Geometric and Electronic Structures of Cyclohexane and Cyclotriborazane, $(BH_2NH_2)_3$

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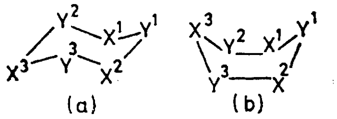
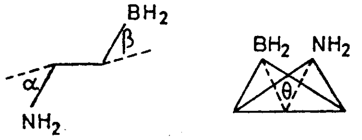
Non-empirical minimal-basis-set calculations of the geometric and electronic structures of cyclohexane and cyclotriborazane predict that the latter is likely to adopt an eclipsed boat conformation in the gas phase, and is also thermodynamically unstable with respect to disproportionation. Changes in ionisation potential and orbital nature are discussed in terms of the relative atomic orbital energies. Several open-shell calculations have been made, giving improved agreement with experimental ionisation energies, while the associated electronic relaxation energies are considered in the context of the $\langle r^2 \rangle$ expectation value.

THE boron–nitrogen analogue of benzene has been the subject of many theoretical studies;[1] experimentally it is the best characterised of the $(BHNH)_m$ series. The 'hydrogenated' derivatives, of general formula $(BH_2NH_2)_n$, have been known for a considerable length of time,[2] but only recently have they been obtained as pure substances[3] from mixtures containing molecules of various n values. One of the most interesting of these is cyclotriborazane ($n = 3$) whose crystal structure has recently been determined.[4] In this paper non-empirical LCGO-MO-SCF calculations of the electronic structure of this molecule are reported and of its organic analogue, cyclohexane.



(I) $X = NH_2$, $Y = BH_2$

(II) $X = Y = CH_2$



Minimal basis sets were used for all atoms with boron, carbon, and nitrogen being represented by 7s and 3p Gaussian-type functions,[5] while hydrogen was represented by 4s functions.[6] All exponents were optimised on atomic calculations thus giving a 'best-atom' basis. The resulting 42 atomic orbitals were used to obtain the ground-state electronic structure of cyclotriborazane (ctb, I) and cyclohexane (chex, II) in a variety of geometric configurations. These were based on the experimental geometries,[4,7] with the C_s symmetry found for ctb in the X-ray crystallographic study slightly adjusted to generate a molecule of C_{3v} symmetry. The electronic structures of some cationic species derived by removal of an electron from ctb and chex are also considered.

RESULTS AND DISCUSSION

Molecular Geometries and Conformations.—Preliminary investigation[8] of the boat and chair conformers of ctb indicated that the boat form was likely to be the preferred geometry, unlike the situation found for chex.[8,9] Accordingly, a limited optimisation of the ctb geometry was undertaken, based on the X-ray crystallographic structure, varying only those parameters shown in (I). For the chair conformation, angles α and β correspond to rotation of the NH_2 group about the B–B axis [Y^2–Y^3 in (Ia)] and of the BH_2 group about the N–N axis [X^1–X^2 in (Ia)] respectively, with $\alpha = \beta = 0$ giving the crystallographic structure; in this manner bond lengths were retained. Ring flattening and clockwise rotation are simultaneously implied by positive values of α and β. The boat conformations, (Ib) and (IIb), were generated by reflection in the four-atom plane $X^1X^2Y^2Y^3$ thereby again maintaining bond lengths. The skew-boat conformations ($\theta \neq 0$) were then obtained by rotation about the axis connecting the mid-points of the Y^2–Y^3 and X^1–X^2 axis in (Ib). However, in this case

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[1] D. R. Armstrong and D. T. Clark, *Chem. Comm.*, 1970, **99**; *Theor. Chim. Acta*, 1972, **24**, 307.

[2] H. I. Schlessinger, D. M. Ritter, and A. B. Burg, *J. Amer. Chem. Soc.*, 1968, **90**, 2297; G. W. Schaeffer and L. J. Basile, *ibid.*, 1955, **77**, 331; A. K. Holliday and N. R. Thompson, *J. Chem. Soc.*, 1960, **2695**.

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[4] P. W. R. Carfield and S. G. Shore, *J. Amer. Chem. Soc.*, 1973, **95**, 1480.

[5] B. Roos and P. Siegbahn, *Theor. Chim. Acta*, 1970, **17**, 209.

[6] S. Huzinaga, *J. Chem. Phys.*, 1965, **42**, 1293.

[7] M. Davis and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181; H. R. Buys and H. J. Geise, *Tetrahedron Letters*, 1970, **34**, 2991.

[8] R. H. Findlay, *J.C.S. Chem. Comm.*, 1975, 98.

[9] J. R. Hoyland, *J. Chem. Phys.*, 1969, **50**, 2775

it was necessary to move the $Y^2X^3Y^3$ group towards the $X^1Y^1X^2$ group in order that the Y^2–X^1 and Y^3–X^2 lengths should be the same as in the remaining molecules.

