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The Electronic Structures and Energies of Borazine, Boronimide and Dimeric Boronimide

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The electronic energies and structures of two proposed models of borazine have been examined by *ab initio* calculations using Gaussian-Type atomic orbitals. It is found that the planar D_{3h} model is energetically preferred. The electronic population analysis reveals that nitrogen and boron atoms in borazine possess a negative and positive charge, respectively. Calculations have also been performed on boronimide and dimeric boronimide. The trimerisation and dimerisation energy of boronimide is calculated to be -193.8 kcal/mole and -63.3 kcal/mole respectively. The reorganisation energy of boronimide in various configurations is obtained and used to discuss the energetics of formation of borazine and dimeric boronimide.

Unter Benutzung Gaußscher Atomorbitale wurden die Elektronenenergien und Strukturen zweier vorgeschlagener Modelle von Borazin mit *ab initio*-Rechnungen untersucht. Man fand, daß das ebene D_{3_h}-Modell energetisch bevorzugt wird. Die Analyse der Elektronenbesetzung ergibt für Stickstoff- und Boratome im Borazin eine negative bzw. positive Ladung. Berechnungen wurden auch durchgeführt für Borimid und dimeres Borimid. Die Trimerisations- und Dimerisationsenergie von Borimid ergab sich zu $-193,8$ kcal/Mol bzw. $-63,3$ kcal/Mol. Die Umlagerungsenergie von Borimid in verschiedenen Konfigurationen wird berechnet und zur Diskussion der Bildungsenergien von Borazin und dimerem Borimid benutzt.

1. Introduction

Borazine has been the subject of both theoretical and experimental interest since the early structural studies established that borazine consisted of a planar hexagonal molecule with alternating B–H and N–H groups [2, 19]. The observed B–N bond distance of 1.44 Å [2, 19] indicated that it was intermediate between that expected for a single and double bond. Because of the isoelectronic and isosteric relationship, borazine was regarded as "inorganic benzene", and this relationship became more credible when a comparison of physical constants of benzene and borazine showed a striking similarity [14]. Furthermore, spectroscopic studies such as infra-red, raman [5, 18] and ultraviolet [11] could all be satisfactorily interpreted on the basis of a benzene like structure. It was, therefore, rather surprising when a recent redetermination of the structure by electron diffraction techniques [13] found that two models of borazine could fit the observed results. These were the "classical" D_{3_h} model and a non-planar twist boat configuration of C_2 symmetry. In order to differentiate between these, we have carried out non-empirical LCAO–MO–SCF calculations on both models.

The electronic structure of borazine has been examined by many semiempirical calculations. The earlier investigations [4, 15] were concerned with the π-electronic system and found that the ultraviolet spectrum could be interpreted on the basis of $\pi \rightarrow \pi$ transitions. The calculations also revealed that the π-electron population of the boron and nitrogen was 0.344 and 1.666 respectively, indicating a π-electron flow towards the boron [15]. Recent studies have covered both the σ- and π-electron systems in an attempt to gauge the extent of both σ- and π-electron movement. Extended Hückel [8] and CNDO [17, 6] calculations on borazine revealed that the classical picture of alternating B^- and N^+ atoms, directly comparable to the electronic situation in benzene, was totally misleading. Both methods showed that the valence electronic population on boron was positive and nitrogen possessed a negative charge. After a preliminary account of this work was published [1] an *ab initio* calculation on the excited states of borazine was reported [16].

2. Results and Discussion

2.1. Energies of the Two Models of Borazine

The first attempt to distinguish between the two models of borazine was made by CNDO SCF MO calculations. It was found that the planar D_{3_h} model was energetically preferred by 1.6 kcal/mole. Considering the semi-empirical nature of the method, however, the difference in energy between the two models was too small for a definite assignment to be made of the preferred structure of borazine.

