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APPROXIMATE RELATIONSHIPS BETWEEN CONFORMATIONAL PARAMETERS IN 5- AND 6-MEMBERED RINGS

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Abstract– The degree of non-planarity of a 5-membered ring can be estimated fairly accurately from a knowledge of the bond angles or torsion angles. The same is true for certain commonly occurring types of 6-membered rings. Some approximate formulae are given with numerical tests of their range of applicability.

INTRODUCTION

IN A 5-membered ring with fixed bond distances the bond angles and torsion angles are related by six equations of constraint (ring-closure conditions). The calculations involved in computing the exact values of the six dependent parameters from values assigned to the four others are quite tiresome and are best carried out by an electronic computer. Even for the relatively simplified cases of equilateral 5-membered rings with C_s or C_2 symmetry imposed (only two independent parameters) the exact values of dependent parameters can only be obtained after extensive arithmetic as indicated by Eq. (1).

C_s (atom 5 on symmetry plane):

$$4\cos\theta_2(\cos\theta_2 - 1) + 2\cos\theta_5 = 1$$

C_2 (atom 5 on symmetry axis):

$$16\cos^2\theta_1 + 4\cos^2\theta_2 - 16\cos\theta_1\cos\theta_2 + 16\cos\theta_1\cos\theta_5 - 8\cos\theta_1 + 12\cos\theta_2 - 14\cos\theta_5 = 5$$

$$\cos\omega_{12} = \frac{1 - 2\cos\theta_2 + 2\cos\theta_1\cos\theta_2}{2\sin\theta_1\sin\theta_2} \qquad (1)$$

$$\cos\omega_{51} = \frac{1 + 2\cos\theta_2 - 2\cos\theta_1 - 2\cos\theta_5 + 2\cos\theta_1\cos\theta_5}{2\sin\theta_1\sin\theta_2}$$

C_s: $$\cos\omega_{23} = 1$$

C_2: $$\cos\omega_{23} = \frac{2\cos^2\theta_2 - 4\cos\theta_2 + 2\cos\theta_5 + 1}{2\sin^2\theta_2}$$

From Eq. 1 it is apparent that the torsion angles ω_{ij} are very sensitive to the *differences* between the bond angles, θ_i. In particular, equality of the bond angles requires that $\theta = 108°$, $\cos\omega = 0$; in other words, the equilateral, isogonal pentagon is constrained to lie in a plane, a most remarkable property.[1]

Many 5-membered rings of organic chemistry are non-planar. Any deviation from planarity must be associated with a decrease in the average bond angle from 108°— the greater the deviation, the smaller the average bond angle. Since the equilibrium bond angles between first-row elements are close to 108° for single bonds and somewhat greater for double bonds, large deviations from planarity cannot occur without excessive bond angle strain. We do not wish to enter here into the energy relationships involved but simply note that the actual deviations from planarity observed in typical 5-membered rings are not very large. Since the bond distances in these rings (e.g. cyclopentane, tetrahydrofurane, pyrrolidine, etc) are approximately equal and the bond angles close to 108°, the rings will project on their mean planes as approximately

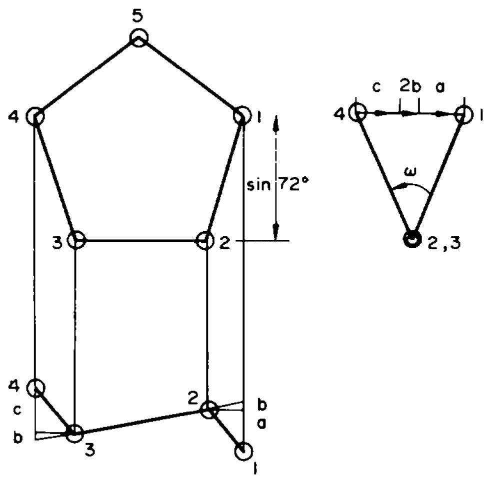

FIG 1. Construction showing how the torsion angles in a non-planar pentagon depend on the displacements of the atoms from the mean plane. For infinitesimal displacements $a = z_1 - z_2$, $b = (z_3 - z_2)\cos 72°$, $c = z_3 - z_4$. In the drawing the torsion angle ω is negative according to the Klyne–Prelog convention [*Experientia* **16**, 521 (1960)]

regular pentagons. This leads to a great simplification for it means that the non-planarity can be described, approximately at least, in terms of the out-of-plane deformations of a regular pentagon. Similarly, non-planar 6-membered rings can be described in terms of the out-of-plane deformations of a regular hexagon.