Cyclohexane is first considered. The total energy of the chair conformation (−233.3219 a.u.) is considerably better than that obtained by Preuss and Janoschek[10] (−229.6239 a.u.) or by Hoyland[9] (−232.9106 a.u.). The binding energy, *i.e.* the difference between the molecular energy and the sum of the atom energies, is estimated to be −1.6676 a.u., *ca.* 62% of the experimental value,[11] a figure typical of minimal-basis-set calculations.[12] The boat conformation is predicted to be less stable (by 38.1 kJ mol^{-1}) than the chair conformation, in agreement with the electron-diffraction study[7] and the work of Hoyland.[9] Experimentally[13] 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. In view of the close similarity between the chair and boat energy differences obtained by Hoyland and myself, it was felt that an investigation of the skew boat of cyclohexane would be a waste of computer resources.

When it was found in the initial stages of this investigation of ctb that the unmodified chair ($\alpha = \beta = 0$) form was 21.2 kJ mol^{-1} less stable than the unmodified or 'eclipsed' boat form ($\theta = 0$), it was considered likely that this represented a true reflection of the behaviour of the molecule since the chair form is very close to an experimental geometry while the boat form is a 'synthesized' structure, *i.e.* the boat form is further from an optimal geometry. Nevertheless it was felt that (*a*) the effect of small independent changes in α and β on the molecular energy should be monitored to test the above assumption, (*b*) it was possible that a skew-boat form of ctb ($\theta \neq 0$) might exist.

It is clear from Table 1 that the slight modification of the chair form results in a deterioration in energy for all values of α and β. Parabolic minimisation of these angles against total energy led to optimal values of −1.5 and −4.0 for α and β; *i.e.* ring puckering is slightly preferred at both the NH_2 and BH_2 ends of the molecule. The predicted total energies for the optimal angles were, however, still greater (less negative) than that of the eclipsed boat. In fact this last conformation represents the best geometry within the optimisation framework examined here. Thus ctb differs from chex not only in that it has a conformational preference for the boat form but also in that the favoured boat is eclipsed rather than skew in nature. 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. One other possibility must be considered, namely 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 ctb would then become only *ca.* 3.7 kJ mol^{-1} more stable than the chair. This would be sufficiently large to give an accurate prediction of conformational preferences. I do not feel that such an assumption is valid, thereby suggesting that the gas-phase structure of ctb will prove to be the boat conformation.

TABLE 1

Energies (kJ mol^{-1}) relative to the boat form ($\theta = 0$) of cyclotriborazane ($E = -243.394\,374$ a.u.)

α	β	ΔE	μ *	θ	ΔE	μ *
+10	0	30.4	5.79	5	7.6	1.96
0	0	21.2	6.01	10	30.9	1.98
−10	0	26.7	6.15	15	70.9	2.02
0	+10	36.4	5.79			
0	−10	22.8	6.15			

* Dipole moment in Debyes.

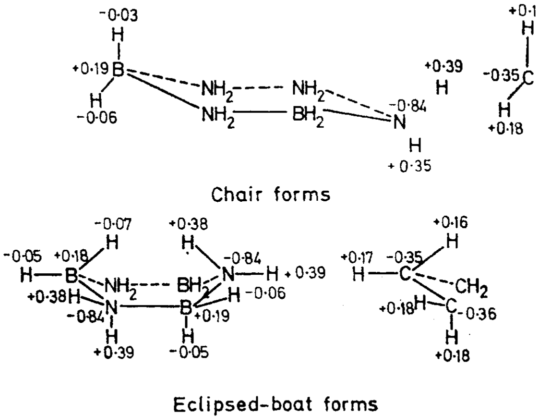

FIGURE 1 Symmetry-unique charge distributions of cyclohexane and cyclotriborazane

The charge distributions obtained by the Mulliken procedure[14] (Figure 1) indicate that electrostatic interactions are likely to contribute heavily in deciding the conformational preference. Generation of the boat forms brings the groups X^3 and Y^1 closer together, as is shown by increases in nuclear repulsion energy.[8] In cyclohexane, although the CH_2 groups are neutral by symmetry in the chair conformations, the hydrogen atoms, which approach each other in the eclipsed boat form, carry a partial positive charge (Figure 1). This will result in an increased electrostatic repulsion, de-

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* 1 a.u. = 2 625.56 kJ mol^{-1}; 1D ≈ 3.3 × 10^{-30} C m; 1 eV ≈ 1.60 × 10^{-19} J.

[10] H. Preuss and R. Janoschek, *J. Mol. Structure*, 1969, **3**, 423.

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[12] M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 778.