It was necessary, therefore, to resort to a non-empirical approach to distinguish between the proposed models of borazine. The calculations [20] were performed using a basis set of Gaussian-type atomic orbitals [3]. The basis set consisted of 7s and 3p atomic Gaussian functions for both boron and nitrogen atoms and 3s atomic Gaussian functions for the hydrogen atoms. The 114 primitive functions were then contracted to 42 functions comprised of 3s and 1p atomic orbitals for the heavy atoms and a 1s atomic orbital for each hydrogen. The nitrogen and boron orbital exponents and coefficients were obtained from the work of Whitman and Hornback [21] and the values for hydrogen from Ref. [10]. The total and orbital energies of the two models of borazine are presented in Table 1. It can be seen that the classical D_{3_h} model is more stable by 40.5 kcal/mole and this large difference in energy effectively rules out the C_2 twisted model proposed by Bauer [2]. Twisting the N–H bonds out of the plane produces an increase in nuclear energy and this is coupled with a smaller decrease in the electronic energy.

The orbital energies of the two models have very similar values, with the highest filled orbitals showing the greatest difference in energy. The highest filled orbitals of the planar D_{3_h} model is a doubly degenerate π-orbital (e'') which is composed mainly of the nitrogen π-orbitals. This orbital will therefore be most affected by the bending of the N–H bonds out of the plane. The UV photoelectron spectrum of borazine [12] confirmed that the highest filled orbital is of e'' symmetry. The lowest virtual orbital of planar borazine is also of e'' symmetry and is concentrated about the π-orbitals of the boron atoms.

Table 1. Total and orbital energies of the two models of borazine (in a.u.)

	Planar D_{3h} model	Twisted boat C_2 model
Electronic energy	−436.7149	−437.1257
Nuclear energy	196.1889	196.6742
Total energy	−240.5260	−240.4515
Virtual orbitals	0.4199 (e')	0.4129 (b)
		0.4093 (a)
	0.3365 (a_1')	0.3589 (a)
	0.2775 (a_2')	0.1996 (b)
		0.1343 (b)
	0.1316 (e'')	0.0810 (a)
Occupied orbitals	−0.4669 (e'')	−0.4583 (b)
		−0.4641 (b)
	−0.4994 (e')	−0.4949 (a)
	−0.5758 (a_1')	−0.5824 (a)
	−0.5783 (a_2')	−0.5858 (b)
		−0.6343 (b)
	−0.6335 (e')	−0.6375 (a)
	−0.6537 (a_1')	−0.6520 (b)
	−0.7687 (a_1')	−0.7583 (a)
		−0.7726 (b)
	−0.7792 (e')	−0.7798 (b)
		−1.1641 (b)
	−1.1662 (e')	−1.1679 (a)
	−1.2483 (a_1')	−1.2505 (a)
	−7.7739 (a_1')	−7.7682 (a)
		−7.7832 (a)
	−7.7743 (e')	−7.7836 (b)
	−15.6070 (e')	−15.5915 (b)
	−15.6072 (a_1')	−15.6050 (a)

2.2 Electronic Population Analysis of Borazine

The electronic population of planar borazine is presented in Table 2. This reveals that the nitrogen atoms possess a large negative charge (0.735) and the boron atoms have a positive charge (0.474). For the nitrogen atoms this charge arises from the bonded hydrogen atom (0.299) and from the boron atoms (0.436). The boron-to-nitrogen electron donation is interesting because it consists of a π-electron delocalisation from the nitrogen to the boron, however, this is coupled with a larger σ-electron polarisation from boron to nitrogen. This electronic description of borazine contradicts the classical picture in which the charges on boron and nitrogen atoms are -1 and $+1$, respectively. It explains, however, the chemical reactions of borazine in which the electrophilic reagent attacks the boron atoms and the nucleophiles react with the nitrogen atoms. Also included in Table 2 are the corresponding electronic population for the C_2 model of borazine. Comparison of the distributions reveals that producing twisted boat C_2 model has only a weak perturbing effect on its electronic population.

