Calculations on the Lowest Energy State of Planar Methane

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Summary Calculations show that the lowest energy state of planar methane is a triplet which is stable to all small distortions; this result is relevant to the possibility of preparing a molecule with planar 4-co-ordinate carbon.

THERE has been some interest in the structure of possible compounds possessing a planar tetraco-ordinated carbon atom. For methane itself the energy required to convert from a tetrahedral to a planar structure has been estimated as 5·5 eV (extended Huckel calculation)[1] or 10·8 eV (approximate *ab initio* calculation),[2] but Hoffmann, Alder, and Wilcox have suggested several molecular systems in which the planar structure could be stabilized relative to the tetrahedral.

In the course of some calculations on the potential energy surface for reaction (1) we have made a fairly extensive

$$^3CH_2 + H_2 \rightarrow {}^3CH_4 \qquad (1)$$

study of the lowest triplet state of methane and have concluded that its equilibrium configuration is square planar. This result is not too surprising in view of the *ab initio* calculations already published on the ground state of CH_4^+ which was shown[3] to have D_{2d} symmetry with two bond angles of 141° and two of 96°. The structure is therefore reasonably close to being planar (for which angles of 180° and 90° would be found).

Calculations have been made with an open-shell SCF program using a minimum basis of Slater orbitals (hydrogen 1*s*, carbon 1s, 2*s*, 2*p*). The evaluation of the three- and four-centre integrals involved some approximations, but past experience with the approximations used shows that the results are close to those of accurate calculations.[4] The open-shell method used different orbitals for different spins with annihilation from the resulting wave function of the quintet component. Although we have investigated the optimum bond length (r) and optimum orbital exponents (ζ) for the system, we give here the results only for the following set of parameters, which are close to optimum:

$$r = 2{\cdot}1 \text{ a.u.}, \ \zeta_H(1s) = 1{\cdot}2, \ \zeta_C(1s) = 5{\cdot}67, \ \zeta_C(2s) = \zeta_C(2p) = 1{\cdot}625$$

Occupied orbitals (see Table) were obtained for the state having two more electrons of α spin than β spin ($S_z = +1$).

TABLE

α spin					
Symmetry	a_{1g}	e_u		a_{2u}	b_{1g}
Energy	−0·9582	−0·6398	−0·6398	−0·3894	−0·2809 a.u.
β spin					—
Symmetry	a_{1g}	e_u			
Energy	−0·8282	−0·5264	−0·5264 a.u.		

The energy of this state was −39·8456 a.u. which is 7·8 eV greater than the ground state of tetrahedral CH_4 calculated with the same basis, but 3·2 eV less than the singlet state with the same square planar structure (our calculated activation energy for the singlet state is 11 eV).

It is to be noted that the two highest occupied α-spin orbitals are non-degenerate so that the total state has symmetry B_{2u} and is not subject to a further Jahn–Teller distortion. We have considered distortions that lower the symmetry to D_{2d} or C_{2v} and have found no configuration of lower energy.

Neither of the two top orbitals of α spin has any C–H bonding characteristics. One of these (a_{2u}) is the π orbital of the carbon, and the other (b_{1g}) is a combination of hydrogen orbitals which has the symmetry of a $d_{x^2-y^2}$ orbital of the carbon. The structures suggested for stabilizing the singlet state, which involve lowering the energy of the a_{2u} orbital, would also stabilize the triplet. In addition the energy of the b_{1g} orbital would be lowered by having ligands more electronegative than hydrogen. Our conclusion is that attempts to prepare a planar 4-covalent carbon system may well lead to a triplet-state molecule.

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