Semi-empirical and *ab initio* Calculations on the Automerization of Methane

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Summary It has been shown by semi-empirical and *ab initio* calculations that pyramidal, and not planar, methane is involved in its hypothetical automerisation reaction.

It is commonly believed that intramolecular enantiomerisation of compounds with tetrahedral carbon involves a transition structure with planar configuration at carbon and several workers have investigated the case of planar methane as an example. Both semi-empirical[1] and *ab initio*[2–4] calculations predict planar methane to be unstable (150—250 kcal mol^{-1} above the ground state of tetrahedral structure) in the decomposition $CH_4 \rightarrow CH_3 + H$ (104 kcal mol^{-1}). However, suitable substituents would be expected to stabilize the planar geometry of the quadrivalent carbon so that it could serve as a thermally accessible transition state of an enantiomerization reaction. This problem has been opened for discussion by calculations of Hoffmann and his co-workers.[1]

Two principal types of deformations of tetrahedral structures have been shown to be responsible for their enantiomerization.[5] The first is the mechanism of the so-called tetrahedral compression (Scheme). The second is the mechanism of digonal twist which reduces to the former for noncyclic compounds.[5]

The automerisation (degenerate enantiomerization) (**1a**) $\rightleftharpoons$ (**1b**) could be related to a group of 'narcissistic' reactions.[6] The reaction pathway is determined by two antisymmetric co-ordinates, by the angles α and β. For reactions of this type there also exists the possibility of totally chiral pathways which do not pass through the planar D_{4h} structure (**2**);

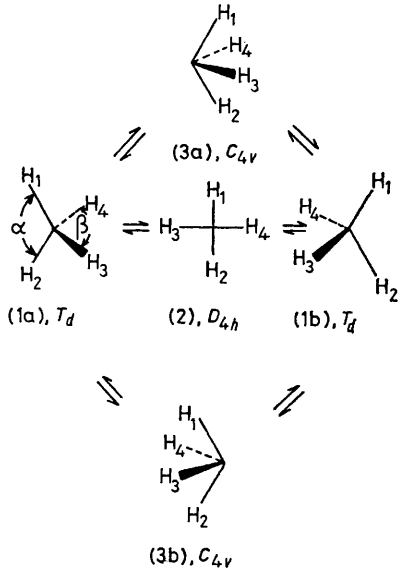
TABLE. Geometries and energies of tetrahedral, planar, and pyramidal methane[a]

Symmetry	Angle/°	l(C–H)/Å	Total energy/a.u.	Relative energy/kcal mol^{-1} *Ab initio*	EHMO	CNDO/2
T_d	109·5	1·093	−40·1830	0	0	0
C_{4v}	130	1·112	−39·9382	147	140	240
D_{4h}	180	1·085	−39·9393	158	150	250

[a] 1 a.u. = 4·3598 × 10^{-18} J. 1 cal = 4·18 J.

this has been found to be the case in one example investigated.

We have calculated the potential energy surface $E = f(\alpha,\beta)$ of the automerization (**1a**) ⇌ (**1b**) by EHMO and CNDO/2 methods and have found that the D_{4h} structure (**2**) is not a saddle point on the potential energy surface but corresponds to the top of a flat maximum (Figure). There are two distinct enantiomeric pathways around this maximum, both having chiral pyramidal C_{4v} structures, (**3a**) and (**3b**), as the saddle points (transition states). The total energy of the pyramidal methane has been estimated by both EHMO and CNDO/2 methods to be 10 kcal mol^{-1} lower than that of the planar form (Table).



SCHEME

This conclusion has been confirmed by *ab initio* calculations of the most important regions of the potential energy surface (T_d and D_h points and C_{4v} section). An extended basis of cartesian Gauss-type functions of double zeta (DZ) quality of types C (10*s* 5*p*/4*s* 2*p*) and H (4*s*/2*s*)[7] has been used and the geometry of all the structures has been optimized. Some of the results are presented in the Table.

The *ab initio* calculations predict the pyramidal structure to be 11 kcal mol^{-1} more stable than the planar structure in agreement with the semi-empirical calculations, both being in singlet electronic states.

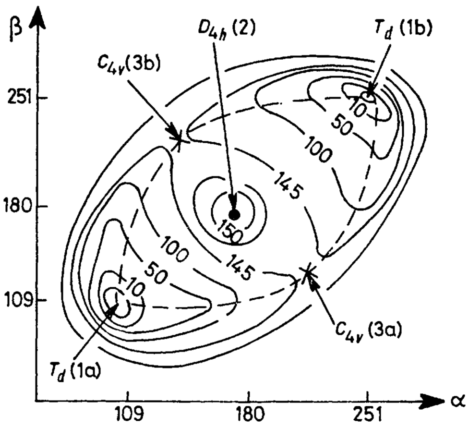


FIGURE. The potential energy surface of automerization of methane calculated by the EHMO method.

It should be noted that Monkhorst,[2] using a minimum STO basis set, found the planar D_{4h} form to be at a minimum with respect to C_{4v} type distortion; this finding is at variance with our calculations. However, minimum basis sets have been shown by special theoretical study[8] to be unreliable for quantitatively accurate *ab initio* geometry predictions for AB_4 molecules, while DZ basis sets generally provide accurate predictions.

In the light of the results obtained, the approach to the problem of stabilization of quadrivalent carbon in organic compounds, other than those having tetrahedral geometry, ought to be reconsidered. The pyramidal form thus appears to be more stable than the planar form.

The possibility of triplet ground states for both or either D_{4h} and C_{4v} forms of methane exists;[4] this requires study. As the correct estimation of singlet–triplet energy separation is in general beyond the scope the single determinant approximation more extensive CI calculations are in progress.

The *ab initio* calculations were carried out with the IBMOL-5 program[9] which was modified for a BESM-6 computer by V.I. Avdeev.

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