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CONFORMATION OF NON-AROMATIC RING COMPOUNDS, Part L (1)
BOAT/TWIST-BOAT PSEUDOROTATION IN SIX-MEMBERED RING COMPOUNDS

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Introduction

Recently, Hendrickson (2) discussed the general features of the pseudorotation in six- and higher-membered rings. As the main characteristic properties of this phenomenon were mentioned:

(i) Pseudorotation may be described as the passage of a ring with a plane of symmetry through an atom to one with an axis of symmetry bisecting the bond adjacent to that atom, and vice versa. The two ring forms of opposite symmetry are called pseudorotation partners (in the case of the flexible form of six-membered rings: boat (C_6-B) and twist-boat (C_6-TB), respectively).

(ii) The dihedral angles about all bonds change smoothly between their maximum and minimum values in the course of the pseudorotation, the ring itself either being asymmetrical when between the pseudorotation partners or retaining a symmetry axis perpendicular to the ring (as in the case of the C_6-B/TB pseudorotation).

(iii) The energy profile during pseudorotation is given by a simple sine curve with maxima and minima only at the symmetric forms. The maximum is usually represented by the form with a plane of symmetry (e.g. the C_6-B), the minimum by that with an axis (e.g. the C_6-TB).

The aim of the present paper is to provide a simple method of determining the geometry of any of the infinity of forms a six-membered ring can assume in the course of the boat/twist-boat pseudorotation itinerary. In previous papers (3,4) such a method was introduced for cyclopentanes, the torsional angles of which appeared to depend on a geometrical parameter φ_{max} (the maximum attainable torsional angle) and a conformational parameter Δ (the phase angle of pseudorotation). The five ring dihedral angles follow from eq.1:

$$\varphi_j = \varphi_{max} \cos\left(\frac{\Delta}{2} + j\delta\right) \qquad (1)$$

where $j = 0,1,2,3,4; \delta = 144^\circ$.

Along the pseudorotation circuit, Δ varying from 0° to 720°, the symmetrical pseudorotation partners appear at $\Delta = 0°, 72°, 144°$ ....(half-chair or C_2 form) and at $\Delta = 36°, 108°, 180°$.......(envelope or C_s form). The geometry of cyclopentane as found by electron diffraction (5) excellently fits to the above description. Strictly speaking, eq.1 is valid only if (i) the endocyclic bond lengths and the force constants governing the bending of the valency angles are equal (i.e. in five-rings with 5 equivalent vertices); (ii) the energy barrier ΔE opposing the pseudorotation is 0, which is only the case for unsubstituted cyclopentane (6,7). When $\Delta E \neq 0$, the molecule may tend to adapt its geometry so that the value of φ_{max} depends on Δ . However, the application of eq.1 to hetero 5-rings (8) and to steroid rings D (4) yields torsional angles deviating only a few degrees from those experimentally obtained by X-ray analysis.

A similar simple cosine function may be applied to the pseudorotating form of cyclohexanes (eq.2):

$$\varphi_j = \varphi_{max} \cos (\Delta + j\delta) \qquad (2)$$

in which $j = 0,1,2,3,4,5$; $\delta = 120°$; φ_0 is the ring dihedral angle about bond (6)-(1) and φ_j about bond (j)-(j+1).

The following characteristics can be concluded from eq.2:

1. Along the pseudorotation circuit, Δ varying from 0° to 360°, the pseudorotation partners appear at $\Delta = 0°, 60°, 120°$......(twist-boat (TB)) and at $\Delta = 30°, 90°, 150°$......(boat (B)), see Fig.1. Ring forms at Δ_1 and Δ_2 are mirror-images if $|\Delta_2 - \Delta_1| = 180°$.
2. For any value of Δ the following equations hold:

$$\varphi_j = \varphi_{j+3} \qquad (3)$$

$$-\varphi_j = \varphi_{j+1} + \varphi_{j+2} \qquad (4)$$

$$\tan (\Delta + 120j) = (\varphi_{j+2} - \varphi_{j+1})/\varphi_j\sqrt{3} \qquad (5)$$

Eq.3 is in agreement with the statement (2) that a symmetry axis perpendicular to the ring is retained during pseudorotation. Experimental knowledge of two torsional angles, not related by eq.3, is sufficient for calculating the other ones (eqs. 3 and 4), Δ (eq.5) and φ_{max} (eq.2).

3. Each torsional angle φ_j varies smoothly between $-\varphi_{max}$ and $+\varphi_{max}$ along the pseudorotation circuit. Therefore, the value of φ_{max} may be regarded as a measure of the puckering of a flexible six-membered ring system.

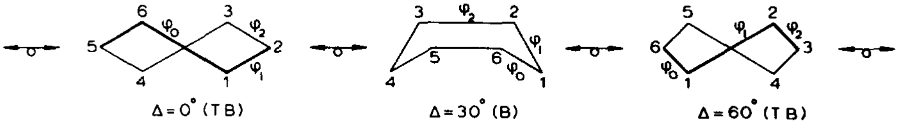
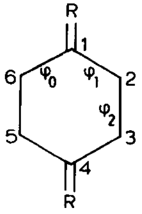


FIG.1. Part of the pseudorotation circuit of the flexible form of a six-membered ring.