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[14] R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 1841, 2338.

stabilising the chair conformation. For ctb, the BH_2 and NH_2 groups carry opposite charges and will thus undergo stabilisation when converted into the boat conformation. This analysis of course assumes that the charge distribution does not materially change on conformational interconversion; that this is a valid assumption can be seen from Figure 1. In the case of the skew-boat form these oppositely charged groups move apart, leading one to expect an eclipsed boat as the preferred structure. This tendency is reinforced by X^3 and Y^2 approaching X^2 and Y^1 respectively as twisting occurs, although this is partially offset by the reduction of electrostatic repulsion as X^3 and Y^3 move away from X^1 and Y^1 (charge distributions in the skew-boat forms differ by <0.01 e from the eclipsed boat).

As a final point in this section, binding energies of -1.3246 and -1.3326 a.u. are reported for the chair and boat forms respectively.

Dipole-moment and Population Analysis.—The dipole moment of ctb has been found [15] to be 3.2 D in *p*-dioxan solution, in better agreement with the boat value of 1.96 D than with that of the chair (6.01 D). While this would appear to indicate the existence of boat ctb in solution, it must be pointed out that minimal-basis-set calculations on boron hydrides [16] give rise to dipole moments which are overestimated by a factor of *ca.* 1.8. If such a factor can be transferred to ctb then the dipole moment of the chair form suggests that this is the preferred structure in solution. In this context it must however be noted that the calculated dipole moment of 2,4-dicarbaheptaborane(7), where atoms other than boron are present in the molecular framework, was in much better agreement with experiment (*ca.* 30% greater).[17] Although the lack of experimental data makes it difficult to estimate how general the effect of incorporation of non-boron atoms may be, ctb is obviously a molecule in which the phenomenon could be important. I cannot therefore entirely rule out the solution-phase structure as being boat.

Another possibility must be considered: solvent–solute interactions may occur in such a manner 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,[2] due to movements of both nuclear and electronic charges. As I have investigated several geometric changes, it is of interest to examine changes in the dipole moment in order to see if the accuracy of the values determined for other molecules [18] can be approached. I feel that skew-boat forms are unlikely as the dipole moment only varies slowly with θ, the maximum value obtained being 2.02 D at $\theta = 15°$. On the other hand, flattening of the molecule at either end does reduce the dipole moment (by *ca.* 0.2 D); thus, if this process were carried out simultaneously on the whole molecule, a substantial reduction could be achieved. However, in my opinion even such a reduction would still give a calculated value in much worse agreement with experiment than those found previously.[18] I therefore conclude that the dipole moment is subject to a similar overestimate as the boron hydrides, and, hence, that the preferred solution-phase structure is chair in nature but may be somewhat flatter than that found in the solid.

Some aspects of the population analysis have been examined above, but other points deserve consideration. The *X*-ray crystallographic study [4] used as a basis for the present work also yielded the (average) charges on the atoms [B, +0.76 e; N, −0.10 e; H(B), −0.40 e; H(N), −0.07 e]. Although there is agreement between the calculated and experimental signs, the magnitudes of the charges are very different. This does not appear to be a function of the basis set as a similar charge distribution was reported in the crystallographic work [4] using Slater-type orbitals. It is quite evident that partition of the Mulliken overlap population using the electronegativities of the component atoms, rather than the usual equipartition procedure, will produce a more positive charge on boron. The value thus obtained (+0.31 e) is in better agreement with experiment but gives considerably worse values for the remaining atoms.

On symmetry grounds the B–N overlap populations of the unmodified chair forms (Table 2) are equal, with variations in the geometry inducing small changes in these populations. For example in the eclipsed boat form, (Ib), the X^3–Y^2 (= X^3–Y^3) overlap population shows an increase to 0.2610 e while that of X^1–Y^2 (= X^2–Y^3) decreases to 0.2488 e, with the remaining two bonds virtually unchanged. It is of interest to compare these overlap populations with the donor–acceptor complex $NH_3{\cdot}BH_3$, the pseudo-olefinic $BH_2(NH_2)$, the aromatic species, borazine, and with the corresponding hydrocarbons. The bond length of chex is slightly shorter than that of ethane, resulting in a small (*ca.* 6%) increase in the overlap population. In contrast the ctb bond length is slightly longer than that of $NH_3{\cdot}BH_3$, but the overlap population is some 2½ times as large. I feel that this implies that the B–N length and overlap populations of ctb should be

TABLE 2

B–N and C–C overlap populations and interatomic distances (Å)

	$NH_3{\cdot}BH_3$/ C_2H_6	C_6H_{12}/ $B_3N_3H_{12}$	C_6H_6/ $B_3N_3H_6$	C_2H_4/ $BH_2(NH_2)$
P(C–C)	0.3441	0.3637	0.5372	0.4724
r(C–C)	1.543	1.520	1.390	1.337
P(B–N)	0.1021	0.2532	0.4292	0.3286
r(B–N)	1.56	1.576	1.434	1.355

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[15] D. R. Leavers, J. R. Long, S. G. Shore, and W. J. Taylor, *J. Chem. Soc.* (*A*), 1969, 1580.

