absolute values and the spread of the effective proton affinities (EPA) are model dependent since the protein and solvent polarization are not considered in detail and the model is both static and highly simplified. Local bonding networks of hydrogen bonds to both the histidine tripod and the water and hydroxide ligands would profoundly affect the magnitude of the EPA. For example, we have recently shown that the ionicity of the first-shell complex is a function of the pH, and proton transfer between the first and second shell of the active site modulates the EPA.[7] The effect of the active site fields and, in particular, the presence of partially ionic H bonds to the active site Thr-199 has also been shown to be large.[31] The basic assumption in the persent calculation is the dominance of the metal-binding interaction in the first shell of the active site in determining the EPA, and the relative EPA are obtained if the metal substitution does not alter the first shell too much.

Examination of Table II shows the number of different factors that are important in determining the EPA. The Born estimate of the reaction field interaction is the most significant. The cavity radius increases by about 0.25 Å in going from ZnCA to CdCA. This leads to a relative stabilization of ZnCA in the protonated state while the high-pH complex has roughly constant Born energy for all the dications. Consequently, the spread in the EPA is reduced by about 7 kcal/mol relative to the SCF cluster values. In one case, the higher moment contributions to the Born energy have a qualitative effect on the relative EPA values. The reaction field stabilization energy of the MnCA high-pH model is smaller than that for the larger CdCA cluster. This is because of the larger M–O–H angle found for Mn (see Table I), giving a more symmetric cluster with smaller dipole and quadrupole moments leading to a smaller reaction field energy.

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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.

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 suggested[1] 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 Figure 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.

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

	$\Delta H_f°$ (kcal/mol)		
compound	MNDO	exptl	ref
C_6H_6	+21.3	+19.8	4
$C_{10}H_8$	+38.3	+36.1	4
$B_3N_3H_6$	−131.1	−124	5
$C_2B_4N_4H_8$	−132		
$B_5N_5H_8$	−225.5		
C_{60}	+869.3	+545	10

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.

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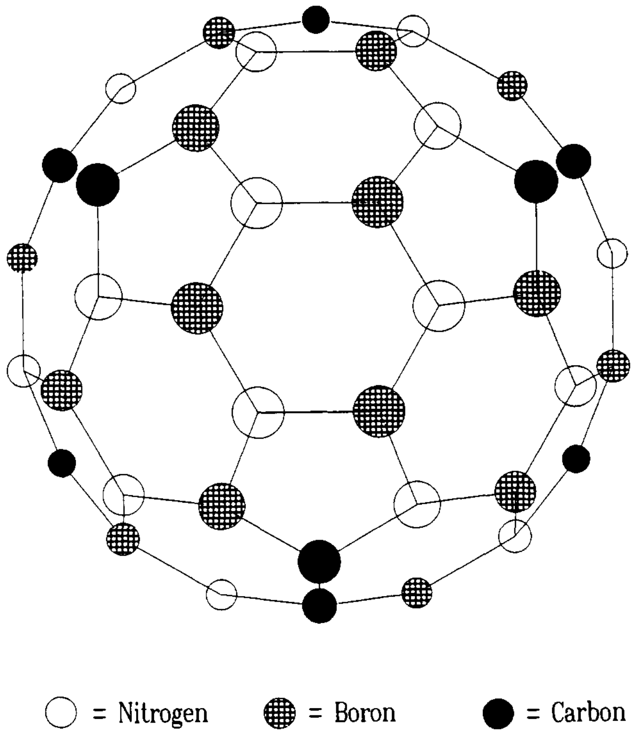


Figure 1. The structure of ($@C_{12}B_{24}N_{24}$) as viewed along the C_3 rotational axis. Nine of the twelve carbons (all six equatorial plus three polar) are shown. Taken from ref 3.

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 calculation[7] 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. Calculated enthalpies of the following reactions are compiled in Table III:

$$10C_6H_6 \rightarrow (@C_{60}) + 30H_2 \tag{1a}$$

$$10B_3N_3H_6 \rightarrow (@B_{30}N_{30}) + 30H_2 \tag{1b}$$

$$6C_{10}H_8 \rightarrow (@C_{60}) + 24H_2 \tag{2a}$$

$$6B_5N_5H_8 \rightarrow (@B_{30}N_{30}) + 24H_2 \tag{2b}$$

$$6C_2B_4N_4H_8 \rightarrow (@C_{12}B_{24}N_{24}) + 24H_2 \tag{2c}$$

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

compound	geometry	energy (eV)	$\Delta H_f°$ (kcal/mol)[a]
C_{60}	I_h	−7636	+869.3
$B_{30}N_{30}$ (**A**)	6 N–N bonds	−8360	−681.5
$B_{30}N_{30}$	8 N–N bonds	−8354	−551.7
$B_{30}N_{30}$ (**B**)	9 N–N bonds	−8351	−489.0
$C_{12}B_{24}N_{24}$	S_6	−8221	−526.8
$C_{58}N_2$	h–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

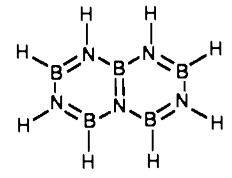
[a] For formation from the standard states of carbon, boron, and/or nitrogen at 25 °C.

