# Molecular Geometry. IV. The Medium Rings[1,2]

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A system for defining all the possible symmetrical medium-ring cycloalkane conformations is presented along with a description of their modes of conformational interconversion. Calculations of the minimum-energy form of each of these symmetrical cycloalkanes ($C_6$–$C_{10}$) are presented and the relation of these conformations to observed physical results and medium-ring chemistry discussed. The results imply two conformations (III and IV) of about equal energy for cyclooctane, a form of $D_3$ symmetry (XIV) for cyclononane, and the BCB form XXIII (Fig. 1) for cyclodecane. Absolute values calculated for the strain energies compare favorably with thermodynamic data.

## Introduction

The feasibility of calculations of conformations and conformational energies of organic molecules from a few primary physical parameters was demonstrated at the beginning of this series[4] and conformational conclusions for cycloheptane and some derivatives were drawn[5a] and tested.[5b] It therefore seemed appropriate, in view of the encouraging correspondence of computed with empirical data, to extend the treatment to the conformationally more complex medium-ring cycloalkanes—molecules which have had a long history of study devoted to delineation of their internal strain energies. As it has been widely accepted that this internal strain arises from nonbonded hydrogen compressions, the medium rings constitute a challenging area for application of the present calculations.

In principle, the method is very simple. The strain energy of a given hydrocarbon conformation[6] is taken as the sum of three independent energies, each related to a single geometrical parameter: bond angle bending strain $(E_\theta)$; torsional strain $(E_t)$ of the dihedral angles $(\omega)$ about single bonds; and nonbonded interactions $(E_{HH})$ of hydrogens in the carbon skeleton. These energies are respectively related to their corresponding geometrical parameters as[4,7]

$$E_\theta = K_\theta(\tau - \theta)^2$$
$$E_t = K_t(1 + \cos 3\omega)$$
$$E_{HH} = 10^{4 - 2r} - 49.2/r^6$$

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(2) Part III: *J. Org. Chem.*, **29**, 991 (1964).

(3) Alfred P. Sloan Foundation Fellow.

(4) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); **85**, 4059 (1963). The second reference contains corrected geometrical parameters for cyclopentanes.

(5) (a) J. B. Hendrickson, *ibid.*, **84**, 3355 (1962); (b) J. B. Hendrickson, *Tetrahedron*, **19**, 1387 (1963).

(6) The method has only been used to compare saturated hydrocarbon conformers for several reasons: The constants used in the energy equations, being derived from relatively sparse physical measurements of questionable generality, are of dubious quality, although their validity is reinforced by the correlation of computed energies with empirical cases.[4] Accordingly, it seems unwise to extend this uncertainty to more complex cases involving additional parameters such as Coulombic interactions and the effects of unshared p- and π-electrons on nonbonded atoms. In the saturated hydrocarbon cases, furthermore, comparisons have been made only between similar conformational isomers in the hope that various secondary parameters not used in the calculations may cancel in the comparison.

(7) Symbols and values[4] used in the subsequent discussion

$K_\theta = 65.0$ kcal./mole/rad² = 0.0200 kcal./mole/deg.² for bending of C–C–C angle $(\theta) > \tau$; see Fig. 1, ref. 4

$\theta$ = C–C–C bond angle

$\tau$ = tetrahedral angle = 109.47°

$K_t = 1.40$ kcal./mole

$\omega$ = C–C–C–C dihedral angle

$r$ = internuclear distance of nonbonded hydrogens, in Å.

$a$ = C–C bond length = 1.533 Å.

$b$ = C–H bond length = 1.108 Å.

The equation for $E_{HH}$ is a simplified form of eq. 3, ref. 4.

The total strain energy for a given conformation is taken as $\Sigma E = \Sigma E_\theta + \Sigma E_t + \Sigma E_{HH}$, summed over all the relevant angles and H–H distances in the molecule. Geometrical equations relating $r$, $\theta$, $\omega$, and $d$ (bond lengths) are given in Appendix B, ref. 4; these are used in solving for all the various angles and distances in a given conformation, which is defined by symmetry and/or by fixing certain angles.[8] Using this procedure, variations may be made systematically in certain angles, the subsequent conformations and their energies so determined, and the conformation of minimum energy selected.

The magnitude of the problem for cycloalkanes increases spectacularly with increasing ring size. Only with cyclopentane was a total solution possible (four independently variable angles); with cyclohexane and cycloheptane, only symmetrical forms were examined, although there is no doubt that these include all the significant minimum-energy forms.[4] To simplify the approach to the larger rings, experience with the correlation of computed and observed energies suggests that the H–H interactions may be ignored between hydrogens bonded to the same or to adjacent carbons on the grounds that they will either cancel in the comparison of conformers, be absorbed in the torsional term $E_t$, or be negligible; similarly, other H–H interactions >2.5 Å. may be ignored as negligible. In summary, then, for the medium-ring cycloalkanes of ring size $n$, $\Sigma E$ consists of $nE_\theta$ and $nE_t$ terms and only a few (4–10) significant $E_{HH}$ terms for each conformation examined. In each case, again, only symmetrical forms were examined, although in the medium rings it is no longer certain that all the energy minima are represented by symmetrical forms.

**Definition of Forms.**—Despite the decision to consider only symmetrical forms, the greater flexibility of the medium rings still affords a large number of different shapes so that it is important to devise a topological convention which will allow us both to see their interrelations clearly and to be sure that none are left out of consideration. To this end we may divide the symmetrical ring forms into two major divisions: those with a plane of symmetry ($C_s$) and those with an axis of symmetry ($C_2$). In the odd-membered rings the symmetry axis or plane must pass through one

(8) It should be emphasized that these equations are much less formidable and *often readily used in hand calculations* when simplied[9]; for example, the distances $r_{14}$ and $r_{15}$ between atoms 1 and 4, and 1 and 5, respectively, with all bond lengths = $a$ and all bond angles tetrahedral, become

$$r_{14}^2 = a^2(41 - 16 \cos \omega)/9$$
$$r_{15}^2 = 16a^2[11 - 4 (\cos \omega_1 + \cos \omega_2) - \cos \omega_1 \cos \omega_2 + 3 \sin \omega_1 \sin \omega_2]/27$$

(9) Copies of a series of useful simplifications of this kind are available on request from the author.

CHART I

NOTATIONS OF THE SYMMETRICAL CYCLOALKANES



atom and bisect the bond opposite it at right angles. In the even-membered rings the axis or plane either passes through two atoms, lying across the ring from each other (type A), or bisects, perpendicularly, two bonds which are opposite (type B). When a plane of symmetry bisects a bond, the bond must have a dihedral angle, $\omega = 0°$, but this is not true when it is bisected by an axis.

In notation, we may represent the axis or plane of symmetry by a horizontal symmetry line above and below which are placed + and − symbols representing the sequence of bonds down each side of the ring by the signs of their dihedral angles (if $\omega = 0°$, the symbol 0 is used instead). When a bond is bisected by a plane or axis, its sign appears at an end of the symmetry line rather than above or below. Each symbol above the symmetry line is reflected below by one of opposite sign for plane symmetry, by the same sign for an axis of symmetry. Since this notation represents the physical ring, it may be turned over or around without altering its identity, or converted to its enantiomer by reversing every sign. In this way one can easily show that a ring with a plane of symmetry is identical with

its mirror image, while one with only an axis is not. These ring notations are also adequate to allow direct translation into molecular models, of which Dreiding models are the most useful for these purposes.

Using this notation system, it is easily possible to generate all possible combinations of + and − signs for consideration. In the convention used here, the left or upper-left sign is taken as $\omega_1$ and + and sequential numbering of the dihedral angles ($\omega_1$, $\omega_2$, $\omega_3$, etc.) of the bonds proceeds from left to right above the symmetry line and then around the other way below. An example of a cyclodecane, with both a plane and axis of symmetry and written both ways, is offered in Fig. 1. Of the rings so generated those with three or more like signs in sequence are either not rings at all or contain such severe interpenetrations of nonbonded atoms as not to be serious candidates for viable molecular conformations. Similarly, viable forms with eclipsed bonds ($\omega = 0$) are only found when the zeroes in the notation are not adjacent and when their replacement by + and − yields viable forms. All the viable symmetrical conformations of the common and medium rings are assembled in Chart I; a few non-
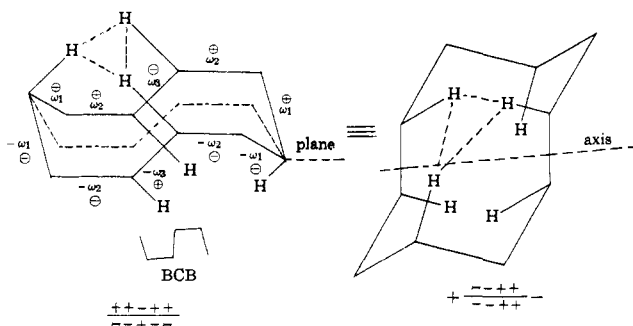
Fig. 1.—Notation of a symmetrical cyclodecane.

viable forms, subsequently to be discussed, are included in brackets. A few forms with eclipsed bonds ($\omega = 0$) above the symmetry line are included to show routes of interchange for certain conformers, to be discussed below; such forms are only particular cases of the more general form with $+$ or $-$ instead of 0.

The majority of forms has a plane of symmetry, especially as a number of the axial-symmetric conformers considered here have planes of symmetry as well, and these may conveniently be organized in more "visual" terms by extending the useful boat–chair distinction of the plane-symmetrical cyclohexanes. The essence of this distinction is seen in the projection of the conformation of each on its mirror plane to yield a three-line figure which has a transoid or zigzag form for the chair and a cisoid or concave form for the boat. The nomenclature may be extended to larger rings by viewing their projections as a sequence of boat or chair subunits and thus labeling the conformation by the sequence of appropriate letters, B and/or C, as shown in the plane-symmetrical cyclodecane example of Fig. 1: dotted lines in the left drawing indicate the plane of symmetry and the projection is shown below it. An odd-membered ring is describable by $(n - 5)/2$ such subunits, while an even-membered ring of type A has $(n - 4)/2$, and an even-membered ring of type B has $(n - 6)/2$. Thus the cyclooctane described as "C" must be type B (with the plane bisecting opposite bonds), i.e., VI, while the CB-cyclooctane (IV) is of type A (with the plane bisecting opposite atoms).

