Geometric Constraints in Six- and Eight-Membered Rings

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Abstract: Geometric constraints in rings are examined from several points of view. It is shown that a six-membered ring with given bond distances and bond angles is rigid unless it possesses a nonintersecting twofold axis of symmetry, in which case it is flexible. Thus the chair forms of all six-membered rings are rigid once bond distances and angles are specified. The eight-membered ring with fixed bond distances, bond angles, and with two torsion angles fixed at zero (*e.g.*, cyclooctadiene) also exists in rigid or flexible forms, depending on the absence or presence of a nonintersecting twofold axis of symmetry. Molecules such as cycloocta-1,4-diene, for which such symmetry can only be approximately fulfilled, may also appear to be flexible. Some relevant experimental findings are summarized.

The best known example of the effects of geometric ring constraints on the properties of certain models of cyclic molecules is the contrast between the rigidity of the chair form and the flexibility of the boat–twist forms of cyclohexane, as first described by Sachse.[2a] Several more recent discussions of the properties of the equilateral, isogonal spatial hexagon are available,[2b,3,4] but for other cyclic systems the influence of ring constraints on molecular structure and flexibility does not seem to have attracted much attention. This lack of interest may be ascribed partly to the mathematical difficulties associated with a formal treatment of all but the simplest cases (although many interesting results can be derived simply if nonrigorously by examining the mechanical properties of Dreiding models[5]) and partly to awareness of the inherent shortcomings of a purely geometric approach to problems of molecular structure. On the other hand, the geometric aspects of molecular structure cannot be ignored. It is obviously very convenient to describe molecular structures in terms of geometric parameters such as bond lengths, bond angles, torsion angles, etc., and it is therefore important to know the kind of restrictions that may hold between such parameters in cyclic and polycyclic molecules. For example, nonplanar conformations of cyclopentane cannot have all C–C bond lengths and all C–C–C bond angles equal since the equilateral, isogonal pentagon is constrained to be planar.[6] In this respect the pentagon is unique since no other equilateral, isogonal polygon (apart from the trivial cases of point, line, and triangle) is constrained to lie in a plane. Neglect or ignorance of this geometrical result can lead to a profitless enquiry into the origin of observed bond angle differences in nonplanar five-ring molecules, and possibly even to an incorrect "explanation." In this paper we examine the influence of geometric constraints in certain six- and eight-membered rings.

For a chain of n atoms the $n - 1$ bond distances, $n - 2$ bond angles, and $n - 3$ torsion angles can be assigned arbitrary values since there are $3n - 6$ of them, exactly the number of degrees of freedom of the system. For a ring of n atoms, the n bond distances, n bond angles, and n torsion angles are not independent, however, since they must be related by six equations of constraint (ring closure conditions). In polycyclic systems of n atoms there are even more equations of constraint since each additional ring involves one additional bond distance, four additional bond angles, and eight additional torsion angles, whereas the number of degrees of freedom remains $3n - 6$. In small polycyclic systems, *e.g.*, bicyclo[1.1.1]pentane, the constraints are especially severe and can lead to highly unusual molecular parameters.

Our problem can be defined in terms of the number of torsional degrees of freedom possessed by an n-membered ring in which the n bond distances and n bond angles are regarded as fixed (a ring built from idealized Dreiding models). If there are no torsional degrees of freedom then the ring is rigid (it can be deformed only if bond distances or bond angles are changed, contrary to the conditions stated) whereas the presence of at least one torsional degree of freedom confers flexibility on the ring. We assume in our discussion that the sum of the n fixed bond angles is less than $(n - 2)\pi$; $n > 3$.

Rigid and Flexible Six-Membered Rings. As is well known, the equilateral, equiangular six-membered ring (*e.g.*, cyclohexane) can exist in a rigid, highly symmetrical chair form (point group D_{3d}) in which the torsion angle ω is related to the bond angle θ by $\cos \omega = -\cos \theta/(1 + \cos \theta)$, or in a family of flexible forms, which can be changed continuously into each other by changing the torsion angles, and which include the boat form (point group C_{2v}) and the symmetrical twist form (point group D_2) as special cases. The only symmetry element common to all the flexible forms of the equilateral, equiangular six-membered ring is a twofold rotation axis that does not pass through any atoms or bonds. We shall refer to such an axis as a nonintersecting axis.

