THE DIHEDRAL ANGLES OF CYCLOHEXANE*

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Some 10 years ago Hazebroek and Oosterhoff (1951) thoroughly analysed the complex geometrical forms which the cyclohexane ring can assume, the mechanical rigidity of the chair form and the contrasting flexibility of the boat form. One single variable suffices to define completely the geometry of the flexible form ; this variable may be any one dihedral angle between three successive carbon–carbon bonds, any one 1–4 carbon–carbon distance, or, as in Hazebroek and Oosterhoff's case, a mathematical variable selected to suit their purpose of describing in a symmetrical way the rotation between staggered and eclipsed conformations. Perhaps because of its formal nature, this important paper has been frequently overlooked, but with the growing interest in the family of cyclohexane conformations which include the boat and the symmetrical skew as extreme cases, it seems important to present material implicit in Hazebroek and Oosterhoff's paper (though reached differently here) with numerical emphasis on angles and coordinates. Further relevant material is presented in papers by Brodetsky (1929) and Henriquez (1934).

Procedure

Using Figure 1, consider two carbon-carbon bonds placed in the xy-plane, with the central atom A at the origin, and with F and B symmetrically disposed about the vertical zy-plane. Atom C is initially placed in the xy-plane, but is free to rotate appropriately about AB produced, and its location is conveniently given by the dihedral angle R between the planes FAB and ABC. The carbon-carbon distance is our unit length. Another atom E is introduced, with z positive, but necessarily placed so that A, E, and C are at the corners of an equilateral triangle of side length 1·6330 if tetrahedral geometry and equal bond lengths are to be preserved. The position of this fifth atom is completely determined by the original location of atom C. By trial and error methods we have determined the coordinates of E for all possible positions of C, and computed the dihedral angle S between the planes EFA and FAB. Furthermore, the original choice for C, and its implied position of E, defines the position of D (at the corners of the equilateral triangle FBD, side 1·6330 ; unit distance from both E and C, and having an x coordinate 0·0000) and fixes the third dihedral angle T between the planes ABC and BCD. There are three further dihedral angles about the bonds CD, DE, and EF, but these are identical with the set S, R, T already discussed.

Results

The dihedral angles about successive bonds, presented in Table 1, change interestingly with the three-dimensional movement of the molecule. We begin at $R=0°$, $T=60°$, $S=-60°$ (the negative sign indicates opposite rotation sense) with the molecule in the F–C boat form with the atoms F, A, B, C in the reference plane. As R increases, C rises above the xy-plane, and so does E, $-S$ increasing slowly. This action continues until $R=33\cdot10°$ and $-S$ has reached its maximum value of $70\cdot67°$. The molecule is now a symmetrical skew with $B-E$ the twofold axis, B, D, E, F coplanar. As R further increases towards $60°$, E descends slowly and at $R=60°$, $-S$ has fallen to $60°$: the model is a second boat, axis AD. All six possible boats, which alternate with six symmetrical skew forms, are
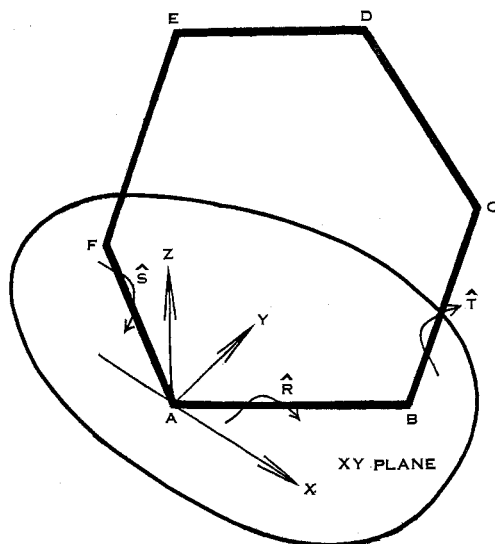

