

SOME NOVEL CONFORMATIONAL EQUILIBRIA*

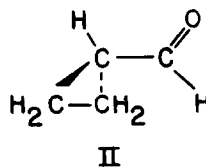
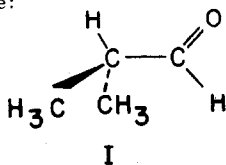
L. S. Bartell, B. L. Carroll, and J. P. Guillory
Institute for Atomic Research and Department of Chemistry
Iowa State University, Ames, Iowa

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In the course of some structural studies of gaseous molecules by electron diffraction, we have observed significant alterations in conformational behavior induced by bond bending and by the lowering of molecular symmetry. Because of the widespread interest in the unsolved theoretical problem of restricted rotation, and in view of possible implications in the field of conformational analysis, it seems appropriate to report the preliminary findings of our investigations.

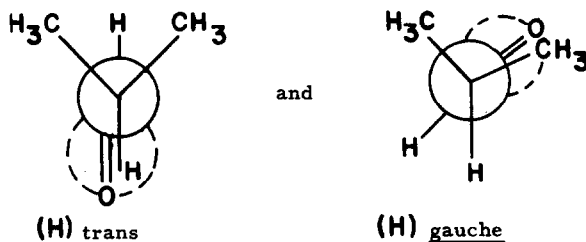
The stable conformations of ethane derivatives are those with staggered bonds. The staggered bond point of view also accounts for the favored configurations in propylene and acetaldehyde, if double bonds are regarded as two bent single bonds (1). Such drastic bending of the bonds at one end of the axis of internal rotation reduces the barrier somewhat but does not destroy the essentially ethane-like 3-fold barrier.

In order to explore the unstudied effect of bending the bonds at the other end of the axis, we have investigated the following pair of molecules in the vapor phase:



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The control molecule I exhibits conformations analogous to those of acetaldehyde, namely



illustrated with bent carbonyl bonds drawn as dashes. It was therefore extremely interesting to discover that molecule II, with bonds bent at both ends, exhibited quite a different behavior. It was found to exist in a trans form and in a cis form with eclipsed bonds.



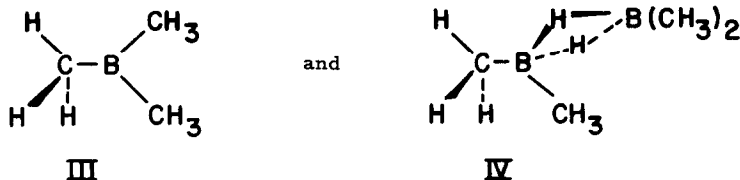
Nearly equal fractions of cis and trans molecules were present in the sample, and the barrier appeared to be in excess of 2 kcal. mole⁻¹.

This behavior, once recognized, can be rationalized in terms of the π -electron characteristics often proposed for the cyclopropane ring (2). Molecule II, consequently, may be regarded as an analog of butadiene for which cis-trans isomerization is usually predicted (3) (although firm evidence exists only for the trans isomer (4)). The most significant finding, then, is that the form of barriers may be substantially altered (in this case

from 3-fold to 2-fold)[†] merely by the bending of adjacent bonds. This fact may be helpful in interpreting the physical nature of barriers to rotation. For example, the observed behavior does not seem to follow the spirit of the simple nuclear repulsion barrier model recently proposed (5).

The control model itself is instructive. It may be considered as a key fragment of 2-methylcyclohexanone, which molecule has been the subject of a certain amount of controversy in conformational analysis. The gauche forms of I, which comprise about 90% of the total gas sample, are analogous to equatorial 2-methylcyclohexanone. The trans form is analogous to the axial conformation except for its freedom from the $\text{CH}_3 \cdots \text{H}$ repulsions encountered in the axial derivative. The present results, unobscured by axial steric effects, show an intrinsic stabilization resulting from eclipsing the $\text{C} = \text{O}$ and CH_3 groups. This is in agreement with inferences made by Abraham and Pople from an NMR study of propionaldehyde (6).

The second pair of molecules investigated includes



Essentially free rotation was observed in III, in contrast to commonly heard hyperconjugative predictions for an appreciable barrier. This is consistent with a microwave study of $\text{H}_3\text{C} - \text{BF}_2$ for which a 6-fold barrier of 0.01 kcal. mole⁻¹ was reported (7). The low barrier is a consequence

[†] It should be pointed out that the difference is one of degree rather than kind. Neither the isopropyl nor the cyclopropyl carboxaldehydes are excluded by symmetry from having 1-fold, 2-fold, 3-fold, etc., components in the Fourier representations of their barrier functions.

of the symmetry which excludes a 3-fold contribution. In IV the symmetry has been broken and the diffraction results indicate a 3-fold barrier of roughly 1 kcal. mole⁻¹. The electronic structure of IV is formally analogous to that of acetaldehyde which has a similar barrier.

Detailed structural analyses of the above molecules will be reported elsewhere.

We should like to thank Professors C. W. Heitsch and C. H. DePuy who donated the compounds for this research.

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