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Ab initio Calculation of the Band Structure of Some Boron–Nitrogen Polymers

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Ab initio calculations using a Gaussian orbital basis set were performed on the two boron–nitrogen polymer systems polyaminoborane and polyboronimide. For the polyaminoborane system an alternating B–N bond model appears to be more stable than a symmetric B–N bond model. An electron drift from the NH_2 group to the BH_2 moiety was calculated for both models although the nitrogen atom was found to possess a negative charge stemming from polarization of the N–H bonds. The energy band diagrams derived from both models show rather featureless bands indicative of weakly interactive systems although that of polyboronimide indicates that it is a more delocalized system than its saturated counterpart. The conduction and valence bands at the X-point are composed of π orbitals and the lowest electronic transition is predicted to be π—π^* in nature. The electron distribution of polyboronimide indicates a movement of σ-electrons from the boron to the nitrogen coupled with a smaller π-electron drift from the nitrogen to the boron.

Key words: B–N polymers, energy band structures and electron distribution of ~

1. Introduction

Numerous theoretical studies [1–4] on molecular compounds containing the B–N bond have shown the charge polarization to differ from the classically expected B^{-}–N^{+}. Moreover, calculations [5] on the polymers $\text{-}[BH_2NH_2]\text{-}_n$ and $\text{-}[BHNH]\text{-}_n$ show that the nitrogen atom is negatively charged. Since the methods

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employed in the latter work can only be considered semi-quantitative we have made a more detailed study, using *ab initio* methods, of the two polymers mentioned above.

2. Calculation Method

The unit cells of polyaminoborane and polyboronimide are illustrated in Fig. 1 and the unit-cell parameters taken from the work of Armstrong, McAloon and Perkins [5] are presented in Table 1. The calculations employed contracted Gaussian basis sets whose expansion [6] simulated Slater-type orbitals (STO) with Clementi's single-zeta exponent [7]. To monitor the effect of basis-set size on the results, two expansion sets were chosen. The first consisted of three Gaussians per STO while in the smaller basis set, each boron and nitrogen atomic orbital was

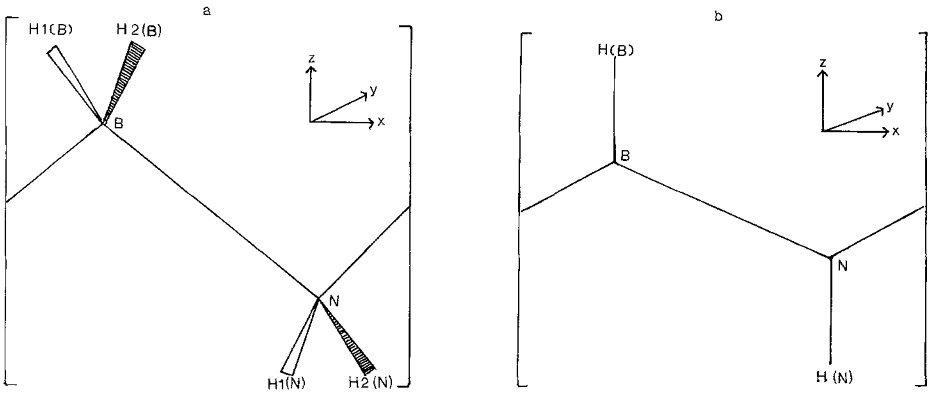


Fig. 1. (*a*) The polyaminoborane unit cell, (*b*) the polyboronimide unit cell

Table 1. The atomic coordinates (in a.u.) for the polyaminoborane and polyboronimide unit cells

	x-coordinate	*y*-coordinate	*z*-coordinate
Polyaminoborane unit cell			
H1(B)	1.267040	−1.849863	2.182480
H2(B)	1.267040	1.849863	2.182480
H1(N)	3.801121	−1.664103	−2.052490
H2(N)	3.801121	1.664103	−2.052490
B	1.267040	0.0	0.887191
N	3.801121	0.0	−0.887191
Unit cell parameter: 5.068161 a.u.			
Polyboronimide unit cell			
H(B)	1.173430	0.0	3.028345
H(N)	3.520289	0.0	−2.656061
B	1.173430	0.0	0.677480
N	3.520289	0.0	−0.677480
Unit cell parameter: 4.693718 a.u.			