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(1) (a) Eidgenössische Technische Hochschule; (b) California Institute of Technology; (c) Contribution No. 4418.

(2) H. Sachse, *Ber.*, 23, 1363 (1890); *Z. Phys. Chem.*, 10, 203 (1895); (b) P. Hazebroek and L. J. Oosterhoff, *Discuss. Faraday Soc.*, 10, 87 (1951).

(3) J. D. Dunitz, *J. Chem. Educ.*, 47, 488 (1970).

(4) H. L. Strauss, *ibid.*, 48, 221 (1971).

(5) We single out Dreiding models not only because they are familiar but also because of the precision with which the units are constructed.

(6) J. Waser and V. Schomaker, *J. Amer. Chem. Soc.*, 67, 2014 (1945); J. D. Dunitz and J. Waser, *Elem. Math.*, 27, 25 (1972).

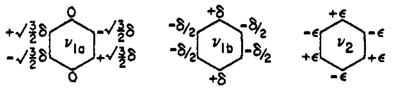
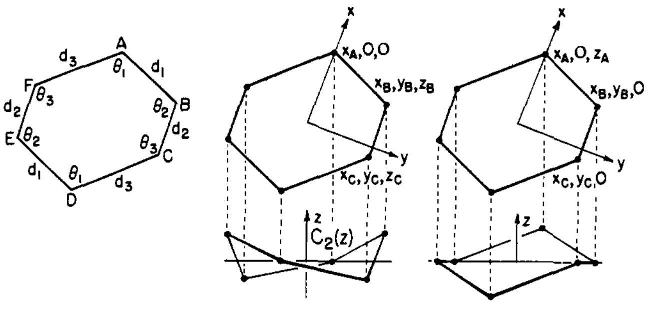


Figure 1. Out-of-plane normal vibrations of a regular hexagon.



(a) (b) (c)

Figure 2. The six-membered ring with bond distances d_1, d_2, and d_3 and angles θ_1, θ_2, and θ_3 as shown on left (a) must have either a nonintersecting twofold axis $C_2(z)$ (b) or a center of symmetry (c). The former needs seven Cartesian coordinates, the latter only 6.

At first sight the existence of the extra degree of freedom in the flexible forms may seem mysterious since the fixing of six bond distances and six bond angles may appear to exhaust the $3 \times 6 - 6 = 12$ degrees of freedom at our disposal. Some insight is achieved by considering the symmetry properties of the three out-of-plane normal vibrations of a regular hexagon (Figure 1).[7]

In terms of the irreducible representations of the point group D_{6h}, ν_2 belongs to B_{2g}; ν_{1a} and ν_{1b} belong to the degenerate representation E_{2u}. Since ν_{1a} and ν_{1b} are degenerate, any normalized linear combination

$$\nu_{1a} \cos \alpha + \nu_{1b} \sin \alpha$$

is also a normal vibration. Values of $\alpha = 0, 60, 120°$, etc., are seen to correspond to the forms with D_2 symmetry, $\alpha = 30, 90, 150°$, etc., to the forms with C_{2v} symmetry, and intermediate α values to forms with only C_2 symmetry. The extra degree of torsional freedom is then nothing else but the phase angle α. The nondegenerate vibration ν_2, corresponding to the chair form, is not associated with any such phase angle. The most serious limitation of this approach is that it applies only to the equilateral, equiangular ring. What about six-membered rings in which the fixed bond distances or bond angles are not all equal?

A Special Case. A simple way of treating certain problems of this kind has been outlined in a previous paper.[3] Consider a six-membered ring in which opposite distances and angles are equal, so that the three different bond distances d_1, d_2, and d_3 and three different bond angles θ_1, θ_2, and θ_3 are arranged as indicated in Figure 2a. For any three-bond train such as A–B–C–D the torsion angle about the central bond B–C is related to the distance between the ends of the train by (Figure 3)

$$(\mathrm{AD})^2 = d_1^2 + d_2^2 + d_3^2 - 2d_1d_2 \cos \theta_2 - 2d_2d_3 \cos \theta_3 + 2d_1d_3(\cos \theta_2 \cos \theta_3 - \sin \theta_2 \sin \theta_3 \cos \omega_2)$$

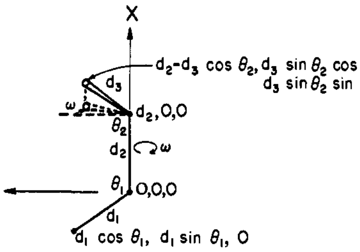


Figure 3. Coordinates of a train of four atoms A–B–C–D.

