Boat *versus* Half-chair Cyclohexyl Rings: Determinants of Conformational Preference

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Bond angles and torsional constraints can lead to a preference for boat conformations over the half-chair expected for cyclohexene-like rings.

The doctrine of six-membered ring conformational preference, chair cyclohexane[1-3] and half-chair cyclohexene,[4] is founded on extensive experimental and theoretical evidence; the chair conformation of cyclohexane is favoured over the alternative twist-boat conformation by 23 kJ mol^{-1} (5.5 kcal mol^{-1}) and the half-chair conformation of cyclohexene is favoured over the boat by 28 kJ mol^{-1} (6.6 kcal mol^{-1}) (Fig. 1). Recent *ab initio* and MM3 calculations accurately reproduce these values.[5] As a centrepiece of the organic chemistry paradigm, the dominating chair conformation for six-membered rings has been a useful analogy in defining the transition states for [3,3] pericyclic reactions[6] and for predicting products derived *via* six-membered transition states.[7] Despite the overwhelming preference for chair and half-chair however, boat cyclohexanes and cyclohexenes have been observed in crystal structures and boat transition states have been proposed for some reactions.[8] We report here a molecular mechanics and crystal structure investigation that correlates specific bond angles with stable boat conformations.

We were initially intrigued by a crystal structure containing a boat cyclohexane ring (Fig. 2).[9] A cyclohexene-like half-chair conformation had been anticipated for this ring as the carbons labelled C(6)–C(1)–C(2)–C(3) are held planar by the fused $[4.2.2^{1,4}.2^{2,5}]$ system. Calculations with MM3*[10] found the boat conformation of this ring to be nearly 25 kJ mol^{-1} (5.9 kcal mol^{-1}) *lower* in energy than the half-chair, the reverse of the situation for cyclohexene, and we suggested that the preference for boat might be due to the sp^3 bond angles of 109 and 112° in **1** rather than the 120° found in cyclohexene.

Additional MM3* calculations have been carried out on boat and half-chair conformations using tricyclodecane **2**.

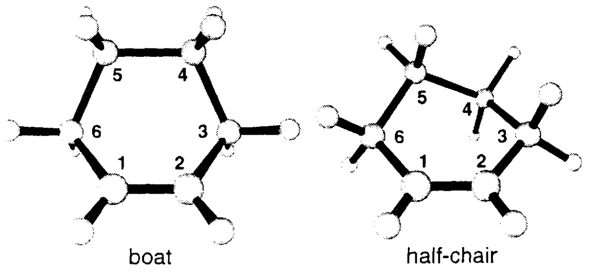
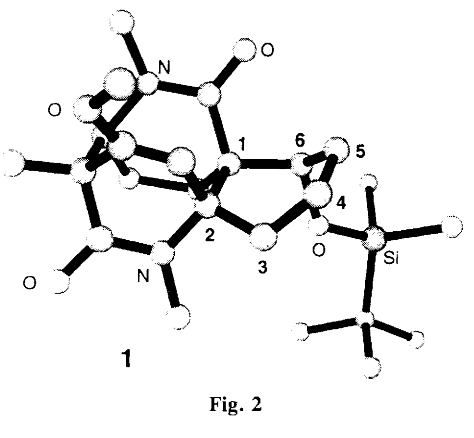


Fig. 1



1

Fig. 2

Structure **2** was chosen for several reasons: the [2.2.0] ring system enforces near planarity on four carbons of the cyclohexane ring, the half-chair and the boat conformations are stable minima (the boat higher in energy by 6.7 kJ mol^{-1}) and the system has more flexibility than cyclohexene. The distance between C(3) and C(6) in **2** was systematically varied by application of a force constant between these atoms and minimization of the structures. Starting from the two conformational minima, moving the C(3) and C(6) atoms closer together or farther apart raises the energy. Fig. 3 shows this effect as a function of the bond angles C(6)–C(1)–C(2) and C(1)–C(2)–C(3). The average value for these bond angles in the lowest energy half-chair is 117.5° and in the boat is 114°. As the bond angles approach 115° the two conformations become equal in energy. That the boat conformation is the more stable below 115° makes sense, as shorter distances between C(3) and C(6) are best accommodated by the small C(3)–C(4)–C(5)–C(6) dihedral angle found in the boat.

