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Modified Neglect of Diatomic Overlap Calculations on Boron-Nitrogen Derivatives of Nonbenzenoid Aromatics. II. The Analysis of the 130 Possible Nonfully Boron-Nitrogen-Alternating Isomers of Pentaazapentaboraazulene

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ABSTRACT

*Modified neglect of diatomic overlap (MNDO) calculations have been used to investigate the ground state properties of the 130 nonfully boron-nitrogen-alternating isomers of pentaazapentaboraazulene (PAPBAZ), $N_5B_5H_8$. The two most stable of these nonfully boron-nitrogen-alternating isomers, 1,2,3a,5,7-pentaaza-3,4,6,8,8a-pentaboraazulene, (1,2,3a,5,7-PAPBAZ) (**3**), and 1,3,3a,5,7-PAPBAZ (**4**) have strongly exothermic heats of formation (−142.5 and −142.4 kcal/mol, respectively), while the two least stable isomers, 1,6,7,8,8a-PAPBAZ (**131**) and 1,2,3,3a,8a-PAPBAZ (**132**), are calculated to have endothermic heats of formation (+95.43 and +96.31 kcal/mol, respectively). Each isomer optimized as a slightly to extremely nonplanar molecule, but each remained a bicyclic system containing a seven-membered ring fused to a five-membered ring. Thus, no ring-opened structures were observed. An empirical relationship between the heat of formation and the number, position, and type of homonuclear (N–N or B–B) bonds present in the molecules could be established, but as the heat of formation for the molecules became more positive, the relationship became less strong. A general trend of diminishing energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was observed as the heat of formation became more positive. In addition to a discussion of the structures of (**3**), (**4**), (**131**), and (**132**), the structures of 2,3a,4,6,8-PAPBAZ (**9**), 2,3a,5,6,8-PAPBAZ (**11**), 1,2,4,6,8-PAPBAZ (**15**), 2,3a,4,7,8a-PAPBAZ (**19**), 1,3a,4,5,8-PAPBAZ (**32**), 1,2,3,5,7-PAPBAZ (**47**), 1,3a,5,8,8a-PAPBAZ (**67**), 1,3a,6,7,8a-PAPBAZ (**87**), 3a,4,6,8,8a-PAPBAZ (**106**), 1,2,3,5,6-PAPBAZ (**109**), 1,2,3a,8,8a-PAPBAZ (**116**), and 4,5,6,7,8-PAPBAZ (**130**) are discussed in detail. Some of these molecules were chosen because they represent the minima and maxima, respectively, in heats of formation [(**3**), (**4**), (**130**), (**131**), and (**132**)], ionization potentials [(**9**) and (**32**)], differences in LUMO and HOMO energies [(**106**) and (**32**)], and dipole moments [(**11**) and (**87**)]. The remaining molecules were chosen because each represents the most stable system containing the following homonuclear chains: B-B-B (**15**), N-N-N (**19**), B-B-B-B (**47**), N-N-N-N (**67**), B-B-B-B-B (**109**), and N-N-N-N-N (**116**).*

INTRODUCTION

There are 132 possible azulene analogs of formula $N_5B_5H_8$ in which the carbon atoms are replaced by boron and nitrogen atoms [1]. Only two of these

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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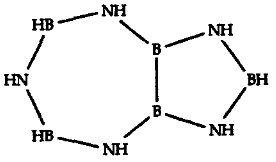
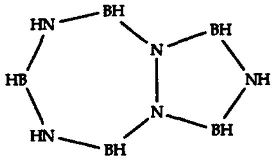
azulene analogs, (**1**) and (**2**), contain a periphery with the boron and nitrogen atoms fully alternating. These two analogs, using the modified neglect of diatomic overlap (MNDO) calculational method, optimize to planar systems [1].