Table 2. Gross and overlap populations of the two models of borazine

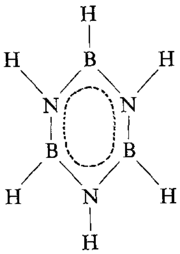
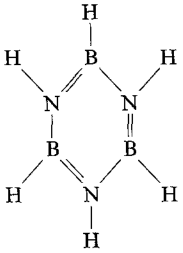
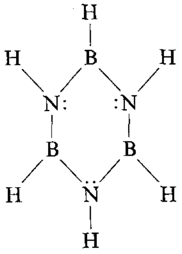
		Planar D_{3h} model	Twisted boat C_2 model	
			A (out of plane)	B (on axis)
Nitrogen	s	3.529	3.532	3.533
	$p\sigma$	2.616	4.211	4.201
	$p\pi$	1.590		
	Total	7.735	7.743	7.734
Boron	s	2.738	2.761	2.749
	$p\sigma$	1.378	1.745	1.786
	$p\pi$	0.410		
	Total	4.526	4.506	4.535
Hydrogen				
(bonded to boron)		1.037	1.035	1.039
(bonded to nitrogen)		0.701	0.710	0.703
B–N	σ	0.327		
	π	0.098		
	Total	0.425	0.420	
B–H		0.446	0.442	
N–H		0.364	0.358	
N–N	σ	−0.024		
	π	−0.003		
	Total	−0.027	−0.298	
B–B	σ	−0.108		
	π	0.003		
	Total	−0.105	−0.108	

2.3. *π-Electronic Energy of Borazine*

In benzene the π-electron system is of paramount importance as it determines the stability and reactivity of the molecule and its derivatives. The delocalisation of π-electrons in borazine is not as extensive as in benzene but is still quite considerable. A possible reason for the relative instability of the C_2 model of borazine is that the bending of the N–H bonds out of plane reduces the π-delocalisation of the lone pair of electrons on the nitrogen atoms. It was therefore of interest to estimate the π-electronic energy of borazine. This was achieved by calculating two models of borazine in which the π-electrons were artificially restricted to a) three boron-nitrogen localised π-bonds b) three nitrogen π-orbitals.

The energies of these models are presented in Table 3. It can be observed that localisation of the π-electrons on the nitrogen orbitals results in a loss of 119.1 kcal/mole, whereas restricting the π-electrons to three B–N localised bonds destabilises the total energy by only 13.1 kcal/mole. Hence, it appears that in borazine the nitrogen π-electrons prefer to be delocalised although the form of

Table 3. The total energies of localised and delocalised models of borazine (in u.a.)

 Delocalised		 Localised bond	 Localised lone pair
Total energy	−240.5260	−240.5051 $\xrightarrow{0.0209}$ $\xrightarrow{0.1689}$ $\xrightarrow{0.1898}$	−240.3362

delocalisation is unimportant. The small value for the resonance energy suggests that localisation of the π-electrons into three bonds is a first step in a reaction process and, with electron bond polarisation, is a major reason why borazine is very reactive compared to benzene.

2.4. Electronic Structure of Boronimide HBNH

In 1948 Wiberg [22, 23] postulated that the formation of borazine from the reaction of diborane and ammonia should proceed stepwise according to

$$H_3N \cdot BH_3 \xrightarrow{-H_2} H_2N \cdot BH_2 \xrightarrow{-H_2} HB \cdot NH \xrightarrow{\quad} \tfrac{1}{3}[HB.NH]_3 .$$

It was assumed that dehydrogenation led to boronimide as a reaction intermediate which rapidly trimerised to the thermodynamically favoured borazine. It was thought relevant that this intermediate should be examined and the energies involved in the trimerisation procedure estimated.

It was first necessary to calculate the equilibrium B–N bond distance for boronimide, as there has been no experimental or theoretical determination of this distance. The total energy of boronimide was calculated at various B–N bond distances using the aforementioned basis set, and an optimum B–N distance of 1.272 Å obtained. In order that trimerisation can occur, the boronimide molecule must reorganise into a non-linear molecule whose B–N bond length and N–B–H and B–N–H angles are equal to those in borazine. The total and orbital energies of boronimide in various configurations are presented in Table 4. The energy gained by the trimerisation of three molecules of boronimide to form one molecule of borazine is 193.8 kcal. The reorganisation energy of the boronimide is 66.6 kcals of which 23.4 kcals is the energy lost in stretching the B–N bond. The energy gained by the three reorganised molecules of boronimide on the formation of borazine is therefore $(3 \times 66.6 + 193.8) = 393.6$ kcals and this energy will arise from the formation of the new B–N σ-bonds. The major term of the reorganisation

Table 4. The total and orbital energies of boronimide (in a.u.)