THE NON-PLANAR PENTAGON

The out-of-plane deformations of a pentagon can be described in terms of only two parameters. For the regular pentagon the most convenient description is in terms of the coordinate system introduced by Kilpatrick *et al.*[2] in their discussion of pseudorotation in the cyclopentane molecule. We define z_j as the displacement of the jth atom perpendicular to the plane of the unpuckered pentagon and write

$$z_j = \sqrt{(2/5)}\, q \cos\left(\frac{4\pi j}{5} + \phi\right) \qquad j = 1, 2, 3, 4, 5 \tag{2}$$

Any out-of-plane deformation is then described in terms of the two parameters, q, the amplitude of the deformation, and ϕ, its phase angle. We obtain the two symmetrical puckered forms by setting $\phi = 36°, 72°, \ldots$ for the C_s (envelope) form and $\phi = 18°$, 54°, 90°, . . . for the C_2 form. Intermediate values of ϕ give puckered rings with no symmetry. We note that q^2 is the sum of squares of displacements of the atoms from the best (least-squares) plane through the ring and shall use this coordinate system to show how the bond angles and torsion angles in a puckered pentagon depend on the out-of-plane amplitude q.

If we take the side of the pentagon as length unity then for an infinitesimal displacement from planarity the bond angle $\theta_j(\theta_{ijk})$ is given by

$$-\cos\theta_j = \frac{2[1+\cos(2\pi/5)] + (z_i - z_k)^2 - 2 - (z_i - z_j)^2 - (z_j - z_k)^2}{2\{1+(z_i - z_j)^2\}\{1+(z_j - z_k)^2\}} \tag{3}$$

Let $\theta_j = (3\pi/5) - \delta_j$ so that δ_j is the *decrease* in the bond angle at atom j resulting from the out-of-plane deformation. Expanding both sides as power series and neglecting higher powers of δ and z we obtain

$$\delta_j = \frac{\{(z_i - z_j)^2 + (z_j - z_k)^2\}\{1+\cos(2\pi/5)\} - (z_i - z_k)^2}{2\sin(2\pi/5)} \tag{4}$$

Cyclic permutation of the indices and addition then gives

$$\sum\delta_j = \frac{2\{1+\cos(2\pi/5)\}\{\sum z_j^2 - \sum z_j z_{j+1}\} - \sum z_j^2 + \sum z_j z_{j+2}}{\sin(2\pi/5)} \tag{5}$$

Fig.1 suggests how an approximate expression for the torsion angle ω_{jk} (ω_{ijkl}) can also be derived for infinitesimal displacements:

$$\omega_{jk} = \frac{z_i - z_j + z_k - z_l - 2(z_j - z_k)\cos(2\pi/5)}{\sin(2\pi/5)} \tag{6}$$

$$\sum\omega_{jk} = 0 \tag{7}$$

$$\sum\omega_{jk}^2 = 8\sum z_j^2 - 4(\sqrt{5}+1)\sum z_j z_{j+1} + 4(\sqrt{5}-1)\sum z_j z_{j+2} \tag{8}$$

Eq (7) says that the algebraic sum of the torsion angles is zero for a slightly puckered 5-membered ring. This is obviously true for the C_s form since torsion angles about bonds related by a mirror plane are equal in magnitude and opposite in sign; according to (7) this result is independent of the phase angle ϕ of the deformation. It can be shown[1] that for an equilateral 5-membered ring

$$\sum\sin\omega_{jk}\sin\theta_j\sin\theta_k = 0 \tag{9}$$

holds exactly, so we can expect that (7) will be approximately true also for larger puckering amplitudes. Examination of experimental torsion angles in a large number of 5-membered rings confirms that this is indeed the case. The sum of the torsion angles is also equal to zero in an equilateral 4-membered ring and we shall see later that this is also approximately true for the equilateral 6-membered ring. It is not true, however, for larger rings in general—only for certain symmetrical forms of these.