In those plane-symmetrical forms in which the plane bisects a bond, one encounters an eclipsed ($\omega = 0°$) assemblage of four carbons symmetrically placed with respect to the mirror plane (e.g., chair cycloheptane has one; the centrosymmetric cyclooctane VI has two). This conformational moiety is intrinsically of high strain, having not only the torsional strain of the eclipsed bond (2.8 kcal./mole) but necessarily also a serious interpenetration of two hydrogens across the ends of the four-carbon unit ($r_1$ in VI). In the tetrahedral-angle cases, the H–H distance is 1.82 Å. in the cyclohexane boat, 1.23 Å. in the cycloheptane chair and cyclooctane VI, and in general even less in reasonable larger rings, the minimum H–H distance of 0.83 Å.[10] being attained in certain cyclodecanes (cf. the CC form). This orientation, therefore, is likely to be avoided altogether as the molecule seeks its minimum-energy conformation. Since odd-membered rings cannot assume a plane-symmetrical form without incorporating this feature, it is not surprising to find that

the most stable forms of odd-membered rings (except cyclopentane) do not have a plane of symmetry.
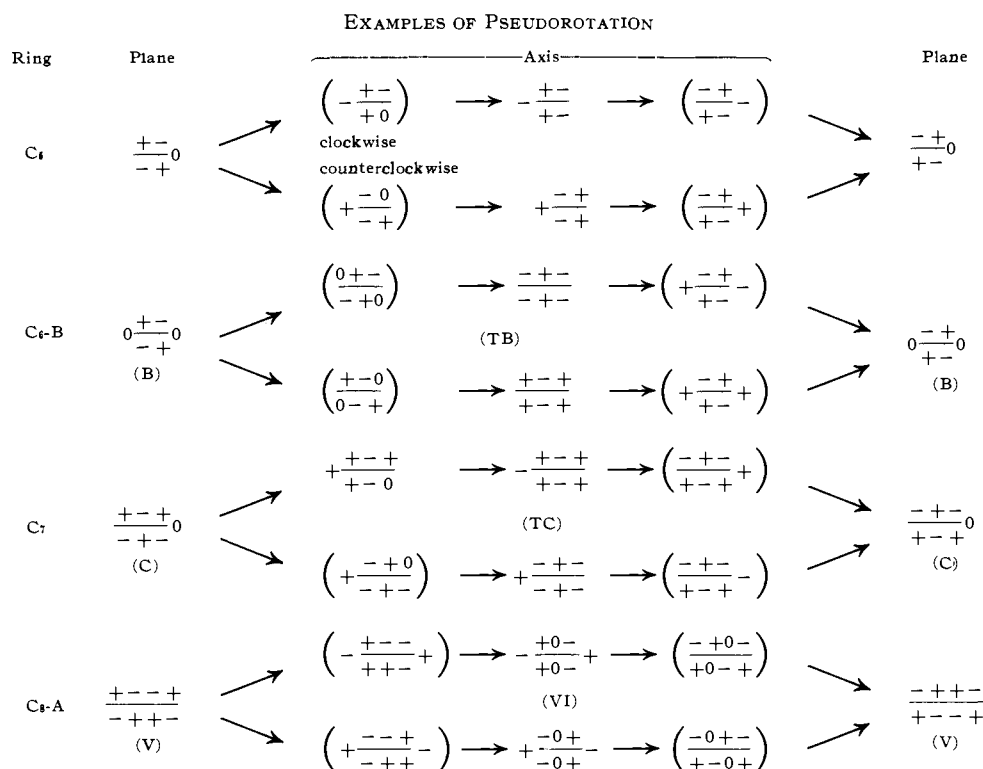
Conformations having only axes of symmetry are more difficult to visualize and more trouble to calculate, yet the most stable conformation for every ring calculated to date has an axis of symmetry. A useful pictorial presentation of these rings (in odd-membered rings) is one looking down the axis,[4] with the atom which lies on the axis (the axis carbon) placed in front. The two substituent positions on the axis carbon are of symmetrical necessity identical, unlike the positions at any other ring atom, and so deserve a designation separate from axial and equatorial, even though they may approximate in terms of strain energy the latter (cf. cycloheptane twist-chair[5a]). The term isoclinal ("equal dip or inclination") has been proposed by Dr. M. C. Whiting[11] and will be used here.

Two modes of interconversion among symmetrical conformations of a given cycloalkane should be discerned. In the first mode the form changes without loss of its basic plane or axis of symmetry; this may be called the symmetrical mode (s) and is embodied in the flip of the chair cyclohexane to the boat via a plane-symmetrical transition state with five atoms coplanar and in the preferred change from the chair to the twist-boat maintaining the axis of symmetry throughout the transition.[4] In the common rings, in which there is little conformational flexibility, this mode requires serious bond-angle bending strain in the transition, but this becomes negligible in the more flexible medium rings which may generally interconvert easily via the symmetrical mode, maintaining constant bond angles and varying only dihedral angles. The symmetrical mode requires at least one pair of opposite dihedral angles to pass through $\omega = 0°$ at some time and several examples are noted in Chart I, e.g., transformation of the CB-cyclononane (XIX) into the BC-cyclononane (XVI) via the $C_{3v}$ form XVII. The arrows represent interconversions in the symmetrical mode.

The other mode is pseudorotation ($\psi$), which may be described as a concerted, continuous change of dihedral angles such that each ring atom (and each ring bond) sequentially takes up each of the possible ring positions; this sequence of ring positions is called the pseudorotation itinerary.[4] In one step of the itinerary for a symmetrical ring the ring must pass out of its symmetry through a continuum of asymmetrical forms, to a form of opposite symmetry, and ultimately back to the initial symmetry form in which each atom now occupies the next ring position on the itinerary. Thus in cycloheptane[4] the atom of position 1 in the chair form finds itself in position 2 after this change and, in subsequent steps, in positions 3, 4, 4', etc., until after a full pseudorotation cycle it is again in position 1. In the course of pseudorotation the axis (or plane) may be thought of as rotating from one location to the next in the ring, e.g., in cyclohexane from 1–4 to 2–5 to 3–6, etc. In the highly symmetrical crown rings a succession of alternating planes and axes is already found in the molecule so that it may be said to undergo pseudorotation without changing form; from another viewpoint this is true (and pseudorotation is meaningless) since all the atoms and bonds in the ring are identical with respect to their conformational environment.

(10) The expression for the minimum case is $r = a(1 - 2 \cos \theta) + 2b \cos 2\theta$ for all bond angles $= \theta$; even with $\theta = 120°$, $r$ is only 1.96 Å.

(11) Private communication.

CHART II

EXAMPLES OF PSEUDOROTATION

| Ring | Plane | ———————Axis——————— | Plane |
|---|---|---|---|



Chart II showing pseudorotation examples for rings $C_i$, $C_i$-B (B), $C_7$ (C), and $C_i$-A (V), with clockwise and counterclockwise rotations, intermediate forms labeled (TB), (TC), (VI).

With less symmetrical rings the conformational notation introduced above may be applied to clarify the pseudorotation process as follows. Each sign in the notation is moved to the next position around the ring ("musical chairs") and the symmetry line is changed from representing plane or axis to the opposite; finally "0" signs are changed to + or — to conform to the requirements of the new symmetry, or, conversely, + or — changed to 0. This is in effect the rotation of a plane to an axis in the next position around the ring and rotation to the right affords a conformation enantiomeric to the one formed on rotating to the left. Even-membered rings of type A yield type B (of opposite symmetry) and *vice versa*. These changes are illustrated by the examples of Chart II[12] and provide a means of examining the interconvertibility of various conformers *via* the pseudorotation mode.

Finally, it should be noted that all the above discussion has been made within the intellectual limits of the idea of symmetry, while favorable conformations for a given cycloalkane are determined by the summation of geometrically interrelated strain energies and so are not, *a priori*, confined to symmetrical forms. However, the experience to date, although admittedly dominated by the unique case of chair cyclohexane, suggests a preference for symmetrical forms. With respect to the nonbonded interactions of hydrogens, this may be justified by the shape of the van der Waals curve in the relevant region (0–5 kcal./mole)[4] which will cause an *increase* in total energy when a symmetrical form with two pairs of nonbonded hydrogens at equal distances is transformed to nonsymmetrical

(12) When the prescribed rotation yields no symmetrical notation (without introducing gratuitous zeroes), subsequent rotations may succeed; thus, in the boat family (B ⇌ TB) of cycloheptanes, two formal rotations of signs in the ring notation are necessary to pass from the plane to the axis of symmetry in pseudorotation; in some rings no pseudorotation is possible (*e.g.*, IV).

ones with the distances of the pairs unequal, one distance increased as much as the other is decreased.

## Results and Discussion[7]

The medium-ring cycloalkanes are separately discussed below with the results of their energy calculations. In general, the highest symmetry commensurate with the notation (Chart I) or boat–chair description of each conformer has been used for the calculations and the formal symmetry designation is appended to the formula in parentheses. The formulas indicate the serious nonbonded hydrogen interactions and axes of symmetry, designated by the symbol — — — —, and are cast in the convention (+ω₁ at left) of the notation system described above. Equations for the geometrical derivations of the ring forms are found in the Appendix.

**The Crown Forms.**—The crown forms of the cycloalkanes $C_n H_{2n}$ ($n$ = even; all bond angles = $\theta$) are the easiest to describe, being in each case simply the single, most symmetrical ($C_{n/2d}$) all-chair form with $n$ planes of symmetry instead of one (these planes

TABLE I

GEOMETRY AND ENERGIES OF THE CROWN CYCLOALKANES

| $n$ | $\theta$ | $\omega$ | $r$ | $E_\theta$ | $E_t$ | $E_{HH}$ | $\Sigma E/n$ | Total energy $\Sigma E$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Energies per $CH_2$ | | |
| | | | (1) | Tetrahedral-angle forms | | | | |
| 6 | $\tau$ | 60.0 | 2.51 | 0.0 | 0.0 | −0.1 | −0.1 | −0.6 |
| 8 | $\tau$ | 97.0 | 2.00 | .0 | 1.9 | .2 | 2.1 | 17.1 |
| 10 | $\tau$ | 115.3 | 1.90 | .0 | 2.8 | .5 | 3.3 | 32.8 |
| 12 | $\tau$ | 126.7 | 1.91 | .0 | 2.7 | .5 | 3.2 | 38.6 |
| 14 | $\tau$ | 134.7 | 1.94 | .0 | 2.4 | .4 | 2.8 | 39.3 |
| 16 | $\tau$ | 140.5 | 1.98 | .0 | 2.1 | .3 | 2.4 | 37.7 |
| 18 | $\tau$ | 145.0 | 2.01 | .0 | 1.8 | .2 | 2.0 | 35.4 |
| | | | (2) | Minimum-energy forms | | | | |
| 6 | $\tau$ | 60.0 | 2.51 | 0.0 | 0.0 | −0.1 | −0.1 | −0.6 |
| 8 | 113.2 | 91.9 | 2.19 | .3 | 1.5 | −0.03 | 1.8 | 14.3 |
| 10 | 112.3 | 112.6 | 2.01 | .2 | 2.7 | .2 | 3.1 | 30.6 |
| 12 | 111.3 | 125.4 | 1.97 | .1 | 2.7 | .3 | 3.1 | 37.6 |
| 14 | 110.6 | 134.0 | 1.97 | .0 | 2.4 | .3 | 2.8 | 38.8 |
| 16 | 110.1 | 140.2 | 1.99 | .0 | 2.1 | .2 | 2.3 | 37.5 |
| 18 | 109.9 | 144.8 | 2.02 | .0 | 1.8 | .2 | 2.0 | 35.3 |

