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THE GEOMETRIES OF PENTAPRISMANE AND HEXAPRISMANE
INSIGHTS FROM MOLECULAR MECHANICS

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Abstract: Molecular mechanics calculations (MM2) have been carried out on pentaprismane and hexaprismane. The results are rationalized and compared to what is known experimentally.

Molecular mechanics calculations are being used increasingly to predict and understand molecular structures.[1,2] In the present work, using the MM2 force field,[3,4] we consider the title compounds and compare the calculated structures with what is known experimentally.

Carbon-carbon single bond lengths are roughly constant in typical organic molecules (averaging 1.534 Å), although there are some conspicuous exceptions. The bond lengths in 5-membered rings are longer (cyclopentane, 1.546 Å)[5] and longer still in 4-membered rings (cyclobutane, 1.549 Å).[6] Why so? One explanation is that as the ring angle gets smaller, the amount of p-character in the endocyclic bonds increases. Accordingly, these bonds are weaker and lengthen.[7] An alternative physical rationale can be put in terms of van der Waal's repulsions. The two carbons bound to a common carbon in a small ring are rather closer together than they would be in an open chain.[5] If van der Waal's repulsion occurs between them, and they cannot move apart by angle bending because of the geometric constraints of the ring, then the bonds stretch to diminish the repulsion. In MM2 (a valence force field), this effect is brought into play by a stretch-bend interaction term.[3] The sign of the stretch-bend interaction constant is such that if a C-C-C angle is pinched, the C-C bonds stretch. Conversely, if the angle is opened, the bond lengths shrink. Working against this is the C-C-H stretch-bend interaction; it is smaller than that for C-C-C.

We consider first cyclobutane. The C-C-C angle is approximately 90°. The stretch-bend interaction constants were chosen to fit the experimental fact of long C-C bonds in 4-membered rings.[3] With these set, we can look at cubane (1). There are two 90° angles at each end of each bond. These bring about a large stretch-bend interaction of the C-C-C variety. Without any stretch-bend interaction the bond length is calculated to be only 1.529 Å. When the C-C-C stretch-bend interaction is added, the length is calculated to be 1.571 Å; inclusion of the C-C-H interaction brings it back to 1.557 Å. The experimental values are 1.549(3) and 1.553(3) Å (the molecule is slightly deformed from O_h symmetry in the crystal).[8] The C-C-C stretch-bend term wins out over the

C-C-H term, partly because of the larger constant, and partly because the deformation of the C-C-C angle is larger (19.5°) than the deformation in the C-C-H angle (15.8°).

Now we come to the interesting case of pentaprismane (2). There are two different kinds of bonds in this molecule; those within a 5-membered ring (and also a 4-membered ring) and those between the 5-membered rings. The MM2 calculated lengths are 1.540 Å for the bond within the 5-membered rings ("short") and 1.566 Å for the bond between the 5-membered rings ("long"). Engel et al. have reported recently the X-ray crystallographic structure for pentaprismane carboxylic acid.[9,10] They found that the 4- and 5-membered rings therein are flat, that the C-C-C internuclear angles are those of the geometric pentaprism, 90° and 108°, and that there is a very significant difference in length between the two kinds of pentaprismane C-C bonds (ignoring the perturbation of the carboxyl substituent). As in our calculation, the bonds within the 5-membered rings are shorter (mean 1.548(8) Å) than those between the 5-membered rings (mean 1.565(4) Å). Interestingly, these values bracket the average C-C bond length of 1.551 Å in cubane (tetraprismane), a close relative.

The "short bond" in pentaprismane has one C-C-C bond angle of 90° at each end and another of 108°. The latter does not contribute much to bond stretching, and so we expect to calculate a bond length similar to that in cyclobutane. This is approximately the case. The calculated bond length is 1.540 Å, versus 1.548 Å in cyclobutane. If the stretch-bend interactions were deleted totally, the value would be 1.529 Å. Adding the C-C-C stretch-bend interaction causes this bond length to stretch to 1.550 Å, while adding the C-C-H interaction brings the value back to 1.540 Å.

The "long" bond in pentaprismane is more like that in cubane. There are two 90° angles at each end of the bond. If the stretch-bend interactions were set to zero, this bond length would be 1.530 Å. Adding the C-C-C stretch-bend interactions stretches it out to 1.572 Å, similar to the effect of the same term in cubane. But in pentaprismane the C-C-H interaction does not bring the bond length back down as far as it does in cubane. The relevant pentaprismane C-C-H angle deviates from the tetrahedral angle by much less (7.1°) than it does in cubane (15.8°).

The C-C-H angle in cubane is 125.3°. The calculated C-C-H bond angles in pentaprismane are 116.6° for carbons between the 5-membered rings and 121.7° for carbons within a 5-membered ring. Why is the smaller angle as small as it is? The calculated distance between the hydrogens on pentaprismane shown in Fig.1 is 2.57 Å; the repulsion energy is 0.11 kcal/mol. If the 116.6° angle were opened, the distance would increase, and the repulsion would be reduced, but, working strongly against this, the concomitant reduction of the 121.7° angle would bring all of the hydrogens closer together on the faces of the 5-membered rings. This would lead to a net increase in repulsion energy. Note that there are twice as many hydrogen-hydrogen interactions on the 5-membered ring faces as between the 5-membered rings. Although this rationalizes the situation, the calculated C-C-H angles and the X-ray results are not in good agreement (found: 121(1)° and 119(1)°).[10] This point must be addressed further.

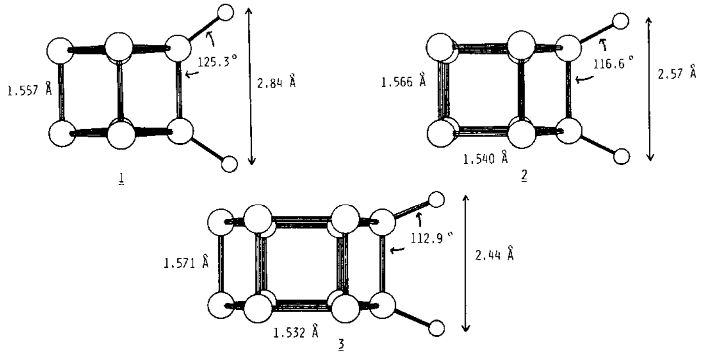

Fig. 1 Some MM2 parameters for cubane (1), pentaprismane (2) and hexaprismane (3)

Next we consider hexaprismane (3). No compound with this carbon skeleton has yet been reported, but work directed to this goal is in progress.[11] The MM2 structure is offered here as a prediction. MM2 calculations indicate that the molecule has D_{6h} symmetry. When the 6-membered rings are distorted to either boat or chair conformations, they return to planarity upon energy minimization. The C-C bonds between the 6-membered rings should be even longer (1.571 Å) than those between the 5-membered rings of pentaprismane, mainly because of the reduced stretch-bend interaction of the C-C-H bonds at the calculated 112.9° angle. Opening this angle would reduce the repulsion between the hydrogens drawn but this would be countered by increased H···H interactions on each of the 6-membered ring faces. The bonds within the 6-membered rings are calculated to be quite short (1.532 Å) because with the C-C-C angle at 120° in the flat 6-membered rings (larger than the tetrahedral angle) the C-C-C stretch-bend interaction acts to shrink the bond length.

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