[16] E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1970, **92**, 3837; E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *ibid.*, 1972, **94**, 4467.

[17] D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 8692.

[18] R. H. Findlay, M. H. Palmer, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 420.

taken as typical of a single bond, *i.e.* ctb cannot be regarded as a donor–acceptor complex. This is further supported by the differences in the charges of boron in $NH_3{\cdot}BH_3$ (−0.18 e) and ctb (+0.31 e) and by the observation that the changes in overlap population along the series ctb, $BH_2(NH_2)$, $B_3N_3H_6$ closely follow those of the hydrocarbon analogues.

Ionisation Potentials.—Using Koopman's theorem (KT)[19] ionisation potentials can be directly compared with the negative of the SCF eigenvalues. There is reasonable agreement between the calculated (Table 3) and experimental (290.3 eV)[20] 1*s* ionisation potential (i.p.) for chex, the difference between the two values being typical of minimal basis calculations. The agreement is much enhanced when the 1*s* i.p. is obtained from the difference of the molecular energies of the ground and (localised) core holes, *i.e.* by the ΔE_{SCF} method. This also produces the correct sign of the chemical shift [i.p. (molecule) — i.p. (reference)] relative to methane, unlike that obtained by the KT method. The chemical shifts of boron and nitrogen, relative to diborane and ammonia respectively, are of the same sign in the KT and ΔE_{SCF} models. In view of the analysis of the bonding in the previous section it is at first sight somewhat surprising to discover that the chemical shifts are the same in sign and similar in magnitude to those found[21] for the complex $NEt_3{\cdot}BH_3$. These can, however, be explained in terms of changes in bonding. In both ctb and $NEt_3{\cdot}BH_3$ the nitrogen has lost some part of the electrons associated with the lone pair of ammonia, and can therefore be expected to have a positive chemical shift. The two three-centre bonds of diborane have been replaced by two normal bonds in ctb, and by one normal plus part of a lone pair in $NEt_3{\cdot}BH_3$; in both cases a negative chemical shift is reasonable, since the electrons are likely to be nearer the boron than they were in the three-centre bonds.

TABLE 3

Chemically distinct 1*s* ionisation potentials (eV) and chemical shifts (eV) *

		Chair	Boat
KT	C	309.9 (+0.22)	309.9, 309.8
	B	211.0 (−3.50)	211.0, 211.4
	N	427.2 (+3.72)	427.1, 426.8
ΔE_{SCF}	C	298.4 (−0.87)	
	B	203.7 (−3.98)	
	N	413.1 (+1.07)	

* Relative to methane, diborane, and ammonia.

Generation of the boat form of chex has virtually no effect on the 1*s* i.p.s indicating that no ring strain is being incurred.[22] As this would be expected to show in the i.p.s of atoms X^1, X^2, Y^2, and Y^3 of (Ib), the small changes in their values (<0.1 eV) indicate that there is hardly any ring strain in ctb. There are, however, quite marked chemical shifts relative to the boat form for the atoms X^3 and Y^1. The boron has a positive chemical shift while the nitrogen has a negative shift; this can be interpreted by examination of the charge distributions in Figure 1, where it can be seen that the negatively charged H(B) has approached the nitrogen atom more closely than in the boat form, *i.e.* it will induce a negative chemical shift. The reverse holds true for the boron shift.

The valence orbital energies for chair chex and the chair and eclipsed-boat form of ctb are shown in Table 4 together with the symmetry of the associated molecular orbitals. In the case of chex the orbitals have been analysed in terms of the sub-group C_{3v} as well as the true point group D_{3d}, the former providing a direct comparison with chair ctb. The eigenvectors of cyclohexane show that the molecular orbitals fall into four groups: carbon 2*s* levels ($3a_1$, $3e$, and $4e$); C–C ring bonding ($1a_2$ and $5a_1$); and axial ($4a_1$, $5e$, $7a_1$, and $7e$) and equatorial ($6a_1$, $6e$, and $8e$) C–H bonding. Since the Hartree–Fock limiting values[23] of the 2*s* and 2*p* orbital energies are (in eV) B 13.46 and 8.43, C 19.20 and 11.79, and N 25.72 and 15.44, the replacement of C–C by B–N is likely to have marked effects on both the nature and the energy of the molecular orbitals. These changes can however be rationalised in terms of the above atomic orbital energies.

