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MNDO Calculations on Boron–Nitrogen Derivatives of Nonbenzenoid Aromatics: I. The Two Fully Boron–Nitrogen-Alternating Isomers of "Inorganic Azulene"[1]

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ABSTRACT

*Modified neglect of diatomic overlap (MNDO) calculations have been used to investigate the ground state properties of the two fully boron–nitrogen-alternating isomers of "inorganic azulene": 1,3,4,6,8-pentaaza-2,3a, 5,7,8a-pentaboraazulene (**1**, 1,3,4,6,8-PAPBAZ) and 2,3a,5,7,8a-pentaaza-1,3,4,6,8-pentaboraazulene (**2**, 2,3a,5,7,8a-PAPBAZ). Both molecules optimize to planar structures, have exothermic heats of formation (−194.4 kcal/mol and −161.4 kcal/mol, respectively), and exhibit some bond delocalization. The relationship of these two PAPBAZ isomers to their organic parent molecule, azulene, is discussed.*

INTRODUCTION

Borazine, $B_3H_6N_3$, first prepared by Stock and Pohland [1] in 1926, has often been referred to as "inorganic benzene" [2]. However, although borazine is planar [3] and exhibits physical properties that closely resemble benzene [4], the chemical properties of borazine suggest little aromatic character [5].

The contrasts between benzene and borazine led us to investigate "hybrids" of these molecules based upon the substitution of [HNBH] fragments for [HCCH] fragments in benzene. Such substitutions result in the three azaborines (C_4H_6BN) [6] and the eleven diazadiborines ($C_2H_6B_2N_2$) [7].

The similarities (and differences) between benzene and borazine can be extrapolated to boron–nitrogen (B — N) analogs of nonbenzenoid aromatics. One of the most well-known nonbenzenoid aromatics is azulene (**AZ**). Unlike borazine, wherein only *one* fully B — N alternating analog of benzene is possible, there are *two* B — N analogs of azulene in which the molecular periphery is fully B — N alternating. For these two cases, the atoms involved in ring fusion are either both boron (**1**) or both nitrogen atoms (**2**). Other isomers are possible: There are 130 distinct isomers, in addition to **1** and **2**, with the formula $B_5H_8N_5$. Each of these isomers contains a seven-membered ring fused to a five-membered ring [8] (Scheme 1).

Apparently, only one report of any of the isomers of pentaazapentaboraazulene (referred to hereinafter as PAPBAZ) has been published [9]. In this report, calculations of ring current contributions to diamagnetic susceptibilities, based upon planar structures with fixed bond lengths, were reported for **1** and **2**. We have not found any experimental or synthetic reports dealing with any of the isomers of PAPBAZ.

Because of the continuing interest in the properties of azulene, both synthetic [10] and theoretical [11], we began an investigation of the structures and ground state properties of the isomers of PAPBAZ.

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[1] This paper is dedicated to the academician A. V. Kirsanov on the occasion of his 90th birthday.

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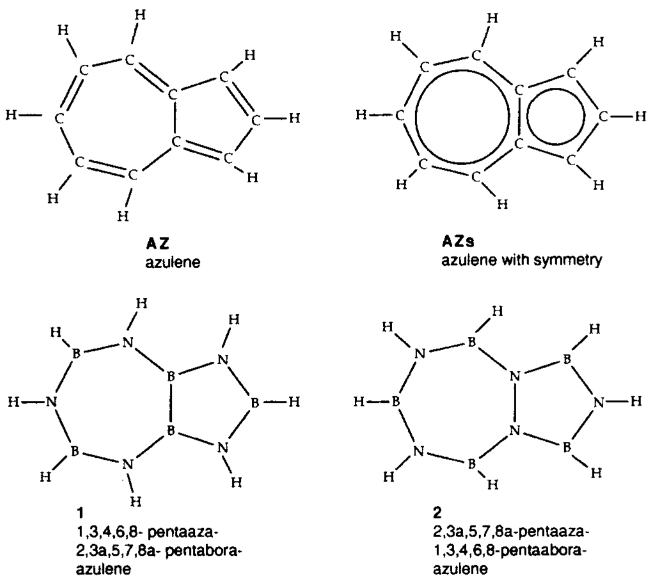

AZ
azulene

AZs
azulene with symmetry

1
1,3,4,6,8- pentaaza-
2,3a,5,7,8a- pentabora-
azulene

2
2,3a,5,7,8a-pentaaza-
1,3,4,6,8-pentaabora-
azulene

SCHEME 1

Herein we report our results for the two fully B–N alternating isomers of PAPBAZ.

