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MNDO Study of Boron-Nitrogen Analogues of Buckminsterfullerene

by

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MNDO STUDY OF BORON-NITROGEN ANALOGUES OF BUCKMINSTERFULLERENE

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ABSTRACT

An MNDO study of boron-nitrogen analogues of buckminsterfullerene is presented. The relative properties of ($@C_{60}$), ($@B_2C_{58}$), ($@N_2C_{58}$), ($@BNC_{58}$), ($@C_{12}B_{24}N_{24}$) and ($@B_{30}N_{30}$) are studied. The heats of formation of such 60-atom systems from benzene, naphthalene and their BN analogues are compared. It is found that all these hybrids are approximately as stable as buckminsterfullerene. Surprisingly, it is predicted that ($@B_{30}N_{30}$) will be stable and should be relatively simple to synthesize from borazine.

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I. INTRODUCTION

Recent experiments have shown that individual boron atoms can displace carbon atoms in the bucky ball molecule, creating "dopey ball" fullerene structures with the stoichiometry $(@B_nC_{60-n})$, where n ranges from 1 to 6.¹ The @ symbol indicates a closed fullerene structure with all atoms forming an integral part of the cage framework.² While it has not yet been demonstrated, it seems reasonable that BN-analogues of buckminsterfullerene could also be synthesized. It has been suggested¹ that $(@B_{30}N_{30})$ would not be stable since it would require that N-N and B-B bonds exist in the molecule, presumably destabilizing it. In particular, it is supposed that N-N σ -bonds would be unfavorable.

In response to this suggestion, we have proposed a molecule in which the largest possible number of carbons are substituted subject to the constraint that there be no B-B or N-N bonds.³ This turns out to imply that each pentagon must contain one carbon atom, yielding the stoichiometry $(@C_{12}B_{24}N_{24})$; the optimal structure is shown in Fig. 1, and belongs to the S_6 point group. A simple Hückel calculation indicated that it would be more stable than buckminsterfullerene. Nothing in what follows changes that conclusion, although we now have considerably more information to report.

We describe here the results of an MNDO study of boron-nitrogen analogues of buckminsterfullerene. Given computational limitations, we are essentially limited to closed shell systems, and hence are restricted to an even number of substituted atoms. Thus we consider $(@C_{60})$, $(@B_2C_{58})$, $(@N_2C_{58})$, $(@BNC_{58})$, $(@C_{12}B_{24}N_{24})$ and $(@B_{30}N_{30})$. There are obviously many possible isomers of most of these species, and we consider several of each.

In order to establish the accuracy of our method, we have compared the MNDO calculated heats of formation for benzene, naphthalene and borazine with experimental values. It is seen that the MNDO calculation overestimates all of these formation enthalpies by about 7%. The data are given in Table I, along with those for two naphthalene analogues. While we have found no comparable experimental data for the latter, this information will be useful in what follows.

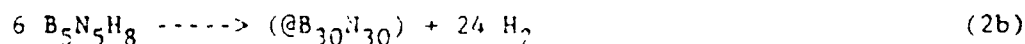
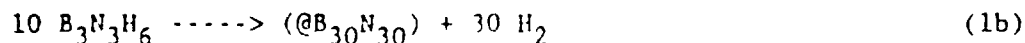
The first MNDO calculation for buckminsterfullerene was performed by Newton and Stanton.⁶ Their value for the standard heat of formation agrees with ours, +869 kcal/mol. A 6-31G SCF calculation⁷ yielded a value of +672 kcal/mol, whereas classical methods gave +574 kcal/mol (MM3)⁸ and +286 kcal/mol (MMP2).⁹ Beckhaus et al report the value measured from bomb calorimetry of crystalline buckminsterfullerene as +545 kcal/mol.¹⁰ Thus it appears that MNDO significantly overstates the heat of formation. Given the relative accuracy of the method for simple rings, one presumes that MNDO overestimates the strain energy involved in sphere closure. If this is true, then our results should nevertheless be qualitatively correct since the strain energy among our various isomers should be relatively constant. On the other hand, classical force-field methods probably do not adequately measure differences in conjugation energy, and hence are less useful

for comparing molecules of similar geometry. In addition, they give no information about charge distribution.