TABLE II

GEOMETRY AND ENERGIES OF THE SYMMETRICAL CYCLOOCTANES[13]

| Description | $\theta$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $r_1$ | $r_2$ | $r_3$ | $r_4$ | $E_\theta$ | $E_t$ | $E_{HH}$ | $\Sigma E$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **(1)** | **Tetrahedral-angle forms** | | | | | | | |
| Crown ($D_{4d}$), I | $\tau$ | 97.0 | ... | ... | 2.00 | .. | .. | .. | 0.0 | 15.2 | 1.9 | 17.1 |
| CC ($C_{2v}$), II | $\tau$ | 83.0 | 108.5 | ... | 1.90 | 2.08 | 2.14 | 1.92 | .0 | 13.8 | 1.8 | 15.6 |
| ($D_2$), III | $\tau$ | 69.5 | 93.0 | 122.0 | 1.93 | 2.22 | 2.03 | .. | .0 | 12.4 | 1.1 | 13.5 |
| BC ($C_s$), IV | $\tau$ | 77.1 | 42.9 | 112.2 | 1.51 | 2.22 | 1.55 | 2.15 | .0 | 8.5 | 15.3 | 23.8 |
| ($C_{2h}$), V | $\tau$ | 124.1 | 36.0 | ... | 1.72 | 1.90 | .. | .. | .0 | 14.9 | 7.8 | 22.7 |
| Chair ($C_{2h}$), VI | $\tau$ | 0.0 | 82.8 | 138.6 | 1.23 | .. | .. | .. | .0 | 13.5 | >30 | >43 |
| BB ($D_{2d}$), VII | $\tau$ | 60.0 | ... | ... | 0.69 | .. | .. | .. | .0 | 0.0 | >30 | >30 |
| Boat ($D_{2d}$), VIII | $\tau$ | 0.0 | 82.8 | ... | 1.23 | .. | .. | .. | .0 | 14.7 | >30 | >44 |
| ($C_2$), IX[a] | $\tau$ | 108.0 | 102.1 | 45.0 | 1.94 | 1.73 | 1.78 | .. | .0 | 10.3 | 6.3 | 16.6 |
| | | | | **(2)** | **Minimum-energy forms** | | | | | | | |
| Crown ($D_{4d}$), I | 113.2 | 91.8 | ... | ... | 2.19 | .. | .. | .. | 2.2 | 12.3 | −0.2 | 14.3 |
| CC ($C_{2v}$), II | 112.7 | 77.4 | 104.8 | ... | 2.02 | 2.22 | 2.30 | 2.03 | 1.7 | 11.7 | .1 | 13.5 |
| ($D_2$), III | 112.0 | 62.8 | 88.6 | 120.6 | 1.99 | 2.37 | 2.13 | .. | 1.0 | 10.8 | .4 | 12.2 |
| BC ($C_s$), IV | 114.3 | 69.2 | 43.5 | 105.5 | 1.90 | 2.47 | 1.80 | 2.35 | 3.7 | 6.4 | 1.8 | 12.0 |
| BC ($C_s$), IV | b | 68.6 | 44.4 | 105.2 | .. | .. | .. | .. | 3.8 | 6.3 | 1.8 | 11.9 |
| ($C_{2h}$), V | 113.0 | 116.4 | 36.5 | ... | 1.98 | 2.00 | .. | .. | 2.0 | 14.8 | 1.6 | 18.4 |
| Chair ($C_{2h}$), VI | 114.8 | 0.0 | 77.7 | 125.0 | 1.79 | .. | .. | .. | 4.5 | 13.3 | 2.2 | 20.0 |
| BB ($D_{2d}$), VII | 118.0 | 53.0 | ... | ... | 1.72 | .. | .. | .. | 11.5 | 0.7 | 3.5 | 15.7 |
| Boat ($D_{2d}$), VIII | 115.9 | 0.0 | 76.4 | ... | 1.92 | .. | .. | .. | 6.6 | 13.1 | 1.9 | 21.6 |
| ($C_2$), IX[c] | 112.7 | 100.8 | 98.0 | 46.4 | 2.07 | 1.91 | 2.08 | .. | 1.6 | 9.8 | 1.4 | 12.8 |

[a] Form IX ($\theta = \tau$), $\omega_4 = 53.6°$, $\omega_5 = 135.6°$, $\phi = 25.9°$. [b] Minimized with variable $\theta$; $E_{min}$ as listed as $\theta_1 = 115.2°$, $\theta_2 = 114.3°$, $\theta_3 = 113.5°$ ($\theta_1$ = in-plane atom). [c] Form IX ($\theta = 112.7°$), $\omega_4 = 50.7°$, $\omega_5 = 126.5°$, $\phi = 25.4°$.

have in common an $n/2$-fold axis through the center of the ring). In each crown (cf. I) connection of alternate atoms yields a regular plane polygon having $n/2$ sides of length $2a \sin \frac{1}{2}\theta$ ($a$ = C–C bond length) and internal angle $\psi = (180/n)(n-4)$. The dihedral angles are all equal in magnitude and alternate in sign. There are two clusters of $n/2$ nonbonded hydrogens each of which have serious repulsions, one forming a circle above, the other be-
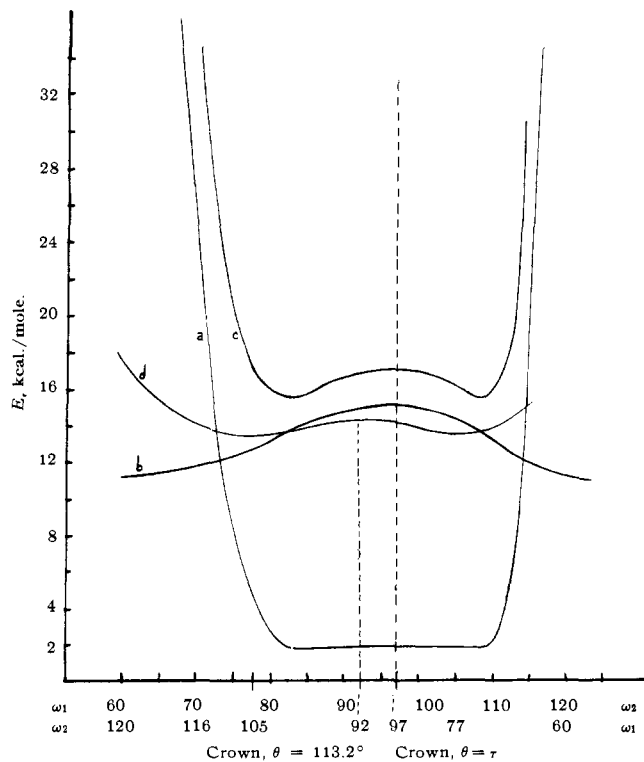


Fig. 2.—Energy profiles of cyclooctane interconversions (variation in CC form (II)). $\theta = \tau$: curve a, $\Sigma E_{HH}$; curve b, $\Sigma E_t$; curve c, $\Sigma E$. $E$-minimum ($\theta = 112.7°$) case: curve d, $\Sigma E$ ($E$-maximum, $\theta = 113.2°$).

low, the general plane of the crown skeleton. Each H–H distance can easily be computed as a 1,5-distance, i.e., $r = f_{15}(b, a, a, b, \theta, \omega, -\omega)$; thus $\Sigma E = n(E_\theta + E_t + E_{HH}) = f(\theta)$, and a search may be made for the minimum-energy form of each crown by varying $\theta$. The results of varying $\theta$ by increments of 0.1° are shown in Table I. It may be noted that crown rings with $n/2$ an odd number have a center of symmetry (cf. chair cyclohexane, crown cyclodecane, etc.), while those with $n/2$ an even number do not.

**Cyclooctane.**—The nine forms of cyclooctane with definable symmetry are shown as formulas I–IX; the results of the computations for these forms are incorporated in Table II. It is convenient in discussing the modes of interconversion of these conformers to assemble them into three groups around the three plane-symmetrical members CC (I, II), CB (IV), and BB (VII). The familiar "extended crown" form (CC, II) has a roughly oval shape when seen from above; if all four dihedral angles $\omega_1$ are changed by the same amount, the symmetry is retained and the oval becomes either more extended or more nearly circular. As the $\omega_1$ values of II are continuously increased, those of $\omega_2$ decrease until they are identical and the conformation has passed from the oval II to the circular crown I; continuing this dihedral angle change leads into another oval II with its major axis perpendicular to the first.

The energy profile of this conformational change in the symmetrical mode is shown in Fig. 2 and illustrates that an extended crown (II) is preferred somewhat (0.8 kcal./mole) over the more symmetrical crown form, which is, in fact, a mild energy maximum over which the molecule must pass in converting (by the plane-symmetrical mode) from one oval CC form to the other one with the perpendicular oval axis. In Fig. 2 the separate energy components (curves a and b) for the variation of tetrahedral-angle species are shown, as well as the total energy sum (curve c) to emphasize the difference in the contribution of torsional strain and van der Waals interactions, the former varying relatively little, the latter passing quickly from negligible to enormous as hydrogens directly across the ring are forced into serious interpenetration. On opening the bond angles from tetrahedral, the latter effect can be drastically reduced, resulting in the more even $\Sigma E$ profile (curve d) of the preferred forms with optimal bond angles. It is important to observe, however, that (within the defined symmetry) the possible variation in torsional strain is correspondingly very limited (compare sections 1 and 2 of Table II).

Pseudorotation ($\psi$) proceeds from II through a continuum of asymmetrical forms to the $D_2$ form (three perpendicular axes) III,[14] and subsequently on to another plane-symmetrical form II.

(13) Rings are described by name and/or symmetry description, the latter in parentheses, as well as formula number. All bond angles = $\theta$, dihedral angles $\omega$, and H–H distances $r$, as shown on formulas I–XXX. Bond and dihedral angles were varied by 0.1° increments in searching for $E_{min}$. Dihedral angles are all listed as positive angles in these tables, their actual signs being obtainable from the notations in Chart I.
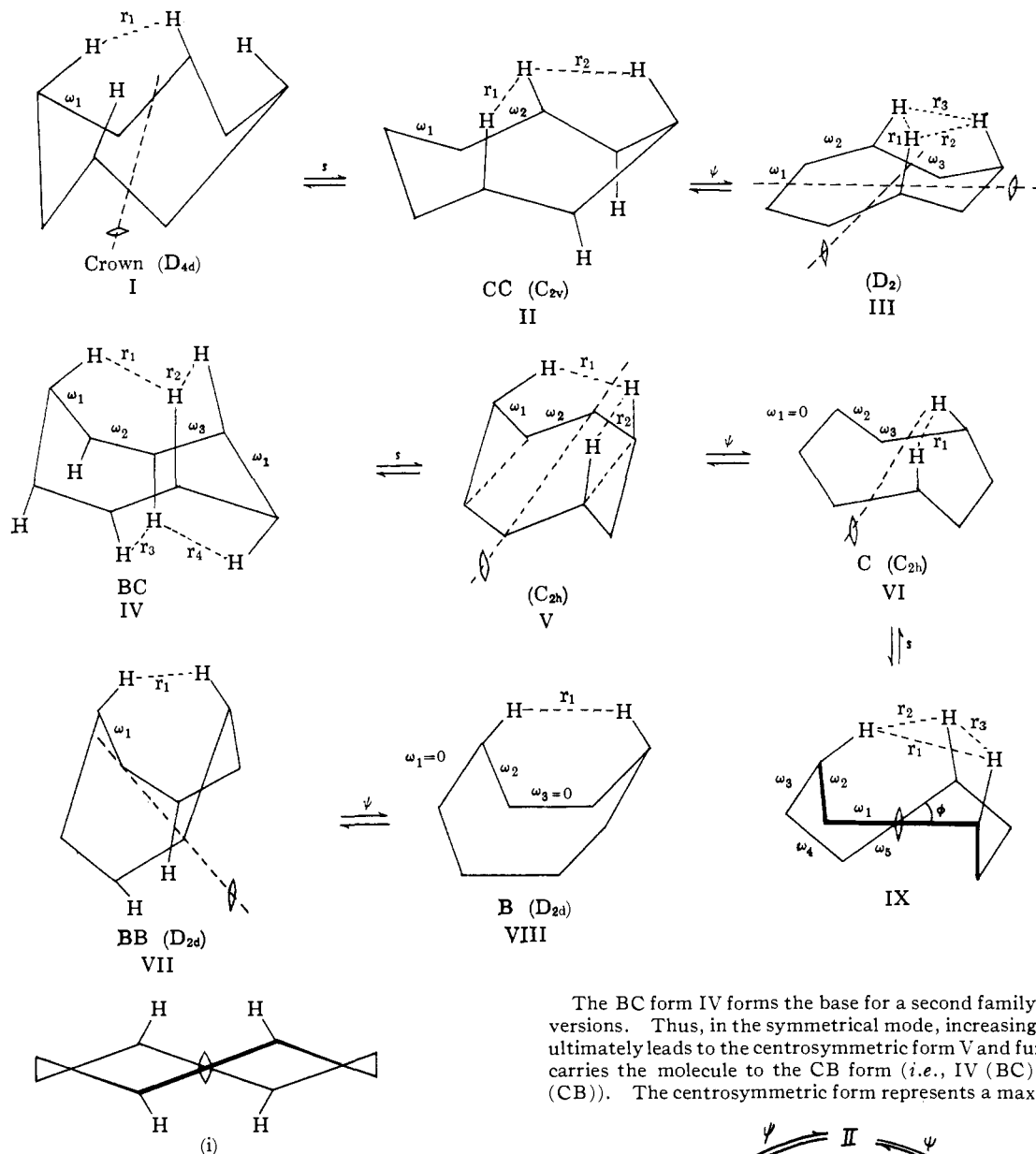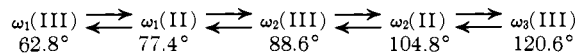
(14) The $D_2$ form is present intact in the twistane molecule[15] as may be seen in the projection (i) of III, seen down the axis (0) through the $\omega_3$ bond; twistane results from replacing the nonbonded hydrogens shown in (i) by