expanded as two Gaussian orbitals and each hydrogen 1*s* atomic orbital was represented by a single Gaussian orbital. The two basis sets may be referred to in the nomenclature used in other polymer calculations [8] as B, N (3,3,3) H (3) and B, N (2,2,2) H (1) where *a*, *b*, and *c* in *X* (*a*, *b*, *c*) refer to the expansion size of the 1*s*, 2*s*, and 2*p* orbitals respectively.

The nearest-neighbour approximation, which allows only the interactions between three adjacent unit cells to be incorporated in the SCF procedure, was imposed on the calculation of both polymers. We recognize that this limits the accuracy of the calculation of the *absolute* total energy but, for the present purposes, this is not important. In any case, such an absolute energy would necessarily be affected by neighbouring strands in a real three-dimensional polymer and the latter would be very difficult to account for accurately.

3. Results and Discussion

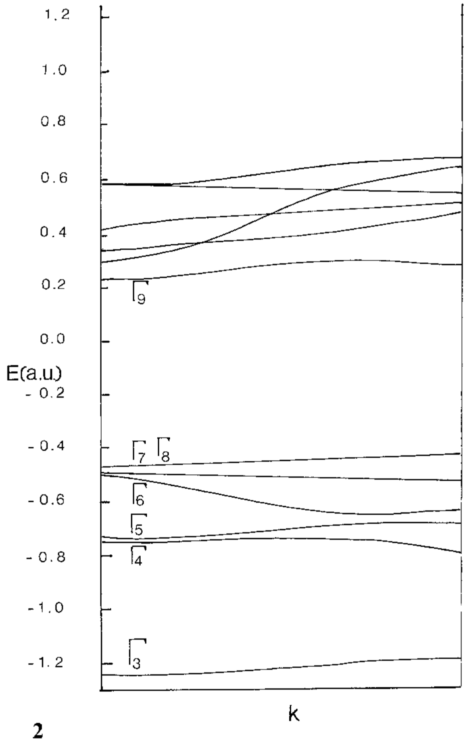
3.1. *The Electronic Energy Band Structure of Polyaminoborane*

The electronic energy band structure of polyaminoborane calculated using the two expansion sets is shown in Figs. 2 and 3.

The lowest-energy bands Γ_1 and Γ_2 are flat and they can be identified as the energy levels of the boron and nitrogen "non-bonding" core 1*s* orbitals, respectively. In the case of the larger basis set, they occur at -15.56 a.u. and -7.60 a.u. and are not shown in Fig. 2. The B, N (2,2,2) H (1) basis set yields higher values of -14.99 a.u. and -7.26 a.u. for the band origins. As the bands are quite flat in both cases, the higher energy values are thought to arise from the use of a less representative 1*s* expansion, rather than as a consequence of any degree of association or electron delocalization.

Minor delocalization is evidenced by bands Γ_5 and Γ_6. The former arise from bonding between the nitrogen $2p_y$ orbital and its associated hydrogens and contains only small contributions from the corresponding boron orbitals; Γ_6, although associated with bonding between the backbone atoms and their hydrogen atoms, exhibits slightly greater *k*-dependence than Γ_5. The bands arising from interactions along the B–N backbone of the polymer, Γ_3 and Γ_7, are not curved to any great extent and contrast strongly with the corresponding bands in polyethylene [9]. The frontier band, Γ_8, has its highest value at the *X*-point ($k=\pi/a$) and is similar in composition to Γ_5, originating from bonding between the boron and nitrogen atom $2p_y$ orbitals and their associated hydrogen atom 1*s* functions. The same value of the Γ_8 band-width, 0.02 a.u., is obtained from both sets of computations and all bands are lower in energy overall in the case of the larger (3-Gaussian) expansion. The main atomic orbital contributions to the bands Γ_1–Γ_8, are given in Table 2.

