radical cation $CH_4^{\cdot+}$ was first studied by Coulson and Strauss [13]. They pointed out that removing an electron from a bonding molecular orbital of methane causes a Jahn-Teller distortion of the tetrahedral symmetry [14–15]. As possible structures of the formed radical cation they considered both tetragonal (D_{2d}) and trigonal (C_{3v}) geometries (Figure 5).

Many other workers followed them in the calculation of $CH_4^{\cdot+}$ structures [16–18]. Dixon carried out ab initio calculations [19] for the three structures (T_d, D_{2d} and C_{3v}) using fixed C–H bond lengths (1.147 Å). He calculated a minimum energy for the T_d structure, −39.66 a. u., for the D_{2d} structure (with two bond angles of 141.2° and four of 96.3°), −39.71, and for the C_{3v} structure (with three HCH angles of 96.9° and three of 118.6°) −39.69 a. u. Pople et al. carried out ab initio calculations [20] for the same ion and found two energy minima in the potential energy surface of the C_{2v} species $C(H_a)_2(H_b)_2^+$. The first minimum corresponds to the following geometries: $r_{CH_a} = 1.100$ Å; $r_{CH_b} = 1.198$ Å; $H_aCH_a = 118.7°$ and $H_bCH_b = 72.4°$. For the D_{2d} structure they calculated equal values for both HCH angles: $r_{CH_a} = r_{CH_b} = 1.134$ Å and $H_aCH_a = H_bCH_b = 137.4°$. They also examined the C_{3v} structure $CH_a(H_b)_3^+$ and found $r_{CH_a} = 1.354$ Å; $r_{CH_b} = 1.108$ Å and $H_bCH_b = 118.8°$. The D_{2d} structure was predicted by them to represent the most stable configuration. Olah and Klopman [21] calculated the various possible configurations of $CH_4^{\cdot+}$ by the PNDO method [22]. They concluded a planar structure of the ion with 2H atoms undergoing a 3 center bond with the C atom as shown in Figure 6.

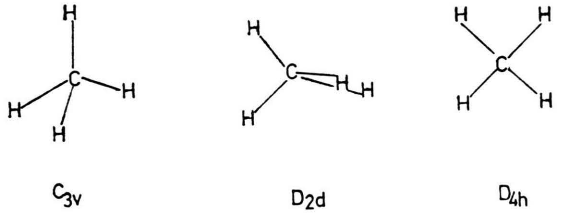


Fig. 5. Possible structures of $CH_4^{\cdot+}$ considered by Coulson and Strauss [13].

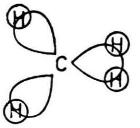


Fig. 6. The planar structure of $CH_4^{+\cdot}$ as calculated by Olah and Klopman [21].

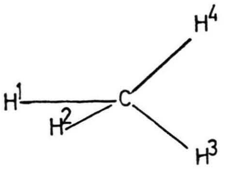
However, they did not minimize the energy with respect to the geometric parameters of the ion.

We have carried out MINDO/3-FORCES calculations for the $CH_4^{\cdot+}$ ion minimizing its energy with respect to all geometric parameters. The initial geometry is considered to be equivalent to the minimized geometry of CH_4 (Table 2). The final molecular geometry (Fig. 7) is obtained after 62 geometric iterations.

Its calculated heat of formation 269.68 kcal/mol, shows good agreement with the experiment [23] (274.0 kcal/mol). The resulting geometry represents an almost D_{2d} structure, in agreement with the conclusions of Dixon [19] and Pople et al. [20]. No detailed experimental evidence about the structure of the cation is known yet.

The path of the decomposition reaction $CH_4^{\cdot+} \rightarrow CH_3^+ + H^\cdot$ was studied by calculating the heats of formation of the cation with different values of the CH^1 bond distance (as reaction coordinate R), and varying the other parameters to obtain minimum energy. The calculated heats of formation are plotted against the $C-H^1$ bond distances (R) in Figure 8. The heat of formation at infinite separation corresponds to the sum of the calculated heats of formation of CH_3^+ and $H^\cdot$ atom. The calculated activation energy of the decomposition reaction is 84.54 kcal/mol. The calculated heat of reaction 42.83 kcal/mol shows a remarkable agreement with the experimental value (38.10 kcal/mol), obtained from the sum of the experimental heats of formation of $CH_4^{\cdot+}$, CH_3^+ and $H^\cdot$.