TABLE 4

Valence-orbital energies (eV) of ctb and chex

ctb		
Boat	Chair	Chair chex
−36.73 ($5a'$)	−36.87 ($3a_1$)	−32.76 ($2a_{1g}$, $3a_1$)
−35.56 ($3a''$)	−35.60 ($3e$)	−29.29 ($2e_u$, $3e$)
−35.33 ($6a'$)	−23.62 ($4a_1$)	−23.98 ($2e_g$, $4e$)
−23.67 ($7a'$)	−22.92 ($4e$)	−21.77 ($2a_{2u}$, $4a_1$)
−23.05 ($8a'$)	−22.85 ($5a_1$)	−19.51 ($3a_{1g}$, $5a_1$)
−22.80 ($4a''$)	−21.86 ($5e$)	−18.12 ($3e_g$, $5e$)
−22.69 ($9a'$)	−18.76 ($6e$)	−18.04 ($3a_{2u}$, $6a_1$)
−21.85 ($5a''$)	−18.34 ($1a_2$)	−16.54 ($1a_{1u}$, $1a_2$)
−21.56 ($10a'$)	−16.82 ($6a_1$)	−16.27 ($3e_u$, $6e$)
−18.72 ($6a''$)	−14.78 ($7e$)	−14.74 ($4e_u$, $7e$)
−18.56 ($11a'$)	−13.50 ($7a_1$)	−13.86 ($4a_{1g}$, $7a_1$)
−18.28 ($7a''$)	−13.19 ($8e$)	−13.56 ($4e_g$, $8e$)
−16.95 ($12a'$)		
−15.05 ($13a'$)		
−14.72 ($8a''$)		
−13.75 ($14a'$)		
−13.46 ($15a'$)		
−13.34 ($9a''$)		

Considering first the carbon 2*s* levels: these would be expected to separate into two groups in ctb where the group at higher i.p. (more negative orbital energy) would be localised on N 2*s* while that at a less negative orbital energy would be predominantly B 2*s* in character. That this does in fact occur for the chex and ctb 2*s* levels can be seen from the correlation diagram (Figure 2). It is also clear from the Figure that orbital 4*e* has

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[19] T. A. Koopmans, *Physica*, 1933, **1**, 104.

[20] T. D. Thomas, *J. Chem. Phys.*, 1970, **52**, 1373.

[21] D. A. Allison, G. Johansson, C. J. Allen, U. Gelius, H. Siegbahn, J. Allison, and K. Siegbahn, *J. Electron Spectroscopy*, 1973, **1**, 269.

[22] M. H. Palmer and R. H. Findlay, *Chem. Phys. Letters*, 1972, **15**, 416.

[23] E. Clementi, *IBM J. Res. Dev.*, 1965, **9**, 2.

been promoted into a region where it is likely to gain some character other than B 2*s*; there is indeed considerable N–H bonding in this orbital. The six orbitals associated with the axial C–H bonds fall into two groups of three. It would then be expected that the separation of these groups would increase with the greater-binding-energy group becoming axial N–H and that at low binding energy being axial B–H in nature. The increase in separation can be seen in Figure 2, where it should also be noted that $4a_1$ in chex correlated best with $5a_1$ in ctb. However, although the $5a_1$ and $7a_1$ orbitals are wholly axial N–H and B–H in character, some mixing of the orbital types (*i.e.* axial, equatorial, ring bonding, or 2*s* levels) that was found in the B 2*s* level also occurs in orbitals 5*e*, where contamination is by equatorial N–H, and in 7*e* where there are contributions from all types of B–H and N–H bonds. In the case of equatorial bonds a somewhat different situation occurs in that from the three orbitals ($6a_1$ and 6*e*) in the higher-binding-energy group of chex two equatorial N–H bonds and one B–H arise, instead of the three expected N–H bonds. The orbital energies still however reflect the nature of the atoms in the molecular orbitals, *i.e.* the N–H pair of orbitals (6*e*) is at higher binding energy than the B–H orbital ($6a_1$); this orbital sequencing is the reverse of that found in chex. Turning now to the ring-bonding orbital, it is noted that $1a_2$ is by symmetry constrained to consist of only 2*p* tangential orbitals, and will therefore not be subject to the mixing with other orbital types. It is not surprising to find then that the orbital energy is more negative in ctb and that nitrogen tangential orbitals predominate. A similar situation occurs in $5a_1$ even though mixing is allowed for this orbital.