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

from benzene or analogue	$\Delta H°$ (kcal/mol)
$10C_6H_6 \rightarrow (@C_{60}) + 30H_2$	+656.3
$10B_3N_3H_6 \rightarrow (@B_{30}N_{30}) + 30H_2$	+629.5,[a] +822.0[b]
from naphthalene or analogues	**$\Delta H°$ (kcal/mol)**
$6C_{10}H_8 \rightarrow (@C_{60}) + 24H_2$	+639.5
$6B_5N_5H_8 \rightarrow (@B_{30}N_{30}) + 24H_2$	+671.5,[a] +864.0[b]
$6C_2B_4N_4H_8 \rightarrow (@C_{12}B_{24}N_{24}) + 24H_2$	+265.2

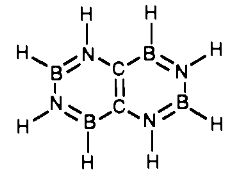
[a] Isomer **A** of ($@B_{30}N_{30}$). [b] Isomer **B** of ($@B_{30}N_{30}$).

Each of these reactions corresponds to the synthesis of a 60-atom fullerene from its benzene- 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 conjecture[3] 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 Figure 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/mol for bucky ball vs +265 kcal/mol for CBN-ball (compare eqs 2a and 2c). This corresponds to a difference of 374 kcal/mol in favor of the substituted derivative. Part of the reason for this result

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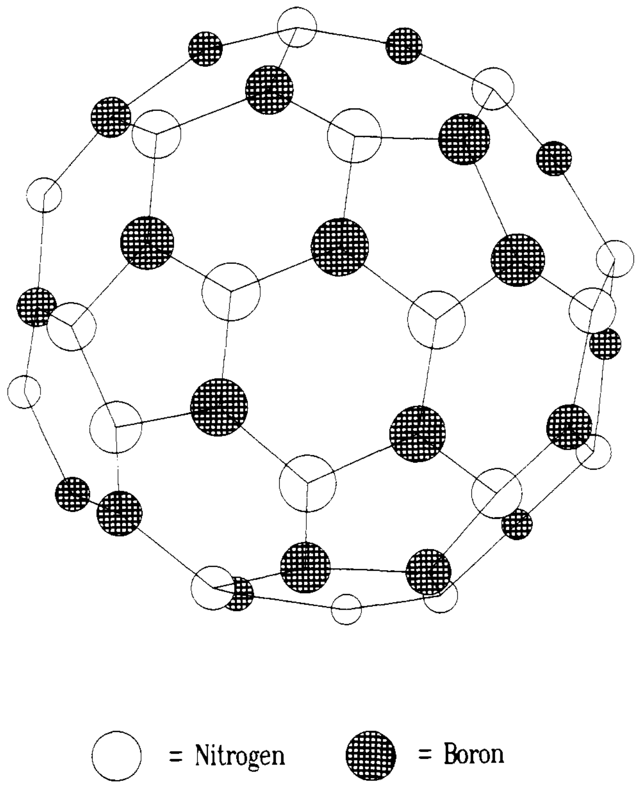

Figure 2. The **A** isomer of ($@B_{30}N_{30}$). Note that if a six-membered ring has an N–N bond, it must also have a B–B bond in order to be isoelectronic with the carbon equivalent. About half the molecule is shown.

appears to be the relative instability of that analogue II 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/mol 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 Figure 2) which is approximately as stable as bucky ball. It contains six B–B and six 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 nine N–N bonds vs six 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 eight or seven 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 nonadjacent 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. However, adjacent dopant atoms break the symmetry of the species, and hence the open-shell problem does not arise in this case. 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 and N on same

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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 semiquantitative 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.

Acknowledgment. We thank Dr. J. Thomas McKinnon for providing us with a useful reference. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research. We acknowledge that this research was partially supported by a grant from the Research Corporation, and we also thank the SUNY Research Foundation for an Equipment Matching Grant. T.F.G. acknowledges support by the Office of Naval Research and the National Science Foundation under Grant No. CHE-9196214.

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Momentum Distributions, Spin Distributions, and Bonding in CH_3NH_2 and Its Radical Cation

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Received February 13, 1992

Abstract: Theoretical spherically averaged momentum distributions for canonical Hartree–Fock and Dyson orbitals are presented for methylamine and compared with the EMS spectra. Theoretical spin densities are also reported for the radical cation and compared with the EPR spectrum. To the first approximation, both of these experiments give information about the HOMO of the neutral molecule. Both results clearly show effects from hyperconjugative delocalization of the nitrogen lone-pair onto the methyl group. The methyl group is found to be electron withdrawing relative to hydrogen in forming methylamine from ammonia. The amino group is similarly electron withdrawing relative to hydrogen in forming methylamine from methane.

Introduction

Data from electron momentum spectroscopy[1,2] and electron paramagnetic resonance spectroscopy[3] are available for methylamine and its radical cation. These results and previous theory[1,2,4–6] for this molecule are interpreted on the basis of new calculations.

Electron momentum spectroscopy[7] (EMS), also known as (e,2e) spectroscopy, has recently proven to be a very effective probe of electronic structure. Experimentally, an electron beam of high energy is directed at gas-phase target molecules, resulting in a scattered electron, an ejected electron, and a molecular cation. The few pairs of outgoing electrons which happen to have equal energies and both paths at an angle θ (usually 45°) to the unscattered beam are selected for detection. The azimuthal angle ϕ between the planes defined by the incoming and outgoing

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