The lowest-energy conduction band, Γ_9, is also associated with B–H and N–H bonding and is localized almost completely on the NH_2 group. The lowest energy



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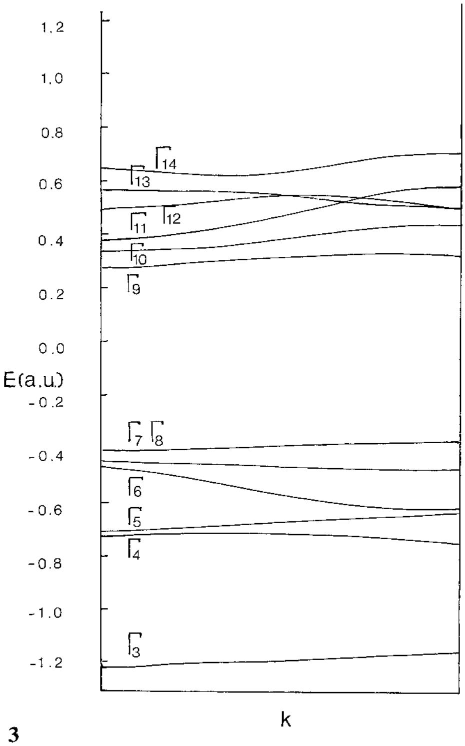

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Fig. 2. The energy-band structure of polyaminoborane using a B, N (3,3,3) H (3) basis set

Fig. 3. The energy-band structure of polyaminoborane using a B, N (2,2,2) H (1) basis set

Table 2. Main atomic orbital contributions to the occupied band structures of polyaminoborane and polyboronimide at the Γ-point

Band	Main contribution (Eigenvector coefficient)					
Polyaminoborane						
Γ_1	N 1*s* (0.99)					
Γ_2	B 1*s* (0.99)					
Γ_3	N 2*s* (0.80)	N 1*s* (0.22)				
Γ_4	N $2p_z$ (0.48)	B 2*s* (0.46)	H(N) (0.22)			
Γ_5	N $2p_y$ (0.56)	H(N) (0.37)				
Γ_6	B $2p_z$ (0.38)	N $2p_z$ (0.32)	N 2*s* (0.32)	H(B) (0.31)	H(N) (0.24)	
Γ_7	N $2p_x$ (0.87)	B $2p_x$ (0.42)				
Γ_8	B $2p_y$ (0.48)	H(B) (0.43)	H(N) (0.27)	N $2p_y$ (0.21)		
Polyboronimide						
Γ_1	N 1*s* (0.98)					
Γ_2	B 1*s* (0.99)					
Γ_3	N 2*s* (0.74)	B 1*s* (0.25)	B 2*s* (0.18)			
Γ_4	N $2p_z$ (0.48)	B 2*s* (0.36)	H(N) (0.35)	H(B) (0.20)		
Γ_5	N $2p_y$ (0.67)	B $2p_y$ (0.46)				
Γ_6	N $2p_x$ (0.59)	B $2p_x$ (0.50)	H(B) (0.30)	H(N) (0.27)	N $2p_z$ (0.26)	
Γ_7	N $2p_x$ (0.50)	H(B) (0.38)	H(N) (0.35)	B $2p_x$ (0.35)	B $2p_z$ (0.31)	N $2p_z$ (0.31)

gap occurs at the Γ-point for both cases and is greater (0.70 a.u.) for the 3-Gaussian basis set than for the smaller 2-Gaussian set (0.67 a.u.).

The energy band structure of polyaminoborane is, therefore, typical of a weakly bonded polymer system. The sole effect of using a larger basis set appears to be to lower the energies of the valence bands without significantly altering their main characteristics. A larger change is observed to occur in the conduction region, in which variations in the relative positions of the bands cause accidental degeneracies to arise.

