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CONFORMATIONAL ANALYSIS OF ALICYCLIC COMPOUNDS—I

CONSIDERATIONS OF MOLECULAR GEOMETRY AND ENERGY IN MEDIUM AND LARGE RINGS

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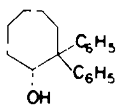
Abstract—The geometry of certain conformations of medium ring cyclo-alkanes and cyclo-alkenes is evaluated by vector methods. Using a potential function for the non-bonded H . . H interactions, the energies of the relevant conformations are compared. The effect of deformations is discussed.

In the recent decade much progress has been made in understanding the stereochemistry of alicyclic systems containing six-membered rings, the impetus having been afforded in many cases by studies of natural products.[1]

The application of this rapidly growing body of knowledge to larger rings has been sporadic. Even the investigators who have contributed most to the field of medium-ring compounds have been wary in extending, by analogy, considerations obtaining in the cyclohexane ring to, e.g. cyclo-octane, cyclononane or cyclodecane compounds.[2] Whilst certain fixed conformations may be used to explain various reactions of the systems involved, it is clear from recent work that the conformational problems in larger rings are more complex than immediately apparent, although superficially it often appears that direct analogies may be made.

For example, the dehydration, accompanied by ring contraction of 2,2-diphenylcycloheptanol (I) to afford benzhydrylidenecyclohexane (II),[3] can be explained



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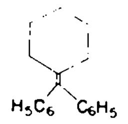

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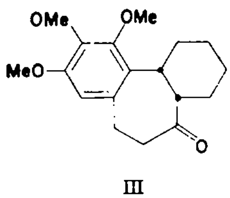

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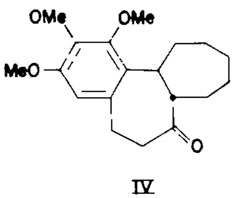

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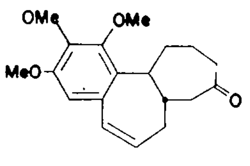

V

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[1] D. H. R. Barton, *J. Chem. Soc.* 1027 (1953); W. Klyne, *Progress in Stereochemistry* Vol. 1 pp. 36–89. Butterworths, London (1954); W. G. Dauben and K. S. Pitzer, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) pp. 1–60. John Wiley, New York (1956).

[2] V. Prelog, in Todd, *Perspectives in Organic Chemistry* pp. 96–133. Interscience, New York (1956); V. Prelog, *Paris Congress lecture, in Experientia Supplementum* VII pp. 261–274. Birkhäuser Verlag, Basel (1957)

[3] R. E. Lyle and R. A. Covey, *J. Amer. Chem. Soc.* 75, 4973 (1953); C. D. Gutsche, N. N. Saha and H. F Johnson, *Ibid.* 79, 4441 (1957).

completely in analogy to the argument used for the dehydration of 3β-hydroxytriterpenes which give the isopropylidenecyclopentane a ring in the corresponding products. Yet, there are differences in behaviour as compared to cyclohexanes, stemming from additional considerations unique to the cycloheptane ring. For example,[4] the highly stereospecific metal hydride reductions of the cycloheptanones III, IV and V in all cases giving the "axial" alcohol, as well as other stereospecific reactions in similar compounds can best be explained by assuming that the cycloheptane and cycloheptene rings in these compounds possess a rigid chair conformation.

As one step in our own studies on conformations of medium and large rings, we present a simple method of calculating the geometry of various conformations and using this method we discuss some of the plausible conformations.

Geometry of the molecules

The most striking stereochemical relations for a given conformation may easily be visualized by employing simple mechanical models.[5] However, in many cases more accurate interatomic distances are needed. This requires evaluation of the molecular geometry. Corey and Sneen[6] have proposed a method for treating this problem using simple trigonometric and vector relations. This method is reconsidered only for certain conformations of cyclo-alkanes and cyclo-alkenes which possess some symmetry since it is simpler at the outset to consider symmetrical models.

The method of calculation

Cyclo-alkanes. In the first step we assume:

(i) a constant C–C bond length, $c = 1{\cdot}542$ A°
(ii) a constant C–H bond length, $d = 1{\cdot}093$ A°
(iii) tetrahedral valency angles, $\gamma = 109^\circ\ 28'$

Subsequently we consider the possibility and effect of small deformations.

Notation. We number the carbon atoms of the molecule from 1 to n and denote the vector connecting the ith C atom with the $(i + 1)$-st by $\mathbf{C}_{i,i+1}$. All these vectors have the same magnitude (c) and their vector sum is zero, as we are dealing with a closed polygon

$$\sum_{i=1}^{n} \mathbf{C}_{i,i+1} = 0 \tag{1}$$

the co-ordinates of the $(n + 1)$-st C atom being indentical with those of the first.

