Nonplanarity of Cyclobutane. Electrostatic Interactions in *cis*-1,2-Dicarboxylic Acids

Layton L. McCoy

Department of Chemistry, University of Missouri at Kansas City, Kansas City, Missouri 64110

Received May 4, 1965

A relation between the amount of bending in a cyclobutane ring and the distance between *cis*-1,2 substituents is formulated. Assuming H–C–H angles of 112–114° in both cyclopropane and cyclobutane, calculations show that the cyclobutane ring must be bent about 50–60° for *cis*-1,2 groups to be the same distance apart as in cyclopropane. It is concluded that, even allowing for slight bending of the cyclobutane ring, *cis*-1,2 groups in cyclobutane are closer together than *cis*-1,2 groups in cyclopropane. In conjunction with additional information from the literature, the consequences of this conclusion in relation to the K_1/K_2 ratio of acid dissociation constants of *cis*-1,2-dicarboxylic acids is discussed.

The possible nonplanarity and related conformational possibilities of cyclobutane have stimulated considerable interest recently. The present work was initiated as a result of a paper by Fonken and Shiengthong.[1] These authors suggested that the decrease in K_1/K_2 ratio for the acid dissociation constants of the series of *cis*-1,2-dicarboxylic acids of cyclopropane, cyclobutane, and cyclopentane was evidence supporting nonplanarity in the cyclobutane system. That is, by being nonplanar, the *cis* groups on the cyclobutane ring would be farther apart than if the ring were planar, and this increased distance would result in a lesser electrostatic interaction, and consequently, a lesser K_1/K_2 ratio. In the present work, examination of Dreiding molecular models suggested that Fonken and Shiengthong's qualitative considerations[1] are erroneous. It is clear from the models that in a planar conformation, *cis*-1,2 groups are closer together on cyclobutane than on cyclopropane, and that even with a 20° bend in the cyclobutane ring this inequality still is very likely correct. However, the precision of measurements with such models is not very high. It seemed worthwhile, therefore, to derive a relation between the amount of bending of the cyclobutane ring and the distances between various substituent locations on the ring in terms of reasonable bond lengths and bond angles. The derivation of this relation, calculations using the derivation, and some specific consequences with regard to *cis*-1,2-dicarboxylic acids are the basis of this paper.

Some preliminary analysis of the motions of various points in a cyclobutane system seems pertinent. For reference, the diagram of Figure 1 will be used. The carbon atoms are numbered 1, 2, 3, 4, and the plane determined by these points when the ring is in a planar conformation will be defined as the *xy* plane. Points lying above this plane and on a C–H axis will be indicated by primed numbers, *e.g.*, 1′, 2′. Similarly, points lying below the initial plane and on a C–H axis will be indicated by double-primed numbers, 1″, 2″. Because of the symmetry of the system and the way it is linked together, bending of the ring across the C-1, C-3 positions also will result in bending across the C-2, C-4 positions, and as C-1 and C-3 move toward each other, C-2 and C-4 will move closer together. If these motions are followed through to a hypothetical extreme of 180° of bend, C-1 and C-3 will coinicde, C-2 and C-4 will coincide, and all four C–C bonds will coincide. During these movements, it should be noted that planes 1′–1–1″ and 3′–3–3″ will coincide and will be perpendicular to another plane containing 2′–2–2″ and 4′–4–4″. A consequence of this is that only in the extreme (180° bend) conformation would substituent groups on C-1 be exactly staggered between groups on C-2.

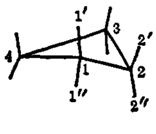

Figure 1.

In order to derive relationships between ring bending and separation of substituents, a coordinate system is defined in the following way. The *x* axis is defined by midpoints of bonds C-1–C-2 and C-3–C-4, the *y* axis by the midpoints of bonds C-2–C-3 and C-1–C-4, and the *z* axis is perpendicular to the *x* and *y* axes at their intersection. With this coordinate system, an alternate description of the folding of the cyclobutane ring may be given. Thus, each C–C bond will rotate about its midpoint; from the origin and looking along either axis, *x* or *y*, the bonds centered on the *x* axis will rotate in one direction, clockwise, for example, while the two bonds centered on the *y* axis will rotate in the opposite direction, counterclockwise. Because the bonds are linked together, they will rotate equally, and move along their respective axes toward the origin. With this description and by straightforward geometrical, trigonometrical, and arithmetical considerations, the following relationships were derived.