We now show that the sums $\sum\delta_j$ and $\sum\omega_{jk}^2$ are also independent of the phase of the puckering and depend only on its amplitude. From (2) we find

$$\sum z_j^2 = q^2$$

$$\sum z_j z_{j+1} = -\left(\frac{\sqrt{5}+1}{4}q^2\right) \tag{10}$$

$$\sum z_j z_{j+2} = \left(\frac{\sqrt{5} - 1}{4}\right) q^2$$

and hence, substituting in (5) and (8), we obtain

$$\sum \delta_j = \frac{5(\sqrt{5} + 1)}{\sin (2\pi/5)} q^2 = 4{\cdot}253\, q^2 \tag{11}$$

$$\sum \omega_{jk}^2 = 20\, q^2 \tag{12}$$

An estimate of the puckering amplitude can therefore be made from a knowledge of the bond angles or torsion angles. Since published values of these quantities are usually given in degrees we express the above relationships in these units

$$\sum \delta_j = 540° - \sum \theta_j(\text{deg}) = 244\, q^2 \tag{11a}$$

$$\sum \omega_{jk}^2(\text{deg}^2) = 6{\cdot}57 \times 10^4\, q^2 \tag{12a}$$

$$\sum \omega_{jk}^2(\text{deg}^2) = 269 \sum \delta_j(\text{deg}) \tag{13}$$

Although the numerical constants in these expressions are strictly valid only for infinitesimal puckering amplitudes they yield reasonable values of q for quite puckered rings. In Table 1 computed values of $\sum \delta/q^2$ and $\sum \omega^2/q^2$ are given for various values

Table 1. Values of various out-of-plane parameters computed for an equilateral pentagon (side = 1) with one atom tilted out of the plane of the other four. The angle α is the dihedral angle between the initial ring plane 1 2 2′ 1′ and the plane 1 5 1′. The bond angles at 2,2′,5 have been held at 108°. For comparison values for cyclopentane[3] are also given. Here $\theta_2 = \theta_{2'} = 106{\cdot}13°$, $\theta_1 = \theta_{1'} = 103{\cdot}95°$, $\theta_5 = 102{\cdot}13°$ for the C_s conformation. In the course of pseudorotation these angles vary but $\sum\delta$ and $\sum\omega^2$ remain constant

α	q	q^2	$\sum\delta$(deg)	$\sum\delta/q^2$	$\sum\omega^2$(deg^2)	$\sum\omega^2/q^2$
0	0	0	0	(244)	0	(65,660)
10	0·065	0·0042	1·02	243	274	65,240
20	0·129	0·0167	4·04	242	1074	64,310
30	0·193	0·0372	8·92	240	2334	62,740
40	0·255	0·0650	15·47	238	3970	61,080
50	0·314	0·0988	23·45	237	5893	59,650
60	0·369	0·1363	32·62	239	8036	58,960
C_5H_{10}	0·281	0·0792	17·70	224	4494	56,740

of q for the case of an equilateral pentagon with one atom tilted out of the plane of the other four. It is seen that for the range $0{\cdot}1 < q < 0{\cdot}3$, in which typical 5-membered rings can be expected to occur, almost perfect agreement can be obtained by using

$$\sum \delta_j(\text{deg}) = 240\, q^2 \tag{11b}$$

$$\sum \omega_{jk}^2(\text{deg}^2) = 6{\cdot}0 \times 10^4\, q^2 \tag{12b}$$

$$\sum \omega_{jk}^2(\text{deg}^2) = 250 \sum \delta_j(\text{deg}) \tag{13b}$$

If we use (11b) and (12b) to estimate the puckering amplitude of cyclopentane from bond angle and torsion angle data[3] ($\sum \delta = 17{\cdot}70$ deg $\sum \omega^2 = 4494$ deg^2) we obtain $q(\delta) = 0{\cdot}272$, $q(\omega^2) = 0{\cdot}269$, compared with the exact value $q = 0{\cdot}281$.