Fig. 1

generated by moving D both above and below the xy-plane, R, S, and T undergoing cyclic permutation but not assuming new values. The intervals have been arranged to facilitate graphical representation, and the number of significant figures is adjusted to the precision of the entries. The coordinates of D, the most laborious to calculate, are presented : those of A, B, and F are respectively $(0\cdot0000,\ 0\cdot0000,\ 0\cdot0000)$ $(+0\cdot8163,\ 0\cdot5774,\ 0\cdot0000)$, and $(-0\cdot8163,\ 0\cdot5774,\ 0\cdot0000)$, whilst C and E can be recovered from

$$x \begin{array}{l} \text{(positive for } C \\ \text{negative for } E) \end{array} = 1\cdot0885 - (0\cdot5443 \cos \text{dihedral}),$$

$$y \text{ (positive)} \quad = 0\cdot7698 + (0\cdot7698 \cos \text{dihedral}),$$

$$z \text{ (positive)} \quad = 0\cdot9428 \sin \text{dihedral}.$$

The calculations have been carried out with four-figure tables so some accumulation of error is inevitable, but it may be safely assumed that the coordinate values permit the calculation of distances to better than 1 in 1000, which comfortably exceeds the usual bond-length accuracy.

It is sometimes convenient to express the movements in terms of the varying distances between opposite carbon atoms. Table 2 shows how any cyclohexane 1–4 distance varies with the associated dihedral angle.

TABLE 1

RELATED VALUES OF R, T, AND S

Dihedral Angles			Coordinates of D		
R	T	$-S$	x	y	z
0·00°	60·0°	60·00°	0·0000	1·7319	0·8166
1·6		61·00			
3·3		62·00	(carbon–carbon bond, unit length)		
5·00	56·8	62·93	0·0000	1·6592	0·9108
5·2		63·00			
7·2		64·00			
9·4		65·00			
10·00	53·2	65·28	0·0000	1·5807	0·9966
11·7		66·00			
14·3		67·00			
15·00	49·6	67·27	0·0000	1·5014	1·0705
17·2		68·00			
20·00	45·4	68·83	0·0000	1·4199	1·1358
20·7		69·00			
25·00	40·9	69·95	0·0000	1·3389	1·1917
25·4		70·00			
29·3		70·50			
30·00	36·2	70·55	0·0000	1·2606	1·2382
33·10	33·1	70·67	0·0000	1·2138	1·2630
35·00	31·2	70·62	0·0000	1·1860	1·2765
37·00	26·8	70·50	0·0000	1·1582	1·2894
40·00	26·0	70·13	0·0000	1·1184	1·3066
40·7		70·00			
44·8		69·00			
45·00	20·4	68·93	0·0000	1·0585	1·3293
47·7		68·00			
50·00	14·2	67·00	0·0000	1·0102	1·3463
52·00		66·00			
53·8		65·00			
55·00	8·0	64·23	0·0000	0·9757	1·3570
55·3		64·00			
56·8		63·00			
58·00		62·00			
59·1		61·00			
60·00	0·0	60·00	0·0000	0·9624	1·3607

The symmetrical skew cyclohexane with neither bond length nor bond angle distortion, alternatively referred to as the stretched conformation or the " half-rotated " form, is shown by the numerical analysis to have dihedral angles of 33·1, 33·1, and 70·67°, and not the 30, 30, 60° values quoted, for instance, by

Klyne and Prelog (1960). The former values are obtained also by straight-forward operations on Hazebroek and Oosterhoff's (1951) equations (9), (8), and (12), and can be verified by accurate models.

TABLE 2

VARIATION CYCLOHEXANE 1–4 DISTANCES WITH DIHEDRAL ANGLE

Dihedral Angle	Associated Distance (Carbon–carbon bond, unit length)		Dihedral Angle	Associated Distance (Carbon–carbon bond, unit length)	
0°	1·6667	Min. Boat	40°	1·7868	
5	1·6684		45	1·8158	
10	1·6745		50	1·8470	
15	1·6845		55	1·8801	
20	1·6980		60	1·9147	Boat
25	1·7156		65	1·9502	
30	1·7365		70	1·9856	
33·1	1·7512	Skew	70·50	1·9911	
35	1·7601		70·67	1·9914	Max. Skew

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