$$x_{1'} = y_{1'} = m \cos \alpha + \left(n \cos \left[\frac{\phi}{2} + \frac{\beta}{2}\right]\right)/\sqrt{2}$$

$$-x_{2'} = y_{2'} = m \cos \alpha + \left(n \cos \left[\frac{\phi}{2} - \frac{\beta}{2}\right]\right)/\sqrt{2}$$

$$z_{1'} = m \sin \alpha + n \sin \left[\frac{\phi}{2} + \frac{\beta}{2}\right]$$

$$z_{2'} = -m \sin \alpha + n \sin \left[\frac{\phi}{2} - \frac{\beta}{2}\right]$$

$$d = \sqrt{(x_{1'} - x_{2'})^2 + (y_{1'} - y_{2'})^2 + (z_{1'} - z_{2'})^2}$$

$$\cos \frac{\beta}{2} = \frac{\cos \alpha}{\sqrt{2 - \cos^2 \alpha}}$$

x, *y*, and *z* are the coordinates of points 1′ and 2′; by consideration of symmetry properties, the coordinates of any other primed or double-primed point may be obtained. *d* is the distance between points 1′ and 2′; *m* the C-1–C-2 bond length; *n* the distance

---

[1] G. J. Fonken and S. Shiengthong, *J. Org. Chem.*, **28**, 3435 (1963).

from the carbon atom of the ring to the primed point; ϕ the H–C–H angle; β the "bend of the cyclobutane ring," the angle between the bisector of angle 1–2–3 and the extension of the bisector of angle 3–4–1, and the angle between the two dihedral planes defined by points 1, 2, 3 and 3, 4, 1; and α is the angle between bond C-1–C-2 and its projection on the xy plane. The first term in each expression defining the x, y, z coordinates of point 1′ or 2′ defines the coordinates for the corresponding ring carbon atom. These expressions, then, can be used directly, or by suitable manipulation, to calculate a variety of distances and angles in the cyclobutane system as a function of the bending of the ring. The calculations are somewhat tedious, but quite simple in nature.

For reference, calculations first were made for cyclopropane, cyclobutane, and cyclopentane assuming in each case that the ring is planar and the C–H bonds are eclipsed. Several variations in angles and distances were allowed. That is, the H–C–H angles (ϕ) in cyclopropane and cyclobutane assumed values of 110, 114, and 120° and in cyclopentane, 108, 110, and 114°. The value of n was taken as 1.50 Å. [a value for the C–C (carboxyl) distance in many acids] and as 3.00 Å. (1.50 Å. plus approximately the additional distance of 1.45 Å. used in some calculations involving electrostatic interactions of carboxyl groups[2]). The cyclopropane C–C bond length is taken as 1.524 Å. while cyclobutane is 1.548 Å. and cyclopentane is 1.540 Å.[3] The results of these calculations are shown in Table I.

TABLE I

CALCULATED DISTANCES (Å.) BETWEEN *cis*-1,2 SUBSTITUENTS ON SMALL PLANAR RINGS

	ϕ, deg.	n = 1.50 Å.	n = 3.00 Å.
Cyclopropane	110	3.014	4.504
	114	2.938	4.352
	120	2.824	4.124
Cyclobutane	110	2.766	3.994
	114	2.701	3.854
	120	2.609	3.670
Cyclopentane	108	2.600	3.660
	110	2.576	3.612
	114	2.522	3.504
Cyclohexane[a]		2.891	4.504

[a] Cyclohexane was taken in a chair conformation with all bond angles as tetrahedral (109°) and C–C bond length of 1.540 Å.

Calculations for various nonplanar conformations of cyclobutane were carried out. Values of d were plotted as a function of β, and the values of β necessary for d to be equal to the corresponding distances in planar cyclopropane were determined. These results are shown in Table II.

TABLE II

THE AMOUNT OF RING BENDING, β, NECESSARY FOR *cis*-1,2 GROUPS IN CYCLOBUTANE TO BE SPACED THE SAME AS IN CYCLOPROPANE

	ϕ (cyclopropane), deg.		
ϕ (cyclobutane), deg.	110	114	120
	n = 1.50 Å.		
110	62	50.5	30
114	69	58.5	41
120	81	71	56
	n = 3.00 Å.		
110	56	46.5	28.5
114	62.5	53.5	37.5
120	72	63.5	50