3.2. The Electron Population Analysis of Polyaminoborane

Figure 4 shows the charge distributions obtained by Mulliken population analysis for the calculations carried out using the B, N (3,3,3) H (3) (*a*) and B, N (2,2,2) H (1) (*b*) bases. The CNDO/2 charge distribution reported by Armstrong *et al.* [5] is also included for comparison (*c*). We expect the changes obtained in the present series of calculations to change little on enlarging the number of interacting unit cells; the essential conclusions of the present paper will be insensitive to this factor.

The most striking feature of the results is the large negative charge on the nitrogen atom. This net negative charge on nitrogen is due to electron donation from its

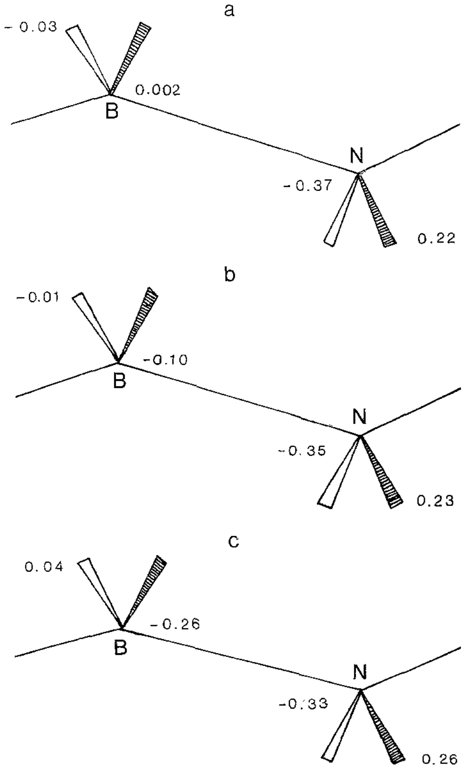


Fig. 4. The charge-distribution for polyaminoborane from (*a*) the B, N (3,3,3) H (3) basis set, (*b*) the B, N (2,2,2) H (1) basis set and (*c*) a CNDO calculation [5]

associated hydrogens and, in fact, surplus density is actually transferred to the BH_2 group. This inter-group electronic migration varies in the calculations from a value of 0.059e in the case of the 3-Gaussian expansion to 0.19e for the CNDO/2 calculation. This feature has been encountered in previous molecular calculations [2].

The electron distribution on the BH_2 group is the feature which shows the greatest variation between the three sets of results. While the *ab initio* treatment favours a withdrawal of electron density from the boron atom to the associated hydrogens, leaving in the case of the 3-Gaussian expansion set a net positive charge on boron and, in the case of the 2-Gaussian expansion, a diminished negative charge on boron, the CNDO/2 calculation predicts the boron atom to accept electron density from the hydrogens, thereby increasing the negative charge arising from B–N donation. Overall, however, electron drift is observed to take place from the NH_2 group to the BH_2 group, in agreement with the classical donor-acceptor hypothesis of bonding in amine boranes.

That the larger, better basis set predicts a much lower $NH_2 \rightarrow BH_2$ drift, suggests that the net drift, might be reduced even further in a calculation employing a larger Gaussian expansion set. This, combined with the nature of the band structure, indicates that it is unlikely that a polymer will exist in the coordination form considered here.

From a classical viewpoint, the polymer can be seen as the product of inter-complexing a number of monomer units of the type BH_2NH_2 by the formation of alternative "dative" and "covalent" bonds. The implications of this view are apparent: i.e., is a bonding scheme involving alternate bond types (and, correlatively, alternate bond lengths) more stable than that of the symmetrical model?

3.3. *The "Alternating Bond" Model of Polyaminoborane*

A conventional conformational analysis of polyaminoborane with respect to the B–N interatomic distance is made impossible, in an absolute sense, by the unreliability of the total electronic energy obtained using a model which is restricted to a finite number of interacting cells. However, the main evidence cited in the preceding section of the non-existence of the symmetric polymer was concerned with the lack of electron delocalization, as interpreted from the energy band structure, and with the weakness of the dative component of the B–N bond. Although not entirely independent of the number of interacting cells considered, these observations probably give a reasonable general indication of the stability of the model.

