Inorganica Chimica Acta, 70 (1983) 255–259

The Stabilities and Geometries of Triborylamines and of Compounds Containing the B_6 Moiety

A. NECKEL

Institut für Physikalische Chemie der Universität, Vienna, Austria

H. POLESAK

Institut für Technische Elektrochemie der Technischen Universität, Vienna, Austria

and P. G. PERKINS

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

Received June 9, 1982

The geometries and relative stabilities of some triborylamines and of some systems based on the B_6 ring have been calculated. It is shown that the triborylamine $N(BH_2)_3$ possesses a stable structure when two of the $N(BH_2)$ units lie in the same plane, whilst the third is rotated so that the H atoms are orthogonal to the plane. This is more stable than the all-planar structure. The parent compound $N(BH_2)_3$ is also shown to be intrinsically thermodynamically stable. Possible dimeric structures for this triborylamine are shown to be more stable than two moles of the monomer. However, amongst the dimers, a structure in which the bridging entities between the units are hydrogen atoms is shown to be more stable than one in which the bridging is brought about by the nitrogen atoms.

We find that the most stable structure in the gas phase of the compound $B_6(NH_2)_6$ is that in which the B_6 ring adopts a planar configuration. This is more stable than either a chair configuration, a boat configuration or an octahedral cage arrangement of boron atoms.

Introduction

The possible occurrence of triborylamines was suggested in a paper by Buckingham *et al.* some years ago [1] (Fig. 1). Compounds of the 'inverse' type, *i.e.*, $B(NH_2)_3$ are well known and in these, the electron deficiency in the boron is, to some extent, satisfied by internal electron donation from the three nitrogen atoms. In the triborylamines, the question arises as to whether one single nitrogen atom satisfies the electron deficiency of three boron atoms and, hence, renders such a material stable, planar, and a non-acceptor of electrons. Examples of both the diborylamines and the triborylamines have now been prepared by Nöth *et al.* [2–4] and they have turned out to manifest interesting chemical and structural properties. It has been found that, in the solid state, the compounds $N(B(SR)_2)_3$ have a planar configuration around the nitrogen atom but only two of the $-B(SR)_2$ groups lie in the same plane [4]. The thrid $(SR)_2$ group is rotated around the B–N bond such that the S atoms lie orthogonal to the main trigonal plane. There are 2 different N–B distances. This is an entirely unexpected geometrical situation for such a system and the question arises as to whether it represents a geometry intrinsic to the free molecule or whether it is one which is only adopted in the crystal. Moreover the parent triborylamine $N(BH_2)_3$ is, as yet, unknown and here the pivotal questions are, *a*) is the compound intrinsically thermodynamically stable; *b*) does it have the above 'rotated' structure; *c*) would it, like many other related boron-nitrogen compounds, dimerise to form a dimer more stable than two monomer units, and *d*) should the monomer units in the dimer be linked by nitrogen bridging or by hydrogen bridging?

The compound $B_6(NMe_2)_6$ has been synthesised [5]. The crystal structure shows that the compound has a basic B_6 ring in chair form. Now, in the borane anion $B_6H_6^{2-}$, the B_6 moiety adopts the configuration of a regular octahedral cage with a terminal hydrogen at each point of the cage. Moreover, the neutral B_6H_6 unit, as such, is electronically unstable and it was originally shown by Longuet–Higgins (and confirmed later) that such a geometry would require an extra pair of electrons to complete the filling of a degenerate set of framework orbitals [6]. Since the chair form of $B_6(NMe_2)_6$ is geometrically not too far removed from the B_6 octahedron and does not confer degeneracy, then it is of interest to inquire what is the energy required to pass from one geometry into the other.