METHODS

Modified neglect of diatomic overlap (MNDO) calculations were performed using QCPE [12] program number 455 (v. 5.0), "MOPAC: A General Molecular Orbital Package," suitably modified to run in a UNIX environment on Apollo DN10000 and DN3550 workstations. This program uses the Broyden–Fletcher–Goldfarb–Shanno [14] method to optimize geometries.

The initial trial geometries (ITGs) for the calculations employed a heavy atom–heavy atom bond distance of 1.5Å with a heavy atom-hydrogen bond distance of 1.1Å. All molecules were assumed to be planar systems composed of a regular heptagon fused to a regular pentagon. No nonplanar ITGs were systematically investigated. Occasionally, tests on certain structures were carried out with different ITGs and/or at higher levels of precision in the gradient norm and self-consistent field (SCF) criteria to investigate the influences of these changes on the final calculated molecular properties. In no case was a difference greater than 0.005 kcal/mol in heat of formation ever demonstrated. The magnitudes of the differences in other molecular properties were similarly small. Molecules were optimized to individual gradients of 0.01 kcal/Å or kcal/radian, and all $3n-6$ degrees of fredom were allowed to optimize (with the exception of **AZs**, *vide infra*).

RESULTS AND DISCUSSION

General Ground State Properties

Table 1 Contains the MNDO-calculated results for the heats of formation, ionization potentials, and dipole moments for azulene and **1** and **2**. Azulene was calculated from two different ITGs. These were **AZ**, in which all degrees of freedom were allowed to optimize, and **AZs**, in which C_{2v} symmetry was forced upon the molecule. Although **AZ** is nearly planar (no carbon atom is more than 0.0009 Å from the *xy*-plane), **AZs** is defined planar, and this difference, coupled with the symmetry forced upon the bond distances, created significant differences in the results for the two structures.

The symmetrical azulene structutre, **AZs**, is slightly less stable than **AZ** by approximately 2.2 kcal/mol; the reported value for the heat of formation of azulene is 73.5 kcal/mol [15], intermediate between the MNDO-calculated values for **AZ** and **AZs**.

The two PAPBAZ isomers, **1** and **2**, which optimize as planar molecules, both have exothermic heats of formation (as was found for borazine [16]), with **1** being more stable than **2** by 33.0 kcal/mol. This significant energy difference between two such similar molecules may be rationalized with reference to the positions of the nitrogen atoms in each molecule. Because nitrogen has a greater electronegativity than does boron, the nitrogen atoms will attain an increased electron density compared to the boron atoms. Placing two nitrogen atoms adjacent to each

TABLE 1 MNDO-Optimized Results[a] for Azulene, **1**, and **2**

Compound	*Heat of Formation (kcal/mol)*	*Ionization Potential (ev)*	*Dipole Moment (debye)*
Azulene (**AZ**)	+72.13	8.067	1.004
Azulene with symmetry (**AZs**)	+74.34	7.791	1.595
1,3,4,6,8-Pentaaza-2,3a,5,7,8a-pentaboraazulene (**1**)	−194.4	9.941	0.02047
2,3a,5,7,8a-Pentaaza-1,3,4,6,8-pentaboraazulene (**2**)	−161.4	9.282	0.03813

[a] All values have been arbitrarily rounded to four significant figures [12].

other, as in **2**, should involve significant electron-electron repulsion, and result in a more positive heat of formation. PAPBAZ isomer **1** has no N—N bonds, resulting in a molecule with greater calculated thermodynamic stability.