Denote the vectors pointing from the ith C atom towards the corresponding H atoms by $\mathbf{r}_i$ and $\mathbf{s}_i$, using the convention that $\mathbf{r}_i$ is above and $\mathbf{s}_i$ is below the plane determined by $\mathbf{C}_{i-1,i}$ and $\mathbf{C}_{i,i+1}$. Their magnitude is d.

On the basis of assumptions *i–iii* we have the following relations:

$$(\mathbf{C}_{i,i-1}\mathbf{C}_{i,i+1}) = c^2 \cos \gamma \tag{2}$$

$$(\mathbf{r}_i\mathbf{s}_i) = d^2 \cos \gamma \tag{3}$$

$$(\mathbf{C}_{i,i+1}\mathbf{r}_i) = (\mathbf{C}_{i,i+1}\mathbf{s}_i) = (\mathbf{C}_{i,i-1}\mathbf{r}_i) = (\mathbf{C}_{i,i-1}\mathbf{s}_i) = cd \cos \gamma \tag{4}$$

where (. . . . .) denotes the scalar product of the vectors.

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[4] H. J. E. Loewenthal, private communication.

[5] Ingeniously constructed models due to A. Dreiding are now available commercially from W. Büchi, Flawil, Switzerland.

[6] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* 77, 2505 (1955).

Evaluation of the molecular geometry may be divided into two steps:
(1) Determination of the C–C skeleton, i.e. the vectors $\mathbf{C}_{i,i+1}; i = 1 \ldots n$ which satisfy relations (1) and (2).
(2) Calculation of the vectors $\mathbf{r}_i$ and $\mathbf{s}_i$, satisfying relations (3) and (4). The latter determine the positions and the distances between the hydrogen atoms. Assuming that the actual conformation is governed by the H . . . H non-bonded interactions and using a semi-empirical potential function for these interactions, we can use the molecular geometry to evaluate the energy of the non-bonded interaction. This affords information with regard to the stability of various conformations.

First we show that step (2) may be simply solved if step (1) is given. We introduce two subsidiary unit vectors $\mathbf{h}_i$ and $\mathbf{n}_i$, defined as follows:

$$\mathbf{h}_i = \frac{1}{2c \cos \gamma/2} (\mathbf{C}_{i-1,i} - \mathbf{C}_{i,i+1}) \tag{5}$$

$$\mathbf{n}_i = \frac{1}{c^2 \sin \gamma} [\mathbf{C}_{i-1,i}\mathbf{C}_{i,i+1}] \tag{6}$$

[. . . . .] denotes vector product. $\mathbf{n}_i$ is orthogonal to the plane of $\mathbf{C}_{i-1,i}$ and $\mathbf{C}_{i,i+1}$ (cf. the definition of the vector product) so it is also orthogonal to $\mathbf{h}_i$. Now, it is easily verified that if $\mathbf{r}_i$ and $\mathbf{s}_i$ are given by (7) and (8)

$$\mathbf{r}_i = d(\mathbf{h}_i \cos \gamma/2 + \mathbf{n}_i \sin \gamma/2) \tag{7}$$

$$\mathbf{s}_i = d(\mathbf{h}_i \cos \gamma/2 - \mathbf{n}_i \sin \gamma/2) \tag{8}$$

then all of the five relations given in (3) and (4) are identically satisfied. Thus having found the vectors corresponding to the C–C skeleton of the molecule, the molecular geometry (including all H . . . H distances) is completely solved.

For the solution of step (1) we can use the $n + 3$ relations (n scalar and one vector equation) given in (1) and (2). We have n unknown vectors of constant length (c), that is $2n$ unknowns. Hence conditions (1) and (2) alone are insufficient for determination of the conformation and we can obtain an unrestricted number of solutions. We may obtain a definite solution only if we introduce additional restrictions, e.g. caused by the presence of a certain symmetry. We shall confine ourselves to the latter case.

We can approach construction of the conformation by utilizing "building units" such as a triangle, one of whose angles is tetrahedral and a trapezoid with two tetrahedral angles. These units are suitably combined in accordance with the presumed properties of the conformation being considered. (See, for example, heavy bonds in cycloheptane chair conformation, Fig. 1.)

To illustrate the method which applies also to larger rings (step 1) we treat two specific cases in detail.