0020-1693/83/0000-0000/$03.00

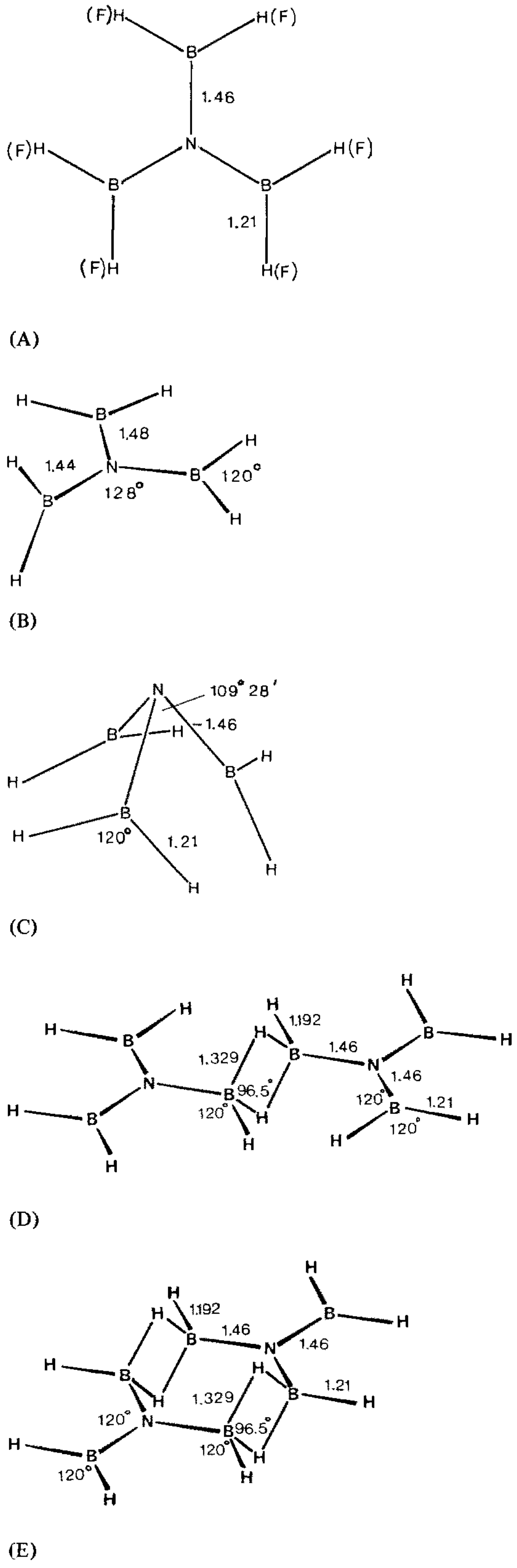


Fig. 1. The triborylamines.

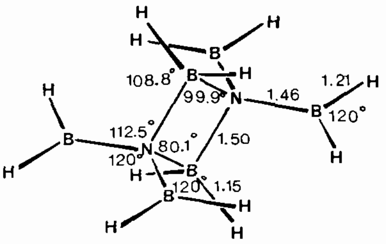
Method

We have attempted to answer these questions by direct calculations based on the molecular-orbital-bond-index method (MOBI) [7, 8]. This is based, essentially, on a CNDO/INDO quantum chemical method [9]. Although such molecules as these are accessible to *ab initio* quantum mechanical computation, the time required for such calculations is somewhat large and indeed, more importantly, the results obtained may well be *less* accurate and reliable than those which can be predicted by the MOBI method.