It is interesting to note the change of the other geometric parameters along the reaction path. The $C-H^4$ bond distance decreases to a minimum (1.122 Å) at $C-H^1$ distance 2.118 Å, then in-



$C-H^1=1.12$ Å $C-H^2=C-H^3=1.234$ Å $C-H^4=1.133$ Å
$H^4-C-H^1=137.4°$ $H^3-C-H^1=102.5°$ $H^3-C-H_2=138.4°$
$H^2-C-H^1=102.3°$ $H^2-C-H^4=91.8°$ $H^3-C-H^4=92.1°$

Fig. 7. MINDO/3-FORCES calculated equilibrium geometry of $CH_4^{\cdot+}$.

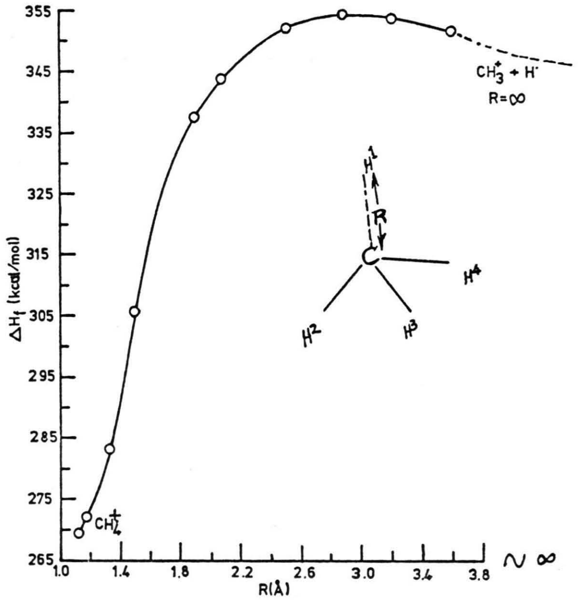


Fig. 8. MINDO/3-FORCES calculated heat of formation of the reaction system $CH_4^{\cdot+} \rightarrow CH_3^{+}+H^{\cdot}$ as a function of the reaction coordinate $R(C \rightarrow H^1)$.

creases to a maximum (1.155 Å) at $C-H^1$ distance 2.5 Å and finally decreases to 1.126 Å at $C-H^1$ 3.5 Å. The $C-H^2$ and $C-H^3$ bonds remain equal in length along the reaction path. They decrease to a minimum (1.095 Å) at $C-H^1$ distance 2.5 Å and remain almost constant as this increases to 3.5 Å (Figure 9).

The bond angle H^2CH^3 increases to a maximum (143.9°) at $C-H^1$ distance 2.9 Å and then increases gradually to 144.3° at $C-H^1$ 3.5 Å. The angles H^3CH^4 and H^2CH^4 remain equal along the reaction path. They increase to a maximum (94.7°) at $C-H^1$ distance 2.118 Å, then remain almost constant to $C-H^1$ 2.9 Å and increase finally to 96.6° at $C-H^1$ 3.5 Å. The variation of these angles and the other two angles H^1CH^4 and H^1CH^2 are shown in Figure 10.

The calculated atomic electron densities of $CH_4^{\cdot+}$ along the reaction path are plotted in Figure 11. It is seen from this figure that the electron density on the carbon atom decreases to approach that of CH_3^{+}