Cycloheptane chair

We assume a plane of symmetry which contains carbon atom 1 and the mid-point between carbon atoms 4 and 5 (Fig. 1). We label this as the yz plane. Let carbon atoms 2, 3, 6, 7 be in the xy plane. The distances 2–7 and 3–6 are given by the relations:

$$\overline{2\text{–}7} = 2c \sin \gamma/2 \qquad \overline{3\text{–}6} = c(1 + 2 \sin (\gamma - \pi/2)) = \overline{2\text{–}7} + 2c \sin \delta \tag{9}$$

These ensure the validity of (2) for $i = 1, 4$ and 5. The plane of atoms 1, 2, 7 forms an angle ϕ with the xy plane. This can be determined on the basis of the condition $(C_{2,1}C_{2,3}) = c^2 \cos \gamma = (C_{7,1}C_{7,6})$

$$\operatorname{Cos} \phi = -\frac{\cos \gamma + \sin \delta \sin \gamma/2}{\cos \delta \cos \gamma/2} \tag{10}$$

Analogously, the angle ψ between the plane of atoms 3, 4, 5, 6 and the xy plane is given on the basis of the condition

$$(C_{3,2}C_{3,4}) = c^2 \cos \gamma = (C_{6,5}C_{6,7})$$

$$\cos \psi = -\frac{\cos \gamma\,(1 + \sin \delta)}{\sin \gamma \cos \delta} \tag{11}$$

Having determined ϕ and ψ we have completely fixed the C–C skeleton. From the method of construction of the $C_{i,i+1} - s$ it is obvious that they also fulfil relation (1).

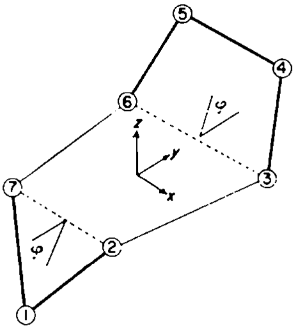

Fig. 1

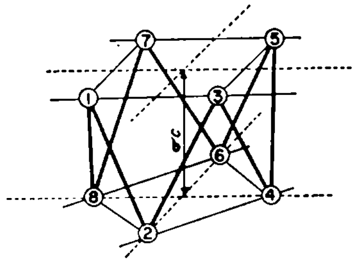

Fig. 2

From the above, the geometry of the boat conformation may be obtained simply by changing the sign of ϕ.

$C_{2n}H_{4n}$ *with* n*-fold rotation symmetry*

We assume the molecule possesses an n-fold rotation axis (conveniently taken as the axis z), i.e. performing rotation through an angle $(2\pi/n)$ about the z axis causes no change in the conformation. Examples are the cyclohexane chair conformation, cyclo-octane crown, cyclodecane crown, etc. Molecular symmetry permits determination of all interatomic distances very simply.

We place the atoms $C_1, C_3, \ldots, C_{2n-1}$ on the n vertices of an equilateral polygon whose centre is on the z axis and its plane parallel to the xy plane. The atoms C_2, $C_4, \ldots \ldots C_{2n}$ are situated on the n vertices of another equilateral polygon with the same centre, its plane parallel to the xy plane, it being rotated through $\frac{1}{2}(2\pi/n) = \alpha$ with respect to the former polygon. (Cf. Fig. 2 for the cyclo-octane crown, $n = 4$; $\alpha = 45°$.)

The distance between the two planes (bc) and the radius of the polygons (rc) are determined on the basis of the condition

$$(C_{i,i+1}C_{i,i-1}) = c^2 \cos \gamma \tag{12}$$

The co-ordinates of the carbon atoms are given by

$$C_{2i} = c\begin{cases} r\sin(2i)\alpha \\ r\cos(2i)\alpha \\ b \end{cases} \qquad C_{2i+1} = c\begin{cases} r\sin(2i+1)\alpha \\ r\cos(2i+1)\alpha \\ 0 \end{cases} \tag{14}$$

The vectors connecting the carbon atoms are as follows:

$$C_{2i-1,2i} = c\begin{cases} r_1\cos(2i-1/2)\alpha \\ r_1\sin(2i-1/2)\alpha \\ b \end{cases} \qquad C_{2i,2i+1} = c\begin{cases} r_1\cos(2i+1/2)\alpha \\ r_1\sin(2i+1/2)\alpha \\ -b \end{cases} \tag{15}$$

$$r_1 = 2r\sin\alpha/2 \tag{16}$$

On the basis of (12) b and r_1 are given as follows:

$$r_1^2 = \frac{1-\cos\gamma}{1+\cos\alpha} \tag{17}$$

$$b^2 = \frac{\cos\alpha + \cos\gamma}{1+\cos\alpha} \tag{18}$$

Having completely determined the C–C skeleton, we immediately obtain the vectors $\mathbf{r}_i$ and $\mathbf{s}_i$ and thence the positions and distances of the hydrogen atoms. The co-ordinates of the hydrogen atoms are given in Table 1, from which all H–H distances may be obtained.

