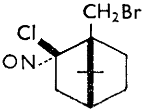
1119. *Molecular Conformations. Part II.*[1] *Conformations and Valency Angles of Five- and Six-membered Rings*

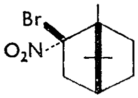
By G. A. Sim

The average valency angle in the five-membered rings in norbornane is deduced geometrically to be about 100°. The interdependence of valency angles and conformation in five- and six-membered rings is derived and related to some bicyclic systems.

X-Ray determinations of the molecular geometries of the bicyclo[2,2,1]heptane derivatives (I)[2], (II)[3], and (III)[4] have demonstrated that the valency angles in the five-membered rings are considerably smaller than tetrahedral. One purpose of the present Paper is to show that the marked reduction from the tetrahedral value is a simple geometrical consequence of two five-membered rings sharing three corners in common.



(I)



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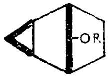
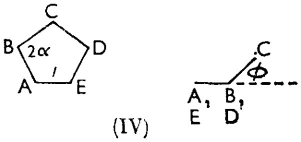


(III: $R = O_2S{\cdot}C_6H_4Br$)

For a regular five-membered ring which is in the " envelope " conformation and has side *l* and internal angle 2α (IV), the angle, φ, between the planes BCD and ABDE is given by:



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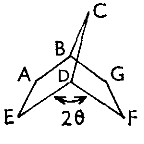

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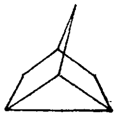

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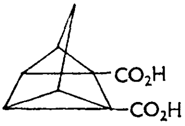

(VII)

$$\cos\phi = \frac{7/4 - 2\cos 2\alpha - \sin^2 2\alpha - \cos^2\alpha}{2\sin 2\alpha\cos\alpha} \qquad (1)$$

The displacement, Δ, of C from the plane ABDE is given by

$$\Delta = l\cos\alpha\sin\phi \qquad (2)$$

Values of φ and of Δ for various values of the angle 2α are shown in Table 1 for $l = 1{\cdot}54$ Å, the normal single-bonded carbon–carbon distance.

TABLE 1

Values of the angle φ and of the displacement Δ of the out-of-plane atom of a five-membered ring in the " envelope " conformation, for various values of the internal angle 2α

2α	108°	107·5°	107°	106°	105°	104°	103°	102°	101°	100°	99°
φ..............	0°	14·5°	20·4°	28·7°	35·0°	40·1°	44·6°	48·7°	52·3°	55·7°	58·8°
Δ (Å)	0	0·23	0·32	0·45	0·54	0·61	0·68	0·73	0·78	0·82	0·86

In the bicyclo[2,2,1]heptane system (V) the angle between the planes ABDE and GBDF is 2φ and if the angles EDF and ABG are 2θ, then

$$\sin\phi = \sin\theta/\sin 2\alpha \qquad (3)$$

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[1] Part I, W. A. C. Brown, J. Martin, and G. A. Sim, *J.*, 1965, 1844; see also W. A. C. Brown, G. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 1964, 57.
[2] G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J.*, 1961, 1976.
[3] D. A. Brueckner, T. A. Hamor, J. M. Robertson, and G. A. Sim, *J.*, 1962, 799.
[4] A. C. Macdonald and J. Trotter, *Acta Cryst.*, 1965, **18**, 243.

When the angles ABG and EDF are tetrahedral (109° 28′) equations (1) and (3) imply that $2\phi = 112°$ and $2\alpha = 99{\cdot}8°$. In this region the angle 2α is not particularly sensitive to small changes in 2θ; thus, for $2\theta = 105°$ we find $2\alpha = 100{\cdot}5°$ and for $2\theta = 114°$ we find $2\alpha = 99{\cdot}1°$. The experimentally determined valency angles in bicycloheptane systems are shown in Table 2. There is good agreement between the theoretical value of about 100° deduced here and the average of the experimentally determined valency angles. The systematic variations in the experimentally determined valency angles [in particular, the extremely small value of the bridge angle BCD in (I) and (II)] can probably be ascribed to the eclipsed interactions of the C–H groupings at positions A, E, G, and F. The incorporation of the cyclopropane ring in (III) relieves these interactions to some extent and the angle BCD is accordingly rather larger than in (I) and (II), though still smaller than the average angle.