We see that $\cos \omega_{BC} = \cos \omega_{EF}$, so that $\omega_{BC} = \pm \omega_{EF}$, and similarly $\omega_{CD} = \pm \omega_{FA}$ and $\omega_{AB} = \pm \omega_{DE}$. Of the eight possible combinations, only two are geometrically feasible. One (with the signs of related ω's equal) corresponds to a ring with a nonintersecting twofold axis (Figure 2b), the other (with opposite signs for related ω's) to a ring with a center of inversion (Figure 2c). In the former case, seven Cartesian coordinates are necessary to define the positions of the three symmetry-independent atoms (*e.g.*, x_A, 0, 0; x_B, y_B, z_B; x_C, y_C, z_C, placing the x-axis through atom A) so that with six internal parameters, d_1, d_2, d_3, θ_1, θ_2, θ_3 fixed there remains one internal parameter that can be arbitrarily assigned within certain ranges. The solution with the nonintersecting twofold axis thus corresponds to a flexible ring. For the centrosymmetric ring, only six Cartesian coordinates are necessary to define the positions of three symmetry-independent atoms (*e.g.*, x_A, 0, z_A; x_B, y_B, 0; x_C, y_C, 0) since the plane defined by the inversion center and two atoms, B and C say, also passes through the two symmetry related atoms (in other words, B, C, E, F are coplanar with the center). This common plane can be chosen as x,y-plane and the x,z-plane passed through A. Hence there can be no free parameter in addition to the fixed bond distances and bond angles and the solution with the centrosymmetric ring corresponds to a rigid ring. The point groups C_2 and C_i are both of order 2, so that flexible forms do not necessarily have a lower symmetry than rigid forms.[9]

We may ask whether other possible symmetries of a six-membered ring with given bond distances and bond angles might convey flexibility upon the ring and consider therefore any of the following four possibilities: a twofold axis through a pair of opposite atoms or bonds, or a plane of symmetry through a pair of atoms or bonds. We see that when either of these symmetry elements passes through a pair of atoms, the bond angles associated with these atoms are not related to others; when either symmetry element passes through a pair of bonds, these bonds are not related to others. In both cases there is then a total of seven unrelated bond angles and distances (4 + 3 or 3 + 4), compared with seven free coordinates, so that no free internal variable remains. Thus the *only* symmetry element that conveys flexibility is a nonintersecting twofold axis.

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(7) H. M. Pickett and H. L. Strauss[8] have used these normal vibrations to develop a system for describing *all* significant nonplanar conformations of cyclohexane in terms of only two coordinates.

(8) H. M. Pickett and H. L. Strauss, *J. Amer. Chem. Soc.*, 92, 7281 (1970).

(9) In a recent article, Strauss[4] has misunderstood earlier arguments[3] presented by one of us. He wrote that "Dunitz pointed out that the boat–twist form of cyclohexane is less rigid than the chair form because of its lower symmetry." Dunitz actually pointed out that an equilateral, equiangular six-membered ring is either rigid or it has a nonintersecting twofold axis. He then showed that all six-membered rings with the latter property and with fixed bond distances and angles are flexible. But a ring, *e.g.*, with six different fixed distances and six fixed angles, has no symmetry and is rigid.

Figure 4. Convex (left) and nonconvex (right) octahedra. All edges of the triangular faces are 1,2 or 1,3 distances of nonplanar six-membered rings.

It must be emphasized here and elsewhere in this paper that we are speaking of rigidity and flexibility in a mathematical rather than a mechanical sense. By rigidity we imply merely the presence of some functional relationship between torsion angles ω_i and the other internal parameters p_j that are held constant; that is, there exist nonzero derivatives $\partial p_j/\partial\omega_i$. By flexibility we imply that all such derivatives are zero in a nonvanishing range of the ω_i. A mechanical model of a six-membered ring with bond distances and angles such that the condition of a nonintersecting twofold axis is approximately but not exactly fulfilled will appear to be more or less flexible, depending on the degree of approximation and the mechanical rigidity of the individual links. The derivatives $\partial p_j/\partial\omega_i$ are close enough to zero in a nonvanishing range of the ω_i to make the mechanical model appear flexible.