The BC form IV forms the base for a second family of interconversions. Thus, in the symmetrical mode, increasing dihedrals $\omega_1$ ultimately leads to the centrosymmetric form V and further change carries the molecule to the CB form (i.e., IV (BC) $\rightleftarrows$ V $\rightleftarrows$ IV (CB)). The centrosymmetric form represents a maximum in the



(i)

The pseudorotation itinerary is a direct sequence: atom 1 in II becomes atom 2 in the next II form, atom 3 in the next, etc. The itinerary for the dihedral angles is as follows, the signs of the angles staying the same throughout the pseudorotation cycle

$$\omega_1(\text{III}) \underset{}{\rightleftarrows} \omega_1(\text{II}) \underset{}{\rightleftarrows} \omega_2(\text{III}) \underset{}{\rightleftarrows} \omega_2(\text{II}) \underset{}{\rightleftarrows} \omega_3(\text{III})$$
$$62.8° \qquad 77.4° \qquad 88.6° \qquad 104.8° \qquad 120.6°$$

The energy profile for pseudorotation is sinusoidal with a minimum at the $D_2$ form III, a maximum at the extended crown II, and a calculated amplitude of 1.3 kcal./mole; in this it closely resembles the energy profile of chair cycloheptane pseudorotation.[4]

Finally, as the crown I has axes as well as planes of symmetry, the symmetrical mode of transition will carry an oval form III through the circular crown I and on to another $D_2$ form with a perpendicular oval axis in a manner analogous to the I $\rightleftarrows$ II change outlined above, except that it occurs with retention of the axis rather than the plane of symmetry. The component and resultant strain energies for this symmetrical conformation change are much the same as those in Fig. 2, but with somewhat lower minima. These conformational changes are summarized in Fig. 3 for the family of forms related to the crown conformation.



Fig. 3.—Conformational interconversions from crown cyclooctane.

energy profile as the crown does in the previous family. Only the centrosymmetric form V in this family, however, undergoes pseudorotation, passing into the chair form VI. Finally, interconversion in the symmetrical mode, but retaining an axis rather than a plane of symmetry (cf. III $\rightleftarrows$ I $\rightleftarrows$ III), is represented by the transformation of the $C_2$ forms IX into VI and back. The familiar chair VI may be considered as the specific case of IX, in which $\phi$

methylene bridges and possesses the same $D_2$ symmetry: three perpendicular axes and no planes of symmetry. The projection (i) corresponds to the view of the other $C_2$ form shown in IX.

(15) H. W. Whitlock, Jr., J. Am. Chem. Soc., **84**, 3412 (1962).

## TABLE III
### Geometry and Energies of Cyclononanes[13]

| Description | θ | ω₁ | ω₂ | ω₃ | ω₄ | ω₅ | r₁ | r₂ | r₃ | Eθ | Et | EHH | ΣE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (1) Tetrahedral-angle forms | | | | | | | | | | | | | |
| CC (Cs), X[a] | τ | 77.0 | 113.4 | 150.0 | 91.4 | 0.0 | 2.16 | 1.52 | 1.07 | 0.0 | 15.1 | 44.4 | 59.4 |
| BC (Cs), XVI[a] | τ | 71.9 | 49.1 | 153.0 | 88.6 | 0.0 | 1.40 | 1.24 | 1.12 | .0 | 8.7 | >50 | >50 |
| (C3v), XVII | τ | 114.7 | 0.0 | ... | ... | ... | 0.84 | .. | .. | .0 | 24.9 | >50 | >50 |
| TCC (C2), XIII | τ | 64.5 | 129.0 | 87.1 | 94.3 | 124.8 | 2.06 | 1.86 | 1.85 | .0 | 13.9 | 3.2 | 17.1 |
| (D3), XIV | τ | 58.5 | 137.3 | ... | ... | ... | 1.67 | .. | .. | .0 | 6.8 | 13.1 | 20.2 |
| (C2), XV | τ | 77.2 | 84.4 | 41.4 | 111.7 | 107.5 | 1.48 | 1.92 | 1.49 | .0 | 12.1 | 25.3 | 37.5 |
| (C2), XX | τ | 78.0 | 109.4 | 0.0 | 95.1 | 143.1 | 0.97 | .. | .. | .0 | 17.4 | >50 | >50 |
| (2) Minimum-energy forms | | | | | | | | | | | | | |
| CC (Cs), X[a] | 116.0 | 66.9 | 108.2 | 139.0 | 83.8 | 0.0 | 2.43 | 1.79 | 1.71 | 6.8 | 14.2 | 2.4 | 23.3 |
| BC (Cs), XVI[a] | 116.0 | 65.0 | 50.8 | 140.0 | 82.1 | 0.0 | 1.88 | 1.70 | 1.73 | 6.8 | 9.1 | 4.5 | 20.3 |
| TCC (C2), XIII | 112.2 | 64.8 | 123.5 | 81.0 | 91.2 | 124.5 | 2.19 | 2.06 | 1.92 | 1.3 | 12.9 | 1.1 | 15.3 |
| (D3), XIV | 113.1 | 57.2 | 130.7 | ... | ... | ... | 1.91 | .. | .. | 2.3 | 7.8 | 3.0 | 13.1 |
| (D3), XIV | b | 57.2 | 129.9 | ... | ... | ... | 1.92 | .. | .. | 2.2 | 7.9 | 2.8 | 12.9 |
| (C2), XV | 115.4 | 70.9 | 77.0 | 45.3 | 105.0 | 94.1 | 1.76 | 2.15 | 1.99 | 6.3 | 8.7 | 3.2 | 18.2 |
| (C2), XX | 117.7 | 69.7 | 99.8 | 0.0 | 87.7 | 124.8 | 1.66 | .. | .. | 12.1 | 15.4 | 4.4 | 31.9 |
| (3) X-Ray comparisons[c] calculated | | | | | | | | | | | | | |
| (D3), XIV (E-min.) | 116.7 | 55.5 | 123.7 | ... | ... | ... | 2.15 | .. | .. | 9.3 | 8.5 | 0.0 | 17.8 |
| (C2), XV | 116.9 | 68.4 | 72.3 | 50.2 | 103.1 | 86.0 | 1.76 | 2.25 | 2.21 | 9.8 | 6.9 | 2.4 | 19.1 |
| (C2), XV | 116.5 | 70.2 | 77.0 | 42.7 | 103.2 | 95.0 | 1.90 | 2.18 | 2.02 | 8.8 | 8.7 | 1.4 | 19.1 |
| (C2), XV | 116.7 | 69.3 | 74.8 | 46.4 | 103.2 | 90.5 | 1.83 | 2.21 | 2.11 | 9.3 | 7.8 | 1.7 | 18.9 |
| (C2), XV (E-min.) | 116.7 | 69.1 | 73.9 | 47.8 | 103.4 | 89.1 | 1.80 | 2.22 | 2.14 | 9.3 | 7.5 | 2.0 | 18.9 |
| (4) X-Ray results[17] | | | | | | | | | | | | | |
| A form | 116.9[d] | 69.0 | 75.5 | 45.5 | 99.0 | 86.0 | 1.81 | 2.36 | 2.09 | .. | .. | .. | .. |
| B form | 116.5[d] | 71.0 | 84.0 | 35.5 | 99.5 | 95.0 | 1.83 | 2.21 | 2.16 | .. | .. | .. | .. |
| Average | 116.7[d] | 70.0 | 79.8 | 40.5 | 99.2 | 90.5 | 1.82 | 2.28 | 2.12 | 9.3 | 8.6 | 1.7 | 19.6 |

[a] Increments of 1.0° for θ and ω used here.   [b] Minimized with variable θ; $E_{min}$ as listed at $θ_1 = 114.4°$, $θ_2 = 112.0°$ ($θ_1$ = axis carbon). [c] See text; first and last examples represent searches for energy minima within the assumption of a bond angle, $θ = 116.7°$; middle three examples are simply the pure C₂ rings of form XV assuming both θ and ω₅.   [d] Averaged angles used here; average deviation of observed bond angles (θ) from 116.7° was 2.5°; of observed dihedral angles (ω) from averages shown, 6°.

= 0°; the view of IX shown is not three dimensional, but the projection seen looking down the symmetry axis.[14] The conversion in the symmetrical mode from IX to VI to IX yields as the second conformation of IX the mirror image of the first, as may easily be seen in Chart I. Of these several interrelated conformations an energy minimum is found in the one BC form (IV) which is comparable to the best D₂ form (III) in calculated strain energy. As a test of the validity of assuming that a reasonable minimum is obtained by allowing, as heretofore, all bond angles to be identical, form IV was computed both with an assumption of all bond angles equal and with independent variation of θ. The results in Table II tend to confirm that differential variation of bond angles affects neither the final energy minimum nor the related geometry significantly. The same effect was observed in differential variation of bond angle in selected cyclononanes and cyclodecanes and affords a defense for the much simpler calculations in which all bond angles are assumed to be equal.

The third family is represented by the cisoid conformation VII which, as it has higher symmetry than II or IV, is uniquely defined by its bond angles (this is true of all symmetrical forms of cyclohexane and cycloheptane but uncommon in larger rings). Conformational change in the symmetrical mode here can only aggravate the already serious H–H interactions in VII and so is not considered in detail. Pseudorotation of VII causes it to pass into the "tub" form VIII, which represents the energy maximum in the itinerary, and then back to VII. Neither of these forms compares favorably in energy with the most stable conformations in the previous two families. Finally, interconversions of the plane-symmetrical members II, IV, and VII of the three families, in the symmetrical mode, are easily envisioned although they may not be the best routes energetically. In any case transformations from one family into another are certainly possible with relatively low transition barriers so that all of the above forms are probably readily interconvertible. This also suggests that, as one form of cyclooctane is not clearly favored energetically as in cyclohexane and cycloheptane, cyclooctane will resemble cyclopentane in being a very mobile conformational mixture at ordinary temperature.

**Cyclononane.**—Ten forms of cyclononane from Chart I are pictured as structures X–XX and calculations for relevant ones

are listed in the first two sections of Table III. There are essentially four plane-symmetrical forms: the chair–chair (X), boat–boat (XII), boat–chair (XVI), and chair–boat (XIX). The first two are interconvertible (i.e. by increasing ω₁) in the symmetrical mode by passage through the form XI which has six carbons coplanar and is therefore describable neither as CC nor BB. The analogous form XVIII serves as the intermediate in the symmetrical mode interconversions (i.e. by continuously changing ω₁) of BC (XVI) and CB (XIX).[16] Plane-symmetrical forms in the odd-membered rings are always strained because of the necessary presence of the eclipsed (here ω₅ = 0°) bond and its attendant H–H repulsions, as discussed above; the latter are also worse in cyclononanes than in cycloheptanes and are reflected in the values of r₃ (and EHH) in Table III, section 1, and the large bond angles (θ) required in section 2 to alleviate this strain. Only the two better forms were actually calculated as even they are relatively poor forms energetically.