It is clear that to achieve equality of spacing between *cis*-1,2 groups in cyclopropane and cyclobutane, appreciable bending of the cyclobutane ring is required. As this bending occurs, the internal angles of the ring will decrease, and this might result in some opening of the external H–C–H angle. However, this effect probably is not of great importance.[4] Assuming that the H–C–H angles remain essentially constant, then with these angles at the reasonable 112–114° value, the bending, β, of the cyclobutane ring will be in the range of 50–60°. Further, for the support of the suggestion by Fonken and Shiengthong,[1] β must be even larger in order for the cyclobutane spacing to be greater than that in cyclopropane. This amount of bending of the cyclobutane ring does not seem reasonable and is in appreciable excess over values previously suggested.[3]

Similar calculations were not attempted for cyclopentane. However, it is obvious from results in Table I that for planar cyclopentane *cis*-1,2 substituents are even closer together than in planar cyclobutane or in cyclopropane. As a first approximation, then, it might be expected that an even greater bending of the cyclopentane ring than of the cyclobutane ring would be required in order that *cis*-1,2 groups be spaced as far apart as they are in cyclopropane. Direct experimental evidence supporting steric compression of *cis*-1,2 groups on cyclopentane as compared to cyclopropane is observed in the work by Curtin and coworkers.[5] This suggests, then, that the cyclopentane ring is not bent excessively.[5a]

Finally, even for cyclohexane in an unstrained chair conformation, *cis*-1,2 groups are no farther apart than they are in cyclopropane (Table I).

It is concluded that *cis*-1,2 groups become more closely spaced as the ring size changes from cyclopropane to cyclobutane to cyclopentane. This discussion does not preclude the possibility of nonplanar cyclobutane (and cyclopentane), but it does eliminate the use of decreasing K_1/K_2 ratios of the *cis*-1,2-dicarboxylic acids with increasing ring size as supporting evidence for that nonplanarity.[1] Instead, it raises a new question: Why does the K_1/K_2 ratio decrease as the carboxyl groups move closer together?

A similar decrease of K_1/K_2 ratios with steric compression has been noted previously in substituted cyclopropane-1,2-dicarboxylic acids[6] and in disubstituted

---

(2) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

(3) The values for cyclopropane and cyclobutane are taken from a review article on cyclobutane chemistry [A. Wilson and D. Goldhamer, *J. Chem. Educ.*, **40**, 504 (1963)]. It should be noted that if the same distance were used for both compounds, the conclusions drawn later in the paper would be even stronger.

(4) If the internal ring angle is called θ, then it can be shown that sin $\theta/2 = (\cos \alpha)/\sqrt{2}$. Using this and previous relationships, it is found that θ changes very slowly for small to moderate values of β. Thus, with $\beta \sim 28°$, $\theta \sim 88°$, and with $\beta \sim 54°$, $\theta \sim 83°$.

(5) D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

(5a) NOTE ADDED IN PROOF.—F. V. Brutcher has suggested (private communication) on the basis of dipole moments of *cis*-1,2-dibromocyclopentane and *cis*-1-bromo-2-chlorocyclopentane (unpublished work) that the torsional angle between the two carboxyl groups of *cis*-1,2-cyclopentanedicarboxylic acid may be close to 60°; this would correspond to appreciable folding of the cyclopentane ring in either the envelope or half-chair conformation.

(6) L. L. McCoy and G. W. Nachtigall, *J. Am. Chem. Soc.*, **85**, 1321 (1963).

maleic acids.[7] Previous consideration of these decreases in K_1/K_2 ratios have "emphasized" an interference with intramolecular hydrogen bonding.[6,7] However, if the suggestion is accepted that for $K_1/K_2 \leqslant 10^4$ intramolecular hydrogen bonding is negligible as a factor contributing to that ratio,[8] then some other explanation must be found.

Electrostatic interaction between the two carboxyl groups is a useful starting point. Such interaction varies with the dielectric constant of the medium. To account for some large K_1/K_2 ratios, and generally to give reasonable correlation between spacing of carboxyl groups and the K_1/K_2 ratio, a cavity of low dielectric constant, the molecule itself, may be considered to be buried in a medium of high dielectric constant, the solvent.[2] On the basis of this model, the relationship

$$\log K_1/4K_2 = \frac{e^2}{2.303kT}\,\frac{1}{r}\,\frac{1}{D_\mathrm{E}} \qquad (1)$$