Six-Membered Rings and Octahedra. So far we have been looking at the six-membered ring as a spatial polygon, but the rigidity problem can also be expressed in terms of the properties of polyhedra. Instead of describing the ring in terms of its bond distances and bond angles we can replace the latter by distances between next-nearest neighbors. For a six-membered ring the resulting arrangement of triangles framed by the 1,2 and 1,3 distances is that of an octahedron. If the ring is in the chair form the octahedron is convex (Figure 4). A theorem due to Cauchy[10] states that if all external faces of a convex polyhedron are rigid then the polyhedron itself is rigid. The octahedron in question must therefore be rigid since all eight external faces are triangles, which are completely defined by the given 1,2 and 1,3 distances. *Thus chair forms of all six-membered rings, regardless of the presence or absence of symmetry, are rigid, once the bond distances and angles are specified.*

For any nonchair nonplanar form of a six-membered ring, the octahedron under discussion is not convex (it does not entirely contain all segments connecting any two points on its boundary (Figure 4)). Cauchy's theorem does not apply to nonconvex octahedra, but they have been analyzed in detail by Bricard[11] (who appears to have been unaware of Sachse's closely related discussion[2a] of the cyclohexane ring a few years earlier).

It is impossible to describe Bricard's algebraic treatment in a short space, but his main conclusions can be summarized as follows. The nonconvex octahedron with fixed faces is rigid in general, but there are three special types that are flexible:

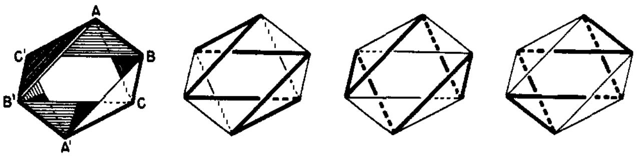

Figure 5. The twofold axis of the nonconvex octahedron ABCA′B′C′ is perpendicular to the paper. The four ways of choosing a hexagon from the 12 edges of the octahedron are shown. In any specific case, only one of these hexagons corresponds to a reasonable molecule.

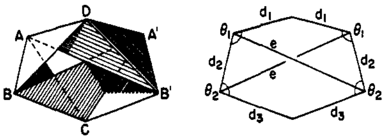

Figure 6. Bricard's nonconvex octahedron with a plane of symmetry through two opposite vertices C and D. (The eight triangular faces are ABC, A′B′C, ABD, A′B′D, AB′C, A′BC, AB′D, and A′BD.) If six edges are identified with 1,2 distances of a hexagon, then four edges correspond to 1,3 distances and the remaining two edges to 1,4 distances.

(1) Those with a nonintersecting twofold axis, shown in Figure 5. The 12 edges of this figure can be identified with the six 1,2 distances and six 1,3 distances of a six-membered ring in four distinct ways. The six-membered rings so described also possess nonintersecting twofold axes and must be flexible, a result we have already derived by counting degrees of freedom.

(2) Those with a plane of symmetry passing through two opposite vertices (Figure 6). In this case the corresponding six-membered ring (which can also be chosen in four ways) also has a plane of symmetry passing through two opposite vertices but it is defined in terms of three pairs of 1,2 distances, two pairs of 1,3 distances (bond angles), and one pair of 1,4 distances (ring diagonals) rather than in terms of bond distances and bond angles alone. The flexibility of this ring can also be derived in a simple manner by counting degrees of freedom since the number of fixed internal parameters just alluded to is six, whereas the mirror-symmetric six-membered ring requires seven Cartesian coordinates for complete specification. Note, as mentioned earlier, that the mirror-symmetric ring with the three symmetry-independent bond distances and the four symmetry-independent bond angles fixed is rigid.

(3) A third type with a special relationship among the four angles at each vertex, opposite angles having to be either equal or supplementary. There are certain difficulties in constructing a model of this type of octahedron and its flexibility is not so intuitively clear as that of the other types. We shall not discuss it further since it is not obviously related to the problem of the six-membered ring.