To further explore the relationship between conformation and bond angles we searched the Cambridge Structural Database[11] for boat and half-chair structures. Only six-membered carbocycles with a C(6)–C(1)–C(2)–C(3) dihedral angle (Fig. 1) less than 30° were considered. No other constraints were placed on C(1) and C(2). Carbons C(3), C(4), C(5) and C(6) were required to be tetravalent and without ring fusions. Monosubstituted cyclohexanes that were part of much larger structures and cyclohexane solvent molecules were rejected, leaving a total of 264 structures. Elimination of disordered structures and those with *R* values above 0.09 brought the number of structures to 186. Finally, structures with the C(1)–C(2)–C(3)–C(4) dihedral angle below 10° were discarded to remove anomalously flat rings.† Data for the final set of 155 structures are shown in Fig. 4 which relates the sum of the bond angles C(6)–C(1)–C(2) and C(1)–C(2)–C(3) and the dihedral angle C(3)–C(4)–C(5)–C(6). For boat cyclohexene this dihedral angle is close to 0° while in the half-chair it is close to 60°. Considering all of the structures, 89% fall within the two boxes with 34% of the data identifying boat‡ structures and 56% half-chairs. Constraining the C(6)–C(1)–C(2)–C(3)

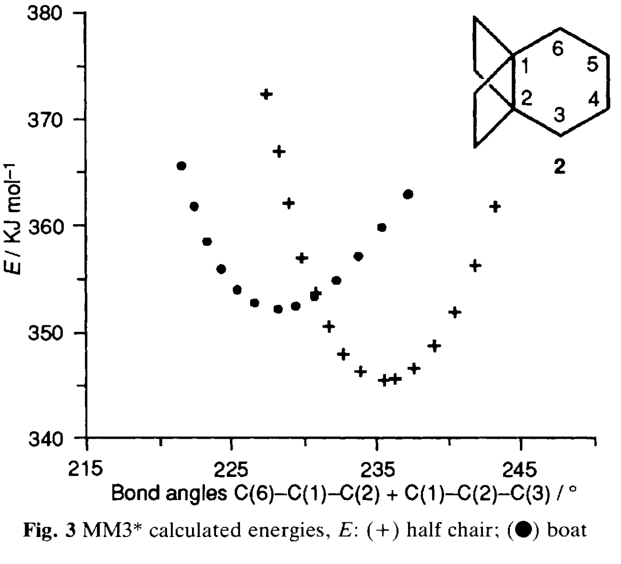


Fig. 3 MM3* calculated energies, *E*: (+) half chair; (●) boat

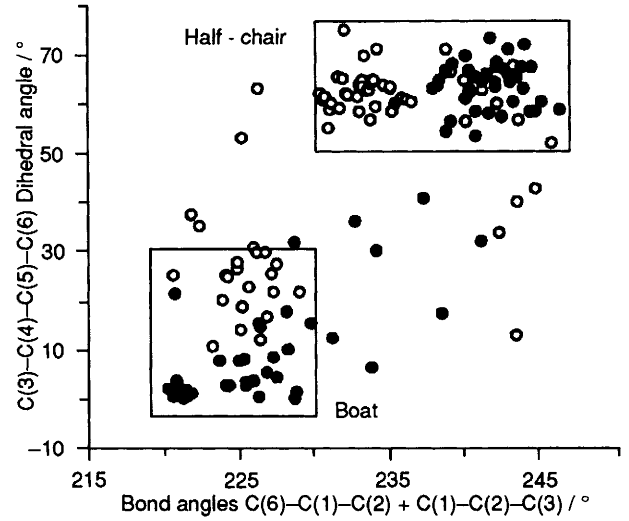


Fig. 4 Data from Cambridge Structural Database for C(6)–C(1)–C(2)–C(3) dihedral angle less than 30° (all circles) and less than 10° (solid circles).

dihedral angle to less than 10° (filled circles) lessens the number of data points to 79, with 89% of these structures within the boxed regions, and the boat and half-chair conformations comprising 40% and 49% of the data points, respectively. Interestingly, by narrowing the range of the C(6)–C(1)–C(2)–C(3) dihedral angle the clusters fall into smaller regions, particularly for the half-chair, indicating that the two conformations have well defined geometries.

Comparing Figs. 3 and 4 one finds the same critical bond angle of 115°. When the C(1)–C(2)–C(3) and the C(6)–C(1)–C(2) bond angles average less than 115° (*e.g.* both are sp^3) a boat conformation is preferred and above this value (both are sp^2) half-chair is preferred. With one sp^2 and one sp^3 centre, the average of the standard bond angles (114.8°) is very close to the 115° mark and small structural changes may tip the balance toward either structure. The calculated structure for half-chair cyclohexene falls nicely within the half-chair region and the cyclohexane ring of **1** lands well within the boat region.

Boat conformations are therefore not merely transition states between lower energy conformers but can be the preferred conformation for a six-membered ring, in spite of the overwhelming preference for the chair and half-chair conformations in cyclohexane and cyclohexene. For partially flattened cyclohexene-like structures, the choice of half-chair or boat conformation appears to be determined by the internal bond angles of the central atoms of the planar portion of the ring.

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Footnotes

† This dihedral angle would be much larger than 10° in the structures being considered: half-chair cyclohexene (63°), boat cyclohexene (45°), twist-boat (30°).

‡ This analysis groups boat and twist-boat conformations together.

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