The experimental dipole moment of azulene is 1.08 debye [17], which compares well to that calculated for **AZ**, but is much lower than that calculated for **AZs**. The dipole moment of azulene is often rationalized [18] through the participation of a resonance structure contributor consisting of a tropylium cation fused to a cyclopentadienyl anion. Such a structure, even if a minor contributor to the resonance hybrid for azulene, would produce a molecule with a definite dipole moment. This dipolar structure also predicts that the negative end of the dipole will point toward the five-membered ring.

The small dipole moments calculated for **1** and **2** may indicate that such dipolar resonance structures are of little to no importance to the electronic structures of these B — N analogs of azulene. Alternatively, because both **1** and **2** each contain five nitrogen atoms with two electrons each, giving a total of ten π-electrons (a Hückel $4n + 2$ value), the possibility exists that either molecule could exhibit bond delocalization and some aromatic character without any dipolar charge requirement.

Structure

The MNDO-calculated bond lengths for azulene, and the experimentally-determined values for three symmetrical derivatives of azulene [19–21], are listed in Table 2. (Azulene itself crystallizes in a disordered fashion [22], and the structure has not been successfully solved [23].)

The substituted derivative **AZdp** and the charge-transfer system **AZnb** both exhibit some bond alternation, with the difference in adjacent bonds of approximately 0.02 Å, while the strained [21] cyclophane (**AZph**) exhibits local C_{2v} symmetry and thus does not exhibit bond alternation in the same fashion as **AZdp** and **AZnb**. The MNDO-calculated structure (**AZ**) overestimates bond alternation (differences in adjacent bonds of approximately 0.09 Å) and localization (i.e., the longer bonds are approximately 0.07 Å longer than experimental values, while the shorter bonds are approximately 0.02 Å shorter). A similar situation is noted in comparing **AZs** to **AZph**. The ring fusion bond lengths (C^{3a} — C^{8a}) in all three crystal structures are well reproduced by the MNDO calculations. These crystal structures indicate that azulenes can adopt a variety of bond length variations through the interactions of appropriate substituents, while still remaining planar [24].

TABLE 2 MNDO-Optimized Bond Lengths[a] for the Azulene Structures

Compnd	*d(C–C)*			*d (C–H)*		
AZ	1.4557[b]	1.3886[c]	1.3749[d]	1.0821[e]	1.0983[f]	1.0976[g]
	1.4736[h]	1.3652[i]	1.4983[j]			
		1.4412[k]				
AZs	1.4117[l]	1.4272[m]	1.4005[n]	1.0820[o]	1.0826[p]	1.0992[q]
	1.4990[j]	1.4001[r]	1.4001[s]	1.0976[t]		1.0989[u]
AZdp[v]	1.412[b]	1.394[c]	1.395[d]			
	1.413[h]	1.380[i]	1.490[j]			
		1.392[k]				
AZnb[w]	1.398[b]	1.404[c]	1.387[d]			
	1.395[h]	1.394[i]	1.498[j]			
		1.394[k]				
AZph[x]	1.399[l]	1.405[m]	1.387[n]			
	1.485[j]	1.405[r]	1.399[s]			

[a] Bond lengths in Ångstroms. [b] Bond d(C^1–C^2). [c] Bond d(C^1–C^{8a}). [d] Bond d(C^2–C^3). [e] Average of d(C^1–H), d(C^2–H, and d(C^3–H). [f] Average of d(C^4–H), d(C^6–H), and d(C^8–H). [g] Average of d(C^5–H) and d(C^7–H). [h] Bond d(C^3–C^{3a}). [i] Average of d(C^{3a}–C^4), d(C^5–C^6), and d(C^7–C^8). [j] Bond d(C^{3a}–C^{8a}). [k] Average of d(C^4–C^5), d(C^6–C^7), and d(C^8–C^{8a}). [l] Bonds d(C^1–C^2) and d(C^2–C^3). [m] Bonds d(C^1–C^{8a}) and d(C^3–C^{3a}). [n] Bonds d(C^{3a}–C^4) and d(C^8–$C8^a$). [o] Bond d(C^1–H) and d(C^3–H). [p] Bond d(C^2–H). [q] Bonds d(C^4–H) and d(C^8–H) [r] Bonds d(C^4–C^5) and d(C^7–C^8). [s] Bonds d(C^5–C^6) and d(C^6–C^7). [t] Bonds d(C^5–H) and d(C^7–H). [u] Bond d(C^6–H). [v] Azulene-1,3-dipropanoic acid [19]. [w] Azulene • 1,3,5-trinitrobenzene complex (1:1) [20]. [x] [2]-5,7-azuleno-[2]-paracyclophane [21].