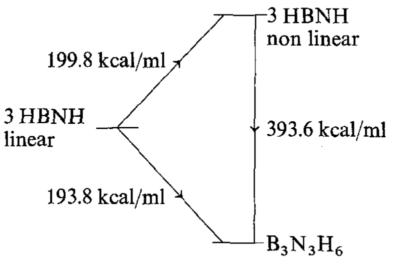
	a) Linear boronimide B–N = 1.272 Å	b) Linear boronimide B–N=B–N distance in borazine	c) Non-linear boronimide in the same configuration as in borazine	d) Non-linear boronimide bending the B–H bond only B–N=B–N distance in borazine	e) Non-linear boronimide bending the N–H bond only B–N=B–N distance in borazine	f) Non-linear boronimide in the same configuration as in dimeric boronimide
Electronic energy	−103.0609	−101.2075	−101.5711	−101.3873	−101.3873	−101.0295
Nuclear energy	22.9885	21.1724	21.6050	21.3920	21.3587	21.0483
Total energy	−80.0724	−80.0351	−79.9661	−79.9953	−80.0286	−79.9812
Virtual orbitals	0.285 (a)	0.242 (a)	0.145 (a'') (π)	0.142 (a'')	0.137 (a'')	0.136 (a')
	0.184 (e)	0.142 (a)	−0.003 (a')	0.052 (a')	0.086 (a')	0.023 (a')
			−0.405 (a'') (π)	−0.407 (a'')	−0.416 (a'')	−0.398 (a'')
Filled orbitals	−0.466 (e)	−0.419 (e)	−0.428 (a')	−0.430 (a')	−0.454 (a')	−0.417 (a')
	−0.611 (a)	−0.610 (a)	−0.591 (a')	−0.577 (a')	−0.606 (a')	−0.593 (a'')
	−0.747 (a)	−0.715 (a)	−0.678 (a')	−0.727 (a')	−0.686 (a')	−0.689 (a')
	−1.130 (a)	−1.076 (a)	−1.098 (a')	−1.084 (a')	−1.107 (a')	−1.075 (a')
	−7.785 (a)	−7.792 (a)	−7.799 (a')	−7.781 (a')	−7.798 (a')	−7.797 (a')
	−15.613 (a)	−15.587 (a)	−15.564 (a')	−15.593 (a')	−15.584 (a')	−15.565 (a')

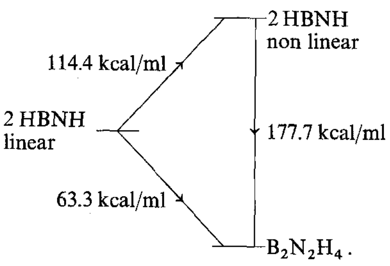
process is the energy required to bend the hydrogen bonds out of the boron-nitrogen plane. In order to determine which bending mode is the more energetic, two calculations were performed on boronimide in which only one hydrogen bond was bent out of the plane. From the results in Table 4 (d–e) it is found that 24.9 kcal/mole are required to bend the B–H bond and 4.1 kcal/mole needed to move the N–H bond out of the plane.

2.5. The Electronic Energy of Dimeric Boronimide

A very intriguing aspect of the production of borazine from boronimide is the absence of dimeric boronimide $(HBNH)_2$ in the process. It is therefore of interest to examine the electronic energies of the dimer of boronimide. In our calculation the boron-nitrogen framework was a square of length 1.47 Å [7] with the hydrogen atoms situated on a line extending along the diagonal by a distance equal to the corresponding hydrogen bond distance in borazine. The total and orbital energies of dimeric boronimide are presented in Table 5. It is found that the dimer is more stable than two molecules of boronimide by 63.3 kcal/mole. This is smaller than the corresponding 193.8 kcals/mole obtained for borazine and explains in part why the trimer is preferred to the dimeric form for boronimide (cf. Ref. [9]).

The energy required to reorganise boronimide into a configuration suitable for dimerisation was calculated to be 57.2 kcal/mole (Table 4a) and f)). This reorganisation energy to the dimer is smaller than to the trimer because of the greater bending of the bonds in the latter case (45° compared to 60°). We are now able to construct energy diagrams comparing the steps in the polymerisation processes.