A series of computations was carried out on the symmetric model of polyaminoborane introduced in the previous section, in which the B–N bond length was allowed to vary from the value (1.637 Å) given by Armstrong *et al.* (The $\widehat{\mathrm{B{-}N{-}B}}$ angle was maintained at 110°.) The smaller B, N (2,2,2) H (1) basis set was chosen for this investigation. The net N–B electron drift was found to increase with increasing B–N bond length and the total energy per cell reached a minimum at a B–N distance of 1.75 Å; at this point the net N→B electronic drift was 0.1314e. Although this energy minimum is not necessarily absolutely significant, it is, nevertheless, a useful starting point for the consideration of the effect of bond alternation on the charge distribution and energy band structure of the polymer.

A further series of calculations was next performed in which two different B–N bond lengths, given by $[r_{BN} + \varDelta]$ and $[r_{BN} - \varDelta]$, were considered to lie at alternate sites along the chain. The effect of alternation on the charge distribution is shown in Table 3. On increasing $\varDelta$ from 0.0 Å to 0.5 Å, net N→B electronic migration is reduced considerably, while the nitrogen-bonded hydrogen atom charge remains almost unaltered. This shows a tendency on the part of the nitrogen atom to retain electron density donated by its hydrogen atoms, instead of in turn donating electrons to the boron atom, as observed in the symmetrical model.

The energy minimum in this set of calculations lies at a value of $\varDelta$ of 0.40 Å. In this model, alternate B–N bonds have bond lengths of 1.35 Å and 2.15 Å, respectively. Although these are, in the absolute, not expected to be accurate, the trend is significant.

The energy band diagram for the alternant, polymer at the minimum of the total energy function is shown in Fig. 5. In common with the band structure of the symmetrical chain, shown in Fig. 2, the band arising from bonding between the backbone atoms and their associated hydrogens, identified as Γ_8 in this case, is observed to exhibit the greatest degree of k-dependence and is raised in energy in the alternant model relative to the remainder of the valence bands. This band is labelled Γ_6 in Fig. 2. The positions of both of the relatively delocalized bands, Γ_5 and Γ_6, obtained in the symmetrical model (Fig. 2) are found to be altered to some extent on alternation.

Table 3. Variation of atomic charges with BN bond length for the alternant bond model of polyaminoborane

BN Bond lengths (a.u.)		Atomic charges				Electronic drift
r'_{BN}	r''_{BN}	B	H(B)	N	H(N)	N→B
3.307	3.307	−0.127	−0.002	−0.328	+0.230	+0.131
3.257	3.357	−0.126	−0.002	−0.329	+0.230	+0.130
3.207	3.407	−0.123	−0.001	−0.334	+0.230	+0.125
3.157	3.457	−0.116	−0.001	−0.342	+0.230	+0.116
3.107	3.507	−0.106	+0.001	−0.354	+0.230	+0.104
3.057	3.557	−0.094	+0.003	−0.369	+0.230	+0.088
3.007	3.607	−0.081	+0.005	−0.387	+0.230	+0.072
2.957	3.657	−0.066	+0.007	−0.408	+0.231	+0.053
2.907	3.707	−0.051	+0.009	−0.431	+0.232	+0.034
2.857	3.757	−0.038	+0.010	−0.455	+0.236	+0.018
2.807	3.807	−0.026	+0.012	−0.480	+0.242	+0.003

The conduction bands which have been labelled Γ_{11} and Γ_{14} in the symmetric scheme vary most in position relative to the remaining conduction bands. Γ_{11} is raised in energy and Γ_{14} lowered in energy. ($\Gamma_{11}-X_{14}$ and $\Gamma_{14}-X_9$). Thus, delocalized bands associated with B–H and B–N bonding constitute the frontier bands in the alternant model of polyaminoborane.

The overall interpretation of Figs. 5 and 2 is that some increase in delocalization is obtained on constraining the B–N backbone of the polymer to be composed of alternate short and long bonds. However, it must be borne in mind that the energy band structure does not, in either case, represent a particularly strongly interactive system and, when combined with the results of the electron population analysis, indicates that the linear polymer is unlikely to be stable in either form. Finally, it should be noted with regard to the energy term at this point that it is heavily dominated by the nuclear repulsion terms and that complete optimization of the geometry of the system may well reveal dissociation into monomeric units.