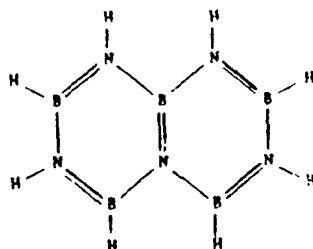
The next section contains the results and discussion of our work. Section III is a brief conclusion.

II. RESULTS AND DISCUSSION

We first report the relative stability of various species. These data are summarized in Table II, where calculated enthalpies of the following reactions are compiled:

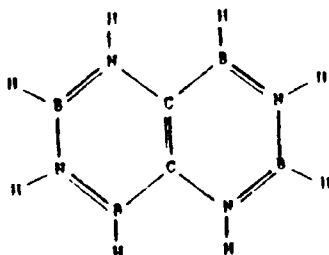


Each of these reactions corresponds to the synthesis of a 60-atom fullerene from its benzene- and/or naphthalene-like precursor. Among the reactants, benzene, naphthalene and borazine are well known. The reactant in Eq. 2b is



(I)

and its synthesis from the pyrolysis of borazine has been reported.¹¹ The reactant in Eq. 2c is



(II)

This precursor has not been made, though something quite similar has been reported.¹²

From Table II we see that our original conjecture³ that ($@C_{12}B_{24}N_{24}$) (which we nickname CBN-ball) is stable is supported by the MNDO calculations. As described in Ref. 3 and shown in Fig. 1, this structure has one carbon on each pentagon, with two pentagons linked by a C-C bond. There is S_6 symmetry, with one C_3 axis. Thus one can distinguish between polar and equatorial carbon atoms, there being six of each.

Most important are the data for the synthesis of CBN-ball from the naphthalene derivatives, shown in Table III: +639 kcal/mole for bucky ball vs. +265 kcal/mole for CBN-ball (compare Eqs. 2a and 2b). This corresponds to a difference of 346 kcal/mol in favor of the substituted derivative. Part of the reason for this result appears to be the relative instability of that analogue (I), and suggests the possibility of successful synthesis via the naphthalene precursor. For comparison, we indicate the enthalpy of the reaction of bucky ball from benzene, and it is seen in Table III to be 17 kcal/mole higher than the formation of C_{60} from naphthalene. Yet C_{60} can be made from the pyrolysis of benzene and other hydrocarbons.¹³ There is no benzene analogue with the same stoichiometry as CBN-ball.

Table III also gives the enthalpy of reaction for the synthesis of ($@B_{30}N_{30}$) (denoted BN-ball) from borazine and the naphthalene analogue. This value is for the formation of an isomer (denoted A, shown in Fig. 2) which is approximately as stable as bucky ball. It contains 6 B-B and 6 N-N bonds, and is generated by substituting all the C-C bonds in CBN-ball with B-N moieties. This can be done in a number of different ways, for example by placing all the borons in polar positions and the nitrogens along the equator. We have not checked all possibilities, but suppose that they will not differ significantly in energy. They may be quite different in their reaction chemistries, however. The original hypothesis,¹ that N-N and B-B bonds will tend to destabilize the structure, is supported by our calculation. Results for a second, less stable isomer (denoted B, with C_{3h} symmetry) are also given in Tables II and III. B is obtained by replacing carbons with nitrogens in the northern hemisphere, and with borons in the southern hemisphere. B is nearly 200 kcal/mol less stable than A, as it contains 9 N-N bonds vs. 6 N-N bonds for A. (The number of B-B bonds in all cases equals the number of N-N bonds.) We also checked intermediate cases where some C-C bonds were replaced by B-N moieties, and others by B-B and N-N moieties, thus producing structures with 8 or 7 N-N bonds. These results confirm the notion that N-N bonds are destabilizing. Presumably, ($@B_{30}N_{30}$) could be made more stable by substituting carbon atoms for each B-B and N-N bond, until the optimal stoichiometry of CBN-ball is reached.