TABLE 1

	H_{2i} axial	H_{2i} equatorial	H_{2i+1} equatorial	H_{2i+1} axial
x	$(e-f)\sin 2i\alpha$	$(e+f)\sin 2i\alpha$	$(e+f)\sin(2i+1)\alpha$	$(e-f)\sin(2i+1)\alpha$
y	$(e-f)\cos 2i\alpha$	$(e+f)\cos 2i\alpha$	$(e+f)\cos(2i+1)\alpha$	$(e-f)\cos(2i+1)\alpha$
z	$-g-h$	$-g+h$	$g-h$	$g+h$

where, $e = r + \frac{d}{c} r_1 \sin\alpha/2 \qquad g = 3/2\, b + b\frac{d}{c}$

$$f = \frac{dr_1 b}{C^2}\,\frac{\cos\alpha/2}{\cos\gamma/2} \qquad h = \frac{1}{2}\,\frac{dr_1^2\sin\alpha}{\cos\gamma/2} \tag{19}$$

Cyclo alkenes. The above treatment can be extended to cyclo-alkenes. The only difference is concerned with the bonds adjacent to the double bond. We must take into account:

(a) the length of the C=C bond, $c = 1{\cdot}334$ A°: the length of the C—H bond attached to the double bond $d = 1{\cdot}079$ A°.

(b) the valence angle 120°

(c) that the five vectors $\mathbf{C}_{i-1,i}$, $\mathbf{C}_{i,i+1}$, $\mathbf{C}_{i+1,i+2}$, $\mathbf{d}_i$ and $\mathbf{d}_{i+1}$ are in the same plane.

Having determined the C–C skeleton, the vectors pointing to the hydrogens adjacent to the double bond are given as follows:

$$\mathbf{d}_i = \frac{d'}{c}\,\mathbf{C}_{i-1,i} - \frac{d'}{c'}\,\mathbf{C}_{i,i+1} \qquad \mathbf{d}_{i+1} = \frac{d'}{c'}\,\mathbf{C}_{i+1} - \frac{d'}{c}\,\mathbf{C}_{i+1,i+2} \tag{20}$$

where c = C–C single bond distance; c' = C=C double bond distance; d' = C–H bond distance for bond adjacent to double bond.

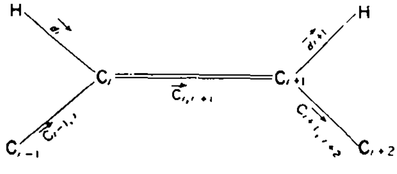

FIG. 3

Energetic relations

To compare the stability of different conformations of a given molecule we must relate their energies to their geometries.

There is a number of potential functions which have been put forward in order to represent the H . . . H non-bonded interaction.

Eyring[7] using the perfect pairing approximation, obtains the interaction energy of two non-bonded hydrogen atoms as follows:

$$E_{\mathrm{H,H}} = Q_{\mathrm{H,H}} - 1/2J_{\mathrm{H,H}}$$

where Q and J are the coulomb and exchange integrals. This corresponds[8] to the interaction of two H atoms with random spin orientation, which in turn can be expressed as:

$$1/4f(^1\Sigma) + 3/4f(^3\Sigma)$$

where $f(^1\Sigma)$ and $f(^3\Sigma)$ are the interaction energies of two hydrogen atoms in the bonding singlet and in the repulsive triplet states, respectively.

This function has the disadvantage that it predicts only 0·4 kcal/mole for the potential barrier in ethane (experimental value about 3 kcal/mole). Barton[9] used a van der Waals interaction type function which also yielded too small values for the potential barrier in ethane. The function he employed contains the van der Waals radius of H which is not defined exactly. Mason and Kreevoy[10] suggested that the appropriate potential function could be represented by the function $Kf(^3\Sigma)$ where K is a numerical constant. The Eyring potential corresponds to a value $\frac{1}{3}$–$\frac{1}{2}$. Pritchard and Sumner[11] used the value $K = 0{\cdot}5$. Mason and Kreevoy suggested $K = 1$ and using this value obtained a better agreement with the experiment for the potential barrier in ethane. This value was used by Howlett[12] who corrected for the angular dependence.

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[7] H. Eyring, *J. Amer. Chem. Soc.* **54**, 3191 (1932).