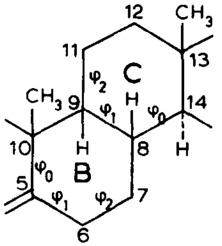
Results

Accurate geometrical information obtained by X-ray analysis is known for the following compounds that contain a six-membered ring in a flexible form:

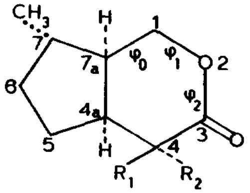
1 cyclohexane-1,4-dione at -140°C (ref.9)
2 idem at room temperature (ref.10)
3 cyclohexane-1,4-dione : $HgCl_2$ (ref.11)
4 cyclohexane-1,4-dioxime (ref.12)
5 22,23-dibromo-8β,9β,10β-ergost-4-ene-3-one, ring B (ref.13)
6 idem, ring C (ref.13)
7 iridomyrmecin (ref.14)
8 isoiridomyrmecin (ref.15)



1 - 4



5 ring B
6 ring C



7 $R_1 = CH_3$, $R_2 = H$
8 $R_1 = H$, $R_2 = CH_3$

Table 1 contains the ring dihedral angles φ_j which were calculated from the atomic coordinates given in the original literature. No experimental data on the geometry of flexible forms of cyclohexane (9) and cyclohexanone (10) are known; the dihedral angle values for the boat and twist-boat forms obtained from theoretical calculations (16,17) are also listed in Table 1 .

Table 1. Ring dihedral angles φ_j, Δ and φ_{max}, and ''standard'' torsional angles φ_j' for some six-membered rings in the flexible form

	Cmpd	φ_0	φ_1	φ_2	φ_3	φ_4	φ_5	Δ	φ_{max}	$\varphi_0'=\varphi_3'$	$\varphi_1'=\varphi_4'$	$\varphi_2'=\varphi_5'$
theoretical models	2*	+62.8	-30.1	-30.1	+62.8	-30.1	-30.1	0	61.5	+61.5	-30.8	-30.8
		+52.1	-52.1	0	+52.1	-52.1	0	30		+53.3	-53.3	0
	2**	+63.1	-30.2	-30.2	+63.1	-30.2	-30.2	0	61.5	+61.5	-30.8	-30.8
		+51.5	-51.5	0	+51.5	-51.5	0	30		+53.3	-53.3	0
	10**	+53.4	-53.4	0	+52.1	-52.1	0	30	60.0	+52.0	-52.0	0
		+20.5	-59.0	+33.2	+24.6	-63.4	+38.6	60		+30.0	-60.0	+30.0
		0	-50.4	+49.8	0	-50.8	+50.7	90		0	-52.0	+52.0
		-28.9	-28.9	+60.2	-29.3	-29.3	+60.2	120		-30.0	-30.0	+60.0
experimental geometries	1	-40.5	-11.6	+52.5	-39.9	-12.4	+53.3	137	55.1	-40.3	-12.4	+52.7
	2	-40.8	-11.4	+52.4	-39.2	-13.8	+54.1	135	55.4	-39.2	-14.3	+53.5
	3	-16.9	-37.2	+55.5	-16.9	-37.2	+55.5	108	56.1	-17.3	-37.5	+54.9
	4	+ 3.3	-51.3	+47.0	+ 2.2	-50.6	+46.6	86.5	56.6	+ 3.5	-50.7	+47.2
	5	-26	-29	+59	-30	-26	+55	120	57.0	-28.5	-28.5	+57.0
	6	-42	-16	+57	-36	-23	+64	130.5	60.8	-39.5	-20.3	+59.8
	7	+48.4	-55.1	+ 2.3	+49.7	-49.9	+ 3.3	33	58.8	+49.3	-52.4	+ 3.1
	8	+53.5	-53.0	- 2.3	+53.7	-49.7	- 3.9	27	60.7	+54.1	-50.9	- 3.2

*Taken from ref.16. **Taken from ref.17.

From the values of φ_j the ''best'' values of Δ and φ_{max} were calculated by means of eqs. 2 and 5. These parameters in turn were used to calculate ''standard'' torsional angles φ_j' with the aid of eq.2.

It should be noted that even for cyclohexane with its six equivalent vertices eq.2 is probably not strictly valid, as a substantial barrier opposing the pseudorotation occurs (18). However, Table 1 shows an excellent agreement between φ_j and φ_j', the deviations being only a few degrees. Only cyclohexanone (10) at $\Delta = 60^\circ$ shows larger deviations, but it cannot be settled whether these deviations are due to violation of eq.2 or to uncertainties in the theoretically calculated geometry.

The degree of puckering (φ_{max}) is not very different for the various compounds listed in Table 1, its value being 55-57° for compounds 1 - 4 and 57-61° for the fused rings 5 - 8. The two theoretical models for cyclohexane (9) calculated by Hendrickson (16) and by Bucourt and Hainaut (17), respectively, show the same φ_{max} (61.5°), whereas that of cyclohexanone is only a little smaller (60°).

The values of Δ depend, of course, on the arbitrarily chosen zero point on the scale. Another choice of φ_0 means a shift of the Δ value by a multiple of 120°.

Conclusion

The application of eq.2 to flexible forms of six-membered rings yields two valuable parameters, defining the degree of puckering (φ_{max}) and the phase angle of pseudorotation (Δ). Although eq.2 is not strictly valid, the results are satisfactory, which has also been found for the application of eq.1 to hetero and fused five-ring systems.

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