We now turn our attention to the less substituted species, ($@C_{58}B_2$), ($@C_{58}N_2$) and ($@C_{58}BN$). Both of the nitrogen-containing compounds have lower total energies than bucky ball, whereas ($@C_{58}B_2$) has higher energy. (Note that heats of formation are not directly comparable, since the reference points are not the same.) This is easily explained by a comparison of atomic sizes and corresponding

electronegativities. Nitrogen is more electronegative than either carbon or boron, and hence its total electronic energy is lower. This is not necessarily a good indication of the relative stability of the cluster. Smalley et al.¹⁴ have reported that the attempted synthesis of N-containing species from N-doped graphite produces N_2 gas rather than substituted bucky ball. He suggests, and our calculations confirm, that beginning from carbon-containing nitrogen compounds will probably be more successful. For example, pyrolysis of benzene doped with pyridine might produce the desired result. However, very recent work has shown that the vaporization of graphite under nitrogen or ammonia gas yield nitrogen adducts of bucky ball, with evidence that some are substituted into the cage.¹⁵

For computer-time reasons, our calculation is restricted to closed-shell systems. Hence we performed calculations only when an even number of carbons are substituted. Our intention was to probe a variety of different isomers, and since the available experimental results seem to indicate that boron dopant atoms are non-adjacent on the bucky ball surface,¹ we wanted to estimate the energy difference as a function of dopant atom separation by studying different isomers of $(@C_{58}B_2)$. This has proved not to be possible since widely spaced dopant atoms yields an open-shell diradical. This indicates that, like polymers, doped bucky ball has a delocalization length beyond which electronic defects are not smoothed out.¹⁶ (This does not contradict the well-known result that the electronic structure of bucky ball is globally delocalized, since the diradical requires electron deficient centers.) While this presents a serious problem for our calculation, it would seem to be a boon for chemists interested in producing exo-derivatives from these species. They would appear to be quite reactive and to have an electronic structure very different from bucky ball. This is confirmed by a recent Car-Parrinello study of $(@C_{59}B)$ and $(@C_{59}N)$.¹⁷

For systems isoelectronic with bucky ball, e.g., $(@C_{58}BN)$, we were able to place the two dopants anywhere in the molecule. Three cases were studied: (1) a B-N bond between two hexagons; (2) the B and N atoms not bonded but on the same hexagon; and (3) the B and N atoms on opposite sides of the molecule. In the first case, the boron was found to be electron deficient and the nitrogen electron rich. This is consistent with the relative electronegativities, and is also the same as the pattern universally observed for all BN-ball isomers. There is a general tendency for σ -electron density to be transferred toward the nitrogen, whereas π -electrons move toward the boron.¹⁸ For boron, the charge density in $(@C_{58}BN)$ is +0.0523, and for nitrogen, it is -0.1450. This compares with the charge distributions in BN-ball, which range around ± 0.23 , though because of the asymmetry there is considerable variation.

If the boron and nitrogen atoms are not bonded to one another, however, then there is obviously little σ -electron transfer between them. Nitrogen is still electronegative, and so borrows electrons from surrounding carbons. The boron forms a hole into which π -electrons sink, and therefore becomes negatively charged despite

its relatively low electronegativity. For the B, N on same hexagon, the charges are -0.1467 and -0.0491 respectively, whereas for atoms on opposite sides of the cluster the comparable values are -0.1292 and -0.0942. In both cases the boron is more negative than the nitrogen. The energies of the three isomers of ($@C_{58}BN$) are almost identical, with the B-N bonded structure slightly favored.

III. CONCLUSION

While we reiterate here the semi-quantitative nature of our results, it must nevertheless be stated that MNDO is best suited to our present purpose. Our intention is to compare a large number of different structures where electrons are globally delocalized. This appears to preclude classical calculations, which would not properly account for the delocalization. Assuming that the discrepancy between MNDO and experiment accrues mostly from strain energy, and noting that the strain energy must be approximately constant among all structures studied, MNDO would appear to be the method of choice.

The essential qualitative result may thus be summarized as follows: It seems that BN-substituted derivatives of ($@C_{60}$) will be stable, especially those species which are isoelectronic with bucky ball. From the reactions described by Eqs. 2a-c, it seems that ($@C_{12}B_{24}N_{24}$) is more stable than bucky ball, which is slightly more stable than ($@B_{30}N_{30}$). The significantly lower reaction enthalpy for the formation of CBN-ball is due in part to the relative instability of the naphthalene-like precursor. But, based on total energies (Table II), all species rival bucky ball with respect to thermodynamic stability.