[8] C. A. Coulson, *Valence* pp. 167–168. Clarendon Press, Oxford (1952).

[9] D. H. R. Barton, *J. Chem. Soc.* 340 (1948).

[10] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.* **77**, 5808 (1955).

[11] H. O. Pritchard and F. H. Sumner, *J. Chem. Soc.* 1041 (1955).

[12] K. E. Howlett, *J. Chem. Soc.* 4353 (1957).

We wish to compare the stabilities of some conformations. In view of the large uncertainty in the choice of the correct potential function we cannot hope to obtain correct figures for the interaction energies. We adopt the following potential function $0{\cdot}5\,f({}^3\Sigma)$, i.e. that used by Pritchard and Sumner. $f({}^3\Sigma)$ is given by the approximation formula of Buckingham[13] which agrees reasonably well with the values obtained from theoretical calculations.[14]

$$f(R) = \frac{627{\cdot}211}{R}\,\{1 + 1{\cdot}167R + 0{\cdot}039R^2 + 0{\cdot}518R^3 + 0{\cdot}864R^4\}\ \exp.\,(-2{\cdot}3R) \qquad (21)$$

R in atomic units (the unit of length $a_0 = 0{\cdot}5292$ A°), $f(R)$ in kcal/mole.

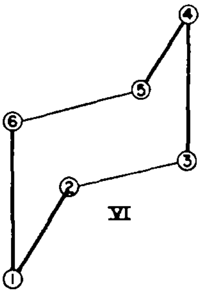
We have determined the geometry of some conformations. Summing over all of the H . . . H interactions, we obtain the results summarized in Table 2.

TABLE 2. ENERGY GIVEN IN kcal/mole

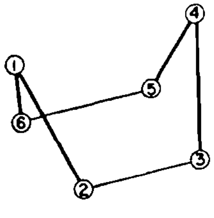
Energy		Energy		Energy		Eneigy		Energy	
VI	15·70	X	66·34	XIV	191·52	XVIII	48·52	XXII	18·60
VII	20·13	XI	107·19	XV	56·56	XIX	48·84	XXIII	31·51
VIII	42·03	XII	38·26	XVI	16·10	XX	61·10		
IX	44·78	XIII	67·30	XVII	15·97	XXI	18·10		

Discussion of results

Cyclohexane (VI, VII). We obtain a difference of 4·43 kcal/mole between the energies of the two conformations (Table 2), the chair (VI) being the more stable. This conclusion is in accord with the experimental findings and yields the same order of magnitude as alternative methods for estimating the energy difference.[15]



VI



VII

Cycloheptane (VIII, IX). Once again the chair conformation (VIII) is the more stable by 2·75 kcal/mole. We must note, however, that the 3–6 interaction is extremely high, due to the fact that the 3a–6a distance is only 1·288 A°, corresponding

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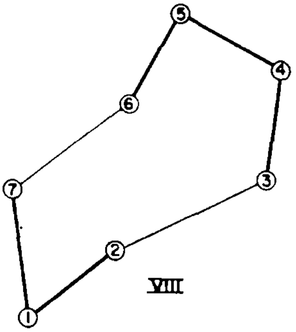
[13] R. A. Buckingham, *Trans. Faraday Soc.* **54**, 453 (1958).

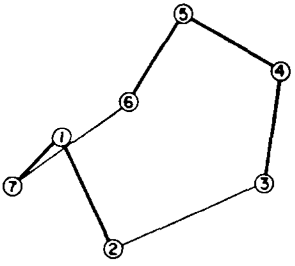
[14] J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.* **18**, 130 (1950); H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.* **4**, 187 (1936).

[15] C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Amer. Chem. Soc.* **69**, 2488 (1947).

to a repulsion energy of 20·01 kcal/mole. It is very improbable that this distance remains unaltered in the real molecule. There must be deformations from the "ideal" structure causing deviations from the strictly tetrahedral bond angles (see below).