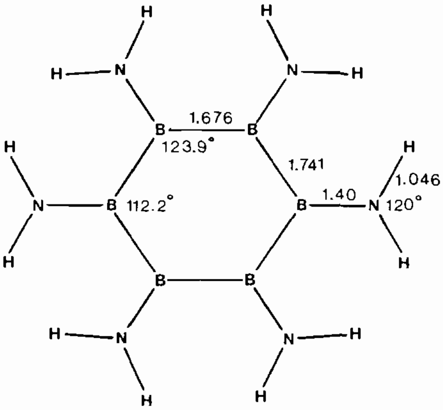
The MOBI method has been fully discussed previously [7, 8] and its use to obtain heats of formation for hydrocarbons and their derivatives has been shown to be accurate and reliable. The present approach is based completely on this method but, in addition, since no boron compounds have previously been investigated in this way, it has been necessary to calculate further bond-energy parameters which heretofore have not been available. In all, for the species mentioned above, bond-energy parameters for the bonds B–B, N–N, B–N, B–H, B–F, N–F and N–H are needed. The bonding parameter for N–H was calculated from the heat of atomisation [10] of NH_3 (derived from its heat of formation) together with an SCF calculation for that molecule, whilst in a similar way, the bonding parameters for B–H and B–B were obtained from the heat of atomisation of B_2H_6 and of BH_3 [10]. This yields the three values for B–H, B–B and N–H given in Table I. The bonding parameter for the B–N bond was then obtained from the heat of formation [10] and a coupled SCF calculation on borazine. The bond-energy parameter for N–N was estimated in a similar way from hydrazine [10] and those for BF and NF from BF_3 and NF_3, respectively [10]. All the derived bond-energy parameters are shown in Table I. The structures considered for monomeric $N(BH_2)_3$ and the derived dimers are shown in Fig. 1 [1]. The bond lengths and bond angles employed in the SCF calculations are also shown in Fig. 2. They are taken from Ref. 11 or reasonable values were assumed. Geometries

TABLE I. Atom Pair Bonding Parameters.

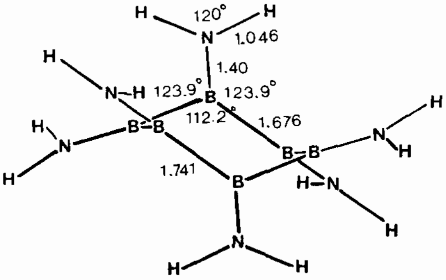
Bond	E, kcal mol^{-1}
B–H	89.2
B–B	71.2
B–N	84.5
B–F	145.6
N–H	93.1
N–N	52.7
N–F	66.7



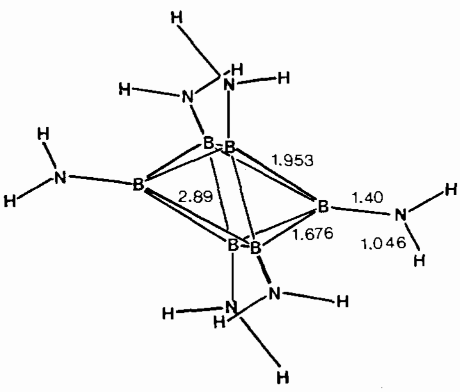
(A)



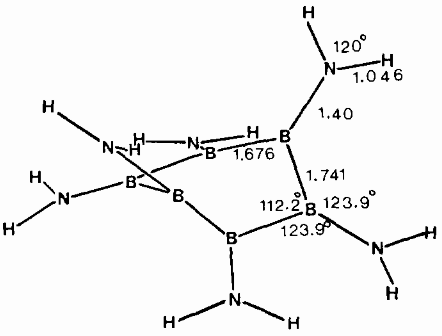
(B)



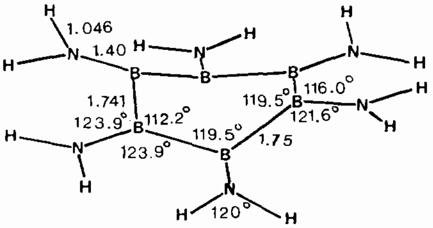
(C)



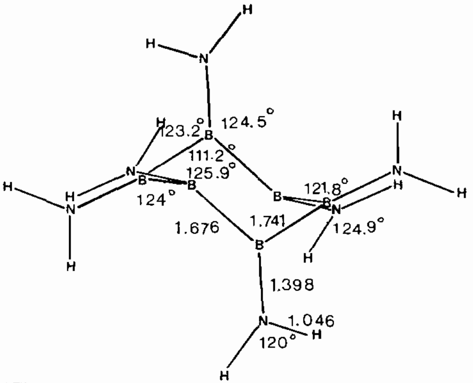
(D)



(E)



(F)



(G)

Fig. 2. Geometries for $B_6(NH_2)_6$.

investigated for the molecule $B_6(NH_2)_6$ are shown in Fig. 2. The basic geometrical data were taken from Ref. 5.