TABLE 3 MNDO-Optimized Bond Lengths(Å) for the Fully Boron–Nitrogen-Alternating Azulene Analogs

Cmpnd	*d(N–N)*	*d(N–B)*		*d(B–B)*	*d(N–H)*	*d(B–H)*
1		1.4433^{a}	1.4323^{b}	1.6926	0.9926^{c}	1.1684^{d}
		1.4124^{e}	1.4266^{f}		1.0021^{g}	1.1804^{h}
		1.4276^{i}			1.0059^{j}	
2	1.3940	1.4278^{k}	1.4615^{l}		0.9913^{m}	1.1640^{n}
		1.4342^{o}	1.4218^{p}		1.0035^{q}	1.1782^{r}
		1.4222^{s}				1.1775^{t}

[a] Average of d(N^1–B^2) and d(B^2–N^3). [b] Average of d(N^1–B^{8a}) and d(N^3–B^{3a}). [c] Average of d(N^1–H) and d(N^3–H). [d] Bond d(N^2–B). [e] Average of d(B^{3a}–N^4) and d(N^8–B^{8a}). [f] Average of d(N^4–B^5) and d(B^7–N^8). [g] Average of d(N^4–H) and d(N^8–H). [h] Average of d(B^5–H) and d(B^7–H). [i] Average of d(B^5–N^6) and d(N^3–B^7). [j] Bond d(N^6–H). [k] Average of d(B^1–N^2) and d(N^2–B^3). [l] Average of d(B^1–N^{8a}) and d(B^3–N^{3a}). [m] Bond d(N^2–H). [n] Average of d(B^1–H) and d(B^3–H). [o] Average of d(N^{3a}–B^4) and d(B^8–N^{8a}). [p] Average of d(B^4–N^5) and d(N^7–B^8), [q] Average of d(N^5–H) and d(N^7–H). [r] Average of d(B^4–H) and d(B^8–H). [s] Average of d(N^5–B^6) and d(B^6–N^7). [t] Bond d(B^6–H).

Table 3 lists the MNDO-calculated bond lengths for **1** and **2**, while Table 4 lists the calculated ring atom bond angles for each of the four NMDO-calculated molecules. Bond lengths in **1** do not indicate significant bond alternation, and the B—B ring fusion bond is quite long. In **2**, there is greater variation in the bond lengths, and the N—N ring fusion bond is short. However, these bond length differences are more likely due to the atoms involved rather than to differences in bonding (*vide infra*).

Ring atom bond angles in all molecules are surprisingly similar for analogous angles. This was not the case when benzene and borazine were compared [6]. Benzene adopts the shape of a regular hexagon with angles of exactly 120°, while borazine had angles of 116.45° (<NBN) and 123.55° (<BNB). In the present instance, the angles of a regular heptagon and a regular pentagon are 128.57° and 108°, respectively. The angles in each MNDO-calculated molecule closely approximate these values, even though the rings of **AZ** and **AZs** are composed solely of carbon atoms, and the rings of **1** and **2** contain only nitrogen and boron atoms. For **1** and **2**, the ring size geometric restrictions apparently play a larger factor in structure than was found for the benzene–borazine system.