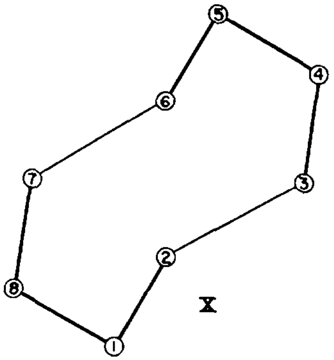


VIII

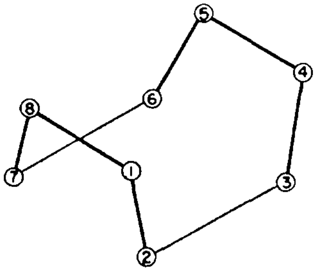


IX

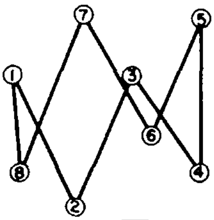
Cyclo-octane (X–XIV). The most stable conformation among the "ideal" structures is the crown form XII (Table 4). However, this conclusion depends largely upon the fact that high repulsions occur in the chair (X) and in the boat (XI) forms (the 2a–7a and 3a–6a H–H distances in X and the 2a–7a, 3a–6a, 1a–4a and 5a–8a H–H distances in XI are all 1·265 A°. This value corresponds to an energy value of 21·11 kcal/mole. Even higher repulsions occur in conformations XIII and XIV. As we have noted above, such small distances are extremely unlikely to obtain in the real molecule and we must consider possible deformations.



X

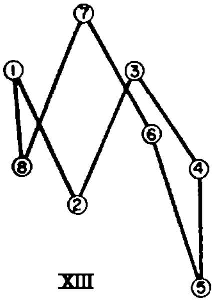


XI

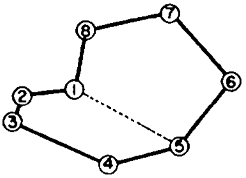


XII

Cyclodecane (XV). In view of the extremely high number of possible conformations it seemed pointless to extend the calculations beyond cyclo-octane. However, the cyclodecane crown form XV is given because its comparison with the cyclo-octane

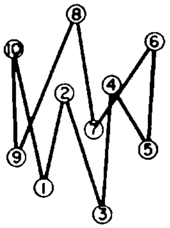


XIII



XIV

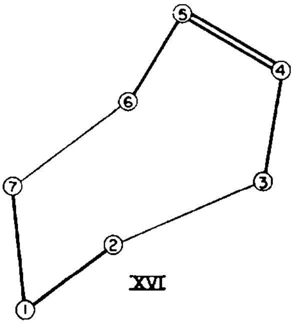
brown form XII is illuminating. The most striking feature of the comparison is the use of the second neighbour interaction (1–3): in XII it is 2·85 kcal/mole; in XV it is 3·74 kcal/mole. This corresponds to the shortening of the la–3a H–H distances: 2·018 A° and 1·924 A°, respectively. This indicates the improbability of the crown form remaining the most stable one in the larger rings.



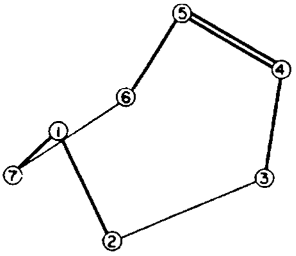
XV

It is clear that both in cyclononane and in cyclodecane the higher flexibility of the molecule makes it more difficult to assign the values for the 1,5 and 1,6 H . . . H non-bonded interactions albeit these values must be relatively high in the transition states for transannular reactions. It is hoped that more light will be shed on this point by our new approach (see below).

Cycloheptene (XVI, XVII). In contrast with the preceding results for cycloheptane, the boat form XVII is the more stable by a value of 0·67 kcal/mole. In this molecule the high 3–6 repulsions present in the saturated compound disappear. With the opening of the valency angle at C_4 and C_5 from the tetrahedral to 120°, the 3a–6a distance becomes 2·108 A°, corresponding to 2·12 kcal/mole only. We note that this distance is very sensitive to the valency angle at C_4 and C_5.



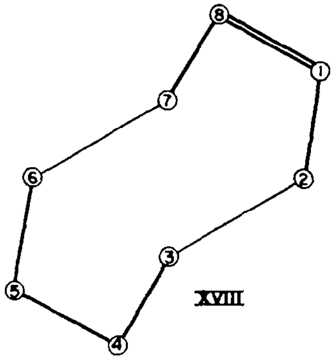
XVI



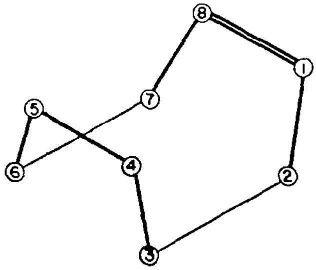
XVII

Cyclo-octene (XVIII–XX). Once again the boat form XIX is more stable but the difference is extremely small, 0·31 kcal/mole. However, we have large repulsions

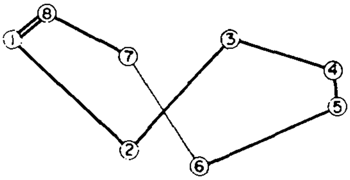
(28·43 kcal/mole) both in XVIII and in XIX, indicating the necessity of altering the situation through small deformations. The same conclusion holds for the skew form XX.