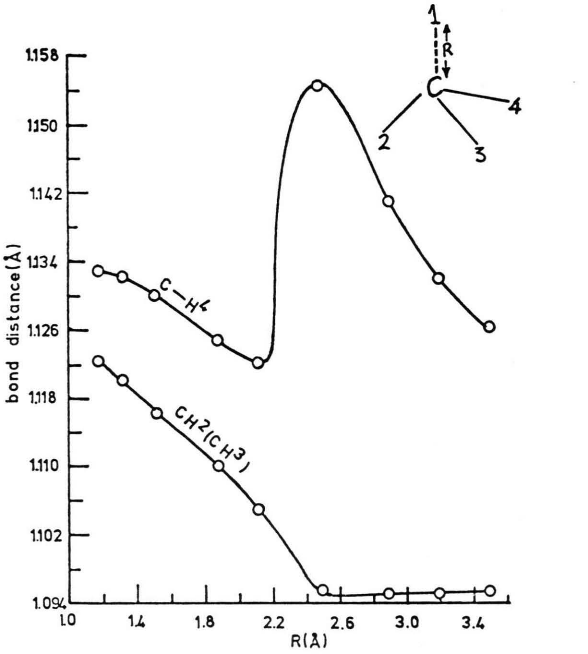


Fig. 9. Variation of the C—H bond distances along the $CH_4^{\cdot+} \rightarrow CH_3^{+}+H^{\cdot}$ reaction path as calculated by the MINDO/3-FORCES method.

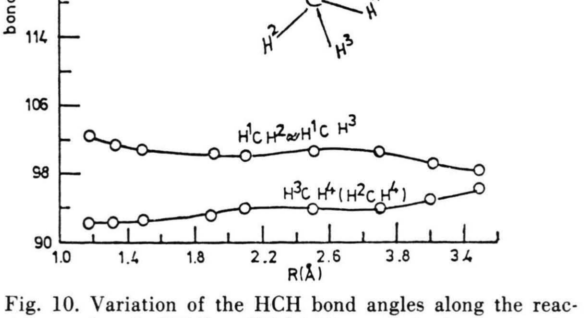


Fig. 10. Variation of the HCH bond angles along the reaction path of $CH_4^{\cdot+} \rightarrow CH_3^{+}+H^{\cdot}$ as calculated by the MINDO/3-FORCES method.

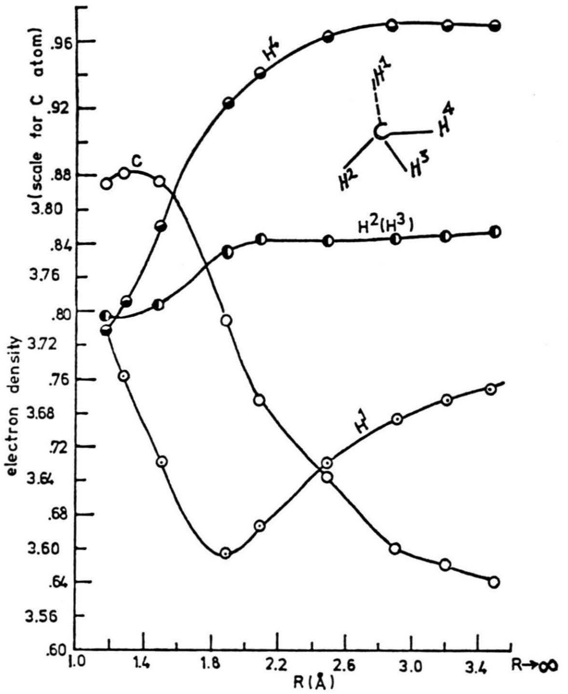


Fig. 11. Change in the electron densities of C and H atoms along the path of the $CH_4^{\cdot +} \rightarrow CH_3^{+} + H^{\cdot}$ reaction.

(3.55) at the end of the reaction ($R = \infty$). The electron density of H^1 decreases to a minimum (0.66) at $C-H^1$ distance 1.915 Å and increases finally to 0.75 at 3.5 Å. Those of H^4, H^2 and H^3 increase continuously along the reaction path; the electron densities on the last two atoms (H^2 and H^3) remaining equal.

The Benzyl Radical

The configuration of the benzylradical was formerly studied by one of us [7] using the π-SCF-MO method Dewar et al [9]. He found that the energy of the radical increased on rotating the CH_2 group up to 50° and then decreased on going to $\Phi = 90°$. According to his calculation the perpendicular structure of the radical forms an intermediate which is less stable than the planar structure by 2.3 kcal/mol. We have carried out MINDO/2- and MINDO/3-FORCES calculations for this radical with different rotation angles. The results listed in Table 3 show that the application of both methods confirms that the perpendicular structure should form an intermediate rather than a transition state of the rotation process. The rotation transition state is equally resembled by the rotation angles 60° and 120°.