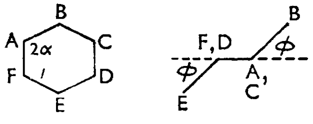
TABLE 2

Valency angles in the bicycloheptane molecules (I), (II), and (III)

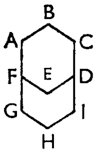
Angle	BAE	BGF	AED	GFD	ABC	GBC	EDC	FDC	BCD	BCD	Av.
(I)	104°	107°	102°	101°	102°	97°	103°	102°	93°	93°	100·4
(II)	106°	105°	103°	100°	101°	98°	104°	101°	93°	93°	100·4
(III)	103°	103°	104°	103°	101°	101°	102°	99°	97°	97°	101·0

Schleyer [5] has shown that nortricyclene (VI), which can be made by a simple reversible thermal rearrangement of norbornene, is thermodynamically slightly more stable than norbornene, the free-energy difference being 0·9 kcal./mole. The nortetracyclene derivative (VII) can be formed in high yield from bicyclo[2,2,1]heptadiene-2,6-dicarboxylic acid by ultraviolet irradiation.[6] The stability, relative to their precursors, of these apparently highly strained cyclopropane derivatives can be attributed to the marked reduction in the angular strain in the five-membered rings on formation of the 2,6- and/or 3,5-bonds with concomitant reduction of the angle 2θ. In nortetracyclene 2θ is reduced to 60° so that $2\phi = 62°$ and $2\alpha = 106°$; such a value for 2α is typical of relatively unstrained five-membered rings (see below). In nortricyclene, the average valency angle will be intermediate between the value characteristic of norbornane (100°) and that characteristic of nortetracycline (106°). The reduction in angular strain in the five-membered ring appears to balance approximately the angular strain involved in forming the cyclopropane rings in (VI) and (VII).

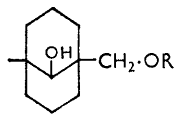
Five-membered rings (cyclopentane, γ-lactone, etc.) with the envelope-like conformation occur in many of the complex organic molecules whose structures have been elucidated by the *X*-ray method in recent years; [7] the average valency angle in these rings is normally about 104—106° and the concomitant displacement of the atom at the flap of the "envelope" about 0·5—0·6 Å. For example, the cyclopentanone ring of 2-bromodihydroisophoto-α-santonic lactone acetate [8] and the γ-lactone ring of 2-bromo-α-santonin [9] have average valency angles of 105° and the out-of-plane atom displaced by 0·54 and 0·61 Å, respectively.



(VIII)



(IX)



(X: $R=O_2S{\cdot}C_6H_4Br$)

In the case of a regular six-membered ring, of side *l* and internal angle 2α, in the chair

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[5] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1958, **80**, 1700.

[6] S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, 1954, **76**, 5000.

[7] J. M. Robertson, *Proc. Chem. Soc.*, 1963, 229.

[8] J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 1962, 111; *J.*, 1965, 1584.

[9] J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 1962, 335.

conformation (VIII), the angle between the planes ABC (or DEF) and ACDF, ϕ, is given by

$$\cos \phi = (1\text{-}2 \cos^2 \alpha)/\cos \alpha \qquad (4)$$

and the displacement of B (or E) from the plane ACDF is given by

$$\Delta = l \sin \alpha \, (4 \cos^2 \alpha - 1)^{\frac{1}{2}} \qquad (5)$$

When $2\alpha = 109° 28'$, $\Delta = 0{\cdot}728$ Å and as 2α increases towards 120° Δ decreases towards zero. Values of ϕ and Δ for various values of 2α are shown in Table 3.

TABLE 3

Values of the angle ϕ and of the displacement Δ of the atoms B and E in a six-membered ring in the chair conformation

2α	109·5°	112°	114°	116°	118°	120°
ϕ	54·7°	47·9°	41·7°	34·2°	24·3	0°
Δ (Å)	0·73	0·64	0·56	0·46	0·33	0

Partially flattened six-membered rings occur in the bicylo[3,3,1]nonane system (IX), in order to provide a transannular B · · · H separation of >3 Å.[1,10] In 1-*p*-bromobenzenesulphonyloxymethyl-5-methylbicyclo[3,3,1]nonan-9-ol,[1] (X), atom E is displaced by 0·72 Å from the planes ACDF and GFDI (cf. the value of 0·728 Å appropriate to tetrahedral angles) whereas atoms B and H are displaced by only 0·48 Å, and there is a resultant increase of the valency angles at A, B, C, G, H, and I to an average value of 114°.

The U.S. National Science Foundation provided financial support of this work.

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[*Received, April* 20*th*, 1965.]

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[10] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695.