XVIII

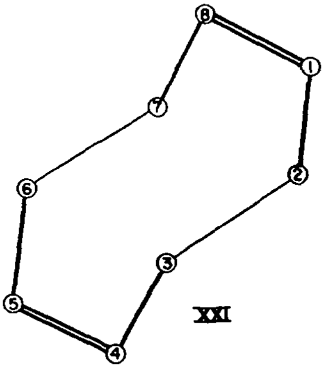


XIX

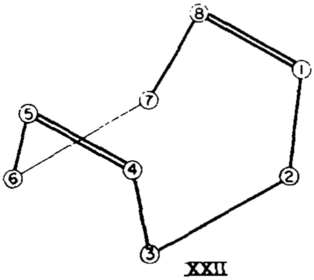


XX

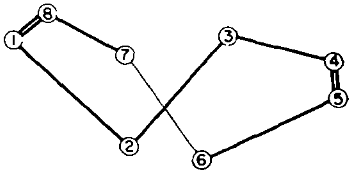
1,5-*Cyclo-octadiene* (XXI–XXIII). Here again we find that the boat form XXII is more stable, the difference being 0·51 kcal/mole. This conclusion is firmer than that for cyclo-octene as here we do not have high repulsions. The skew form XXIII is less stable than either the boat or the chair XXI form.



XXI

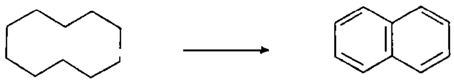


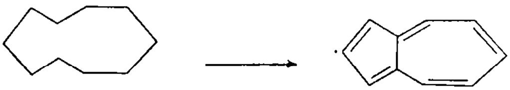
XXII

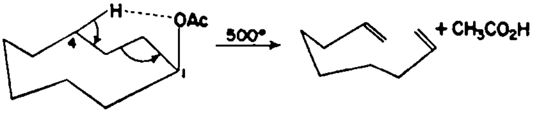


XXIII

The formation of indane by dehydrogenation of cyclononane with palladized charcoal and the formation of naphthalene or azulene by similar treatment of cyclodecane[16] makes certain conformations of the cyclo-alkanes appear particularly attractive. However, both the fact that the reactions are carried out at 400° and the high H–H interaction energies between the 1,5 and the 1,6 positions make such an assumption appear as an oversimplification. So would also appear an explanation such as given for ring cleavage of cyclononyl acetate at 500° to yield 1,8-nonadiene via a 1,4-transannular elimination.[17]







Conformation XIV for cyclo-octane was taken as a model calculation for a case in which 1,5-transannular reaction may take place. If we apply the assumption used throughout, namely that the H–H interaction is the same as the repulsive interaction of the hydrogen atoms in the anti-bonding state, multiplied by a factor of ½, we obtain an enormous repulsion energy for the 1,5-hydrogens (160 kcal/mole). Yet the formation of XXX from XXIX by 1,5-transannular interaction followed by dehydration, does take place.[18]

Many further examples of transannular interactions are known to occur.[19]

From this it follows that in the above and in analogous cases we may reasonably assume that deformations from the "ideal" more symmetrical conformations, as exemplified above, must in fact occur. This would permit decrease of repulsions at various points in the molecule whilst still permitting the formation of the transition state required for driving these transannular reactions to their respective goals.

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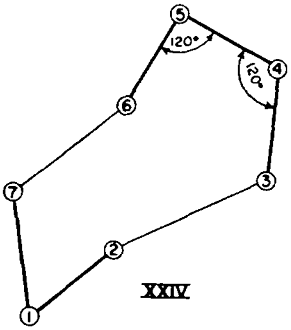
[16] V. Prelog, V. Boarland and S. Polyak, *Helv. Chim. Acta* 38, 434 (1955).

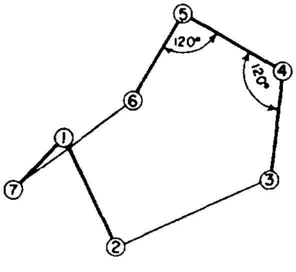
[17] A. T. Blomquist and P. R. Taussig, *J. Amer. Chem. Soc.* 77, 6399 (1955).

[18] A. C. Cope, S. W. Fenton and C. F. Spencer, *J. Amer. Chem. Soc.* 74, 5884 (1952); A. C. Cope and W. R. Schmitz, *Ibid.* 72, 3056 (1950).