We thus conclude from the results obtained that a strictly linear polymer of this type is likely to dissociate into its constituent monomeric units. The primary source of this instability is the tendency of the nitrogen electron lone pairs to avoid separation (a condition which is required in the symmetrical polymer model). This observation may have some important implications in connection with the interpretation of the Jahn-Teller theorem. Although not specifically covered by the theorem, this phenomenon does have its origins in molecular symmetry and may have some bearing on the stability of other coordinated systems.

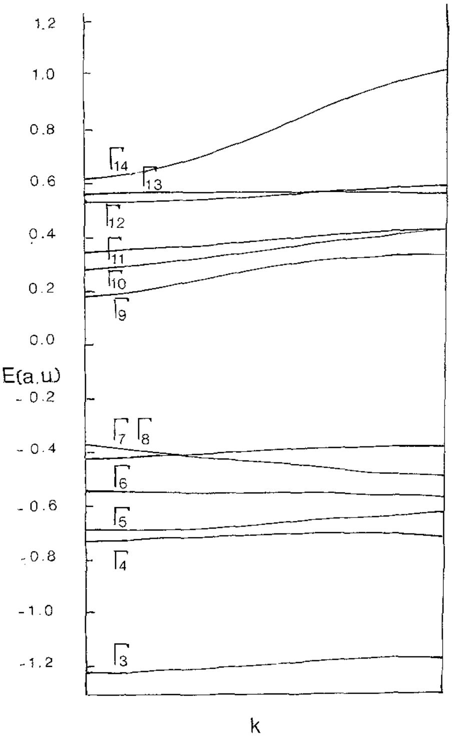
The slight improvement found on introducing bond alternation confirms this observation and suggests that some complexing of aminoborane units might take place. The lack of any appreciable degree of energy-band broadening, indicative of delocalization, however, would tend to suggest that any association of monomer units would be restricted to the formation of dimers, trimers and, possibly, tetramers. If these species do form (and there is some evidence that they might [10]) they will almost certainly be cyclic at lower temperatures.

3.4. *The Electronic Band Structure of Polyboronimide*

Since general agreement was found for the band structures obtained by the use of two different basis sets for polyaminoborane, the use of the smaller expansion set was considered applicable in this case. The resulting electronic energy band structure is depicted in Fig. 6 and the composition of the bands at the Γ-point is given in Table 2.

Two narrow bands (not shown) at -14.95 a.u. and -7.34 a.u. are identified as the nitrogen and boron 1*s* energy levels, respectively and, as might be anticipated, do not take part in bonding to any great extent.

Bands (Γ_5-X_7) and (Γ_9-X_8) constitute the π-electron system and are observed in Fig. 6 to be the frontier bands at the X-point; at this point, the ionization potential and the energy band gap are lowest. Thus, the first transition in polyboronimide



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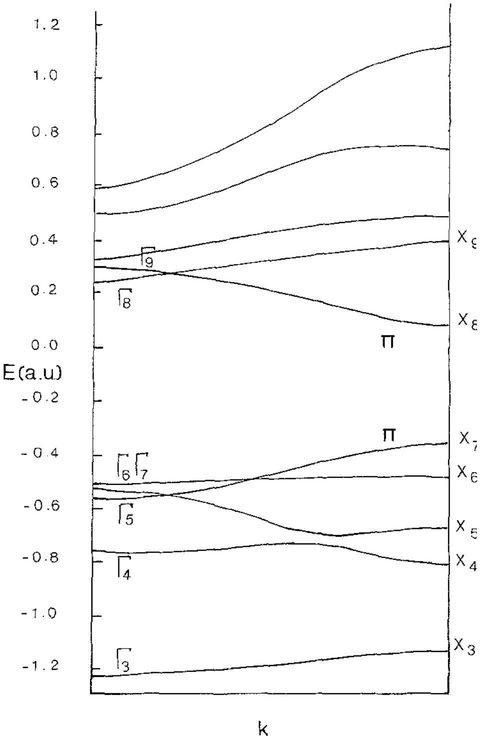

