A Note on the Calculation of the Space Displacements of Terminal Carbon Atoms in Ring Formation.

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Short (*Chem. News*, 1926, **133**, 149) points out that in certain cases a good measure of the tendency to ring formation of a uniplanar polymethylene chain is given by what he calls the "approach value". This conception was first introduced by Ingold (*J. Chem. Soc.*, 1921, **119**, 307), whose definition is, however, rather vague. He merely refers to his values as showing "by how much" the terminal carbon atoms of a normal polymethylene chain must approach one another in forming the corresponding uniplanar *cyclo*-paraffin ring. An examination of his results indicates that, taking as the unit, the distance between two adjacent carbon atoms in the unstrained chain, the "approach value" is half the difference in the distance between the terminal carbons before and after displacement.

Approach values have been calculated for special cases by Ingold and Short, but the general formula relating them to the valency angle (*i.e.*, the angle between each pair of carbon-to-carbon valencies in the unstrained chain), and to the number of carbon atoms in the chain, has not yet been given. The derivation of the formula is shown in what follows.

The general formula for approach values.—Consider an unstrained chain with n methylene groups, and join without displacement the terminal carbon atoms 1 and n. Let a be the distance between the adjacent carbon atoms in the chain, and let $2\theta°$ be the valency angle.

If $(1, n)$ is the distance between the terminal carbon atoms before ring formation, then half the difference in the distances between the terminal carbon atoms before and after displacement is

$$\frac{(1, n)-a}{2},$$

and since the approach value is this quantity when a is taken to be the unit of distance, we have, approach value

$$= \frac{(1, n)-a}{2a}.$$

The angle between (1, n) and (1, 2) is given by

$$\left[\frac{(n-1)(180)-180-2\theta(n-2)}{2}\right]^\circ = (90-\theta)(n-2)^\circ.$$

This can be seen by joining any point O in (1, n) to all the carbon atoms, and considering the angles of the $(n-1)$ triangles so formed. The sum of these angles amounts to $(n-1)(180)^\circ$. From this must be deducted the angle of 180° at O, and also $(n-2)$ angles each equal to $2\theta^\circ$, in order to obtain the sum of the two equal angles between (1, n) and, respectively, (1, 2) and $(n-1, n)$.

The angle between (1, n) and (2, 3) is

$$[(90-\theta)(n-2)-(180-2\theta)]^\circ = (90-\theta)(n-4)^\circ.$$

Proceeding in this way we obtain,

$$(1, n)=a[\cos(90-\theta)(n-2)^\circ+\cos(90-\theta)(n-4)^\circ+\ldots+\cos(n-2)(n-1)(90-\theta)^\circ] = \frac{a\sin(n-1)(90-\theta)^\circ}{\cos\theta^\circ}.$$

From which we have, approach value

$$=\frac{(1,n)-a}{2a} = \frac{\sin(n-1)(90-\theta)^\circ}{2\cos\theta^\circ}-\cdot5. \quad \ldots (1)$$

This general formula yields the values given by Ingold and Short for the particular cases they considered.

Thus for $2\theta=115\cdot3^\circ$, the valency angle assumed by Ingold, and $n=4$, we have, approach value

$$= \frac{\sin(4-1)(90-57\cdot6)^\circ}{2\cos 57\cdot6^\circ}-\cdot5 = \frac{\sin 97\cdot2^\circ}{2\cos 57\cdot6^\circ}-\cdot5$$

$$= \frac{\cdot992}{1\cdot07}-\cdot5 = \cdot427$$

which agrees with the value given by Ingold.

Since the general formula for the angle of strain is

$$\alpha^\circ = \left[\frac{\theta - 90(n-2)}{n} \right]^\circ, \qquad \ldots \quad (2)$$

it is clear from a comparison of (1) and (2), that there is no simple relation between α and the approach value. Accordingly the comparison made by Ingold (*loc. cit.*) between the heats of formation of a series of *cyclo*paraffin rings, the Baeyer values for α, and the approach values calculated from the Ingold value for θ, is meaningless and cannot lend support to any theory. Short (*loc.cit.*) has in fact shown by calculation that the approach values calculated from the Baeyer value of θ are in as good functional agreement with the thermal values as those calculated from Ingold's value of θ.

The discussion has here been confined to uniplanar rings. Ruzicka and his collaborators have shown (*Helv. Chim. Acta*, 1926, 9, 230, 249, and subsequent papers) that polymethylene rings containing a large number of carbon atoms can be formed, strain being relieved by the rings ceasing to be uniplanar. We hope to investigate the general conditions under which the approach value for a multiplanar ring can become zero. This involves complete removal of strain.

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