The four plane-symmetrical forms have their counterpart in four forms with axes of symmetry but the very convoluted one corresponding to the boat–boat has not been included here because of its excessive strain. The chair–chair X undergoes pseudorotation carrying it into the "twist-chair–chair" (TCC) XIII and subsequently back to the next sequential CC (X), in a transition completely analogous to the chair ⇌ twist-chair (TC) pseudorotation of cycloheptane.[4] Here also the form with the axis of symmetry is the more favored, by a calculated 8.0 kcal./mole compared to 2.2 kcal./mole for cycloheptane (and 0.0 for cyclopentane). To complete the symmetry operation, we may note that a transition in the symmetrical mode (varying dihedrals and retaining the axis of symmetry) carries the TCC form XIII into the unpictured "TBB" form just as the same mode carries their pseudorotational counterparts X and XII into each other.

The cyclononane of greatest interest is the most highly symmetrical (D₃) conformation XIV, which has three identical axes

(16) The form XVIII has its parallel in the cyclooctane V which stands between BC- and CB-cyclooctanes (IV) in the analogous way. Similarly, form XI has a cyclooctane counterpart (not pictured) which stands between the CC (II) and BB (VII) conformers in their interconversion via the symmetrical mode.

(17) R. F. Bryan and J. D. Dunitz, Helv. Chim. Acta, 43, 1, 3 (1960).

CC
X

XI

BB
XII

TCC
XIII

(D₃)
XIV

XV

BC
XVI

BC (C₃ᵥ)
XVIII

XX

CB
XIX

XVIII
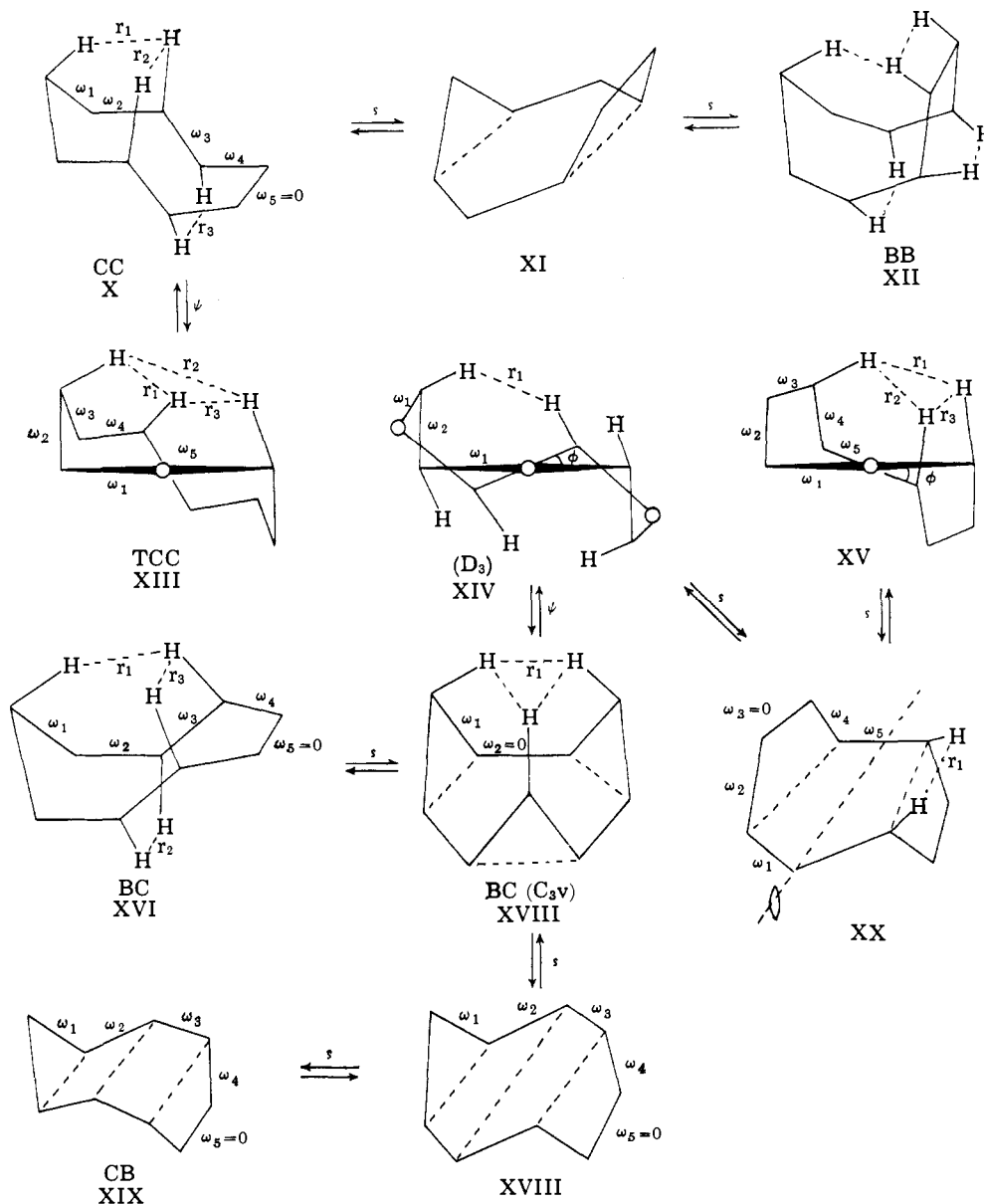
of symmetry in the plane of the molecule, passing through atoms 1, 4, and 7, which are circled in XIV; it has two parallel planes of three nonbonded hydrogens each interacting above and below the molecular plane. In this and other geometrical respects (cf. its threefold symmetry) this form bears a marked resemblance to chair cyclohexane. This form is computed to be the most stable cyclononane by 2.2 kcal./mole over the next best form, the TCC (XIII), and was chosen also as a test of variable bond angle calculation which showed, as with cyclooctane, no significant improvement in energy (Table III). Furthermore, the $D_3$ is only one of a continuum of forms (with five different dihedrals $\omega_{1-5}$) in the particular $C_2$ symmetry described by its notation in Chart I and the projection XIV; examination of the energy profile of this continuum showed, however, a minimum at the most symmetrical ($D_3$) form. Thus $D_3$ is the most stable of all forms XIV (the other forms of XIV may be arrived at by varying angle $\phi$). Furthermore, this variation of XIV in the symmetrical mode until the angle $\phi$ goes to zero leads to the form XX, with five atoms coplanar and $\omega_3 = 0°$, which is the in-symmetry transition between the axial-symmetric conformers XIV and XV; XX represents an energy maximum arising from eclipsed bonds and serious nonbonded hydrogen interpenetration. Finally, pseudorotation of $D_3$ carries it into the equally symmetrical $C_{3v}$ (three planes at 120° in place of three axes), which is one of the boat–chair form (XVIII), and pseudorotation of XV carries it into the chair–boat form XIX with $\omega_3 = 0°$.

**Cyclodecane.**—The rapid increase in complexity on increasing ring size is reflected in the cyclodecane cases in Chart I and

formulas XXI–XXX; computations for certain cases are presented in Table IV, but not all forms were examined in this detail since preliminary examination in the light of the foregoing experience easily eliminated some forms, as discussed below. The plane-symmetrical forms are of two types, A and B, each conformation of type A, with two atoms in the plane of symmetry, being represented by three conformational subunits (BCB, BBC, etc.); it is convenient to break down these type-A cyclodecanes into two groups based on whether the central subunit is boat or chair. Of the former the BBB conformer is not viable and is omitted; the other two are the CBB (XXIV) and CBC (XXV). All three forms suffer seriously from nonbonded interactions as a result of the confining quality imposed by the central boat unit and all three have two eclipsed bonds ($\omega_3$) as well, so that none were examined in detail; the best, the CBC form XXV, must have dihedral angles of about 90° for $\omega_1$ and 120° for $\omega_2$ and so a crippling torsional strain of about 22 kcal./mole.

The forms with the chair central subunit are far more viable and are listed in Table IV; the CCB (XXII) is merely intermediate in form between the more symmetrical ($C_{2h}$) CCC (XXI) and BCB (XXIIII) conformers. The all-chair XXI (the "stair" form) is simply an extended crown and bears a direct resemblance to the corresponding cyclooctane II in that conformational change in the symmetrical mode carries it to the crown which represents an energy maximum. However, owing to its different symmetry ($C_{2h}$) from that of the cyclooctane extended crown ($C_{2v}$), this form always contains both a plane and perpendicular axis of symmetry and so exhibits no pseudorotation (cf. chair cyclo-
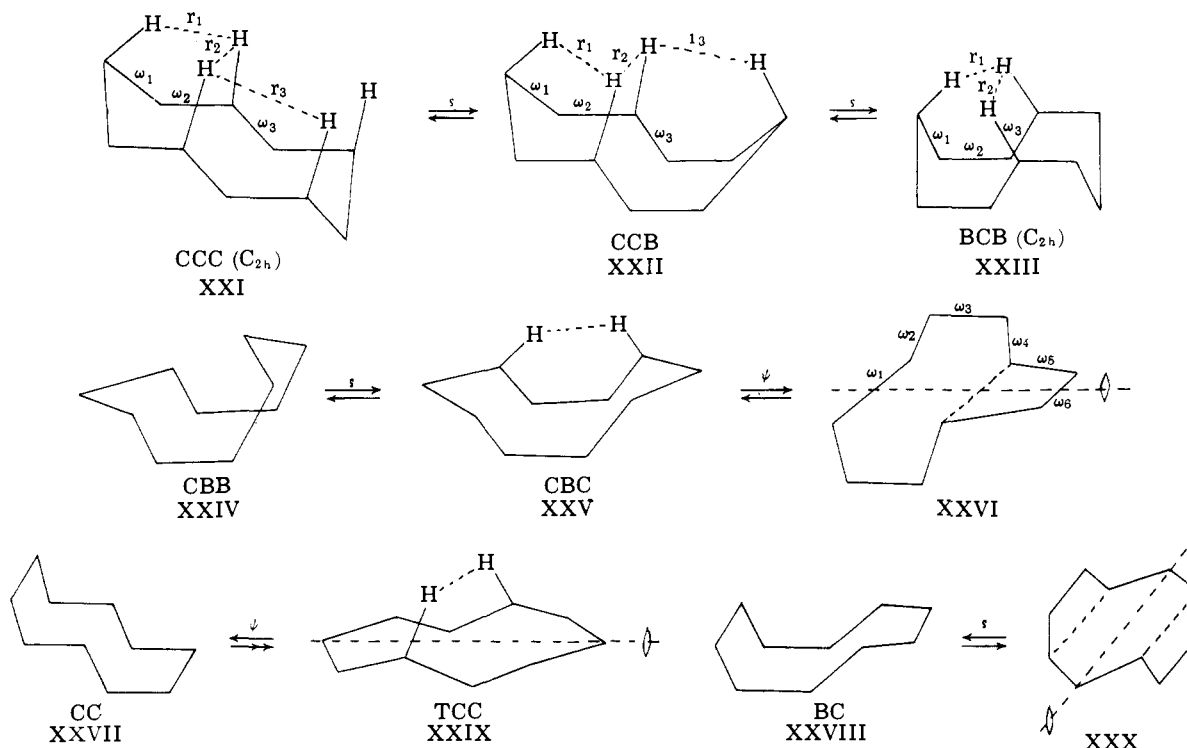
TABLE IV