Although the nonconvex octahedra we have been describing do not have a volume in the usual sense, nevertheless they can be assigned a definite volume in the generalized sense of Möbius.[12] This is possible since a sense of circuit can be associated with each of their faces without violating the Möbius law of edges,[12] that in completing this procedure for all faces of a polyhedron each edge is traversed in opposite directions with respect to the two faces meeting at that edge.

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(10) See A. D. Alexandrow, "Konvexe Polyeder," Akademie-Verlag, Berlin, 1958, pp 112–113; L. A. Lynsternik, "Convex Figures and Polyhedra," Dover, New York, N. Y., 1963, pp 60–66.

(11) R. Bricard, *J. Math. Pures Appl.*, (5) **3**, 113 (1897); see also G. T. Bennett, *Proc. London Math. Soc.*, (2) **10**, 309 (1911).

(12) See F. Klein, "Elementary Mathematics from an Advanced Standpoint," Vol. 2, Geometry, Dover, New York, N. Y., 1939, pp 16ff.

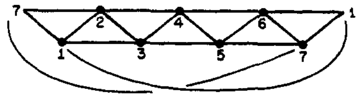

Figure 7. Joining the ends of the ribbon of triangles to give a seven-membered ring produces a Möbius strip. The drawing illustrates the case of equal distances and angles.

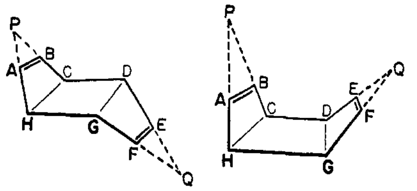

Figure 8. Two forms of eight-membered rings with two opposite torsion angles fixed at zero.

The generalized volume of the polyhedron is defined as the algebraic sum of the volumes of the pyramids formed by the faces and some arbitrary point P, where these volumes are taken positive or negative depending on whether the sense of circuit as seen from P is counterclockwise or clockwise. Because of the law of edges the location of P can be seen to be immaterial. When the law of edges is not satisfied it is impossible to assign a definite volume to the polyhedron. For a convex octahedron the generalized volume just defined is identical with the conventional volume.

It can be shown that for any flexible octahedron the generalized volume is zero. For the types 1 and 2 the proof is simple. We illustrate it for type 1. In Figure 5 suppose the arbitrary point P to be on the twofold axis of the nonconvex octahedron ABCA′B′C′. The tetrahedra PABC and PA′B′C′ are congruent in the strict sense because they are related by the twofold rotation axis. The senses of circuit of the triangles ABC and A′B′C′ as seen from P are therefore the same. The triangles ABC and A′C′B′ have then opposite senses of circuit and, because of the congruence of the two tetrahedra, their contributions to the volume of the octahedron exactly cancel. Similarly, the contributions of the triangles CA′B′, B′C′A, and ACB′ exactly cancel the contributions of C′BA, BA′C, and A′BC′, respectively. When the triangles are circuited in the senses indicated, each edge is traversed twice in opposite directions. Hence a generalized volume can be assigned, and its value is zero. A similar proof can be given for the flexible octahedra of type 2. For the octahedra of type 3 the proof is somewhat more difficult but the result is the same.[13]

We may summarize the discussion so far as follows: *a six-membered ring with given bond distances and angles is rigid unless it possesses a nonintersecting twofold symmetry axis, in which case it is flexible provided the sum of the bond angles is less than 720°.*[13a]

Seven-Membered Rings. A seven-membered ring with $7 + 7 = 14$ fixed bond distances and angles is flexible, since seven atomic positions require $3 \times 7 - 6 = 15$ coordinates, leaving at least one degree of freedom. It is interesting that the polyhedron formed by linking 1,2 and 1,3 neighbors is bounded by a ribbon of the Möbius type and has no assignable volume (Figure 7). This is true for all odd-membered rings. If one torsion angle in a seven-membered ring is fixed in addition to the bond distances and angles then the ring in general is rigid; the remaining torsion angles are then in general functions (but not necessarily single-valued functions) of the 15 assigned parameters. In special cases, however, a seven-membered ring is flexible even when one of the torsion angles has been fixed.

