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THE CONFORMATION OF SIX-MEMBERED RINGS INVOLVING A PLANAR GROUP

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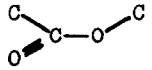
It is of interest to consider the restraints imposed on the stable conformation of a six-membered ring by the presence of a planar group forming part of the ring and how the specific dimensions of the planar group may determine the conformational selection.

The principal groups for which evidence is available are the carbon-carbon double bond and the lactone group  for which we have recently presented evidence[1,2,3] that its characteristic shape is planar. Closely allied to the lactone group in shape and disposition is the amide (peptide) group and conclusions regarding one may be considered to apply to the other.

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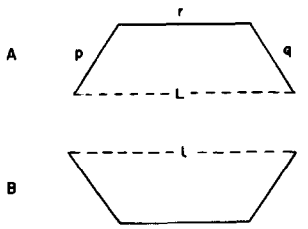
[1] J. Fridrichsons and A. McL. Mathieson, Acta Cryst., 15, 119 (1962).

[2] A. McL. Mathieson and J. C. Taylor, Tetrahedron Letters, No. 17, 590 (1961).

[3] J. F. McConnell, A. McL. Mathieson and B. P. Schoenborn, Tetrahedron Letters, No. 10, 445 (1962).

A planar constraint on four atoms of a six-membered ring can lead to either a boat or a half-chair conformation. Evidence of sufficient detail regarding conformation is only available in a few cases but, within these limits, the pattern is consistent. Where the carbon-carbon double bond occurs, as in lanostenol[4] (two examples) and thelepogine,[5] the conformation in each case is the half-chair. On the other hand, where the lactone group is concerned,[2,3,6] the conformation is invariably boat. In the recent analysis of sporidesmin,[7] which contained two planar amide groups, again the boat conformation occurred.

From this limited but consistent selection, one may consider how the dimensional shape of the groups concerned may determine the conformation achieved. A six-membered ring may be decomposed into two groups A and B each of four atoms, the terminal atoms of each group being common, Fig. 1. The planar group B is defined by its dimensions whereas the group A by its flexibility has an extra degree of freedom through the variation



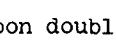
[4] J. Fridrichsons and A. McL. Mathieson, J. Chem. Soc. 2159 (1953).

[5] J. Fridrichsons and A. McL. Mathieson, Tetrahedron Letters, No. 26, 18 (1960).

[6] M. MacKay and A. McL. Mathieson, unpublished data.

[7] J. Fridrichsons and A. McL. Mathieson, Tetrahedron Letters, in press.

of the dihedral angle between bonds p and q around r. With this extra degree of freedom, group A can adjust to accommodate itself to the constraint of group B. Even allowing for the mutual adjustment of the two groups, group A is potentially more flexible.

In the case of the lactone group, the distance ℓ is smaller than the relaxed distance L and the group A is modified accordingly. This we have shown previously in the analysis of the bromdilactone from jacobine where the exo-ring bonds α and β are deflected in the direction corresponding to the constraint (see Fig. 1 of ref. (2)). To maintain L at the value permitted by linkage to the lactone group, the dihedral angle between p and q is minimized, i.e. the four atoms of group A are held in a plane and the conformation of the six-membered ring in such a case is therefore the boat. On the other hand, when group B involves a carbon-carbon double bond  then ℓ is larger than in the case of the lactone group, according to the exact dimensional data of Dowling and Stoichieff for ethylene[8] and this increase in ℓ can be accommodated by an increase in L permitted by the adjustment of the dihedral angle between p and q. The resultant conformation is therefore the half-chair.[9]

Although the present proposal is based on somewhat limited data, it may provide some guidance in dealing with structures

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[8] J. M. Dowling and B. P. Stoichieff, Canadian J. Physics, 37, 703 (1959).

[9] A demonstration of the dimensional difference between the boat and half-chair conformation may be made with a Dreiding model of a six-membered ring with a planar group. For the boat configuration, the "para" distance is about 2.7 Å while, for the half-chair, it is about 3.0 Å in accord with the conclusions above.

involving planar groups, in particular lactone groups which occur frequently in many natural products, e.g. (10).

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10 Abstracts, 2nd International Symposium on Natural Products, Prague (1962).