GEOMETRY AND ENERGIES OF CYCLODECANES[13]

| Description | $\theta$ | $\omega_1$ | $\omega_2$ | $\omega_3$ | $r$ | $r_2$ | $r_3$ | $E_\theta$ | $E_t$ | $E_{HH}$ | $\Sigma E$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (1) Tetrahedral-angle forms | | | | | | | | | | | |
| Crown ($D_{5d}$) | $\tau$ | 115.3 | ... | ... | 1.90 | .. | .. | 0.0 | 27.6 | 5.2 | 32.8 |
| CCC ($C_{2h}$), XXI | $\tau$ | 87.0 | 121.4 | 150.0 | 2.09 | 1.77 | 2.05 | .0 | 18.7 | 3.5 | 22.2 |
| CCB ($C_s$), XXII | $\tau$ | 88.0 | ( 48.1) | 148.8 | 2.08 | 1.82 | 1.99 | .0 | 14.1 | 3.1 | 17.2 |
|  |  |  | (121.3) |  |  |  |  |  |  |  |  |
| BCB ($C_{2h}$), XXIII | $\tau$ | 89.0 | 47.7 | 147.6 | 2.00 | 1.86 | .. | 0.0 | 9.6 | 2.5 | 12.1 |
| (2) Minimum-energy forms | | | | | | | | | | | |
| Crown ($D_{5d}$) | 112.3 | 112.6 | ... | ... | 2.01 | .. | .. | 1.6 | 27.0 | 2.1 | 30.6 |
| CCC ($C_{2h}$), XXI | 112.4 | 81.0 | 118.7 | 150.4 | 2.24 | 1.84 | 2.15 | 1.7 | 17.0 | 1.3 | 20.0 |
| CCB ($C_s$), XXII | 112.4 | 81.0 | (both) | 150.4 | 2.24 | 1.84 | 2.22 | 1.7 | 11.8 | 1.3 | 14.8 |
| BCB ($C_{2h}$), XXIII | 112.4 | 81.0 | 49.8 | 150.4 | 2.22 | 1.84 | .. | 1.7 | 6.6 | 1.3 | 9.6 |
| BCB ($C_{2h}$), XXIII | 116.0 | 71.0 | 52.4 | 152.1 | 2.54 | 1.88 | .. | 8.4 | 3.8 | 0.7 | 12.9 |
| (3) X-Ray results[18] | | | | | | | | | | | |
| cis-1,6-Diamino[a] | 116.2 | 66.5 | 55.5 | 152.6 | .. | .. | .. | 8.7 | 3.0 | (1.7) | (13.4) |
| trans-1,6-Diamino[a] | 116.1 | 68.2 | 55.6 | 153.5 | 2.07 | 1.83 | .. | 8.9 | 3.1 | 1.7 | 13.7 |
| Average | 116.2 | 67.4 | 55.5 | 152.6 | .. | .. | .. | 8.8 | 3.1 | (1.7) | (13.6) |

[a] Averaged angles used here; average deviation of observed bond angles ($\theta$) from values shown was 1.9° (cis) and 1.2° (trans); for dihedral ang'es ($\omega$), 2.4° (cis) and 1.7° (trans).

hexane). The BCB form XXIII, also illustrated in Fig. 1, is the preferred cyclodecane owing to its peculiarly favorable torsional energy, which outweighs a nonbonded hydrogen strain situation somewhat *more* crowded than that of the extended crown. This form also has an axis perpendicular to its plane of symmetry and exhibits no pseudorotation; two parallel planes of three seriously interacting hydrogens each are found above and below the molecular plane. As with cyclooctane and cyclononane, computations of the three forms with independent variation of bond angles created only negligible improvement in over-all energy.

above since it has two perpendicular mirror planes to consider; thus XXV and XXVII are merely different views of the same molecule. Considered as the CC form, its pseudorotation leads to the $D_2$ conformer XXIX with only axes of symmetry; a parallel may be made to the pseudorotation of the CC form of cyclooctane (II) with the axial-symmetric $D_2$ form III. (In fact, XXIX may be looked upon as the $D_2$ form III with an atom inserted, on the axis, into each of the two end bonds.) The $D_2$ cyclodecane (XXIX) is estimated at over 16 kcal./mole for the best tetrahedral-angle form and is incapable of escaping serious nonbonded



CCC ($C_{2h}$)
XXI

CCB
XXII

BCB ($C_{2h}$)
XXIII

CBB
XXIV

CBC
XXV

XXVI

CC
XXVII

TCC
XXIX

BC
XXVIII

XXX

Consideration of the type B cyclodecanes (with symmetry plane bisecting two opposite bonds) yields the three forms CC (XXVII), BC (XXVIII), and BB, of which the last is not viable. All three forms have two of the energetically unfavorable eclipsed butane units as in chair and tub cyclooctane (VI and VIII) but with even somewhat worse H–H interpenetrations. The CC form is identical with the symmetrical CBC conformer considered

interactions so that a detailed computation was not carried out. Finally the BC form XXVII is similarly analogous to the BC form of cyclooctane in undergoing no pseudorotation but passing *via* the symmetrical mode into a form (XXX) with an axis perpendicular to the plane of symmetry which is analogous to V. The estimated torsional strain in XXX is nearly 20 kcal./mole, so that it cannot be a serious competitor as a favored form. The last viable form predicted by the notations of Chart I is XXVI, illustrated with $\omega_3 = 0$ but capable of easy conversion to + or − values of $\omega_3$ while retaining its axis of symmetry; it is clear that

(18) E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta.*, **43**, 760 (1960); **44**, 2027 (1961); **45**, 1036 (1962); J. D. Dunitz and K. Venkatesan, *ibid.*, **44**, 2033 (1961).

the forms with acceptable nonbonded interactions must have three bonds ($\omega_3$ and $\omega_8$) nearly eclipsed.

**Comparisons with Observed Results.**—Determinations by X-ray crystallography of the solid state structures of cycloalkyl ammonium halides have been carried out by Dunitz for the cyclononane[17] and cyclodecane[18] cases. In both the 1,6-*cis*- and 1,6-*trans*-diaminocyclodecane salts the form of the ring was found to be the same, namely, the BCB form of XXIII and Fig. 1. In Table IV the X-ray results, averaged to fit $C_{2h}$ symmetry, are presented in the format of the calculated results for comparison. It is quite clear that both are in close agreement as to the detailed geometry of the stable cyclodecane ring. Furthermore, some assurance that this BCB form represents a substantial energy minimum (like chair cyclohexane) derives both from the large $\Delta E$ separating it from the other cyclodecanes in the calculations and from the presence of the same conformation in both the *cis*- and *trans*-1,6-diamino derivatives. The calculations suggest it is 5.2 kcal./mole more stable than its nearest competitor (about the same as the energy preference for chair cyclohexane).

The major discrepancy between the calculated minimum-energy cyclodecane and the X-ray-derived form lies in the somewhat larger bond angles (116°) in the latter; when the form is calculated assuming this bond angle (and allowing $\omega$'s to vary to locate the energy minimum), it can be seen that the ring form and its energy are both virtually identical with the observed structure, the energies of which were calculated from the observed geometrical parameters for comparison. This discrepancy may well arise from the assumption[4] of the tetrahedral angle as the energy minimum for $E$ for a methylene group in the calculations. As this assumption is certainly correct only for carbon with four equal substituents, it is reasonable to suppose that the C–C–C angle at methylene prefers to be more open than 109.5° and, indeed, recent electron-diffraction studies[19] on *n*-alkanes afford an angle of about 112°. Making this assumption has the effect of shifting the parabolic $E_\theta = f(\theta)$ curve to higher values of $\theta$ by about 3° for the same energy and so its use in the energy-minimization process would yield virtually the same *geometry*[20] as that observed, at an energy of about 10 kcal./mole.

In the cyclononanes the case is not so clear. In the crystallographic determination[17] it was found that crystals of cyclononyl-ammonium bromide contained molecules in two different conformations, said to be asymmetrical but similar. In fact, these two observed conformations are each very close to the $C_2$ form XV. When the observed bond angles and four pairs of dihedrals are averaged, the two observed cyclonanes appear as in section 4, Table III. A ring of form XV with $C_2$ symmetry is defined by assumption of the bond angle $\theta$ and one dihedral angle; for comparison with the observed ring, true $C_2$ rings of the same $\theta$ and $\omega_5$ as the observed rings are presented in the middle three examples of section 3; furthermore, the minimum-energy ring of form XV and $\theta = 116.7°$ was also computed for comparison (last example in section 3). From these it will be seen that the observed rings are very close indeed, not only to conformations of true $C_2$ symmetry but also in fact to that $C_2$ conformation calculated to have minimum energy for the same assumed bond angle $\theta$.

On the other hand, the more symmetrical $D_3$ form was found (section 2) to be about 5 kcal./mole better than the conformer XV for the best cases (section 2, Table III). Accordingly, the general $C_2$ ring of form XIV was also calculated for $\theta = 116.7°$ (first example, section 3). It was found that the minimum-energy form, as before, had indeed the higher $D_3$ symmetry and that it was still the preferred form energetically, although by a very much smaller margin (1.1 kcal./mole). Such energy differences are small enough that it is not therefore clear that the $D_3$ form has a clear superiority. On the other hand, it is also not certain that the crystallographic conformer XV will be preferred in the parent case, and more seriously that it will retain its preference in solution, in the absence of crystal-packing forces.

No empirical evidence of comparable precision is available for cyclooctane, but such evidence as exists generally implies a skewed or extended crown form[21–23]; this evidence is compatible with form III but probably not with IV.

## Summary of the Calculations

Every conformation computed to be the most stable has an axis of symmetry, from cyclopentane to cyclodecane, although in the cyclopentanes and cyclooctanes the energy of the best axial-symmetric form is matched by one with a plane of symmetry; in cyclopentane the two forms simply pseudorotate at about equal energy.[4,24] Cyclooctane appears to have two symmetrical forms, III and IV, of about equal energy, between which a decision is not possible. Cyclononane shows a small computed preference for the 3-fold symmetry ($D_3$) of XIV, and cyclodecane a really clear preference for the BCB form XXIII. It may be noted that in all these preferred $C_6$, $C_9$, and $C_{10}$ rings, there are three axial hydrogens seriously interacting in a plane above, and three more in a parallel plane below, the molecular plane. Besides these six hydrogens, chair cyclohexane has six equatorial hydrogens as well, $D_3$ cyclononane has six equatorial and six isoclinal hydrogens, all relatively unhindered, and BCB-cyclodecane has two further pairs of axial hydrogens (on each side) of much less consequence (less than axial H in cyclohexane), and essentially uninvolved with the two trios of bad hydrogens, as well as the ten equatorial hydrogens.

The computed energies of the several molecules reveal some significant trends, the most salient being the importance of the torsional energy component. Not only is this source of strain a major part of the total energies in the preferred forms, it is also the one least subject to alteration within any one family of forms. Nonbonded repulsions of hydrogens *can* give rise to the largest strain components but small increases in bond angles, within a very low energy range for angle-bending strain, usually serve to wipe out the van der Waals component, at least in the favorable conformations. Hence each symmetrical family has a more or less characteristic torsional strain, not subject to much variation *via* bond-angle opening, which usually therefore determines which family will be the preferred one; the detailed form within that family which is most stable is then determined by angle variation largely to eliminate nonbonded repulsions.[25,26] In some very severe boat conformations the torsional strain may be mild, but the transannular hydrogen compressions are so severe that they remain a predominant source of strain, not alleviated adequately by angle opening; in such cases the simplification that torsional strain is determining breaks down and nonbonded interactions must be seriously considered. This effect is noticeable in the twist-boat cycloheptane[27] and especially in the BB form of cyclooctane[28] (VII), which yields adamantane ($\Sigma E_t = 0$) on replacing the two pairs of interpenetrating hydrogens by two methylene bridges.