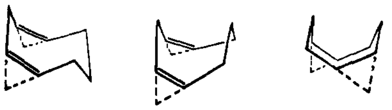

Figure 9. Left and center structures are rigid and flexible conformations of cycloocta-1,4-diene, both with mirror plane through two opposite atoms. Right structure is conformation with C_{2v} symmetry obtained by slight deformation of flexible conformation.

Eight-Membered Rings. An eight-membered ring with given bond distances and bond angles has (at least) two degrees of torsional freedom, which are in general frozen by assigning fixed values to two torsion angles. There are again certain special cases where such rings are flexible even when the torsion angles are fixed. We shall discuss here only cases where two torsion angles are fixed at zero, as realized in the cyclooctadienes, for example. The simplest way of visualizing the geometric constraints in these eight-membered rings is to derive them from the known constraints present in six-membered rings.

This is illustrated here for the case where the bonds about which the two torsion angles are fixed are opposite one another, *e.g.*, as in cycloocta-1,5-diene. Figure 8 (left) shows a ring conformation in which the two fixed bonds AB and EF are on opposite sides of the mean plane of the other four atoms C, D, G, and H. The quadrilateral ABCH is planar and defined by the given distances HA, AB, and BC and given angles A and B so the lines through HA and CB must intersect at some point P in the plane ABCH to yield a triangle HPC with fixed sides. Similarly, a triangle GQD with fixed sides can be obtained from the planar quadrilateral GFED. The figure PCDQGH is a hexagon with fixed sides and fixed angles. Since it is in the chair form it is rigid and hence the original octagon must be rigid.

If the fixed bonds AB and EF are on the same side of the mean plane of C, D, G, and H, the above construction yields a hexagon with fixed sides and angles in some boat–twist form (Figure 8, right). If the original octagon has a nonintersecting twofold axis then so does the hexagon, which is therefore flexible, in which case the original octagon must also be flexible. The rigidity of the chair form and the flexibility of the twist–boat family of forms of such an eight-membered ring is readily seen by examining Dreiding models of cycloocta-1,5-diene.

Dreiding models of cycloocta-1,4-diene suggest that there is a rigid conformation as well as a family of flexible conformations of this molecule, which obviously does not possess a nonintersecting twofold axis. The rigid conformation has a mirror plane passing through two opposite atoms. It is illustrated in Figure 9 and

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[13] J. Waser, unpublished work.

[13a] Note Added in Proof. H. A. Lauwerier, *Proc. Kon. Ned. Akad. Wetensch.*, **69**, 330 (1966), and O. Bottema, *ibid.*, **70**, 151 (1967), have discussed the mathematical properties of flexible hexagons and have come to conclusions that are essentially the same as ours. We thank Professor L. J. Oosterhoff for having drawn our attention to these papers.

its rigidity follows easily from the kind of geometric arguments given earlier. As seen from Figure 9 it can be developed into the chair form of a hexagon. There is also a mirror-symmetric form among the flexible conformations of cycloocta-1,4-diene but the hexagon into which it can be developed does not possess a nonintersecting twofold axis and it should therefore be rigid, like the other form.

Why does one form of the 1,4-diene appear to be flexible? The conformation shown in the center of Figure 9 is seen from the figure to have *approximate* C_{2v} symmetry (its exact symmetry being C_s). Indeed if some of the bond distances were adjusted upward or downward by 5% and the angles by 5° the model would have exact C_{2v} symmetry in this conformation, with four torsion angles of the eight-membered ring equal to zero. In this case the construction shown in Figure 9 (right) would yield a hexagon whose flexibility would be assured by the presence of the nonintersecting dyad axis. We have not solved the actual equations of constraint for the case of only approximate C_{2v} symmetry but it is clear that the rate of change of any bond angle, for example, with change in one of the nonfixed torsion angles must be so small as to be undetectable with normal Dreiding models for a considerable range. The range is, however, definitely limited, which is not the case for the analogous form of the 1,5-diene. This example illustrates the distinction between rigidity of a geometric figure and rigidity of a mechanical model.