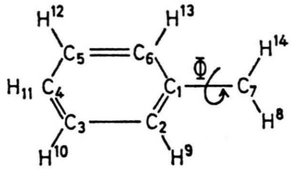


Table 3. MINDO/2-FORCES and MINDO/3-FORCES calculated heats of formation (kcal/mol) of the benzyl radical with different rotation angles and the corresponding MINDO/3-FORCES calculated geometric values.

	Heat of formation	ϕ ^{A}	I ^{B}	Molecular geometries ^{C}
	MINDO/3	MINDO/2		
0	67.93	48.40	7	C^7H^8, 1.111; C^1C^7, 1.380; C^1C^2, 1.464; C^2H^9, 1.107; C^2C^3, 1,386; C^3C^4, 1.416; $H^8C^7H^{14}$, 114.6; $H^{14}C^7C^1$. 120.6; $C^7C^1C^6$, 125.9; $C^2C^1C^6$, 113.5; $C^1C^6H^{13}$, 118.5; $C^1C^6C^7$, 122.7; $C^6C^5H^{12}$,120.7; $C^6C^5C^4$, 120.6; $C^3C^4C^5$, 119,3; $C^5C^4H^{11}$, 120.7.
60	74.97	54.5 (55°)	6	C^7H^8, 1.109; C^1C^7, 1.408; C^1C^2, 1.444; C^2H^9, 1.108; C^2C^3, 1.397; C^3C^4, 1.411; $H^8C^7H^{14}$, 118.9; $H^{14}C^7C^1$, 119.4; $C^7C^1C^6$, 122.7; $C^1C^6H^{13}$, 117.9; $C^2C^1C^6$, 115.8; $C^1C^6C^5$, 122; $C^6C^5H^{12}$, 119.9; $C^6C^5C^4$, 120.1; $C^3C^4C^5$, 120.1; $C^3C^4H^{11}$, 119.9.
80	70.63	49.12	7	C^7H^8, 1.106; C^1C^7, 1.431; C^1C^2, 1.432; C^2H^9, 1.109; C^2C^3, 1.403; C^3C^4, 1.407; $H^8C^7H^{14}$, 119.8; $H^{14}C^7C^1$, 119.1; $C^7C^1C^6$, 121.9; $C^1C^6H^{13}$, 118.3; $C^2C^1C^6$, 116.4; $C^1C^6C^5$, 121.8; $C^6C^5H^{12}$, 119.8; $C^6C^5C^4$, 119.9; $C^3C^4C^5$, 120.1; $C^3C^4H^{11}$, 119.9.
90	69.96	47.50	8	C^7H^8, 1.120; C^1C^7, 1.443; C^1C^2, 1.436; C^2H^9, 1.115; C^2C^3, 1.408; C^3C^4, 1.412; $H^8C^7H^{14}$, 121.6; $H^{14}C^7C^1$, 118.2; $C^7C^1C^6$, 121.2; $C^1C^6H^{13}$, 118.4; $C^2C^1C^6$, 117.7; $C^1C^6C^5$, 121.0; $C^6C^5H^{12}$, 119.4; $C^6C^5C^4$, 119.9; $C^3C^4C^5$, 120.5; $C^3C^4H^{11}$, 119.8.

A Rotation angles in deg.
B Number of geometric iterations.
C In Å and deg.

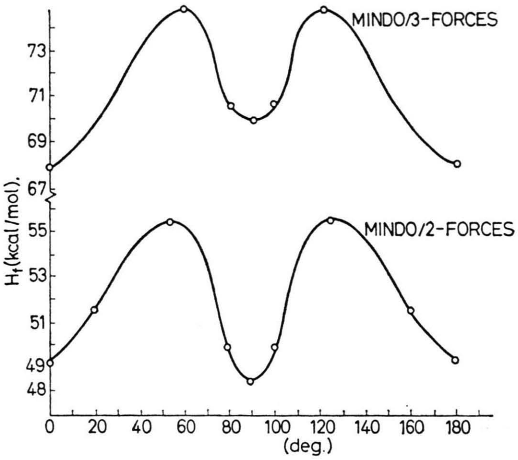


Fig. 12. MINDO/2- and MINDO/3-FORCES calculated heat of formation (kcal/mol) of the benzyl radical as a function of the dihedral angle (Φ).