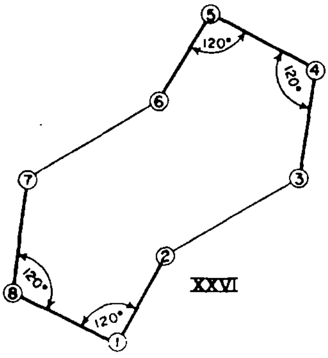
[19] *Inter alia*, A. C. Cope, S. W. Fenton and C. F. Spencer, *J. Amer. Chem. Soc.* 79, 3905 (1957) and many preceding papers; A. T. Blomquist and P. R. Taussig, *Ibid.* 79, 3505 (1957) and many preceding papers; V. Prelog and W. Küng, *Helv. Chim. Acta* 39, 1394 (1956) and many preceding papers.



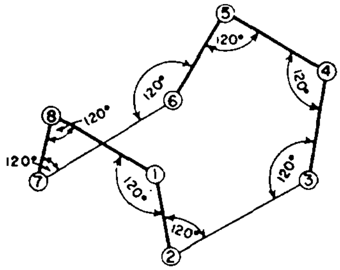
XXIV



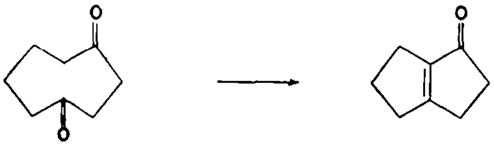
XXV



XXVI



XXVII



XXIX XXX

Indeed, Dunitz's recent X-ray diffraction measurements show that there are considerable deviations from tetrahedral angles in the carbon skeleton of certain cyclononane,[20] cyclodecane,[21] and cyclododecane derivatives.[22,23]

We therefore turn to a short discussion of the effect of introducing certain deformations into some of the above more idealized conformations.

Deformations

Barton[9] noted in his early calculations on cyclohexane that the results largely depend upon a few small interatomic distances and that the molecule would probably gain stability by undergoing deformations which alter these distances. The deformations can occur variously. If we alter the skeletal bond angles the energy rises but concurrently there is a great decrease in the H . . . H non-bonded interaction. Little experimental data are available for the variation of the energy with the skeletal bond

[20] R. F. Bryan and J. D. Dunitz, unpublished work.

[21] E. Buser and J. D. Dunitz, unpublished work.

[22] J. D. Dunitz and H. M. M. Shearer, *Proc. Chem. Soc.* 348 (1958).

[23] We gratefully acknowledge private communications from Professors Dunitz and Prelog on this point. Prof. Prelog has disclosed results leading to the formulation of the cyclodecane conformation at the Colloque International de Stereochemie at Montpellier on Sept. 8, 1959.

angle. Evans,[24] using thermochemical data and force constants, estimates the energy required to decrease the skeletal angle from the tetrahedral value by 5°, 10° and 20° to be only 0·4, 1·8 and 7 kcal/mole, respectively. Assuming that the same figures apply to the increase in bond angles, then an increase of 11° raises the energy by about 2 kcal/mole. At the same time the greatest H . . . H interactions drop very sharply by about 20 kcal/mole. Table 3 summarizes calculations in which we have used this deformation for cycloheptane and cyclo-octane.

TABLE 3

Interaction energy		Energy of deformation (kcal/mole)
XXIV	24·87	4
XXV	33·00	4
XXVI	32·72	8
XXVII	32·93	16

We see that for cycloheptane it is again predicted that the chair form is the more stable, the energy difference being increased to 8·13 kcal/mole. For cyclo-octane the energies are in the same range as for the crown form, the chair (with deformation) being the most stable.

In the preceding illustrative calculations we changed only those angles (while preserving the symmetry of the conformation) which affect mostly the shortest H . . . H distances. Evidently a more thorough treatment is needed which allows for the variations of all of the angles and takes into account unsymmetrical conformations too. However this exceeds the scope of this simple method which is suitable only for preliminary information regarding the geometry of the molecule. We intend to return to this problem using a more general method which was applied by Lifson[25] to a study of long chain polymer structures. Use of the electronic computer facilities (Weizac) of the Weizmann Institute of Science permits introduction of changes in a number of conformational parameters simultaneously. The results will be reported in a subsequent paper.[26]

Tables of distances between non-bonded hydrogens and their interaction energies for the various conformations discussed above may be obtained from the authors.

Acknowledgement—One of us (D. G.) is grateful of Prof. V. Prelog for stimulating discussions.

[24] A. C. Evans, *Trans. Faraday Soc.* **42**, 719 (1946).
[25] S. Lifson, *J. Chem. Phys.* **29**, 80, 89 (1958); **30**, 964 (1959).
[26] S. Lifson, R. Pauncz and D. Ginsburg, to be published.