Activation Energy for Interconversion of Enantiomers containing an Asymmetric Carbon Atom without breaking Bonds

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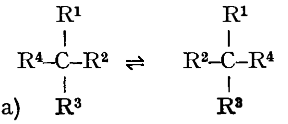
INTERCONVERSION of enantiomers containing asymmetric carbon atoms can in principle occur with or without breaking of the bonds attached to the asymmetric carbon atom. For the simplest case, namely



$$\underset{R^3}{\overset{R^1}{R^4\text{–}C\text{–}R^2}} \rightleftharpoons \underset{R^3}{\overset{R^1}{R^2\text{–}C\text{–}R^4}}$$

(Ia) (Ib)

this interconversion without breaking of bonds could occur by bending of the bonds, but this pathway has been generally rejected, because it would require too much energy.[1]

There is no calculation known to the author which supports this contention. It was therefore interesting to calculate the activation energy for the hypothetical interconversion (Ia) ⇌ (Ib) when no bonds are broken. Two pathways can be distinguished. One involves a transition state with a planar configuration of the four bonds originating from the asymmetric carbon atom. This configuration has a plane of symmetry. The pathway is shown in Figure 1.

The other pathway involves an "umbrella" configuration of the bonds with the carbon atom at the top of it. This is shown in Figure 2.

We used the methane molecule as a representative model to calculate the interconversion barrier. We performed LCAO–SCF calculations on methane in its (normal) tetrahedral configuration and the hypothetical configurations of the C–H bonds as discussed above. In these calculations a minimal basis of Slater-type orbitals is used.[2] The one-electron, one- and two-centre integrals and two-electron, one-centre integrals have been calculated accurately, and the remaining integrals have been evaluated approximately, using a modified Mulliken approximation.[3] Slater exponents[2] were used for the carbon atom, and an exponent of 1·2 for the hydrogen atoms, in accordance with the work of Palke and Lipscomb.[4] Details of the method will be published elsewhere. Bond lengths

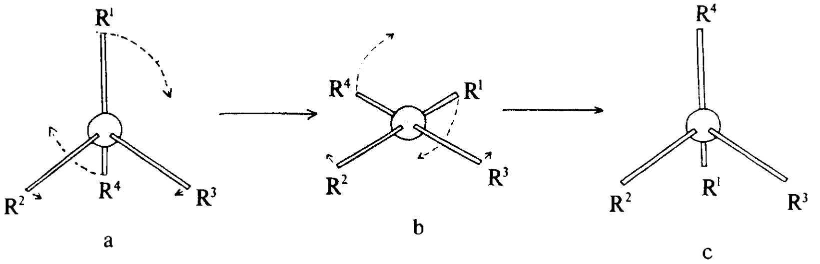


FIGURE 1. *Interconversion of the enantiomers of* $CR^1R^2R^3R^4$ *without breaking bonds, involving a transition state with a planar configuration;* a *and* c *are mirror images.*

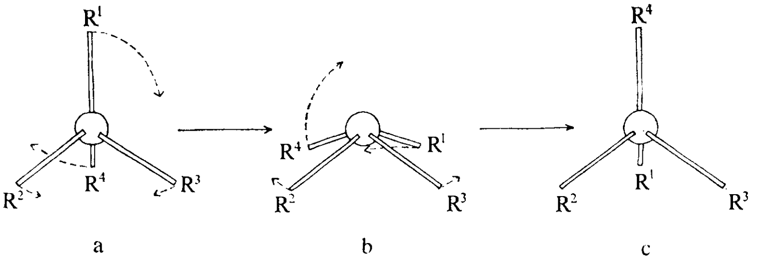


FIGURE 2. *Interconversion of the enantiomers of* $CR^1R^2R^3R^4$ *without breaking bonds, involving a transition state with a pyramidal configuration;* a *and* c *are mirror images.*

have been varied in order to minimize the total energies. We can summarize the results as follows:

(1) The energy of the planar configuration is about 250 kcal./mole above the energy of the tetrahedral configuration; the C–H bonds have practically the same length as those in tetrahedral methane.

(2) The planar configuration constitutes a minimum with respect to the following deformations: (a) from a square-planar to a rectangular-planar configuration; (b) from equal to different lengths of the C–H bonds; (c) out-of-plane deformations of the C–H bonds, that lead to an "umbrella" configuration.

From these results we may conclude that the interconversion (Ia) $\rightleftharpoons$ (Ib) without breaking bonds is in fact impossible: the "best" pathway (involving a planar configuration of the bonds around the asymmetric carbon atoms) would require at least 2·5 times the carbon–carbon bond energy. In actual enantiomers this amount of energy will be even greater because of steric hindrance of the groups bonded to the asymmetric carbon atom. Similar calculations on NH_4^+ lead to an interconversion barrier of the same order of magnitude (200 kcal./mole).

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[4] W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1966, **88**, 2384.