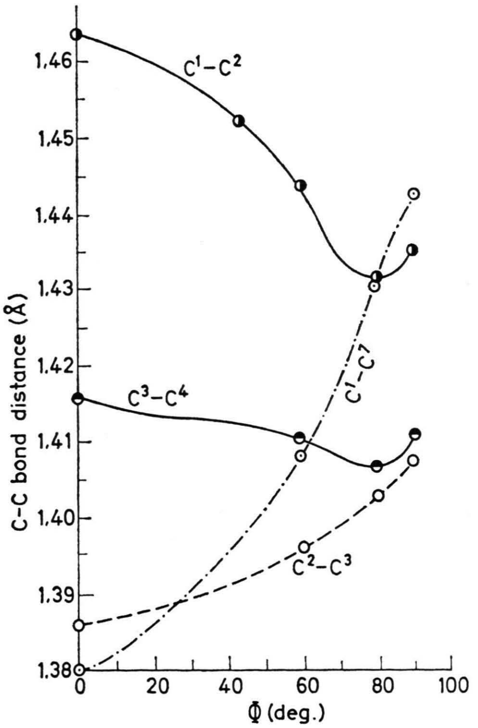


Fig. 13. MINDO/3-FORCES calculated bondlengths of the benzyl radical with different rotation angles. Changes in the Φ(deg) C–C bond distances as functions of the dihedral angle Φ) in the Ph–CH_2·.

It is seen that, whereas the MINDO/2-FORCES results include the stability of the perpendicular over the planar conformation, the MINDO/3-FORCES calculation yield that the planar conformation is by approximately 2.0 kcal/mol more stable than the perpendicular one. This figure is of a remarkable agreement with the value 2.3 kcal/mol obtained from the π-SCF calculation [7].

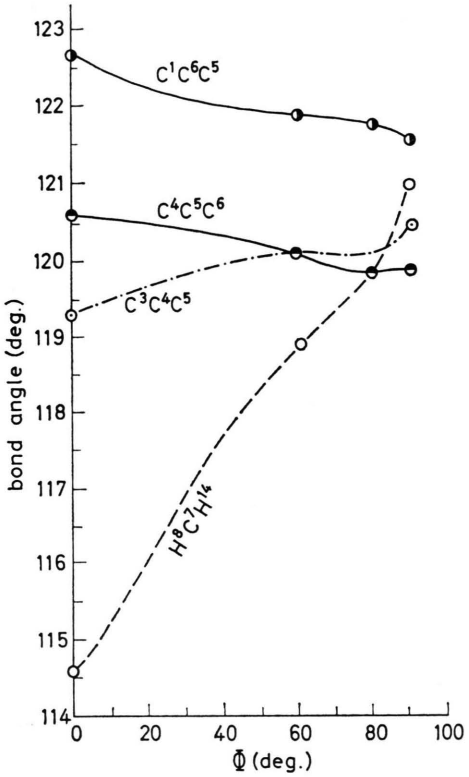
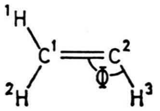


Fig. 14. MINDO/3-FORCES calculated bond angles of the benzyl radical with different rotation angles. Changes in the bond angles as function of the dihedral angle (Φ) in the Ph–CH_2·.

Also the MINDO/3-FORCES calculated rotation barrier, 7.03 kcal/mol, is in agreement with the value 8.54 kcal/mol of the π-SCF calculation. It is to note, however, that the calculated heat of formation of the radical (67.93 kcal/mol) is greater than the values of MINDO/2-FORCES (48.40 kcal/mol), the π-SCF method (53.20 kcal/mol) [7] and the experiment (45.0 kcal/mol) [11].