Results and Discussion

The results are most conveniently presented and discussed under two heads.

The Triborylamines

Table II shows the calculated heats of atomisation and standard heats of formation for the structures shown in Fig. 2. It is immediately obvious that the pyramidal structure, in which the configuration around the nitrogen atom is non-planar, is

TABLE II. Heats of Atomisation and Formation of Triborylamines.

Structure	ΔH_{atom}	ΔH^{o}_{f}
	kcal mol^{-1}	
I	852.0	−23.6
II	863.2	−35.7
III	730.3	97.2
IV	1203.7	−575.3
V	1730.8	−75.8
VI	1752.7	−97.7
VII	1687.4	−32.4

considerably less stable than either of the other two monomeric forms. Hence, this structure for the ground state can be dismissed. Its energy does, however, lead to a value for the reorganisation energy of the $N(BH_2)_3$ molecule and this will be discussed later. Of the two structures based on a planar configuration around nitrogen, the most symmetrical (D_{3h}) structure is less stable, by 12.1 kcal mol^{-1}, than the C_{2v} structure in which one of the N–B bonds is rotated. This is consistent with the experimental evidence for the crystal structure of $N(BSR_2)_3$ determined by Nöth *et al.* [4] and implies, moreover, that the structure should persist in the free molecule also. Nöth *et al.* recently adduced evidence from the n.m.r. spectra of $N(BSR_2)_3$ in solution that the molecule has equivalent B–N bonds in this medium. For $N(BH_2)_3$ the rotation barrier between the rotated and planar forms seems too high to allow this, although in the related molecule studied by Nöth it appears to be far lower. We have not yet examined this case. We see, too, that the parent compound $N(BH_2)_3$ is intrinsically thermodynamically stable with respect to dissociation to the element in the gas phase. Of the possible dimer structures, those which have hydrogen bridging are both more stable than that in which nitrogen forms the bridge between the two moieties. It may be further seen that dimerisation of two monomers to give the H-bridged dimer is an exothermic process yielding 28.6 kcal mol^{-1}. This is of the same order as the dimerisation energy of borane itself, although some 10 kcal mol^{-1} less, as might be expected since BH_3 is more electron-deficient. It is notable that corresponding dimerisation to a nitrogen-bridged dimer is an endothermic process. This correlates with the prediction made some years ago [12] with respect to hydrogen versus nitrogen bridging in such B–N complexes. As far as we are aware, this is the first time that such a quantitative comparison between nitrogen bridging and hydrogen bridging has been made.

Of the two possible dimers, it is seen, as expected, that the one in which only one hydrogen bridge appears is more stable than that possessing two hydrogen bridges. It would be interesting to discover to what extent this feature depends on the nature of the groups substituted on boron.

Of the three monomer structures, the pyramidal structure is the only one which is not intrinsically thermodynamically stable with respect to dissociation to the elements. The difference between this structure and the most stable one yields in principle the reorganisation energy. From the calculation this amounts to 121 kcal mol^{-1}. The reorganisation energy obtained here is very much in excess of what has been found for other boron-containing molecules, *e.g.*, BF_3 has a reorganisation energy amounting only to 34.2 kcal mol^{-1} [13]. We believe that this calculated reorganisation energy for $N(BH_2)_3$ is probably too large and that the bond lengths assumed in the pyramidal geometry are inappropriate. It is probable that, assuming the tetrahedral angle at the nitrogen atom, a longer N–B bond length would bring about stronger B–H and less B–B bonding in the reorganised species. This would lower its energy and make the reorganisation energy more realistic. Unfortunately, at present the MOBI technique does not afford a method of varying bond lengths so as to obtain a minimum value of energy, with a fixed interbond angle. Hence, there is nothing further we can add here at present.