The difference between the two processes is the larger stabilisation energy gained by trimerisation than by dimerisation. If we can make the assumption that this stabilisation is due to the energy gained by the formation of new boron-nitrogen bonds, then the energy of the new boron-nitrogen bond is 131.2 kcal/mole and 88.8 kcal/mole for borazine and dimeric boronimide respectively. The difference between these two values represents to some extent the strain energy involved in the bonds of the dimeric species. From reorganisation energy considerations, it is expected that with certain boronimide derivatives the reorganisation term would be the most important and in these cases the dimeric boronimide derivative would be formed. This would obtain when the derivative

Table 5. The total and orbital energies of dimeric boronimide $(HBNH)_2$ (in a.u.)

Electronic energy	-256.1485	
Nuclear energy	95.9027	
Total energy	-160.2458	
Virtual orbitals	0.228	$(b_{1u})\ \pi$
	0.079	$(b_{3g})\ \pi$
	-0.400	$(b_{2g})\ \pi$
	-0.500	(b_{3u})
	-0.555	$(b_{1u})\ \pi$
	-0.570	(b_{1g})
	-0.575	(b_{2u})
	-0.602	(a_g)
Filled orbitals	-0.733	(b_{3u})
	-0.769	(a_g)
	-1.082	(b_{2u})
	-1.252	(a_g)
	-7.796	(a_g)
	-7.796	(b_{3u})
	-15.560	(b_{2u})
	-15.561	(a_g)

is a bulky organic group or a group bonded strongly to the boron or nitrogen atoms.

The orbital energies of boronimide and dimeric boronimide listed in Tables 4 and 5 respectively, show that the highest filled orbital in both molecules is π-type and is largely concentrated about the nitrogen atoms. The π-electronic delocalisation energy of the dimeric boronimide is estimated by repeating the calculation with the π-electrons restricted to the nitrogen π-orbitals. The total energy of the localised model is -160.1177 a.u. which means that the π-delocalisation energy of dimeric boronimide is 80.3 kcal/mole. After adjustment for the differing number of π-electrons the delocalisation energy of dimeric boronimide is very similar to that of borazine. It would seem therefore that this value might be a constant transferable from molecule to molecule.

2.6. *The Electronic Population of Boronimide and Dimeric Boronimide*

The electronic population of boronimide is presented in Table 6. The electron densities are similar to the values in borazine, with the nitrogen and boron atoms possessing a large negative and positive charge, respectively. The B–N bond population, as expected, is greater in boromimide than in borazine, reflecting the shorter bond length and the involvement of more electrons in the B–N bond of the former. On examining the change in bond population of boromide with the change in configuration it is found that increasing the B–N bond length to that of borazine produces a small decrease in the B–N bond population ($\sigma = 0.351$, $\pi = 0.188$, $\pi' = 0.188$, total $= 0.727$). However, on moving the B–N and N–H bonds out of a linear configuration, there is a substantial decrease in the B–N bond population ($\sigma = 0.322$, $\pi = 0.208$, total $= 0.530$).

Table 6. The gross and overlap electronic populations of boronimide and dimeric boronimide

		Boronimide	Dimeric boronimide
Boron	S	2.767	2.815
	X	0.811	0.583
	Y	0.579 (π′)	0.822
	Z	0.579 (π′)	0.297 (π)
Total		4.736	4.517
Nitrogen	S	3.493	3.510
	X	1.288	1.288
	Y	1.421 (π′)	1.278
	Z	1.421 (π)	1.703 (π)
Total		7.623	7.729
Hydrogen (B)		0.965	1.016
Hydrogen (N)		0.676	0.738
B–N	σ	0.321	0.323
	π	0.222	0.069
	π′	0.222	
Total		0.765	0.392
H–B		0.434	0.427
H–N		0.369	0.364

The electronic population of dimeric boronimide presented in Table 6 shows that the electronic charge pattern is the same as in borazine. The π-electronic drift towards the boron is not as great as in the trimer but this is offset by a smaller σ-electron polarisation. The boron-nitrogen overlap population, however, is lower in dimeric boronimide than in borazine entirely due to a smaller π-electron contribution in the former.

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