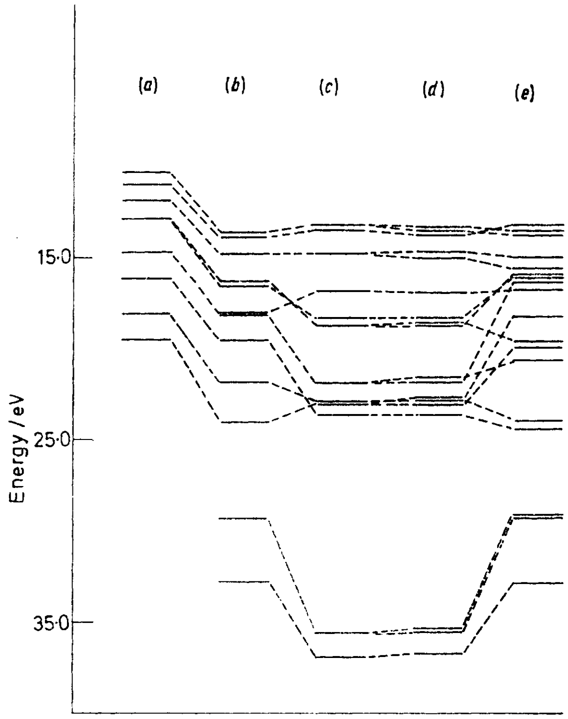

FIGURE 2 Orbital correlation diagram: (*a*), experimental cyclohexane; (*b*), chair cyclohexane; (*c*), chair cyclotriborazane; (*d*), boat cyclotriborazane; (*e*), boat cyclohexane

The correlation of the boat forms of ctb and chex follows a similar pattern to that of the chair forms (Figure 2). Since generation of the boat form of ctb reduced the molecular point group to C_s, the orbitals of *e* symmetry lose their degeneracy, each separating into an *a*′ and *a*″ pair. Examination of Figure 2 shows that the grouping of the i.p.s is almost identical to that of the chair form, *i.e.* the only change is an increase in the number of discrete energy levels within each band. From this it would be reasonable to expect that the nature of the orbitals in the boat form would be almost identical to that in the chair form, bearing in mind that there will be an increase in the number of types of N–H, B–H, and B–N bonds. The eigenvectors confirm this view, with the only significant change in the bonding being the partial disappearance of the largely B 2*s* level (4*e* in the chair form). It will be remembered that this had a significant proportion of N–H bonds and was almost accidentally degenerate with the $5a_1$ orbital which was predominantly N–H bonding. Removal of the degeneracy in the boat form allows these levels to mix (within the *a*′ representation) resulting in a pair of N–H levels and one only having a large B 2*s* character. A similar situation occurs, but to a lesser extent, for the orbitals 6*e* and $1a_2$ in the chair form (6*a*″, 11*a*′, and 7*a*″ in the boat form) of ctb.

There have been several studies of the valence region of cyclohexane using He(I) spectroscopy, the most complete being that of Heilbronner and his co-workers.[24a] This spectrum has been included in the orbital correlation diagram (Figure 2) where it was found necessary to assign two calculated energy levels to each of the 4th and 5th peaks, these being somewhat broader than the other bands. The least-squares analysis of the calculated and experimental i.p.s leads to a reasonable fit, with an equation of i.p.(expt.) $= 0.885$ i.p.(calc.) $-$ 1.410 and standard deviations of 0.026 (gradient), 0.458 (intercept), and 0.260 (overall); there is little scatter in the line (Figure 3). Despite this good agreement for chex, the similarity in the groupings of the chair and boat forms make it unlikely that a distinction between these forms will be possible using photoelectron spectroscopy. The best opportunity occurs in the 15 eV region where the separation from adjacent levels is 1 eV.

Although Koopmans' theorem has been widely used to assign ionisations in photoelectron spectroscopy, it suffers from two principal defects. First, correlation-energy differences between the molecule and ion are neglected, thereby giving rise to calculated i.p.s smaller than the true values. Secondly, no account is taken of

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[24] (*a*) P. von Bischoff, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 1969, **52**, 1745; (*b*) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, 1969, **50**, 654; (*c*) M. I. Al-Jobury and D. W. Turner, *J. Chem. Soc.*, 1964, 4434; (*d*) D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 31.

electron relaxation (reorganisation) on ionisation; omission of this leads to calculated i.p.s greater than those found experimentally. These two effects are to a certain extent self-compensating but the magnitude of the relaxation energy is greater than that associated with neglect of correlation energy, as examination of the least-squares analysis of the i.p.s of chex will reveal. Accordingly I made restricted Hartree–Fock open-shell calculations on the lowest i.p. from each of the occupied symmetry representations in chex and from the a_1 and e representations of ctb.* It can be seen from Table 5 that in all cases the i.p. is lower than that obtained from Koopmans' theorem, as expected, and that the open-shell values also give a better agreement with experiment. Although the relaxation energy varies quite considerably for the five chex cases, there is no change in the order of adjacent i.p.s. However in ctb the first two ionisations are reversed in order.