(**1**)



(**2**)

The remaining 130 azulene analogs with the formula $N_5B_5H_8$ have also been investigated using MNDO. (We refer to these molecules as pentaazapentaboraazulene (PAPBAZ) isomers. Analogs (**1**) and (**2**) can then be systematically named 1,3,4,6,8-pentaaza-2,3a,5,7,8a-pentaboraazulene (1,3,4,6,8-PAPBAZ) and 2,3a,5,7,8a-pentaaza-1,3,4,6,8-pentaboraazulene (2,3a,5,7,8a-PAPBAZ), respectively.) There are apparently no reports in the literature concerning these nonfully boron-nitrogen (B-N) alternating PAPBAZ isomers [2]. Because of the continuing synthetic [3] and theoretical [4] interest in the properties of azulene, we began an investigation of the structures and ground state properties of the PAPBAZ analogs of azulene, and we report our results herein.

METHODS

The MNDO calculations were performed using QCPE [5] program number 455 (v. 5.0), "MOPAC: A General Molecular Orbital Package," suitably modified to run in a UNIX environment on Apollo DN3550 and DN10000 workstations. This program uses the Broyden-Fletcher-Goldfarb-Shanno [6] method to optimize geometries.

The initial trial geometries (ITGs) for the calculations employed a heavy atom–heavy atom bond distance of 1.5 Å with a heavy atom–hydrogen bond distance of 1.1 Å. All molecules were assumed to be planar systems composed of a regular heptagon fused to a regular pentagon for the ITGs. No nonplanar ITGs were systematically investigated, but, occasionally, certain molecules were calculated beginning from different ITGs or at higher levels of precision 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. All $3n - 6$ degrees of freedom ultimately optimized to individual gradients of 0.01 kcal/Å or kcal/radian.

RESULTS AND DISCUSSION

Ground State Heats of Formation

Table 1 contains the MNDO-calculated results for the heat of formation, ionization potential, the energy difference between the lowest unoccupied molecular orbitals and the highest occupied molecular orbitals (LUMO − HOMO), and the dipole moment for each of the nonfully B–N alternating PAPBAZ isomers. These molecules range in heat of formation from −142.5 kcal/mol for the thermodynamically most stable isomer, (**3**), to +96.31 kcal/mol for the least stable isomer, (**132**). The two possible fully B-N alternating PAPBAZ isomers, (**1**) and (**2**), were previously calculated to have more exothermic heats of formation than any of the 130 isomers listed in Table 1 [1].

The heats of formation exhibit a generally linear and continuous trend when the data are plotted vs. compound number, as shown in Figure 1. (Such a nearly continuous graph should not be considered unusual, since with a range of less than 240 kcal/mol in heat of formation from (**3**) to (**132**), the *average* difference between any two molecules is expected to be approximately 1.8 kcal/mol.) Although discontinuities in this plot can be noted and the expected average difference in heats of formation of 1.8 kcal/mol is met or exceeded 44 times, only *six times* are the differences in heats of formation greater than three times the expected average differences. These six differences occur between (**14**) and (**15**), with a difference of 10.2 kcal/mol, between (**18**) and (**19**), 21.5 kcal/mol, between (**59**) and (**60**), 6.4 kcal/mol, between (**123**) and (**124**), 5.7 kcal/mol, between (**129**) and (**130**), 13.1 kcal/mol, and between (**130**) and (**131**), a difference in heats of formation of 6.7 kcal/mol.

The two most stable azulenoid $N_5B_5H_8$ isomers, (**1**) and (**2**), indicated that, other factors being equal, a B–B bond was less destabilizing than an N–N bond in the ring fusion position and that the most stable isomers would be those with the most B–N alternating bonds [1]. Since only six heats of formation differences are considered significant for the 130 isomers discussed here, only overall trends as to the relative stabilizing or destabilizing nature of groups within these isomers can be drawn. An overall picture can be framed, but specific differences between any two molecules will, in general, be too small to be statistically significant.