may be formulated where r equals the "distance" between the carboxyl groups and D_E is an "effective" dielectric constant.[2] In order to calculate r and D_E, the carboxyl groups must be "buried" in a spherical or ellipsoidal cavity of low dielectric constant, usually assumed as 2 (hydrocarbon), and in the ellipsoidal case, the carboxyl groups must be located at the foci. In actual molecules where the carboxyl groups may lie at opposite ends of the cavity as in *trans* conformations of acyclic 1,2-dicarboxylic acids or in long straight-chain diacids, or they lie within a spherical cavity as in some disubstituted malonic acids or racemic di-*t*-butylsuccinic acid, then the theory works reasonably well. However, in some *cis*-1,2-dicarboxylic acids, the carboxyl groups clearly project from the hydrocarbon cavity and lie very close to each other; *i.e.*, there is no medium of low dielectric constant between the two carboxyl groups, nor do they lie within the cavity. The compounds do not resemble the spheres or ellipsoids necessary for quantitative application of the theory, and qualitative application is of dubious value since it leaves open the question of what effective dielectric constant should be used. Using K_1 and K_2 for *cis*-1,2-cyclobutanedicarboxylic acid and r equal to 4.00 Å., about a 15° bend in the cyclobutane ring, in eq. 1 gives D_E as 37. This is appreciably larger than values of D_E usually "found" with this "shape" and size of hydrocarbon residue, but it might not be unreasonable if the acid molecule, the cavity, is considered to be divided into a hydrocarbon portion, $D = 2$, and a carboxyl portion, $D \sim 58$, all buried in the solvent, $D \sim 80$. The rationale for the carboxyl region is that two very closely spaced carboxyl groups might be looked upon as comparable to a small volume of formic acid, $D = 58$. To the extent that any of these values have any real meaning at the molecular (or very small volume) level, it suggests that very careful examination must be made of the orientation of closely spaced carboxyl groups with regard to the attached "hydrocarbon cavity." That is, for *cis*-1,2-diacids, as the groups come closer together, the "medium" between them might be expected to change in nature from hydrocarbon to carboxyl and solvent with attendant rise in "effective" dielectric constant. From eq. 1, then, for some ranges of change in molecular structure of the *cis*-1,2-diacids, D_E might be expected to increase more rapidly than r decreased. The net result would be a decrease in K_1/K_2 ratio as the spacing between groups decreases.[9]

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation.

---

(7) L. Eberson, *Acta Chem. Scand.*, **18**, 1276 (1964).

(8) L. Eberson and I. Wadsö, *ibid.*, **17**, 1552 (1963). This lower limit for intramolecular hydrogen bonding as a contributing factor could be lowered to 10^3 without effecting the present discussion. The range of K_1/K_2 ratios in which the decreases have been observed in the examples cited is about 10^3–10^2.

(9) Presumably, if the groups could be forced closer together, a minimum would be reached and then the K_1/K_2 ratio again would rise, probably very rapidly. However, sufficiently close approach to reach such a minimum undoubtedly would raise a variety of other problems.

The Stereochemistry of Free-Radical Addition of Thiolacetic Acid to Cyclohexenes[1,2]

FREDERICK G. BORDWELL, PHILIP S. LANDIS, AND GEORGE S. WHITNEY

Chemistry Department, Northwestern University, Evanston, Illinois

Received January 7, 1964

Free-radical addition of thiolacetic acid to 4-*t*-butyl-1-methylcyclohexene resulted in about 80% of *trans*-diaxial adduct (SAc group axial) and 20% of *cis* adduct (SAc· group equatorial). This is explained by assuming that in each instance the AcS·radical initiates a perpendicular attack on the C=C bond, but that attack from the "top" side of the cyclohexene molecule is preferred for steric reasons. The radical intermediates formed from addition of the AcS· radical to 4-*t*-butyl-, 3-methyl-, and 2-methyl-1-methylenecyclohexanes were found to abstract a hydrogen atom from AcSH preferentially into an axial position.

Free-radical addition of hydrogen bromide, thiolacetic acid, and the like to 1-substituted cyclohexenes has been shown to proceed to give predominantly the *cis* product.[3] It has been suggested that the major (*cis*) product is formed by *trans*-diaxial addition,[3] but its origin, and that of the smaller amount of *trans* product, is rendered uncertain by the possibility of chair–chair interconversion preceding the hydrogen

---

(1) Abstracted in part from the Ph.D. Dissertation of G. S. Whitney, Northwestern University, 1962.

(2) These results were reported at the Fifth Annual Conference on Organic Chemistry at the U. S. Army Natick Laboratories, Natick, Mass., Oct. 1961, and in part at 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962; Abstracts, p. 64Q.

(3) (a) H. L. Goering, D. I. Relyea, and D. W. Larsen, *J. Am. Chem. Soc.*, **78**, 348 (1956); (b) F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).