Are the bonds in the azulene structures and **1** and **2** delocalized? Table 5, which lists MNDO-calculated bond indices, gives some indication of the extent of delocalization. In **AZ**, double (bond index, bi, of approximately 1.7) and single bonds (bi = 1.1) are localized, while in **AZs**, delocalization only

TABLE 4 MNDO-Optimized Ring Atom Bond Angles[a]

Cmpnd	*∠123*	*∠218a and ∠233a*	*∠18a3a and ∠33a8a*	*∠3a8a8 and ∠43a8a*	*∠3a45 and ∠788a*	*∠456 and ∠678*	*∠567*
AZ	108.84°	109.27°	106.31°	127.52°	128.64°	129.19°	129.29°
AZs	109.04°	109.20°	106.28°	127.36°	128.85°	129.10°	129.37°
1	112.47°	109.47°	104.29°	127.89°	126.73°	126.08°	138.60°
2	108.43°	107.39°	108.05°	129.62°	125.51°	133.64°	122.46°

[a] Angle numbers refer to the ring atom numbering, beginning with the five-membered ring. Nitrogen atoms, when present, are given the lowest numbers consistent with IUPAC systematics. Where two angles head a column, the value is the average of the angles.

TABLE 5 MNDO-Optimized Ring Atom Bond Indices[a]

Cmpnd	*bi(1–2)*	*bi(6–7)*	*bi(2–3)*	*bi(7–8)*	*bi(3–3a)*	*bi(8–8a)*	*bi(3a–4)*	*bi(1–8a)*	*bi(4–5)*	*bi(3a–8a)*	*bi(5–6)*
AZ	1.1256	1.1141	1.7242	1.7180	1.0783	1.0911	1.6739	1.6604	1.1173	1.0052	1.7101
AZs	1.4053	1.3867	1.4049	1.3911	1.3411	1.3494	1.3491	1.3407	1.3914	1.0033	1.3864
1	1.1448	1.1723	1.1445	1.1701	1.1528	1.1860	1.1857	1.1525	1.1705	0.8863	1.1721
2	1.1908	1.1658	1.1908	1.1651	1.1289	1.1342	1.1341	1.1288	1.1652	0.9269	1.1657

[a] Heading numbers refer to the ring atom numbering, beginning with the five-membered ring. Nitrogen atoms, when present, are given the lowest numbers consistent with IUPAC systematics.