The results infer that the nitrogen atom in the borylamines should be a very poor donor of electrons towards acceptors but the question of whether the boron atoms in the borylamines are good electron acceptors remains theoretically an open one. We have not carried out the calculation in which one or more boron atoms is reorganised to the pyramidal form. The acceptor boron atom must, of course, attain this configuration in the formation of a donor–acceptor bond and such planar-tetrahedral reorganisation energy is known to be an important factor in the energetics of donor–acceptor bond formation in bond complexes.

The Molecule $B_6(NH_2)_6$

Results of the MOBI calculation for all the geometries of $B_6(NH_2)_6$ shown in Fig. 2 are listed in Table III At the present time no structural data are

TABLE III. Heats of Atomisation and Formation of $B_6(NH_2)_6$ Isomers.

Structure	ΔH_{atom}	ΔH^{o}_{f}
VIII	2255.5	−148.7
IX	2213.3	−106.5
X	2227.3	−120.5
XI	2203.3	−96.5
XII	2254.9	−148.1
XIII	2214.5	−107.7

available for the basic B_6 compounds in solution; the known information (for $B_6(NMe_2)_6$) refers to the solid state. In solution, however, higher symmetry is indicated by n.m.r. measurements [5].

We find from the calculations that the order of stabilities in planar B_6 rings (VIII) ~ twisted ring (XII) > octahedral B_6 (X) > chair (XIII) ~ chair (IX) > boat form (XI). It seems, therefore, that a different sequence of stability is appropriate to the gas phase of $B_6(NH_2)_6$ and probably in solution also. Thus, the stability of the *chair* form of the real compound in the solid must stem from strong steric effects and favourable crystal packing which accommodates the N–Me groups and allows donor bonding interactions with the boron atoms of neighbouring molecules. The stable planar form predicted would fit with the higher symmetry of $B_6(NMe_2)_6$ evidence by the observed n.m.r. results [5] although the octahedral B_6 cage form would also contain equivalent boron atoms.

The latter geometry is interesting in that it is accessible from both the planar and the chair forms and does not lie too far in energy above the former. Clearly, in contrast to the B_6H_6 species, the -NR_2 groups internally satisfy the electron deficiency of the B_6 cage and render the system more stable than one where the substituents are not electron donors. The octahedral form is hence a plausible intermediate in transformations of the ring.

References

1 A. D. Buckingham, *Proc. Chem. Soc.*, 351 (1962).
2 W. Storck and H. Nöth, *Angew. Chemie, 88*, 231 (1976).
3 W. Storck and H. Nöth, *Chem. Ber., 110*, 1636 (1977).
4 H. Nöth, R. Staudigl and W. Storck, *Chem. Ber., 114*, 3024 (1981).
5 H. Nöth, private communication.
6 H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc., A224*, 336 (1954).
7 T. N. Bell and P. G. Perkins, *J. Phys. Chem., 81*, 2012 (1977).
8 T. N. Bell, K. A. Perkins and P. G. Perkins, *J. Chem. Soc., Faraday Trans. I*, 1779 (1981).
9 D. R. Armstrong, P. G. Perkins and J. J. P. Stewart, *J. Chem. Soc. A*, 3654 (1971).
10 R. T. Sanderson, 'Chemical Bonds and Bond Energy', Academic Press, New York (1976).
11 A. F. Wells, 'Structural Inorganic Chemistry', 3rd Edn., Oxford University Press, London (1962); Tables of Interatomic Distances in Atoms and Ions, *Chem. Soc. Spec. Publ. 11*, 18, Chemical Society, London, 1958, 1965.
12 D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 2748 (1970).
13 D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta, 15*, 413 (1969).