(19) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491, 4765 (1959).

(20) Since it is clear that the minimization process arrives at almost the same values of $\omega$ and $r$ whether $\theta = 112.4°$ or 116.0°, the effect of shifting the $E_\theta$ curve up by 3° can only change the optimum $\theta$ parameter significantly.

(21) F. A. L. Anet and J. S. Hartman, *J. Am. Chem. Soc.*, **85**, 1204 (1963).

(22) N. L. Allinger, S. P. Jindal, and M. A. DeRoage, *J. Org. Chem.*, **27**, 4290 (1962), and previous papers cited therein.

(23) J. D. Dunitz and V. Prelog, *Angew. Chem.*, **72**, 896 (1960).

(24) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

(25) See, for example, the intrinsically better $E_t$ for the BCB-cyclodecane over its competitors whatever the bond angles or the fact that $E_t$ changes very little with general or variable bond angle changes in the extended crown cyclooctane (II) or $D_3$ cyclononane (XIV).

(26) Differential variation in bond angles ($\theta$) has surprisingly little effect and can apparently be ignored as a mode of little value for energy minimization. This seems to be true partly because variation in $\theta$ has a negligible effect on the torsional energy component and partly because uniform enlargement of all bond angles (as usually done in these calculation), by causing generalized ring flattening, thereby serves about equally well to destroy serious nonbonded hydrogen repulsions across the ring.

(27) *E.g.*, ref. 4, footnote 39.

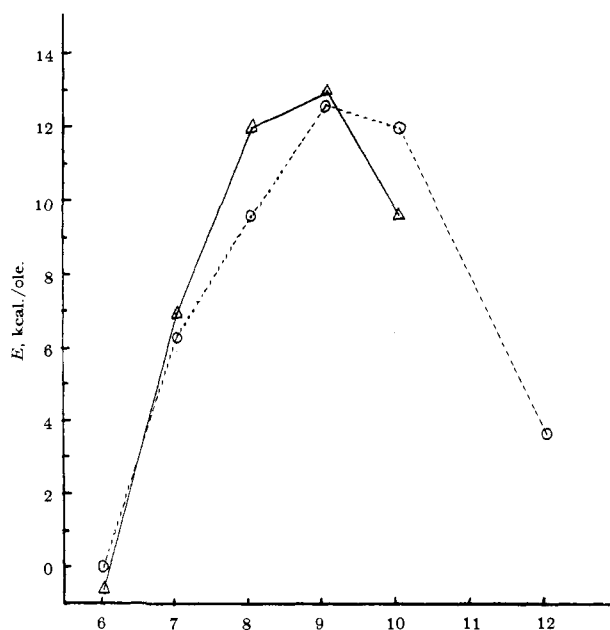(28) J. Dale, *J. Chem. Soc.*, 93 (1963).

Fig. 4.—Summary of medium-ring cycloalkane strain energies: O. . . ., observed data[22]; △———, calculated data; the values for cyclohexane and cycloheptane are taken from the data of ref. 4 with nonbonded interactions recalculated to include only "axial" H–H, $\leq 2.5$ Å., in order to conform to the procedure used in the present calculations.

The calculated strain energies for preferred conformers of the medium-ring cycloalkanes are shown in Fig. 4 compared to the experimental values[29] of $\Delta H$ compared to cyclohexane set at 0.0 kcal./mole. The agreement between the two sets is gratifying in view of the many uncertainties and simplifications implicit in the method and the parameters used.

**Chemistry and Conformational Analysis of the Cycloalkanes.**—Application of these computed conformations to chemical considerations is not difficult, following the analysis of Prelog[23] and the discussions and selected examples below. The stereoelectronic requirements of most reactions involving two adjacent carbons fall generally into two categories, with the involved substituents either at a dihedral angle of $0°$ or $180°$, the former exemplified by reactions involving five-membered ring intermediates or transition states, the latter by the widespread *trans*-antiparallel elimination.[30] Since the dihedral angle of two *cis* substituents is the same as the dihedral in the ring itself at that bond, and of two *trans* substituents is the ring $\omega \pm 120°$, the requirements for a reaction may easily be translated into the dihedral angles of the preferred rings in Tables I–IV. Similarly, fusion of small rings in bicyclic compounds will occur only at bonds in which *cis*- or *trans*-vicinal substituents can lie at $\omega \simeq 0°$. Finally, although the nonbonded interaction component of the strain energy in the preferred forms is usually small, release of this strain by removal of the offending hydrogens is energetically important since it allows the molecule to relax some angle-bending strain as well and seek a less constricted conformation which can therefore also be somewhat better in torsional energy. The latter consideration implies that change of an $sp^3$ to an $sp^2$ carbon will be preferred at a carbon bearing

one of the most severely axial hydrogens. These rules have been very effectively applied by Prelog[23] to explain the behavior of cyclodecane derivatives[31] in terms of removal of the compressed hydrogens on the central ($\omega_3$) bonds of the BCB form.[32] It may be noted that antiparallel eliminations occur at $\omega_3$ between *cis* substituents since it is these which, having the same dihedral angle as the ring has at that bond ($\sim 150°$), are nearly at the ideal $180°$; these eliminations yield the *trans*-olefin. Fusions of small rings or transition cycles at about $\omega = 0°$ will occur in cyclodecane preferentially across *trans* positions of the $\omega_3$ bond ($\omega = \omega_3 \pm 120° = 30°$); accordingly, the epoxide of the *trans*-olefin should appear at the $\omega_3$ bond and so be stereoelectronically well suited for migration of an axial hydrogen from the opposite $\omega_3$ bond (XXXI) and formation of the observed 1,6-*trans*-diol on formic acid solvolysis.[33] Similarly, one would predict the conformation XXXII for the diketone resulting from oxidation of a $\Delta^{5,10}$-olefin in the steroids since the ketone groups are to be found replacing bad axial hydrogens on the $\omega_3$ bond and the other substituents will all be equatorial.
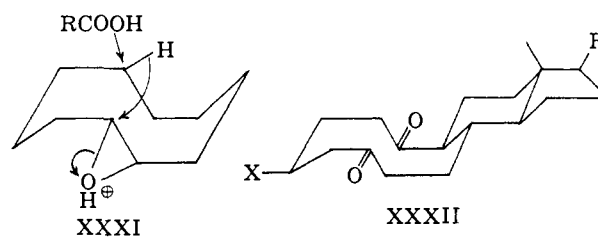


In the cyclononane derivatives, *trans* fusion of small rings (at $\omega_2 \simeq 130°$ in the $D_3$ form) should be preferred over *cis* and be as favorable as in cyclodecanes ($\omega_3 \simeq 150°$) or more; this appears to be borne out by rates of oxazoline formation from *cis*- and *trans*-2-thiobenzamidocycloalkanols[34] and the preferential formation of *trans*-olefin from amine oxide pyrolysis.[35] The solvolysis of cyclononene epoxide is reported[36] to afford the same mixture of *cis*- and *trans*-1,5-diols from both the *cis*- and *trans*-epoxides. This result suggests that the intermediate[23] 2-hydroxycyclononylcarbonium ion formed from each epoxide is identical, an inference which requires the hydroxyl group to occupy either of the two identical isoclinal positions of a $C_2$ form. Collapse of the carbonium ion by hydride transfer from either of the axial hydrogens on the bond bisected by the $C_2$ axis will then yield the same mixture of *cis*- and *trans*-1,5-diols as observed. The analysis parallels that for the cyclodecane examples[23] and is *uniquely* consistent for the $D_3$ form (*cf.* XXXIII, $R_1$ or $R_u =$

(31) Prelog has used in his discussions the perspective of the BCB-cyclodecane shown on the right side in Fig. 1; for many chemists, however, this has not the three-dimensional immediacy of the entirely equivalent picture at the left side. In both representations the relation to the conformations of diamond and chair cyclohexane may be seen by replacing the four axial hydrogens on the $\omega_3$ bonds with two methylene bridges.

(32) The estimate[23] that removal of one of these releases one-third of the total strain, or about 4 kcal./mole, is probably unrealistic since neither the torsional strain nor the angle-bending strain is likely to be reduced by as much as one-third in such a change.

(33) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

(34) J. Sicher, J. Jonas, M. Svoboda, and O. Knessl, *Collection Czech. Chem. Commun.*, **23**, 2141 (1958).

(35) A. C. Cope, D. C. McLean, and N. A. Nelson, *J. Am. Chem. Soc.*, **77**, 1628 (1955); A. C. Cope, M. Brown, and H. H. Lee, *ibid.*, **80**, 2855 (1958); M. Svoboda and J. Sicher, *Collection Czech. Chem. Commun.*, **23**, 1540 (1958); *Chem. Ind.* (London), 290 (1959).

(36) V. Prelog, K. Schenker, and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).

(29) J. Coops, H. von Kamp, W. A. Lambregets, J. Visser, and H. Dekker, *Rec. trav. chim.*, **79**, 1226 (1960).

(30) J. Sicher, "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworths, London, 1962, p. 202.

Ac), but it requires both *cis-* and *trans-*epoxides to be fused across the $\omega_1$ bond, although the $\omega_2$ bond should be preferred for the *trans-*epoxide.



**XXXIII**    **XXXIV**
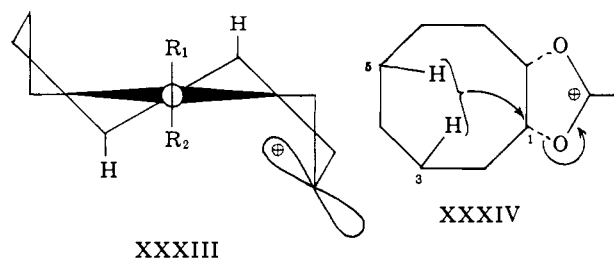
In contrast to these results with the 9- and 10-rings, reactions of cyclooctane derivatives are characterized by more diversity of products, as would be expected from a mixture of preferred conformers. Thus the products obtained by treating cyclooctene dibromide with silver acetate in glacial acetic acid[37] are all rationalized by collapse of the intermediate ion XXXIV *via* 1,3- or 1,5-hydride shifts; the $D_2$ form III is stereoelectronically well disposed for the former (XXXV), while the BC form IV is appropriate for the latter (XXXVI). Solvolysis of the epoxides implies another, similar dichotomy, for the *cis-*epoxide should take up



**XXXV**    **XXXVI**
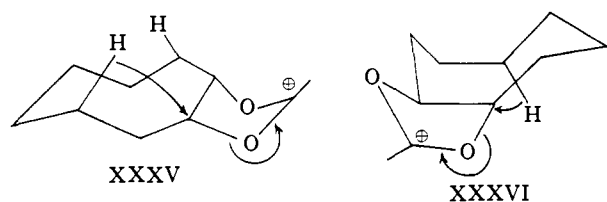
conformation IV with the most favorable dihedral for *cis* fusion ($\omega_2 = 43°$) while the *trans-*epoxide is perfectly fitted for conformer III ($\omega_3 \simeq 120°$). Stereoelectronic analysis of the intermediate 2-hydroxycyclooctylcarbonium ions, as above, implies that the *cis-*epoxide will then yield the *cis-*1,4-diol and the *trans-*epoxide the *trans-*1,4-diol, as observed.[38] Hence the several experimental results may be said to be consistent with the predictions of the calculations of cycloalkanes presented here.

**Acknowledgment.**—The author wishes to acknowledge helpful discussions of symmetry properties with Prof. T. N. Margulis of this department and financial support from the National Institutes of Health. The author also expresses gratitude to the Brandeis Computer Center for use of the IBM 1620 computer.