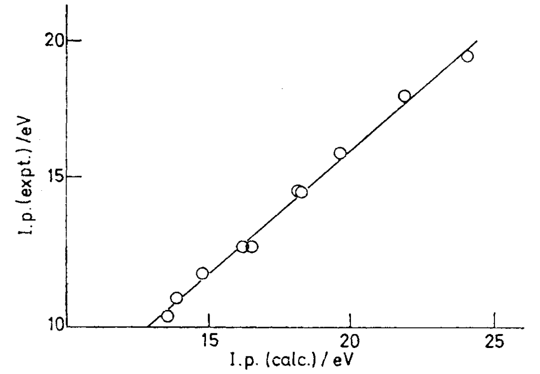

FIGURE 3 Least-squares analysis of cyclohexane ionisation potentials

TABLE 5

Ionisation potentials (eV) and relaxation energies (r.e.) (eV) for chex and chair ctb

Orbital	Principal characteristic	I.p.	R.e.	$\langle r^2 \rangle$
$4e_g$	4 equatorial C–H	13.00	0.56	16.04
$4a_{1g}$	6 axial C–H	13.48	0.38	15.03
$4e_u$	4 axial C–H	14.23	0.51	16.05
$1a_{1u}$	6 C–C ring	15.71	0.83	11.82
$3a_{2u}$	6 equatorial C–H	17.77	0.27	18.14
$8e$	All B–H and N–H	12.87	0.32	19.41
$7a_1$	3 axial B–H	12.63	0.87	17.40

The magnitude of the relaxation energy appears to be dependent on the nature of the associated molecular orbital (Table 5). Thus orbitals which are concentrated in particular regions of space, such as the axial B–H and C–C ring-bonding levels, have high (*ca.* 0.8 eV) relaxation energies, while the diffuse orbitals such as $8e$ in ctb (all types of B–H and N–H bonds) and $3a_{2u}$ in chex (all equatorial bonds) have low relaxation energies. It would obviously be useful, both for correcting orbital ordering (and hence leading to better assignments of spectra) and improving agreement with experiment, if the relaxation energy could be related in a quantitative manner to the diffuse natures of the ground-state orbitals. [Direct calculation of all i.p.s by the ΔSCF method is not practicable as (*i*) each i.p. requires a separate SCF calculation, although this situation can be somewhat relieved (as has been found for small molecules) by using the combined ΔSCF technique,[26] and (*ii*) open-shell SCF calculations often converge more slowly than the closed shell (for example, the fastest of the chex set took 1.7 times as long as the closed shell).] Hillier proposed [27] that the necessary quantification could come from the expectation value $\langle r^2 \rangle$, there being an inverse relation between the two parameters. This proposal was based on finding considerable differences between the $\langle r^2 \rangle$ values and relaxation energies of the mainly non-bonding single-centre metal $3d$ orbitals and those which were delocalised over the entire ligand framework. This situation is somewhat different from that of the present work where we are attempting to distinguish between orbitals which are all multicentre bonding, although concentrated in different molecular regions.

In Table 5 are reported the second moment expectation values for each ground-state molecular orbital whose open shell has been investigated. Several points are worthy of consideration. First there is broad agreement between the reciprocal of $\langle r^2 \rangle$ and the relaxation energy † in that large differences in $\langle r^2 \rangle$ are reflected in large values of the relaxation energy. However, finer differences such as those of the $4e_g$ and $4a_{1g}$ orbitals are not so well reproduced. The second point is closely related to the first; the range of values for both parameters is fairly restricted, making extrapolation to other i.p.s (using least-squares analysis, say) somewhat uncertain. In organometallic compounds where relaxation energies are much greater [29] (up to *ca.* 6 eV) such an analysis may be more fruitful; further, it is in this type of compound that Koopmans' theorem breaks down most readily. Finally, the differences in $\langle r^2 \rangle$ for chex and ctb with orbitals having similar relaxation energies show that, at best, any analysis is going to depend on the constituent atoms of the molecule. At worst it may vary from molecule to molecule thus necessitating the establishment of a relation by evaluating the relaxation energy using a few orbitals and

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* Convergence could not be obtained within a reasonable amount of computer time for the $1a_2$ orbitals of ctb despite extensive manipulation of damp factors and level shifters [25] even though canonicalisation methods were chosen to give optimal convergence rates.[25,26]

† Relaxation energy is defined [28] as the difference in i.p. as determined by Koopmans' theorem and SCF methods. The values of Table 5 are somewhat smaller than those obtained by more flexible bases. For example, relaxation energies of 0.5—2.6 eV (lower values predominating) have been found for valence-shell double-zeta calculations on small molecules,[26] while a basis close to the Hartree–Fock limit gave rise to values of 1.2—3.1 eV (higher predominating) for a sub-set of the same molecules.

[25] M. F. Guest and V. R. Saunders, *Mol. Phys.*, 1974, **28**, 819.

[26] M. F. Guest and V. R. Saunders, *Mol. Phys.*, 1975, **29**, 873.

[27] I. H. Hillier, Quantum Chem. Conf., Oxford, April 1973.

[28] D. T. Clark and I. W. Scanlan, *J.C.S. Faraday II*, 1974, 1222.