Kinetic stability is harder to judge. As was noted above, bucky ball has been synthesized by the pyrolysis of benzene.¹³ This suggests that ($@B_{30}N_{30}$) might be obtained from borazine either by thermal degradation as per Eq. 1b, or by high-temperature air oxidation.¹⁹ ($@C_{12}B_{24}N_{24}$) represents a more difficult synthetic problem. Precursors having C:B:N atomic ratios of 1:2:2 would be especially attractive, as illustrated by Eq. 2c, but such species are rare. However, a synthetic route to compounds having fused CB_2N_2 rings has been described.¹²

Once made, both BN-ball and CBN-ball are expected to have significantly different chemical properties from those of ($@C_{60}$). Bucky ball itself is reactive toward both nucleophiles and electrophiles.²⁰ The uneven charge distributions of the B- and N-doped clusters should increase both types of reactivity, making them attractive as ligands, electron transfer agents, etc. They would be important additions to the chemical arsenal.

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Table I: Calculated vs. Experimental Enthalpies of Formation for Selected Compounds.

<u>Compound</u>	<u>ΔH_f° (kcal/mol)</u>		<u>Reference</u>
	<u>MNDO</u>	<u>Expt.</u>	
C_6H_6	+ 21.3	+ 19.8	4
$C_{10}H_8$	+ 38.3	+ 36.1	-
$B_3N_3H_6$	-131.1	-124	5
$C_2B_4N_4H_8$	-132	-	
$B_5N_5H_8$	-122.5	-	
C_{60}	+869.3	+545	10

Table II: Calculated Total Energies and Enthalpies of Formation for Some Sixty-Atom Clusters.

Compound	Geometry	Energy (eV)	ΔH_f° (kcal/mol) ^a
C ₆₀	I _h	-7636	+869.3
B ₃₀ N ₃₀ (A)	6 N-N bonds	-8360	-681.5
B ₃₀ N ₃₀	3 N-N bonds	-8354	-651.7
B ₃₀ N ₃₀ (B)	9 N-N bonds	-8351	-489.0
C ₁₂ B ₂₄ N ₂₄	S ₆	-8221	-526.8
C ₅₈ N ₂	n-p bond	-7795	+888.3
C ₅₈ N ₂	h-h bond	-7795	+905.2
C ₅₈ B ₂	h-h bond	-7521	+864.9
C ₅₈ BN	h-h bond	-7660	+834.4
C ₅₈ BN	same hex	-7659	+861.6
C ₅₈ BN	opposite	-7658	+881.5

^afor formation from the standard states of carbon, boron and/or nitrogen at 25°C.

Table III: Enthalpies for Selected Synthetic Reactions Producing Sixty-Atom Clusters, as Calculated from MNDO Data in Tables I and II.

<u>From Benzene or Analogue</u>	<u>ΔH° (kcal/mole)</u>
10 C ₆ H ₆ -----> (@C ₆₀) + 30 H ₂	+656.1
10 B ₃ N ₃ H ₆ -----> (@B ₃₀ N ₃₀) + 30 H ₂	+629.5 ^a +822.0 ^b
<u>From Naphthalene or Analogues</u>	<u>ΔH° (kcal/mole)</u>
6 C ₁₀ H ₈ -----> (@C ₆₀) + 24 H ₂	+639.3
6 B ₅ N ₅ H ₈ -----> (@B ₃₀ N ₃₀) + 24 H ₂	+671.5 ^a +864.0 ^b
6 C ₂ B ₄ N ₄ H ₈ -----> (@C ₁₂ B ₂₄ N ₂₄) + 24 H ₂	+265.2

^aIsomer A of (@B₃₀N₃₀).