## Appendix

**Calculation of Geometry of the Various Conformations.**—Let all bond angles $= \theta$, all C–C bond lengths $= 1$ and, for identification, letter the atoms in the forms sequentially clockwise (A, B, C, etc.) in such a way that the AB bond has dihedral angle $\omega_1$, BC bond has $\omega_2$, etc., as in the cycloheptane chair shown below. The functions $f_{14}$, $f_{15}$, and $f_{16}$ refer to the relation of the distance $S$ between two points (1–4, 1–5, and 1–6 atoms apart, respectively) and the intervening bond angles, $\theta$, and dihedral angles, $\omega$.[8] These equations allow simple solution of unknown dihedral angles; $f_{15}$ and $f_{16}$ each have two solutions for an unknown $\omega$.

(37) A. C. Cope and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 3885 (1957).

(38) A. C. Cope, S. W. Fenton, and C. F. Spencer, *ibid.*, **74**, 5884 (1952); A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, and G. W. Wood, *ibid.*, **79**, 3900 (1957); A. C. Cope, A. Fournier, and H. E. Simmons, *ibid.*, **79**, 3905 (1957).
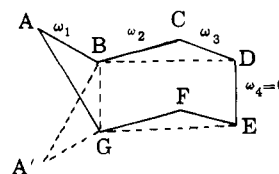
1. Cycloheptane chair and boat:

$$S_{BF}^2 = 1 + 2 \sin \tfrac{1}{2}\theta(1 - 2 \cos \theta) = f_{14}(\theta, \omega_1)$$

$$S_{BE}^2 = 2(1 - \cos \theta) + 2 \sin \tfrac{1}{2}\theta = f_{14}(\theta, \omega_3) = f_{15}(\theta, \omega_1, \omega_2)$$

These equations lead to

$$\cos \omega_1 = \frac{(1 - \cos \theta)^2 - \sin \tfrac{1}{2}\theta(1 - 2 \cos \theta)}{\sin^2 \theta}$$

$$\cos \omega_3 = \frac{1 - 2 \sin \tfrac{1}{2}\theta - 2 \cos \theta(1 - \cos \theta)}{2 \sin^2 \theta}$$

and solution of $f_{15}$ for $\omega_2$ leads to the two angles corresponding to $\omega_2$ for the chair and the boat, respectively.

2. Crown cycloalkanes (even-membered, $n$ atoms)

$$\cos \omega = (1 - \cos \theta - 2 \sin \tfrac{1}{2}\psi)/(1 + \cos \theta)$$

where $\psi = (180/n)(n - 4)$

3. Cyclooctanes II, IV, V, and VII all have four alternate (B, D, F, H) atoms lying in a square plane of side $2 \sin \tfrac{1}{2}\theta$. In II and IV, assumption of $\theta$ does not yield a unique solution; if $\omega_1$ is given, then $S_{BF}^2 = 8 \sin^2 \tfrac{1}{2}\theta = f_{15}(\theta, \omega_1, \omega_2)$ and the two solutions for $\omega_2$ yield both $\omega_2$ and $\omega_3$ of the BC form IV; $\omega_2$ for II is the same as for IV. In V and VII, however, the dihedral angles are fixed by $\theta$ and the symmetry

Form V:

$$\cos \omega_1 = \frac{\cos \theta(\cos \theta - 1) - \sin \theta}{\sin^2 \theta}$$

$$\cos \omega_2 = \frac{\sqrt{1 + \sin \theta}}{\sin \theta \sin \tfrac{1}{2}\theta} - 1$$

Form VII:

$$\cos \omega = \frac{\sqrt{2}}{\sin \theta} - 1$$

4. The cyclooctanes VI and VIII have the same $\omega_2$ for a given $\theta$; both forms are fully determined by symmetry and $\theta$

$$\cos \omega_2 = \cos^2 \theta/\sin^2 \theta$$

$$\cos \omega_3 = (3 \cos^2 \theta - 1)/\sin^2 \theta$$

5. The $C_s$ cyclononanes (CC, BC, CB, BB) are analogous to the $C_s$ cycloheptanes above except that the greater conformational freedom allows a single defined form only when $\theta$ and one dihedral angle, $\omega$, as well, are specified; if $\omega_1$ is given

$$S_{CH} = \frac{(1 - \cos \theta)^2 - 2 \sin^2 \theta \cos \omega_1}{\sin \tfrac{1}{2}\theta}$$

$$\cos \omega_4 = \frac{2 \cos \theta(\cos \theta - 1) + 1 - S_{CH}}{2 \sin^2 \theta}$$

$$S_{BG}^2 = 2 \sin \tfrac{1}{2}\theta(1 - 2 \cos \theta + 2 \sin \tfrac{1}{2}\theta) = f_{15}(\theta, \omega_1, \omega_2) = f_{16}(\theta, \omega_3, \omega_4, \omega_5 = 0)$$

and solution of $f_{15}$ for $\omega_2$ leads to two angles corresponding to chair and boat orientations in the left ($\omega_1$) end of the molecule (*cf.* CC (X) and BC (XVI)), while solution of $f_{16}$ leads to two values for $\omega_3$, representing chair and boat orientations at the other end (*e.g.*, the CB- and BB-cyclononanes).

6. The $C_{3v}$ cyclononane XVII is uniquely defined for any given $\theta$

$$\cos \omega_1 = \frac{-1 - 2 \cos \theta \sin \frac{1}{2}\theta}{2 \sin \frac{1}{2}\theta (1 + \cos \theta)}$$

7. The $C_s$ cyclodecanes CCC (XXI), CCB (XXII), and BCB (XXIII) are analogous to the cyclooctanes (II, IV, VII) above and a unique solution requires assignment of one dihedral angle as well as $\theta$; if $\omega_1$ is given

$$\cos \omega_3 = \frac{1}{2} \left( \frac{\cos^2 \theta - \sin^2 \theta \cos \omega_1 - \cos \theta}{\sin \theta \sin \frac{1}{2}\theta} \right)^2 - 1$$

$$S_{DJ}^2 = 2(\cos^2 \theta - \sin^2 \theta \cos \omega_1 - 3 \cos \theta + 2) = f_{15}(\theta, \omega_1, \omega_2)$$

and solution of $f_{15}$ for $\omega_2$ leads to two angles corresponding to $\omega_2$ for boat and chair subunits at the ends of the molecule.

8. The $C_s$ cyclodecanes CBC, BBC, and BBB are similarly defined by assumption of $\omega_1$ and $\theta(\omega_3 = 0)$

$$S_{DJ}^2 = 2(1 - \cos \theta)(\cos \theta + \cos \theta \cos \omega_1 + \cos \omega_1) = f_{15}(\theta, \omega_1, \omega_2)$$

and solution of $f_{15}$ for $\omega_2$ leads to two angles as in 7, above.

9. Common procedure with the more difficult rings containing only axes of symmetry has been to utilize an iterative approach to discover the true ring as may be seen in the $C_2$ cyclononanes which are defined by assumption of $\theta$ and one $\omega$(here $= \omega_5$)
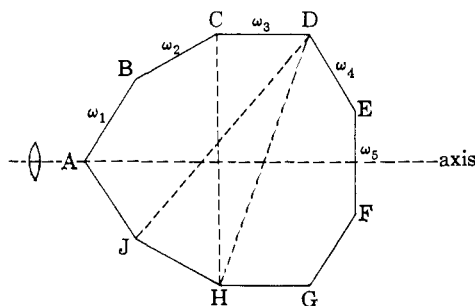


(a)  assume a value for $\omega_4$

(b)  $S_{CH} = f_{16}(\theta, \omega_4, \omega_5, \omega_4) = f_{15}(\omega_1, \omega_1)$; yields $\omega_1$

(c)  $S_{DH} = f_{15}(\theta, \omega_5, \omega_4) = f_{16}(\omega_1, \omega_1, \omega_2)$; yields $\omega_2$

(d)  $S_{DJ} = f_{15}(\theta, \omega_1, \omega_2) = f_{16}(\omega_5, \omega_4, \omega_3)$; yields $\omega_3$

(e)  $S_{HH} = f_{1-10}(\theta, \omega_1, \omega_1, \omega_2, \omega_3, \omega_4, \omega_5, \omega_4)$

(f)  vary $\omega_4$ and repeat until $S_{HH} = 0$, a condition of a closed ring.

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# Strained Ring Systems. I. Peroxidation Studies with Certain Acetylenes. The Relevance of Oxirene Intermediates

By Richard N. McDonald and Peter A. Schwab[1]

Organic peracid oxidations of phenyl- and diphenylacetylene have led to the formation of three different types of products. Each is explicable in terms of an oxirene intermediate reacting to give products (1) of further oxidation, (2) of rearrangement, and (3) of addition, depending on the reaction conditions. Trifluoroperacetic acid treatment of diphenylacetylene gave benzil and benzoic acid. Phenylacetylene when allowed to react with trifluoroperacetic acid gave phenylacetic and benzoic acids, while with perbenzoic acid methyl and ethyl phenylacetates, methyl benzoate, benzaldehyde, and benzoic acid were produced. Peracetic acid reacted with phenylacetylene to give benzyl acetate, acetylmandelic acid, phenylacetic acid, and benzoic acid. The modes of formation of these products are discussed as is the nature of the proposed oxirene intermediates. Treatment of desyl chloride with tritylsodium gave benzilic and benzoic acids. Desyl chloride also reacted with potassium t-butoxide in dimethyl sulfoxide to give a mixture of cis- and trans-dibenzoylstilbenes.

The synthesis and chemistry of small-ring compounds has been and continues to be of interest to chemists. The simplest oxygen-containing heterocycle, oxirene (I), has not yet been fully described or characterized. It may bear some interesting relationships with two hydrocarbon small-ring compounds.
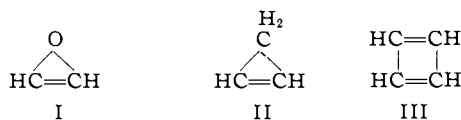
Its hydrocarbon analog, cyclopropene (II), has been reported as having various substituted derivatives, and a considerable amount is known concerning its physical and chemical behavior. Oxirene (I) may also be considered to be iso-$\pi$-electronic with cyclobutadiene (III) just as furan is to benzene. Simple molecular orbital calculations[2] predict zero delocalization energy and a singlet ground state for I, as opposed to the zero delocalization energy and triplet ground state predicted for III.[3]

An estimate of the strain energy of I is also available from its hydrocarbon counterparts. The strain energy (s.e.) of ethylene oxide, taken as the difference between the calculated and experimental heats of formation, has been found to be 13 kcal./mole.[4] Assuming the same differential in strain energy holds between cyclopropane and cyclopropene ($\Delta$s.e. $\approx$ 27 kcal./mole)[5] as in ethylene oxide and oxirene (I), we see the total s.e. of I to be $\sim$40 kcal./mole. In addition, since the s.e. of cyclopropane is $\sim$12 kcal./mole more than for ethylene oxide,[4] we might expect I to be more stable than II and isolable, at least on the basis of this one criterion.

(1) This paper comprises a portion of the dissertation submitted by P. A. Schwab to the Graduate School of Kansas State University in December, 1963, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) We wish to thank Dr. D. E. Applequist, personal communication to R. N. McDonald, 1959, for the results of these calculations.

(3) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, J. Am. Chem. Soc., 74, 4579 (1952).



|  I  |  II  |  III  |

(4) R. A. Nelson and R. S. Jessup, J. Res. Natl. Bur. Std,. 48, 206 (1952); Chem. Abstr., 46, 8505i (1952).

(5) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, J. Am. Chem. Soc., 84, 3980 (1962).