Molecules (**3**) and (**4**) are the first to contain both an N–N and a B–B bond. In each molecule, these homonuclear bonds are adjacent, the B–B bond is involved in the N–B ring fusion bond, and the N–N bond is part of the five-membered ring. Since nitrogen is more electronegative than boron, placing the nitrogen atoms in the five-membered ring might be expected to impart increased stability to the molecule if dipolar resonance struc-

TABLE 1 MNDO Optimized Results[a] for the Nonfully Alternating Isomers of PAPBAZ

Compound[b]		*Heat of Formation* (*kcal/mol*)	*Ionization Potential* (*eV*)	*LUMO − HOMO* (*eV*)[c]	*Dipole Moment* (*debye*)
1,2,3a,5,7-PAPBAZ	**(3)**	−142.5	9.773	10.42	0.9797
1,3,3a,5,7-PAPBAZ	**(4)**	−142.4	9.645	10.40	1.402
1,2,3a,5,8-PAPBAZ	**(5)**	−138.4	10.02	10.50	1.408
1,2,3a,6,8-PAPBAZ	**(6)**	−136.9	9.942	10.38	2.428
1,3,3a,6,8-PAPBAZ	**(7)**	−136.8	9.788	10.49	3.135
1,3,3a,5,8-PAPBAZ	**(8)**	−135.7	9.767	10.44	1.990
2,3a,4,6,8-PAPBAZ	**(9)**	−132.6	8.735	9.285	0.7997
2,3a,5,7,8-PAPBAZ	**(10)**	−132.1	9.104	9.837	0.6338
2,3a,5,6,8-PAPBAZ	**(11)**	−131.4	9.080	9.656	0.1004
1,3a,4,6,8-PAPBAZ	**(12)**	−127.6	9.129	9.658	2.102
1,3a,5,6,8-PAPBAZ	**(13)**	−125.2	9.305	9.860	2.770
1,3a,5,7,8-PAPBAZ	**(14)**	−124.4	9.460	9.954	2.624
1,2,4,6,8-PAPBAZ	**(15)**	−114.2	9.462	9.769	1.495
1,3,4,5,8-PAPBAZ	**(16)**	−111.8	9.492	10.21	2.190
1,3,4,6,7-PAPBAZ	**(17)**	−109.1	9.480	9.947	1.292
1,3,4,5,7-PAPBAZ	**(18)**	−107.3	9.250	9.585	1.548
2,3a,4,7,8a-PAPBAZ	**(19)**	−85.77	9.605	10.28	3.021
2,3a,4,6,8a-PAPBAZ	**(20)**	−84.48	9.519	10.17	2.816
1,3a,5,7,8a-PAPBAZ	**(21)**	−79.72	9.361	9.958	3.074
2,3a,5,6,8a-PAPBAZ	**(22)**	−77.68	9.301	9.990	2.000
1,2,4,6,8a-PAPBAZ	**(23)**	−75.49	10.01	10.48	1.951
1,2,5,7,8a-PAPBAZ	**(24)**	−74.47	10.09	10.26	2.211
1,2,4,7,8a-PAPBAZ	**(25)**	−74.19	10.04	10.44	2.630
2,3a,6,7,8-PAPBAZ	**(26)**	−70.89	10.44	11.00	1.809
2,3a,4,5,8-PAPBAZ	**(27)**	−69.12	9.737	9.948	3.066
2,3a,4,5,7-PAPBAZ	**(28)**	−68.58	10.43	10.38	1.206
1,3,3a,4,7-PAPBAZ	**(29)**	−68.35	9.371	9.462	1.883
2,3a,5,6,7-PAPBAZ	**(30)**	−68.02	10.41	10.39	1.281
1,3a,5,6,7-PAPBAZ	**(31)**	−67.73	10.46	10.52	2.466
1,3a,4,5,8-PAPBAZ	**(32)**	−67.07	10.88	11.04	1.950
1,3a,4,5,7-PAPBAZ	**(33)**	−66.29	9.829	9.911	2.076
1,3a,6,7,8-PAPBAZ	**(34)**	−62.74	10.83	11.00	3.112
1,3,3a,6,7-PAPBAZ	**(35)**	−62.40	9.785	10.43	2.927
1,2,3a,4,7-PAPBAZ	**(36)**	−62.21	9.904	10.07	1.320
1,3,3a,4,6,-PAPBAZ	**(37)**	−60.82	9.157	9.161	0.9825
1,2,3a,6,7-PAPBAZ	**(38)**	−60.25	9.785	10.39	2.590
1,3,3a,4,8-PAPBAZ	**(39)**	−59.05	9.631	9.958	2.890
1,2,3a,4,6-PAPBAZ	**(40)**	−55.99	9.785	9.853	1.104
1,2,3a,5,6-PAPBAZ	**(41)**	−55.23	9.783	9.872	1.499
1,3,3a,5,6-PAPBAZ	**(42)**	−54.48	9.422	9.468	1.392
1,2,3a,4,8-PAPBAZ	**(43)**	−54.32	9.848	10.10	2.097
1,2,3,4,7-PAPBAZ	**(44)**	−52.76	9.745	9.544	2.236
2,3a,4,7,8-PAPBAZ	**(45)**	−52.40	8.889	9.475	2.603
1,2,3,4,8-PAPBAZ	**(46)**	−52.00	9.542	9.959	2.499
1,2,3,5,7-PAPBAZ	**(47)**	−51.40	9.730	9.728	0.8454
2,4,5,6,8-PAPBAZ	**(48)**	−50.90	9.585	9.982	0.7250
1,2,3,4,6-PAPBAZ	**(49)**	−50.87	9.570	9.812	1.621
1,2,3a,7,8-PAPBAZ	**(50)**	−49.52	9.663	9.870	2.725
1,3,3a,7,8-PAPBAZ	**(51)**	−48.33	9.551	9.842	3.804
1,3,5,6,7-PAPBAZ	**(52)**	−48.23	9.585	9.455	1.202
1,3,4,5,6-PAPBAZ	**(53)**	−47.89	10.11	10.23	1.202
1,4,6,8,8a-PAPBAZ	**(54)**	−47.42	9.111	8.777	1.725
1,3a,4,6,7-PAPBAZ	**(55)**	−46.91	9.130	9.099	2.328
2,3a,4,6,7-PAPBAZ	**(56)**	−46.64	8.943	8.903	1.681
1,3a,4,7,8-PAPBAZ	**(57)**	−46.03	9.954	9.962	2.035
1,4,5,6,8-PAPBAZ	**(58)**	−45.33	10.18	10.35	1.749
1,4,6,7,8-PAPBAZ	**(59)**	−44.95	9.954	10.13	1.899
1,4,5,7,8a-PAPBAZ	**(60)**	−38.56	8.916	8.559	1.656
1,4,6,7,8a-PAPBAZ	**(61)**	−37.23	8.952	8.482	1.778