A conflict between a geometric conclusion and the result of experience gained from handling molecular models does not necessarily involve a contradiction. In the case of six-membered ring, for example, the geometric condition for flexibility is the presence of a nonintersecting twofold axis, whereas a Dreiding model of a six-membered ring that lacks this symmetry may appear to be fairly flexible in its boat form. For the geometric analysis it is the symmetry of the geometric figure that is relevant, not the symmetry of the molecules, whereas for molecules, or models thereof, the metric aspect of the required symmetry need be satisfied only approximately. When these symmetry conditions for molecules or models are satisfied only approximately the flexibility extends in general only over a limited range, the range being determined by the degree of deviation.

We are not aware of the existence of a general treatment of such "almost poristic" solutions to the equations of condition.

Implications for Structural Chemistry. In talking about the rigidity or flexibility of molecules it is very important to distinguish carefully between the properties of geometric figures and those of actual molecules. The latter involve energy considerations, whereas it is an intrinsic limitation of the geometric approach described in this paper that energy changes associated with conformational changes are totally ignored. Our molecular model is essentially one in which bond distances and bond angles are regarded as invariant while torsion angles are free to adopt any values whatsoever unless arbitrarily fixed at some definite value. This is obviously unrealistic when we consider the energy increments associated with deformations of actual molecules from their equilibrium conformations by changes in bond lengths, bond angles, and torsion angles. One set of potential functions[14] that reproduces the strain enthalpies and equilibrium conformations of cycloalkanes reasonably well is (energies in kcal mol^{-1}, d in Å, angles in degree)

$$\text{bond length deformation } E(d) = 300\,(d - 1.533\text{ Å})^2$$

$$\text{bond angle deformation } E(\theta) = 0.025\,(\theta - 112.7°)^2$$

$$\text{torsion angle potential } E(\omega) = 1.70\,(1 + \cos 3\omega)$$

Thus changing a torsion angle by 3–4° from its equilibrium value of 60 or 180° costs roughly the same as stretching a bond by 0.01 Å or deforming a bond angle by 1°.

This limitation is so serious that it raises the question whether anything at all about the structures and properties of molecules can be learned from the geometric approach. The answer must be a cautious affirmative. We can not expect to be able to explain the quantitative details of molecular structures by studying geometry but we can hope to recognize which features of molecular structures are "built in" by geometric necessity and which require discussion in terms of a detailed theory of valency. A trivial example: we shall not learn much from a theoretical model designed to reproduce the experimental observation that the sum of the ring angles in cyclopropane carboxamide is exactly 180°!

As far as six-membered rings are concerned the results of the geometric analysis seem to have only a limited relevance to actual molecules. For cyclohexane itself the twist–boat forms have never been observed experimentally; they are estimated to lie at least 5 kcal mol^{-1} higher in energy than the chair form, mainly as a result of energetically unfavorable torsion angles and steric repulsion between nonbonded atoms. The same factors are probably responsible for the greater stability of the chair form in related six-membered ring molecules such as dioxanes, etc. The normal preference for the chair form can be reduced by interactions between substituents. There is evidence that *trans*-1,3-di-*tert*-butylcyclohexane[15] and *cis*-1,4-di-*tert*-butylcyclohexane-2,5-diol[16] exist in nonchair forms; in the former case the large positive entropy change ($\Delta S° = 4.9 \pm 1.0$ eu) for the cis → trans isomerization has been attributed to the greater flexibility of nonchair over chair forms. Cyclohexa-1,4-dione[17,18] and the corresponding dioxime[19] have been shown by X-ray analysis to occur in nonchair forms. The reasons for this are not clear. The observed rings are not boat forms lacking "flagpole" interactions between H atoms but are markedly twisted. The torsion angles around the ring bonds in the diketone, beginning at a bond adjacent to C=O, are 12, −53, 40, 12, −53, and 40° (calculated from information given in ref 14), showing that the ring has effective C_2 symmetry. The crystal structure analysis[17] (carried out at −140°) does not provide any indication of unusually

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(14) M. Bixon and S. Lifson, *Tetrahedron*, 23, 769 (1967).

(15) N. L. Allinger and L. A. Freiburg, *J. Amer. Chem. Soc.*, 82, 2393 (1960).

(16) R. D. Stolow and M. M. Bonaventura, *ibid.*, 85, 3636 (1963).