The approximate validity of (13b) has been checked by evaluating $\sum \omega^2/\sum \delta$ from the data collected by Altona *et al.*[4] for ring D in several steroid molecules and for the 5-membered rings in several corrinoid structures[5] (Fig 2). In evaluating out-of-plane parameters for small rings it would be helpful if authors would cite bond angles to 0·1° even when the absolute accuracy does not seem to merit this.

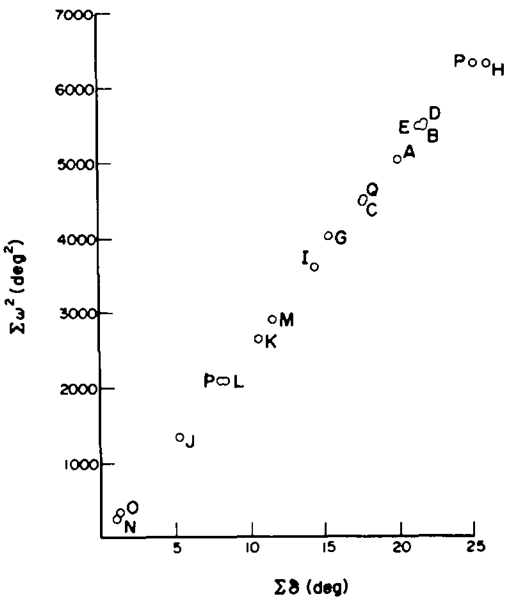

FIG 2. Relationship between $\sum\delta$ and $\sum\omega^2$ in 5-membered rings. The points indicated refer to ring D in several steroid derivatives collected in Ref 4 (A–H), rings A, B, C, D in cobyric acid (I–L) and in a seco-corrinoid derivative (M–P) (Ref 5) and to cyclopentane itself, Q (Ref 3)

Substitution of (2) in Eq (6) leads to

$$\omega_{jk} = 2\sqrt{(2)}q \cos\left\{\frac{4\pi}{5}\left(\frac{j+k}{2}\right) + \phi + \frac{\pi}{2}\right\} \tag{14}$$

thus providing a mathematical derivation of the empirical relationship discovered by Altona, Geise and Romers.[4] We note that the maximum torsion angle attainable in a pseudorotational circuit is given by

$$\omega_{max} = 2\sqrt{2}q = 2{\cdot}828\, q \tag{15}$$

$$\omega_{max}(\text{deg}) = 162\, q \tag{15a}$$

for infinitesimal q. For finite q in the range $0{\cdot}1 < q < 0{\cdot}3$ better results are obtained by taking

$$\omega_{max}(\text{deg}) = 150\, q \tag{15b}$$

As Altona, Geise and Romers[4] have pointed out, ω_{max} and ϕ can be derived from knowledge of two torsion angles. Hence the puckering amplitude can also be obtained from this information.

THE NON-PLANAR HEXAGON

To describe the out-of-plane deformations of a hexagon requires in general three parameters. Fortunately the non-planarity of many of the 6-membered rings of organic chemistry can be described reasonably accurately in terms of only one or two parameters. For "chair" forms with approximate D_{3d} symmetry, for example, the displacement of the jth atom from the mean plane of the unpuckered polygon is given by

$$z_j = \frac{1}{\sqrt{6}} q \cos(\pi j) \tag{16}$$

while for the flexible forms belonging to the pseudorotating "boat-twist" family, the corresponding displacement is characterized by an amplitude and a phase and is given by

$$z_j = \frac{1}{\sqrt{3}} q \cos\left(\frac{2\pi j}{3} + \phi\right) \tag{17}$$

With $\phi = 0°, 60°, \ldots$ we obtain the symmetrical (C_{2v}) "boat" forms, with $\phi = 30°$, $90° \ldots$ the symmetrical (D_2) "twist" forms. Intermediate ϕ values yield non-planar rings that have a twofold rotation axis. More general non-planar distortion of hexagons can be described by taking suitable linear combinations of (16) and (17).