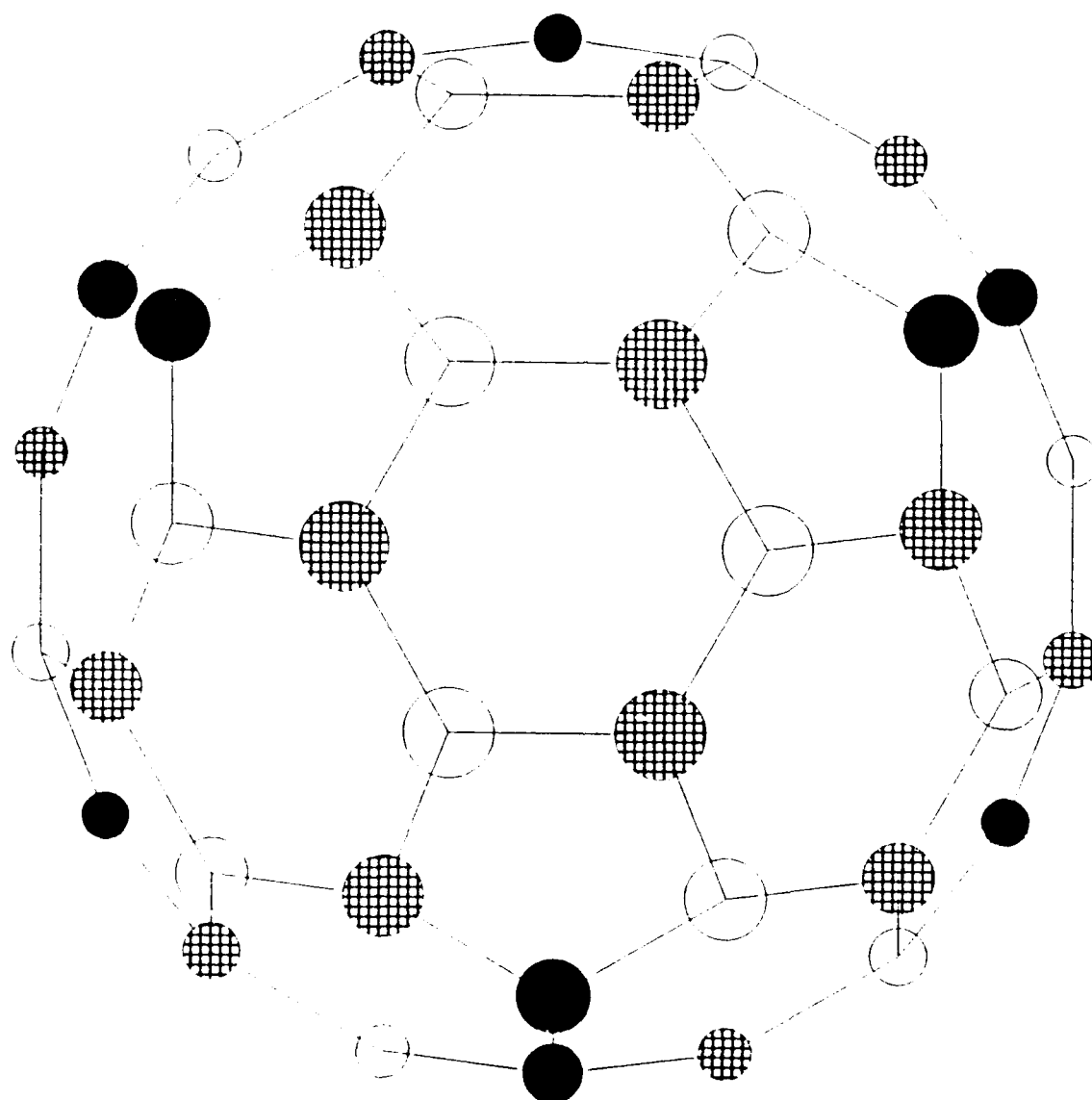
^bIsomer B of (@B₃₀N₃₀).

FIGURE CAPTIONS

Figure 1: The structure of $(@C_{12}B_{24}N_{24})$ as viewed along the C_3 rotational axis. Nine of the twelve carbons (all six equatorial plus three polar) are shown. Taken from Ref. 3.

Figure 2: The A isomer of $(@B_{30}N_{30})$. Borons are shown as hatched circles, the others being nitrogen atoms. Note that if a six-membered ring has an N-N bond, it must also have a B-B bond in order to be isoelectronic with the carbon equivalent. About half the molecule is shown.

Fig. 1



○ = Nitrogen

▨ = Boron

● = Carbon

Fig. 2

