Conformation of 1,4,7-Trioxacyclononane

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Summary ^{13}C n.m.r. and i.r. spectroscopy show that 1,4,7-trioxacyclononane has in solution and in the solid an unsymmetrical [234] conformation.

THE most stable conformation of cyclononane, predicted from strain-energy calculations[1–3] and established experimentally in solution by n.m.r. spectroscopy,[4] has D_3-

symmetry; it is here designated as [333] to indicate three "sides" each having three bonds.[3] Also 4,4,7,7-tetramethylcyclononanone and derived compounds,[5] as well as trimeric acetone peroxide,[6] which are all biased by *gem*-dimethyl substitution, take the same conformation. On the other hand, simple derivatives like cyclononylammonium bromide[7] and cyclononanone,$HgCl_2$[8] crystallise in the [12222] conformation,[3] possibly because of packing forces in these dominantly inorganic crystal lattices. A third conformation, [234], having no symmetry, is calculated to be of intermediate energy.[3]

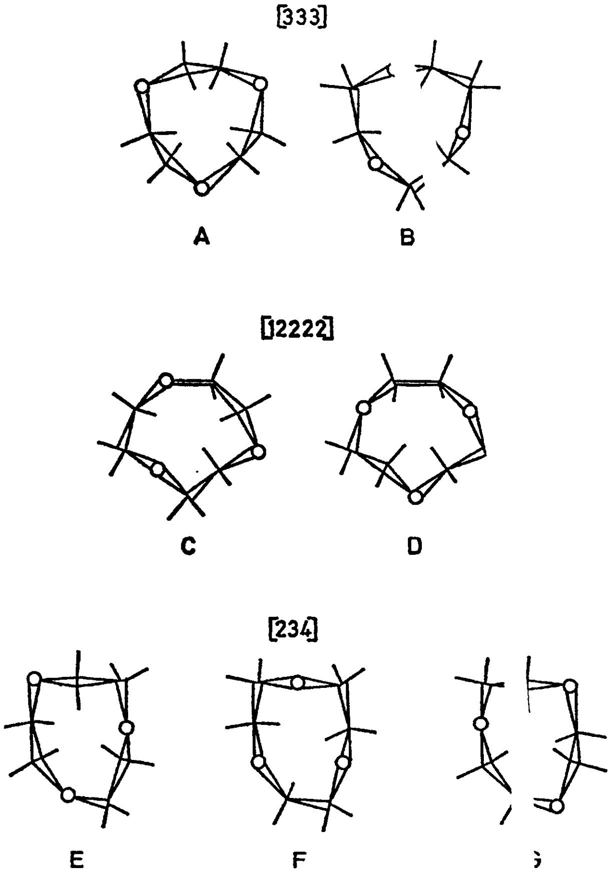

FIGURE. The possible conformations of 1,4,7-trioxac lononane.

For 1,4,7-trioxacyclononane, m.p. 0°, recently s nthesized in one step from ethylene oxide,[9] there are altc ther two possible [333] conformations (A and B, Fi re), two [12222] conformations (C and D), and three 34] conformations (E, F and G). We now present ev ence that the exclusive conformation in solution and in the olid lacks symmetry, hence is not A, B, or D and that the ost likely conformation is F.

The i.r. spectrum is identical in solution (35°) and in the solid (−70°), and, in contrast with the higher cyclic oligomers of ethylene oxide,[10,11] all i.r. bands are equally sharp in solution as in the crystal. We therefore conclude that only one conformer is present and that it is near a deep conformational minimum. The presence of three strong bands (835, 885, 910 cm^{-1}) and four weaker bands (805, 820, 860, 900 cm^{-1}) in a region where just two bands occur whenever all monomer units are identical,[10,11] shows that the molecule contains more than one type of CH_2CH_2 unit, whereby conformations A and B can already be ruled out.

The ^1H n.m.r. spectrum at 251 MHz is temperature dependent. The single line (at 4·05 p.p.m. from Me_4Si in $CHCl_2F$ at −60°) splits on further cooling into a broad, complicated, unsymmetrical pattern which could not be analysed, but the spectral changes show that more than one process is involved. The ^{13}C spectrum at 63·1 MHz, on the other hand, clearly revealed two processes; the single line (at 73·3 p.p.m. in $CHFCl_2$) broadens on cooling and starts to develop two broad lines, intensity 2 : 4 ($T_c = -94°$; $\Delta G^‡ = 7{\cdot}9$ kcal/mol), but before these become sharp (three lines are to be expected; the high-field resonance consists of two unresolved lines) a further splitting starts ($T_c = -112°$; $\Delta G^‡ = 7{\cdot}3$ kcal/mol), so that the low-temperature spectrum contains five lines, intensity 1 : 1 : 1 : 2 : 1. These must represent six different carbon atoms. Not only conformations A and B, but also D, are thereby ruled out.

To decide between the four unsymmetrical conformations, which all satisfy the final low-temperature spectrum, it is necessary to consider which of them can, by conformational site-exchange processes, have the six different carbon atoms averaged pair-wise over some barrier which has to be lower than the critical barrier on any path leading to averaging of all carbons. Adopting the conformational interconversion paths and relative barrier values calculated for cyclononane,[12] it can be shown that the [12222] conformation C is excluded since any interconversion must go through a [234] intermediate, E or F, from which it is separated by a [*1*224] barrier[12] which is higher than any subsequent barrier leading to full exchange. Similarly, there is no process which can average any pair of carbons in conformation E without averaging all carbons. Conformation G can achieve partial averaging by passing twice over a [*1*224] barrier to an equivalent conformation, whereby the symmetry of the intermediate D is acquired, but the [*1*233] barrier separating G from A is expected to be lower, and a single passage over it would make all carbons identical. Finally,conformation F can obtain partial exchange by passing over the lowest calculated barrier, [*1*323] or "boat-chair",[1] to its mirror image and acquire the symmetry of the barrier with three pairs of carbon atoms, while it has to pass over higher [*1*233] barriers *via* B to A to obtain full exchange of all carbon atoms. Thus, if the relative magnitude of the calculated barriers is significant, conformation F is more likely than G.

The low observed dipole moment in benzene solution, 1·55 *D*, is on the other hand in better agreement with conformation G, since F has roughly parallel ether dipoles. However, in the case of the higher cyclic oligomers of ethylene oxide,[10,11] the dipole moment was in conflict with other evidence and had to be disregarded, so we hesitate to base any conclusion on it in the present case of the trimer, even if there is no indication in the i.r. spectrum of a particularly loose molecule, as observed for the higher homologues.[10,11]

We conclude that the conformation of 1,4,7-trioxacyclononane is either F or G, but we favour F on the basis of the general *gauche*-preference for the CC-bond and *anti*-preference for the CO-bond observed for polyethyleneglycol[10] and because of its similarity with the conformation of 1,4,7,10-tetraoxacyclododecane.[11]

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