Methylene Rocking and Minimum Bond Tortuosity in Cyclobutane

By Lawrence S. Bartell*
(*Department of Chemistry, University of Michigan, Ann Arbor, Michigan* 48104)
and Birgit Andersen
(*Department of Chemistry, University of Oslo, Blindern Oslo* 3, *Norway*)

Summary A principle of minimum bond tortuosity leads naturally to an equation representing an important contribution to static rocking deformations of groups in four-membered rings.

Although the concept of bent bonds is widely accepted, chemists are in the habit of drawing straight lines to represent the bonds between covalently bonded atoms. This may sometimes obscure the origin of deformations of groups from idealized geometries. A case in point seems to be the methylene orientation in cyclobutane. We suggest a simple interpretation of certain rocking displacements noted in recent theoretical[1] and experimental[2] structural investigations of cyclobutane systems.

Planar (D_{4h}) cyclobutane has C–CH$_2$–C groups with local C_{2v} symmetry. If the ring is puckered to D_{2d} symmetry preserving the local C_{2v} configuration of the C–CH$_2$–C units (with methylene groups bisected by their associated C–C–C planes) the C–C and C–H bonds escape the eclipsed conformations they suffered in the D_{4h} structure. Indeed, this diminished eclipsing is generally considered to be responsible for the puckering of cyclobutane rings. Little attention was paid to possible interactions between ring puckering and methylene rocking displacements until calculations by Salem[1] led to the "surprising result" that planar cyclobutane is more stable than puckered cyclobutane unless the local C_{2v} symmetry of methylene groups is broken.

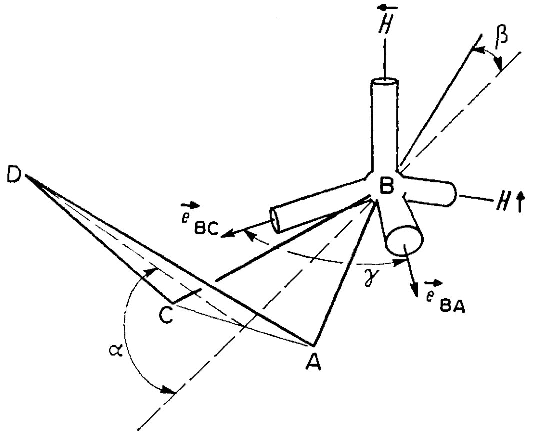

Figure. D_{2d} cyclobutane ring ABCD with flap angle α, methylene rock angle β, and vectors $\vec{e}_{ij}$ representing emerging C–C bond lines radiating from carbon i in the sense of carbon j. Emerging bond rays are depicted for carbon B and are imagined to be distributed about B with local C_{2v} symmetry. The C_A–C_B–C_C rays $\vec{e}_{BA}$ and $\vec{e}_{BC}$ leave B with an intervector angle γ and lie in a plane that bisects H–C_B–H and aims away from plane CBA by an angle β.

There is evidence in favour of a localized bond picture in which bonds radiating from a given atom follow the Valence-Shell-Electron-Pair-Repulsion model[3] advanced by Gillespie and Nyholm. It is natural, then, to view the –CH$_2$– units in cyclobutane as possessing C_{2v} symmetry with respect to the emergent localized bond lines radiating from the carbon atoms rather than with respect to the C–C–C internuclear vectors. So, for example, the local C_{2v} symmetry expected in the chemists' "prong and tubing model" (Prentice-Hall

Framework Molecular Model) of C_4H_8 should apply to the geometry of the 4-pronged metal inserts representing carbon valence lines instead of to the C–CH_2–C atomic positions. In a prong and tubing model of cyclobutane, the C–CH_2–C bonds are bent and, furthermore, if the ring is puckered, the tubular connectors are bent in a tortuous, snaky path unless the CH_2 group bisector moves away from the C–C–C local plane. We suggest that the CH_2 rocking angle, β, giving the minimum bond snakiness, is a plausible gauge of the natural angle in the molecule. A mathematical expression of the result requires the internal co-ordinates and bond vectors illustrated in the Figure.

The condition for minimum bond tortuosity is that the i to j bond arcs are each constrained to lie within a plane; they must not snake away from it. That is, the vectors $\vec{r}_{ij}$, $\vec{e}_{ij}$, and $\vec{e}_{ji}$ must lie in a common plane. It may be shown that this condition is met if the angle β satisfies equation (1).

$$(\tan \tfrac{\alpha}{2})[\cos(\tfrac{\alpha}{2} + \beta) + \tan \tfrac{\gamma}{2}] - 2 \sin (\tfrac{\alpha}{2} + \beta) = 0 \qquad (1)$$

If we adopt a value of 30° for α, a common value for cyclobutane derivatives,[4] and assume that the carbon bond lines emerge at tetrahedral angles ($\gamma = 109{\cdot}47°$) the natural (minimum bond snakiness) value of β is 3·45°. If α or γ is increased ($\angle$CCC = 112·5° in n-alkanes[5]), β is increased somewhat.

The above result may be compared with the CNDO/2 calculations on cyclobutane by Wright and Salem[1] where $\beta = 3°$ yielded an energy minimum at $\alpha = 20°$, and $\beta = 4°$ yielded $\alpha = 40°$. *Ab initio* results also favoured a planar ring when β was constrained to equal zero but the calculations were not extended to $\beta \neq 0$.[1] Meiboom and Snyder[2a] have interpreted the n.m.r. spectrum of cyclobutane in a nematic solvent in terms of $\alpha = 27°$ and $\beta = 4°$. An apparently related deformation has been seen experimentally in spiro[3,3]heptane where each cyclobutane ring is puckered with α *ca.* 26·5° and where the value of β at the quaternary carbon is *ca.* 5°.[2b]

The principle of minimum bond tortuosity is not a new one.[6] It has been invoked, for example, to account for the difference between the force constants for E_g and E_u methyl rocking deformations in ethane.[6a] Lest the principle appear whimsical, we point out that it is fully in keeping with considerations of σ-bond orbital overlap, on the one hand, and applied to ethane at least, it is in accord with the pseudo-Jahn-Teller implications of electron density polarization and softening of force constants.[7]

Furthermore, rocking also results in additional staggering, at fixed α (*cf.* ref. 1), of which account should be taken. Unfortunately, no reliable model applicable to four-membered rings exists. For sake of argument, a model can be constructed by incorporating hydrocarbon force constants[8] · and an ethane-like torsional potential into the emergent bond ray representation. The emergent bond ray picture implies a significantly greater staggering for the C–C–C–C bond sequences than does the conventional picture of C–C–C–C straight internuclear vectors. The above model suggests a rocking displacement of several degrees to be added to the result of equation (1).

We thank the National Science Foundation for support.

(*Received*, 13*th July* 1973; *Com.* 1000.)

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