The non-planarity of the chair form is described by a single parameter, which may be taken as the mean bond angle or the mean torsion angle or the puckering amplitude q. There are exact relationships between these quantities:

$$\cos\theta = q^2 - \frac{1}{2} \tag{18}$$

$$\cos\omega = \frac{1 - 2q^2}{1 + 2q^2} \tag{19}$$

$$\cos\omega = \frac{-\cos\theta}{1 + \cos\theta} \tag{20}$$

so that the approximate treatment is superfluous. However, we reproduce it briefly since its range of applicability may serve as a guide in dealing with other systems. If $\delta = (2\pi/3) - \theta_j$ is the decrease in a bond angle from 120° resulting from the out-of-plane deformation it is easy to show that

$$\delta = \frac{2}{\sqrt{3}} q^2 = 1{\cdot}155\, q^2 = 66{\cdot}2\, q^2(\text{deg}) \qquad \sum\delta = 4\sqrt{3}\, q^2 = 6{\cdot}928\, q^2 = 397\, q^2(\text{deg}) \qquad (21, cf\ 11)$$

$$\omega^2 \doteq 8\, q^2 = 2{\cdot}63 \times 10^4 q^2(\text{deg}^2) \qquad \sum\omega^2 = 48\, q^2 = 15{\cdot}76 \times 10^4 q^2(\text{deg}^2) \qquad (22, cf\ 12)$$

In Table 2 exact values of δ/q^2 and ω^2/q^2 are given for increasing values of q for the regular hexagon. As in the 5-membered ring case δ/q^2 is nearly constant so that q can be estimated quite accurately from known values of the bond angles using (21).

TABLE 2. VALUES OF VARIOUS OUT-OF-PLANE PARAMETERS COMPUTED FOR AN EQUILATERAL HEXAGON (SIDE = 1) WITH D_{3d} SYMMETRY

θ(deg)	q	q^2	ω(deg)	δ/q^2(deg)	ω/q^2(deg^2)
120	0	0	0	(66·2)	(26,260)
118	0·175	0·0305	27·8	65·6	25,340
116	0·248	0·0616	38·7	64·9	24,310
114	0·305	0·0933	46·7	64·3	23,380
112	0·354	0·1254	53·2	63·8	22,570
110	0·397	0·1580	58·7	63·3	21,810
109° 28′	0·408	0·1667	60·0	63·2	21,600

The pseudorotational family of non-planar hexagons with out-of-plane displacements given by (17) has a twofold rotation axis common to all its members since $z_j = z_{j+3}$. The decrease in bond angle (from 120°) is given (*cf* (4)) by

$$\delta_j = \frac{3(z_i - z_j)^2 + 3(z_j - z_k)^2 - 2(z_i - z_k)^2}{2\sqrt{3}} \tag{23}$$

whence

$$\sum \delta_j = \frac{4\sum z_j^2 - 6\sum z_j z_{j+1} + 2\sum z_j z_{j+2}}{\sqrt{3}} \tag{24}$$

and the approximate expression for the torsion angle is given by

$$\omega_{jk} = \frac{z_i - z_j + z_k - z_l - 2(z_j - z_k)\cos(\pi/3)}{\sin(\pi/3)}$$

$$= \frac{-4}{\sqrt{3}}(z_j - z_k) \tag{25}$$

using $z_l = z_{i+3} = z_i$. We obtain the relationships

$$\sum \omega_{jk} = 0 \tag{26}$$

$$-\omega_{j-1,j} = \omega_{jk} + \omega_{k,k+1} \tag{27}$$

$$\sum \omega_{jk}^2 = \frac{32}{3}(\sum z_j^2 - \sum z_j z_{j+1}) \tag{28}$$

From (17) it can easily be shown that

$$\sum z_j^2 = \sum z_j z_{j+3} = q^2 \tag{29}$$
$$\sum z_j z_{j+1} = \sum z_j z_{j+2} = -q^2/2$$

