1-Aza-4-boratricyclo[2.2.2.$0^{1,4}$]octane and 1-Aza-4-borabicyclo[2.2.2]octane: Stable Bond-stretch Isomers? An *ab initio* Study

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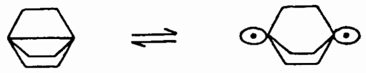
Summary *Ab initio* molecular orbital theory is used to demonstrate bond-stretch isomerism in the 1-aza-4-boratricyclo[2.2.2.$0^{1,4}$]octane–1-aza-4-borabicyclo[2.2.2]-octane system; the effect of solvent and substituents on the bond-stretch equilibrium is discussed.

Recent theoretical calculations on the [2.2.2]propellanes (**1**) and (**2**), and related systems, have revealed a novel type of isomerism in which the two isomers are related by a simple bond stretching, *i.e.* (**1**) ⇌ (**1a**) and (**2**) ⇌ (**2a**).[1] Such bond-stretch isomers are generally described by different electronic configurations, the result of interplay between through-space and through-bond interactions.[2] Unfortunately experimental observation of bond-stretch isomerism in the propellanes, (**1**) and (**2**), is thwarted by the extreme ease with which the isomers (**1a**) and (**2a**) undergo a 'symmetry-favoured' Grob-type fragmentation.[3]


(1) (1a)

(2) (2a)

(3) (3a)

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We believe, on the other hand, that the azaborabicyclo-[2.2.2]octane (ABBO) (**3a**) should be more resilient to this type of fragmentation§ and that the azaboratricyclo-[2.2.2.0^{1,4}]octane (ABTO) (**3**)–ABBO (**3a**) system therefore offers a much better prospect for the experimental observation of bond-stretch isomers. We report herein results of *ab initio* molecular orbital calculations[4] which appear to confirm our expectations.

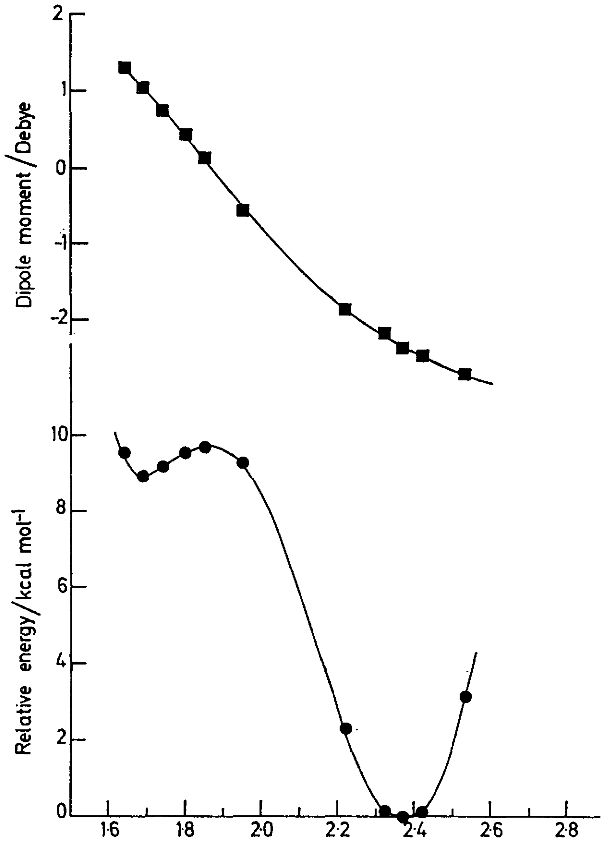


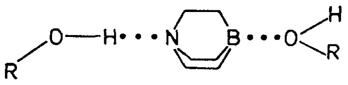
FIGURE. Variation in calculated energy and dipole moment accompanying bond-stretching in the ABTO–ABBO system.

We have calculated the energy of the ABTO–ABBO system as a function of the interbridgehead distance *R*.¶ The resulting potential energy curve is shown in the Figure along with the variation in the calculated dipole moment.

