A Non-empirical LCGO-MO-SCF Study of the Boat and Chair Conformers of Cyclohexane and Cyclotriborazane

By Robert H. Findlay

(*Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, Cathedral Street, Glasgow G1 1XL*)

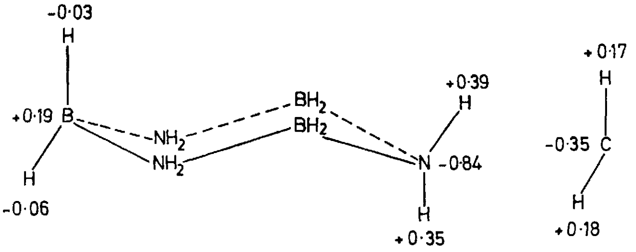
Summary Minimal basis set calculations predict that cyclotriborazane could exist as the boat form in the gas phase with electrostatic attraction being a contributing factor.

Recently, the structure of cyclotriborazane, $B_3N_3H_{12}$, has been determined by X-ray crystallography.[1] This molecule is of interest because of its analogy with cyclohexane, and we now report the results of a non-empirical LCAO-MO-SCF study of the chair and boat forms of cyclohexane and cyclotriborazane.

Table

	Cyclohexane		Cyclotriborazane	
	Chair	Boat	Chair	Boat
Total energy/a.u.	−233·321902	−233·307406	−243·386314	−243·394374
Nuclear repulsion energy/a.u.	257·219817	258·344115	255·508875	256·455709
μ/debye	—	0·005	6·01	1·96
E(chair) − E(boat)/kJ mol^{-1}	−38·1		+21·2	

The atomic orbitals were formed by taking linear combinations of Gaussian functions with boron, carbon, and nitrogen being represented by seven s-type and three p-type functions[2] and hydrogen by four s-type.[3] Cyclohexane was studied at the experimental geometry determined by electron diffraction;[4] the C_s symmetry found for cyclotriborazane was slightly adjusted to C_{3v} symmetry. Boat conformations retained the bond lengths of the chair forms and were obtained by reflection in an appropriate four-atom plane. This results in boat forms intermediate between two equivalent skew boat conformations.



Figure

The total energies in the Table predict that cyclohexane exists in the chair conformation, in agreement with the electron diffraction study[4] and the results of Hoyland.[5] Experimentally[6] the chair form has been estimated to be 20·0—24·7 kJ mol^{-1} more stable than the boat form. This is less than that found in the present work, although the difference can be largely attributed to the skew boat form being more stable than that considered here. Thus, in cyclohexane the calculations reasonably reflect the experimental data. In contrast, the preferred structure for cyclotriborazane is predicted to be the boat conformation. While this disagrees with the structure found by X-ray methods, it must be remembered that the calculations refer to an isolated molecule, best represented by the gaseous state. It must also be considered possible that the overestimate of the calculated energy differences in cyclohexane is an intrinsic feature of the calculations and not attributable to boat–skew boat energy differences; the boat form of cyclotriborazane would then become only 3—7 kJ mol^{-1} more stable than the chair. This would be insufficiently large to give an accurate prediction of conformational preferences. We do not feel that such an assumption is valid and therefore suggest that the gas-phase structure of cyclotriborazane will prove to be the boat conformation.

The dipole moment of the boat conformer is in better agreement with the experimental value[7] of 3·2D obtained in p-dioxan solution, indicating that the boat form could also exist in solution. However, as the accuracy is much less than that found previously,[8] this interpretation must be viewed with caution and another possibility considered, namely, that solvent-solute interactions occur in such a way as to alter the dipole moment. In oxygen-containing solvents such as p-dioxan, intermolecular $N \cdots H \cdots O$ bonding will occur, giving rise to structural changes likely to be most marked in the NH_2 regions. This will then lead to a change in the dipole moment, owing to movements of the centres of gravity of both nuclear and electronic charges. Thus, in view of the unusually high difference between calculated and experimental dipole moments, we feel that the solution-phase data apply to a molecular structure differing from those considered here.

The charge distribution obtained by the Mulliken procedure[9] (Figure) indicates that electrostatic interactions are likely to contribute heavily in deciding the conformational preference. Generation of the boat form brings the non-bonded atoms closer in both systems, shown by the increase in nuclear repulsion energy (Table). In the case of cyclotriborazane, the BH_2 and NH_2 groups are oppositely charged, stabilising the boat form by an increase in electrostatic attraction. For cyclohexane, symmetry requires a neutral CH_2 group in the chair conformation. The slightly positive charges in the boat conformation result in an increased electrostatic repulsion, destabilising the chair conformation.

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