whence we obtain by analogy with (11) and (12)

$$\sum \delta_j = 2\sqrt{(3)}q^2 = 3{\cdot}464\, q^2 = 198\, q^2(\text{deg}) \tag{30}$$

$$\sum \omega_{jk}^2 = 16\, q^2 = 5{\cdot}25 \times 10^4 q^2(\text{deg}^2) \tag{31}$$

$$\sum \omega_{jk}^2(\text{deg}^2) = 265 \sum \delta_j(\text{deg}) \tag{32}$$

Equation (26) implies that the sum of the torsion angles is zero for any slightly puckered regular hexagon belonging to the boat-twist family. The equation holds approximately for quite large puckerings of such hexagons, even when the bond lengths are not exactly equal. Eq (27) says that in a slightly puckered hexagon of the boat-twist family every torsion angle is the sum of the preceeding two torsion angles with reversed sign, a relationship that has already been noted by Buys and Geise.[6] Eqs (30)–(32) give the linear relationships between out-of-plane parameters valid for infinitesimal displacements from the plane. The numbers given in Table 3 show the range of applicability of these linear relationships.

TABLE 3. VALUES OF VARIOUS OUT-OF-PLANE PARAMETERS COMPUTED FOR AN EQUILATERAL ISOGONAL HEXAGON (SIDE = 1) WITH C_{2v} SYMMETRY ("BOAT" FORM). IN THE COURSE OF PSEUDOROTATION VALUES OF $\sum \delta/q^2$ AND $\sum \omega^2/q^2$ REMAIN VIRTUALLY CONSTANT

θ(deg)	q	q^2	ω(deg)	$\sum\delta/q^2$(deg)	$\sum\omega^2/q^2$(deg^2)
120	0	0	0	(198·4)	(52,520)
118	0·245	0·0598	27·8	200·6	51,678
116	0·344	0·1182	38·7	203·1	50,688
114	0·418	0·1749	46·7	205·8	49,869
112	0·479	0·2298	53·2	208·9	49,262
110	0·532	0·2827	58·7	212·3	48,758
109° 28′	0·544	0·2963	60·0	213·3	48,601

Substitution of (17) in Eq (25) leads to

$$\omega_{jk} = \frac{4}{\sqrt{3}} q \cos\left[\frac{2\pi}{3}\left(\frac{j+k}{2}\right) + \phi + \frac{\pi}{2}\right] \tag{33}$$

which provides the derivation of the cosine dependence

$$\omega_{jk} = \omega_{max} \cos\left(\frac{2\pi}{3} j + \Delta\right)$$

proposed by Buys and Geise[6]. The value of ω_{max} is proportional to the puckering amplitude.

$$\omega_{max} = \frac{4}{\sqrt{3}} q = 2{\cdot}309\, q = 132\, q(\text{deg}) \tag{34}$$

Finally it may be useful to give the approximate linear expressions for the individual torsion angles in the two special forms of C_{2v} and D_2 symmetry:

$$C_{2v}\begin{cases}\omega_{12} = \omega_{45} = 0 \\ \omega_{23} = \omega_{56} = -\omega_{61} = -\omega_{34} = -2q = -115\,q(\text{deg})\end{cases} \tag{35}$$

$$D_2\begin{cases}\omega_{12} = \omega_{45} = -\dfrac{4}{\sqrt{3}}q = -132\,q(\text{deg}) \\ \omega_{23} = \omega_{56} = \omega_{61} = \omega_{34} = \dfrac{2}{\sqrt{3}}q = 66\,q(\text{deg})\end{cases} \tag{36}$$

It should be emphasized that the relationships and formulae derived in this paper are purely geometrical in nature and do not depend on any features of the molecular force field. More rigorous discussion of the geometric constraints in 6-membered and other rings has been given elsewhere.[7]

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