[29] M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.

extrapolating to the remaining orbitals using $\langle r^2 \rangle$. This latter possibility would of course greatly reduce the usefulness of the method.

Nevertheless, despite the drawbacks in the method which have been revealed by the present work, I feel that sufficient evidence has been found of its viability to justify a fuller investigation and propose to pursue the method further using a series of simple molecules.

Molecular Stability.—On the basis of binding energy, chex is more stable than ctb, with both molecules being thermodynamically stable with respect to decomposition to the constituent atoms. Although such a comparison is useful, atomisation is not likely to happen under normal chemical conditions, decomposition to and reaction with smaller molecules being much more conceivable occurrences. The thermochemistry of such reactions can be studied using Pople's isodesmic method.[30]

An isodesmic reaction is one in which there are the same numbers of bonds of the same types in both products and reactants, a typical example being reaction (1) of Table 6, where there are 6 C–C and 36 C–H bonds on each side of the equation. The agreement between calculated and experimental[11] heats of reaction is excellent bearing in mind that there are 13 molecular species involved. Reaction (1) also exemplifies the problem in isodesmic reactions involving ring fission, that hydrogen atoms have to be introduced since the cycloalkane has a general formula of C_nH_{2n} while that of the resulting open-chain species is C_nH_{2n+2}. This would similarly apply to ctb where the species corresponding to CH_4 would be $[NH_4]^+$ and $[BH_4]^-$. While such species could readily be included, the isodesmic nature of the reaction would not be preserved since, as we have seen, the character of the B–N bond is quite different in ctb and $NH_3 \cdot BH_3$. The stabilities of ctb and chex are therefore compared using a set of parallel reactions of the same type for both molecules; these are aromatisation [(2), (3)], fragmentation [(4), (5)], and hydrogenation [(6)—(8)].

TABLE 6

Reactions of cyclohexane and cyclotriborazane (boat conformation) *

No.	Reaction	E/kJ mol^{-1}	
		Calc.	Expt.
(1)	$C_6H_{12} + 6CH_4 \longrightarrow 6C_2H_6$	+17	+64
(2)	$C_6H_{12} \longrightarrow C_6H_6 + 3H_2$	+561	+206
(3)	$B_3N_3H_{12} \longrightarrow B_3N_3H_6 + 3H_2$	−720	
(4)	$C_6H_{12} \longrightarrow 3C_2H_4$	+471	+280
(5)	$B_3N_3H_{12} \longrightarrow 3BH_2(NH_2)$	+1 517	
(6)	$C_6H_{12} + 3H_2 \longrightarrow 3C_2H_6$	−131	−131
(7)	$B_3N_3H_{12} + 3H_2 \longrightarrow 3NH_3 \cdot BH_3$	−327	
(8)	$B_3N_3H_{12} + 3H_2 \longrightarrow 3BH_3 + 3NH_3$	+275	
(9)	$2B_3N_3H_{12} \longrightarrow B_3N_3H_6 + 3NH_3 \cdot BH_3$	−1 047	

* Calculations on smaller molecules were made at the experimental geometry using the same bases as for ctb and chex.

There is excellent agreement between the calculated and experimental values for reaction (6) which is the most isodesmic in nature; the other two chex reactions [(2), (4)] overestimate the endothermic nature of the reaction. While fragmentation is predicted to be markedly endothermic in nature for both chex and ctb, hydrogenation is exothermic provided that the ammonia–borane adduct is formed from ctb. The heat of formation of this adduct from ammonia and borane is predicted to be −200 kJ mol^{-1}. The major difference between chex and ctb lies in the aromatisation reaction where ctb is unstable with respect to formation of borazine (plus hydrogen). Indeed when this reaction is coupled with a hydrogenation reaction [(7)] the resulting disproportionation reaction [(9)] is exothermic to such a great extent that calculated errors of a magnitude found in the carbon-containing species are not likely to be sufficiently large as to reverse the sign of the heat of reaction. In other words, reaction (9) represents a real reaction of ctb in the gas phase, and presents a possible decomposition path.

Conclusions.—Although ctb has been shown to possess a single B–N bond comparable to the C–C bond in chex, the conformational preference of the former molecule is an eclipsed boat. This can be rationalised in terms of the charge distributions arising from the different orbital energies of the constituent atoms, as can the nature and ionisation potentials of the molecular orbitals. Open-shell calculations show improved agreement with experimental ionisation potentials, with the relaxation energy differing as the extent of the localisation changes. Attempts to quantify this localisation using $\langle r^2 \rangle$ are inconclusive, but indicate that a relation could be achieved given sufficiently large ranges of relaxation energies and second moments. Finally, sets of parallel reactions suggest that ctb is thermodynamically unstable with respect to disproportionation.

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[30] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4796.