Structure of the Vinyl Radical

The structure and heat of formation of the vinyl radical was subject to various experimental [24, 25] and theoretical studies [26–29]. We have carried out a MINDO/3-FORCES calculation of the vinyl radical, minimizing its energy as a function of all geometric parameters.



The calculated results are listed in Tables 4 and 5. A plot of the calculated heats of formation against the bond angle $C^1C^2H^3$ (Φ) shows that the minimum heat of formation 69.81 kcal/mol corresponds to $\Phi = 151.1°$ (Figure 15). The calculated heat of formation shows good agreement with the experiment (65 kcal/mol) [30] and with the value published by Dewar et al. [4] 68.7 kcal/mol.

The calculated ground state equilibrium geometry compared with that of Pople et al. [27] and Linnett et al. [29] is shown in Table 6. The C = C bond (1.275 Å) is calculated shorter than that of ethylene (1.316 Å) and the $C^1 - H^2$ bond is longer than the other two C – H bonds, in agreement with the results of Linnett et al. [29]. Deformation of the $C^2 - H^3$ bond from its equilibrium position causes a considerable change in the other two C – H bond lengths.

The calculated spin densities of the unpaired electron on H^1, H^2 and H^3 are 0.0518, 0.1715 and 0.0333 respectively. The e.s.r. measurements [26] indicated three non-equivalent protons, with the largest spin on H^2, in agreement with the present calculated spin densities.

Table 4. MINDO/3-FORCES calculated heats of formation (kcal/mol) of vinyl radical with different values of the $C\dot{C}H$ angle (Φ).

Heat of formation	(deg.)	I A	F B
70.12	174.9	4	6×10^{-3}
69.99	170.0	4	6×10^{-3}
69.84	160.3	4	5×10^{-3}
69.81	151.1	5	5×10^{-3}
70.43	142.3	5	4×10^{-3}
70.74	139.8	24	6×10^{-3}
70.93	139.3	47	6×10^{-3}
71.07	138.5	52	6×10^{-3}

A number of geometric iterations. B maximum force (a.u.).

Table 5. MINDO/3-FORCES calculated molecular geometries (Å, deg.) of the vinyl radical with different $C-\dot{C}-H$ bond angles.

(deg.)	Molecular geometries
174.9	C^2H^3, 1.087; C^1C^2, 1.268; C^1H^1, 1.116; C^1H^2, 1.118; $H^1C^1H^2$, 107.7; $H^1C^1C^2$, 126.1.
160.3	C^2H^3, 109; C^1C^2, 1.272; C^1H^1, 1.112; C^1H^2, 1.119; $H^1C^1C^2$, 126.1; $H^1C^2H^2$, 108.0.
151.1	C^2H^3, 1.089; C^1C^2, 1.275; C^1H^1, 1.108; C^1H^2, 1.121; $H^1C^2H^2$, 108.3; $H^1C^1C^2$, 126.5.
139.8	C^2H^3, 1.085; C^1C^2, 1.275; C^1H^1, 1.091; C^1H^2, 1.119; $H^1C^1C^2$, 109.3; $H^1C^1C^2$, 129.1.

Table 6. MINDO/3-FORCES calculated bond lengths (Å) and bond angles (deg.) of vinyl radical compared with the values of ab initio calculation.

	MINDO/3-FORCES	FSGO [29]	STO-3G [27]
		Distances (Å)	
C^1-C^2	1.275	1.347	1.357
C^2-H^3	1.089	1.110	1.083
C^1-H^2	1.121	1.099	1.085
C^1-H^1	1.108	1.098	1.083
		Angles (deg.)	
$C^1-C^2-H^3$	151.1	124.6	130.8 (138) [28]
$C^2-C^1-H^2$	125.2	120.4	122.3
$C^2-C^1-H^1$	126.5	120.4	121.4
$H^1-C^1-H^2$	108.3	119.2	116.3

