Linnett Planar Methane

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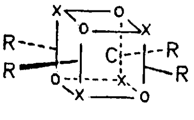
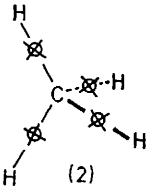
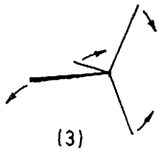
Summary In contrast with the results of all MO calculations, planar methane is predicted by the L-strain theory to be capable of existence.

INTEREST in strained hydrocarbons is high, and among the foremost types not yet prepared is that containing a planar tetravalent carbon atom. A number of recent calculations by various MO methods have placed the energy of planar methane at 248,[1] 127,[2] 187,[2] 168,[3] 250,[4] and 180[4] (triplet) kcal mol^{-1} above that of tetrahedral methane. Since the bond dissociation energy of CH_3–H is only 104 kcal mol^{-1}, all these studies predict that planar methane cannot exist.


(1)


(2)


(3)

A different result is obtained for Linnett planar methane, (**1**) (R = H). Although Linnett tetrahedral methane (**2**)[5,6] is identical with that pictured in the conventional way, structure (**1**) has no counterpart in MO theory as yet. It is higher in energy than (**2**) because (i) the C–H bonds are each L-strained[6] by 70½°, and (ii) the hydrogen atoms are closer together in (**1**), causing an increase in core–core repulsion among the atoms not bonded to each other.

The empirically determined energy price for an L-strain of 70½° is 6·8 kcal mol^{-1} per isolated C–C bond,[6] or (from the ratio of bond energies) 8·1 per C–H bond. An additional *ca.* 3 kcal mol^{-1} of secondary L-strain must be assumed when R is alkyl,† not counting steric repulsion, which is neglected. The total L-strain in (**1**), then, is 32 kcal mol^{-1} when R is H, and 40 when R is alkyl.

If the hydrogen atoms were bare protons, and all C–H distances were 1·093 Å in (**1**) (R = H) and (**2**), the total interproton electrostatic repulsion in (**2**) would be 6(331·6)/1·785 = 1114 kcal mol^{-1}, and in (**1**) 4(331·6)/1·546 + 2(331·6)/2(1·093) = 1161 kcal mol^{-1}, for a net destabilization of 47 kcal mol^{-1} for (**1**) relative to (**2**). However, the hydrogen nuclei are heavily screened from one another by the bonding electrons, which spend much of their time around the atomic nuclei, so that the repulsion energy term, which falls off with the square of the effective charge, is actually very much less than 47. If the hydrogen nuclei are 50% screened, the core–core repulsion term becomes 12 kcal mol^{-1}, and for 75% screening it drops to only 4 kcal mol^{-1}.

Thus the total strain in (**1**) relative to (**2**) can be estimated at about 35—40 kcal mol^{-1} for R = H, and about 8 kcal mol^{-1} higher for R = alkyl. These numbers are probably on the low side because the scissoring deformation (**3**), which is available for all the bent-bonded molecules on which the L-strain curve is based,[6] is impossible for (**1**). However, since the strain energies for (**1**) are substantially lower than the respective bond dissociation energies, the prediction can be made that planar tetravalent carbon is capable of existence.

A more difficult question is whether tetrahedral carbon can be thermally racemized. It is clear that (**1**) lies in a potential well, since twisting one RCR group relative to the other increases L-strain sharply. If the transition state is half twisted, *i.e.* with the two RCR planes at a 45° angle, the L-strain in two of the C–R bonds goes up to one-half of 141°. This is so far off the L-strain curve[6] that extrapolation is unreliable; an activation energy for racemization in the neighbourhood of 50—55 kcal mol^{-1} (not counting the increase in core–core repulsion) is estimated. By another, more empirical method,‡ the barrier to racemization is 73 kcal mol^{-1}, so that by either standard the racemization of a molecule with no especially weak bonds, such as 3-methylhexane, should be possible.

Closely related to planar methane is perpendicular ethylene, which is also predicted to lie in a potential well. It will be discussed in a subsequent article.‡

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† Secondary L-strain is about one-half of primary L-strain for isolated C–C bonds.[7]

‡ Manuscript in preparation.

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