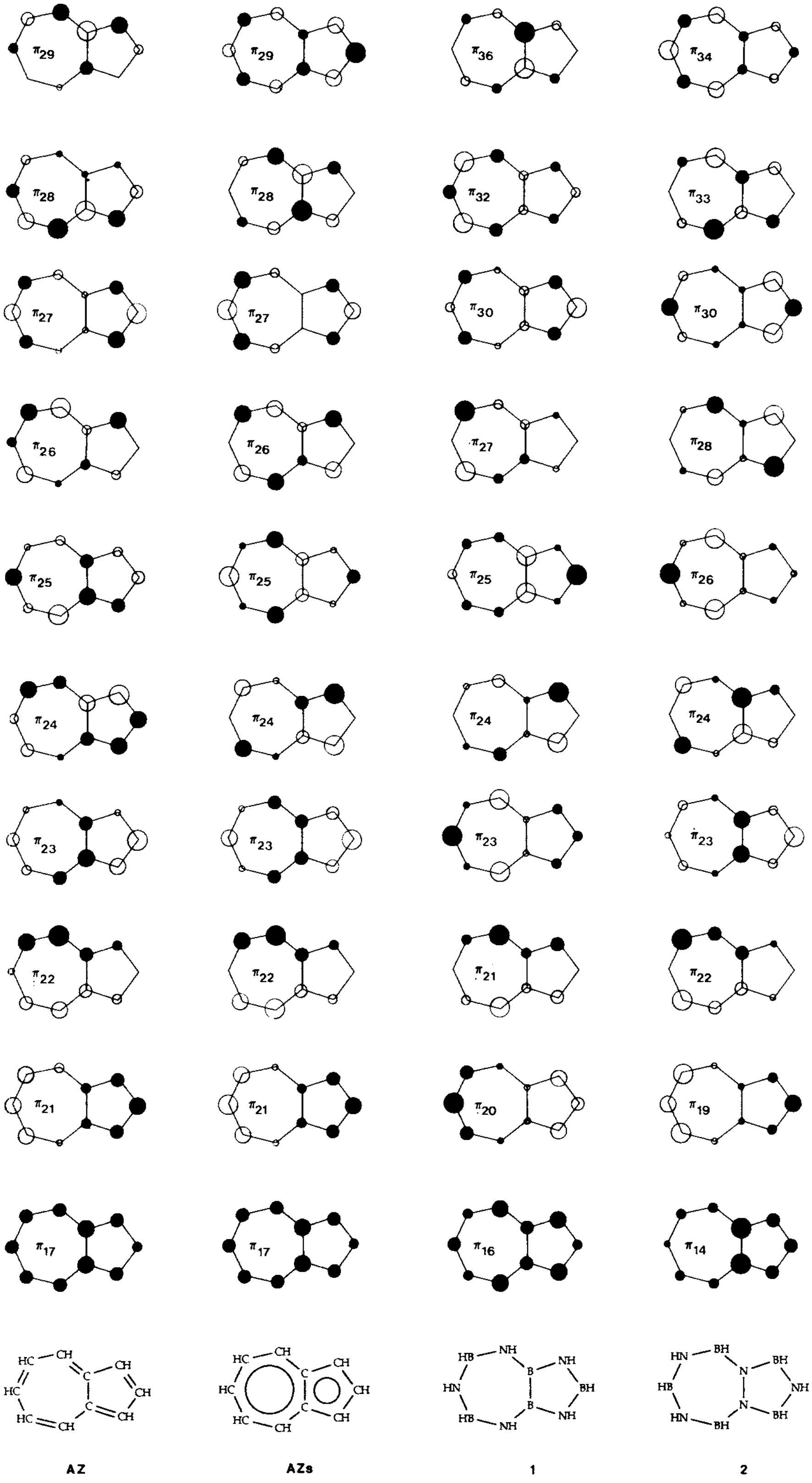

FIGURE 1 The π-molecular orbitals of **AZ**, **AZs**, **1**, and **2** as calculated by MNDO. The upper lobe of each atomic π-orbital is depicted with filled circles positive and open circles negative; the size indicates the relative contribution of the atomic orbital to the molecular orbital. Orbitals are numbered in their MNDO-determined order.

slightly less than that of benzene (bi = 1.41 [6]) is calculated to be present. For **1** and **2**, the extent of delocalization is much less than **AZs** (as was found for borazine, bi = 1.18), but some delocalization may still be present.

Molecular Orbitals

The π-mainfold molecular orbitals of azulene and **1** and **2** are depicted in Figure 1. Barring the sign conventions assigned by the MNDO calculations, the π-molecular orbitals of the PAPBAZ isomers are extremely similar to those of azulene. Two significant differences do arise, however.

First, the orbitals of **1** and **2** are less evenly distributed about the ring atoms than in azulene. This observation was noted with borazine as well [6]. The explanation for this orbital unevenness relies upon the greater electronegativity of nitrogen compared to boron. Thus, the contributions of the nitrogen atomic orbitals should be greater in the filled, bonding orbitals, while the contributions of the boron atomic orbitals should be greater in the empty, antibonding orbitals, just as is calculated by MNDO.

The second difference apparent is in the ordering of the orbitals. For the azulene structures and for **1**, the highest occupied molecular orbital (HOMO, orbital 24) and the lowest unoccupied molecular orbital (LUMO, orbital 25) are both π-orbitals, while for **2**, the HOMO is a π-orbital, and the LUMO is a σ-orbital. In addition, the ordering of the two highest energy π-orbitals for **1**, π-orbitals 32 and 36, are reversed for **2**, π-orbitals 33 and 34. Figure 2 illustrates the relationship of the π- orbitals to all of those ς-orbitals within the π-molecular orbital manifolds of the azulenes and **1** and **2**.