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large amplitude of internal motion, as has been observed in certain crystal structure analyses of larger membered rings.[20] An nmr investigation[21] of tetramethyl-*s*-tetrathiane strongly suggests that for this molecule the twist form of D_2 symmetry (the only possible form in which the four methyl groups are symmetry equivalent) is more stable than the chair form. From the temperature dependence of the equilibrium it was estimated that the D_2 form is ~0.5 kcal mol^{-1} lower in enthalpy and ~1.0 eu higher in entropy than the C_{2h} chair. When account is made for the different symmetry numbers of the two forms the higher entropy of the D_2 form would suggest that it has a greater flexibility. Almost all energy calculations based on the most various interatomic potential functions do support the idea that the twist–boat family of forms can easily undergo pseudorotational interconversion. For cyclohexane, the conformation with D_2 symmetry appears to represent the energy minimum in the pseudorotational itinerary, the boat form the energy maximum, but the energy barrier is very small[8,14,22] (less than 1 kcal mol^{-1} and as low as 40 cal mol^{-1} according to one estimate).[23] Although the agreement with the results obtained from geometric analysis should not blind us to the limitations of the latter, we may echo a statement (actually made for cyclopentane) that "the existence of an equipotential path is more due to the geometry of cyclohexane than to the exact nature of the intermolecular forces."[23]

For eight-membered rings with two opposite torsion angles frozen at zero the energy difference between the chair and twist–boat forms should depend on very different factors from those that favor the chair form of cyclohexane. In cycloocta-1,5-diene, both chair and boat forms show eclipsing around the $-CH_2-CH_2-$ bonds, the torsion angles being 120 and 0°, respectively. Any slight preference accruing to the chair form from this factor ought to be reinforced by the greater separation between the double bonds in this form. Nowadays almost everyone knows that the parallel approach of two ethylene molecules in their ground states is a symmetry-forbidden process.[24] The closer the approach between the two molecules, the greater the repulsion energy between them should be.[25] On the other hand, the boat form, because of its flexibility, can ameliorate these unfavorable features by twisting about the $-CH_2-CH_2-$ bonds without any concomitant deformation of bond angles, whereas the chair form can only avoid its unfavorable features at the cost of introducing bond angle strain.

An electron diffraction investigation has shown that gaseous cycloocta-1,5-diene exists as an equilibrium mixture of chair and boat forms with the latter, presumably twisted, predominating.[26] Roberts found that 1,6-dichlorocycloocta-1,5-diene has a dipole moment,[27] which is not possible for the chair form. On the other hand, crystal data reported for dibenzocycloocta-1,5-diene[28] indicate a molecular center of symmetry, which is only possible for the chair form. X-Ray analyses have been reported for several metal complexes of cycloocta-1,5-diene.[29–31] In all the cases studied, both double bonds are π bonded to the same metal atom, which is only possible for the boat–twist forms of the diene. From the two analyses for which fairly reliable carbon positions have been published, it is evident that the complexed cyclooctadiene molecules are markedly twisted out of the ideal boat conformation; the torsion angles about the $-CH_2-CH_2-$ bonds are 24–29° in one case (cyclooctadieneduroquinonenickel(0)[30] with two independent sets of molecules with C_2 symmetry in the crystal), and 30–36° in the other ((cyclooctadiene)$_2$nickel(0)[31] with two sets of crystallographically independent molecules with approximate C_2 symmetry).

The balance of evidence suggests that the boat–twist forms of cycloocta-1,5-diene are at least as stable as the chair form and that they tend to avoid eclipsing by adopting a twisted conformation with torsion angles of 25–35° about the $-CH_2-CH_2-$ bonds, which would not be possible in the chair form without bond angle deformation.

Another molecule containing an eight-membered ring in which two opposite torsion angles are effectively fixed at zero is cyclo(di-β-alanyl).[32] The electric moments of the two peptide groups are oriented much more favorably in the centrosymmetric chair form than in the boat form with C_2 symmetry. But the boat form can avoid eclipsing by twisting around the $-CH_2-CH_2-$ bonds without concomitant bond angle deformation, whereas the chair form is rigid. X-Ray investigation[33] has shown that crystals of cyclo(di-β-alanyl) are built from molecules in a markedly twisted C_2 conformation (torsion angle of 28° about $-CH_2-CH_2-$ bonds).

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