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Fig. 5. The energy-band structure of the alternating-bond model of polyaminoborane

Fig. 6. The energy-band structure of polyboronimide

is predicted to be $\pi \rightarrow \pi^*$ in nature. The σ-band (the band $\Gamma_6 - X_5$) in Fig. 6) arising from H–N–B–H bonding in the polymer backbone is found to be much lower at the X-point relative to the π-bonding band, than that obtained in the CNDO/2 calculation by McAloon *et al.* [5]. The observation, in this work, of a $\pi \rightarrow \pi^*$ first transition as opposed to the $\sigma \rightarrow \pi^*$ transition described by McAloon, is therefore explicable in terms of the extent of destabilization of the π-bonding band in the region of the X-point in the Brillouin zone.

Although not in accord, in this respect, with the *ab initio* molecular calculation on aminoborane due to Armstrong, Duke and Perkins [3] (in which a $\sigma \rightarrow \pi^*$ transition is also predicted), the X-point eigenvalues obtained in the present calculation on polyboronimide do compare quite reasonably with the molecular energy levels reported in that work. It is possible that bond alternation, as observed for the isoelectronic system polyene [11] might reduce the X-point π-band energy to some degree, such that the first transition would take place from a σ band. There is, however, no prior justification for this in terms of the Jahn-Teller theorem, as there was for polyene, as no degeneracy is directed by structural symmetry.

3.5. Electron Population Analysis of Polyboronimide

The gross atomic charge distribution as obtained by Mulliken population analysis is shown in Fig. 7, with the results obtained by Armstrong *et al.* [5] given for comparison.

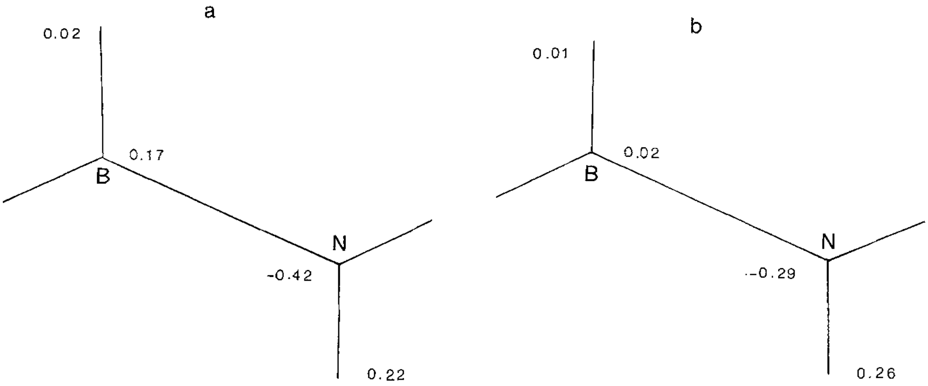

Fig. 7. The charge-distribution for polyboronimide from (*a*) an *ab initio* calculation and (*b*) a CNDO calculation [5]

All the calculations agree that an overall drift of electrons takes place from boron to nitrogen. This is in accordance with the revised theory applicable to aminoboranes in general [1]. The two methods appear, however, to differ over the magnitude of this drift, the source of the disagreement becoming more apparent on inspection of the σ and π components of the B–N bond.

Both the *ab initio* and CNDO/2 methods estimate the σ component to consist of a donation of approximately 0.7e from boron to nitrogen. The CNDO/2 calculation, however, finds the competing donation of nitrogen "lone-pair" electrons to balance this drift almost exactly, with the result that the overall B→N electronic migration is very small. The *ab initio* result, on the other hand, shows the degree of π-electron donation to be much less than the σ drift, giving rise to a very strong net migration towards the nitrogen atom. This trend, it will be recalled, has already been observed in the case of polyaminoborane, in which the CNDO/2 method was found to obtain a stronger B–N donation than that predicted from the *ab initio* calculation.

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