Benzene's HOMO and LUMO are each π-orbitals, while borazine's HOMO is calculated to be a π-orbital and its LUMO to be a σ-orbital [6]. The chemical differences between benzene and borazine [4,5] may arise in part from these HOMO/LUMO differences. If so, the chemical properties of **1** may be more like those of azulene and benzene, while the chemical properties of **2** might be more like those of borazine. Molecule **1** may, in fact, exhibit some of the chemical manifestations of aromaticity exhibitied by azulene [10].

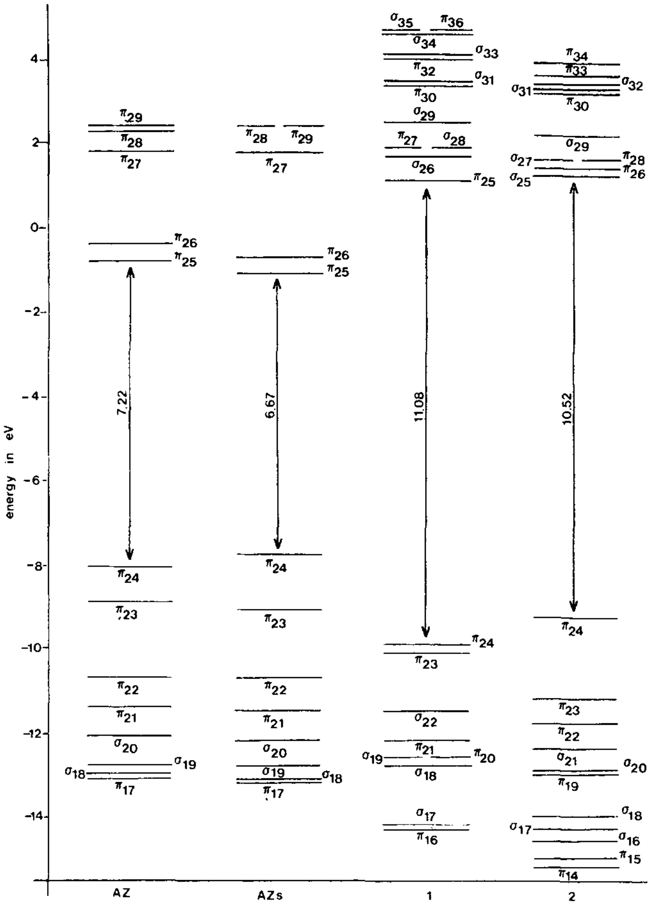

FIGURE 2 The relative energies (in eV) of the π-manifold molecular orbitals of **AZ**, **AZs**, **1** and **2**. The difference in energy between the HOMO and LUMO for each molecule is indicated by a double-headed arrow.

CONCLUSIONS

The PAPBAZ isomers **1** and **2** have apparently not been studied experimentally, and only one computational report [9] mentions these molecules. However, because the MNDO method has been shown [17, 25–28] to be a reliable indicator of the ground-state properties of boron-nitrogen-containing molecules, there exists a solid basis upon which to establish the structures of these molecules.

The PAPBAZ isomers **1** and **2** are calculated to be planar molecules, possibly containing π-systems at least as delocalized as in borazine. Further, **1**, from an examination of its π-molecular orbitals and a HOMO/LUMO analysis, may exhibit aromatic character similar to those of benzene or azulene (albeit in lesser degree), while **2** is predicted to exhibit chemical properties similar to those of borazine.

Is either **1** or **2** aromatic? This question is not directly addressable without the choice of a proper reference molecule with which to compare selected calculated properties. The most stable PAPBAZ isomer, **1**, through comparison of its calculated properties and orbitals, appears to exhibit the promise of aromaticity. A more definitive answer awaits the synthesis of the molecule either as the unsubstituted parent or as a closely-related derivative.

Computational studies on these and other boron–nitrogen nonbenzenoid molecules are continuing [28].

ACKNOWLEDGMENTS

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of the determination of the nonduplicating isomers of PAPBAZ and, for **AZ**, **AZs**, **1**, and **2**, the final atomic coordinates and molecular orbital energies (17 pages) may be obtained from one of the authors (R.W. Z.) on written request.

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