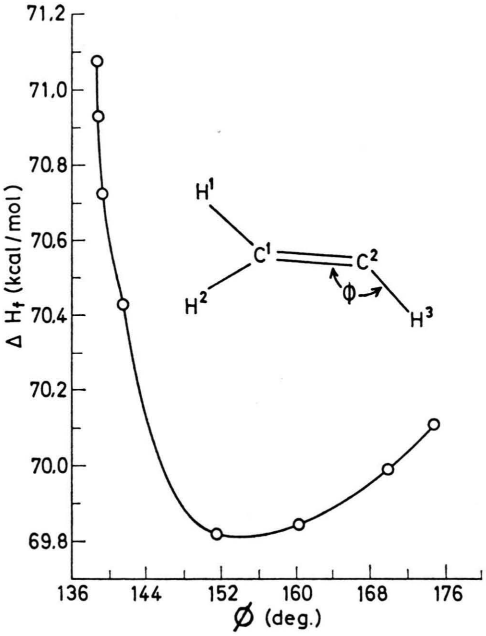


Fig. 15. MINDO/3-FORCES calculated heat of formation of vinyl radical as a function of the $H-\dot{C}-C$ bond angle.

[1] S. M. Khalil and M. Shanshal, Theor. Chim. Acta **46,** 23 (1977).
[2] B. A. Murtagh and R. W. H. Sargent, Comput. J. **13,** 185 (1970).
[3] P. Pulay, Mol. Phys. **17,** 197 (1969).
[4] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. **97,** 1285 (1975); ibid, 1294.
[5] H. M. Frey and R. Walsh, J. Chem. Soc. A, **1970,** 2115.
[6] C. P. Baskin, C. F. Bender, C. W. Bauschlicher, Jr., and H. F. Schaefer III, J. Amer. Chem. Soc. **96,** 2709 (1974).
[7] M. Shanshal, Molec. Phys. **23,** 441 (1972).
[8] J. N. Murrell, J. B. Pedley, and S. Durmaz, J. Chem. Soc. Faraday Trans. **2,** 69, 1370 (1973).
[9] M. J. S. Dewar and A. Harget, Proc. Roy. Soc. **A 315,** 443 (1970).
[10] W. Braun, A. M. Bass, and M. Pilling, J. Chem. Phys. **52,** 5131 (1970).
[11] J. A. Kerr, Chem. Rev. **66,** 465 (1966).
[12] G. S. Hammond, J. Amer. Chem. Soc. **77,** 334 (1955).
[13] C. A. Coulson and H. L. Strauss, Proc. Roy. Soc. **A 269,** 443 (1962).
[14] H. A. Jahn and E. Teller, Proc. Roy. Soc. **A 161,** 220 (1937).
[15] H. A. Jahn, Proc. Roy. Soc. **A 164,** 117 (1938).
[16] G. S. Handler and H. W. Joy, Int. J. Quantum Chem., Symp. **No. 5,** 529 (1970).
[17] F. A. Grimm and J. Godoy, Chem, Phys. Lett. **6,** 336 (1970).
[18] J. Arents and L. C. Allen, J. Chem. Phys. **35,** 73 (1970).
[19] R. N. Dixon, Mol. Phys. **20,** 113 (1971).
[20] W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc. **93,** 808 (1971).
[21] G. A. Olah and G. Klopman, Chem. Phys. Lett. **11,** 604 (1971).
[22] M. J. S. Dewar and G. Klopman, J. Amer. Chem. Soc. **89,** 3089 (1967).
[23] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Braxl, Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS-26, National Bureau of Standard, Washington D.C., see Ref. [29].
[24] F. P. Lossing, Can. J. Chem. **49,** 357 (1971).
[25] E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. **40,** 213 (1964); R. W. Fessenden, J. Phys. Chem. **71,** 74 (1967).
[26] See Ref. [4].
[27] W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc. **93,** 808 (1971).
[28] P. Millie and G. Berthier, Int. J. Quantum Chem. **2 S,** 67 (1968).
[29] P. H. Blustin and J. W. Linnett, J. Chem. Soc. Faraday II, **71,** 1071 (1975).
[30] J. L. Franklin, J. D. Dillard, H. M. Rosenstock, Y. T. Herron, K. Draxl, and F. M. Field, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. No. 26 (1969).