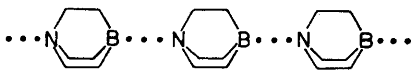
There are two potential minima although the one which corresponds to the ABTO structure (**3**) is very shallow. The barriers to stretching and contraction are *ca.* 1 and 9 kcal mol^{-1}, respectively. These results are very encouraging but, because of approximations in our treatment associated with the use of a single determinant wave function and a small basis set, should be taken as indicative rather than definitive. More sophisticated calculations are clearly desirable and we can only speculate here on their effects. Inclusion of polarisation functions in the basis has previously been found[5] to favour preferentially cyclic over acyclic molecules and could therefore be expected to stabilize the inner minimum more than the outer one and hence to reinforce the bond-stretch isomerism. Results of configuration interaction calculations at the INDO level[6] suggest that electron correlation does not strongly influence the ABTO–ABBO equilibrium. We should stress in addition that our calculations refer to isolated vibrationless molecules in the gas phase at 0 K. Population of the ground and higher vibrational levels will facilitate interconversion of the isomers at ordinary temperatures.

Although the ABTO–ABBO system lacks the symmetry which would strictly permit the classification of the B–N orbitals as *S* (**4**) and *A* (**4a**), it is convenient for descriptive purposes to think qualitatively in these terms. We find that there is an intended but avoided crossing between the B–N HOMO and LUMO and, at *R ca.* 2·05 Å, the topology of the HOMO changes from pseudo-*S* ($R < 2{\cdot}05$ Å, through-space domination) to pseudo-*A* ($R > 2{\cdot}05$ Å, through-bond domination). This change is strikingly reflected in a reversal in direction of the dipole moment (Figure) from $N^{\delta+}$–$B^{\delta-}$ ($R < 2{\cdot}05$ Å) through zero (*R ca.* 2·05 Å) to $N^{\delta-}$–$B^{\delta+}$ ($R > 2{\cdot}05$ Å).

(4) (4a)



(5)



(6)

Whereas ABTO and ABBO are strongly polar species, the transition state which separates them is essentially non-polar. The observation of bond-stretch isomers will therefore be sensitive to choice of solvent. In particular, dipolar aprotic solvents which will stabilize ABTO with respect to ABBO and both isomers with respect to the transition state offer the best conditions for observing the ABTO isomer (**3**).

Application of simple PMO arguments[6] leads to the prediction that both hydrogen-bonding solvents (*e.g.* alcohols) and nucleophilic solvents (*e.g.* amines, ethers) stabilize ABBO with respect to ABTO. Therefore solvents which are capable of acting both as electron donors and as hydrogen-bonding agents will be particularly effective in stabilizing ABBO. Alcohols belong in this category, (**5**). Because ABBO itself has both donor and acceptor sites, the formation of linear molecular complexes of the type (**6**) will compete with intramolecular association (**3**) in sufficiently concentrated solutions.

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§ The fragmentation product, 1,4-bismethyleneperhydro-1,4-borazine, will be formed with difficulty on account of its zwitterionic character and because it contains a carbanionic centre.

¶ C_{3v} symmetry was maintained throughout and the C–N and B–C bond lengths were set equal to 1·49 and 1·57 Å respectively.[6]

Finally we note that the instability of ABTO compared with ABBO may be attributed to weak through-space interaction between the B and N orbitals which is not strong enough to compensate satisfactorily for the additional ring strain. The through-space interaction [and hence the stability of (**3**)] can be increased by narrowing the energy gap between the $2p$ atomic orbitals on boron and nitrogen. This may be achieved by a substitution pattern in which electron-withdrawing groups (*e.g.* CN, F) are attached to positions 3, 5, and 8 (thus stabilizing the boron orbital) and electron-releasing groups (*e.g.* Me) attached to positions 2, 6, and 7 (thus destabilizing the nitrogen orbital).

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[6] A. R. Gregory, M. N. Paddon-Row, L. Radom, and W.-D. Stohrer, to be published.