TABLE 1 Continued

Compound[b]		*Heat of Formation (kcal/mol)*	*Ionization Potential (eV)*	*LUMO − HOMO (eV)*[c]	*Dipole Moment (debye)*
1,2,4,5,8-PAPBAZ	**(62)**	−34.21	9.581	9.871	1.568
1,2,4,7,8-PAPBAZ	**(63)**	−31.15	9.458	9.476	2.548
2,4,5,7,8-PAPBAZ	**(64)**	−30.77	9.046	9.616	1.217
1,2,4,5,7-PAPBAZ	**(65)**	−27.72	9.339	9.792	0.7251
1,2,4,6,7-PAPBAZ	**(66)**	−26.73	9.238	9.597	1.481
1,3a,5,8,8a-PAPBAZ	**(67)**	−26.10	10.38	10.53	0.6707
1,3a,6,8,8a-PAPBAZ	**(68)**	−24.49	10.28	10.31	2.799
1,2,3a,6,8a-PAPBAZ	**(69)**	−23.88	9.615	9.761	1.127
1,4,5,7,8-PAPBAZ	**(70)**	−21.37	8.970	9.117	1.968
1,2,3a,5,8a-PAPBAZ	**(71)**	−20.03	9.400	9.532	2.081
1,2,5,6,8-PAPBAZ	**(72)**	−18.25	9.411	8.845	2.999
1,2,5,7,8-PAPBAZ	**(73)**	−16.35	9.336	8.674	3.582
1,2,3a,7,8a-PAPBAZ	**(74)**	−15.90	9.137	9.178	1.878
1,2,3,3a,5-PAPBAZ	**(75)**	−15.05	9.412	9.054	0.6194
1,2,3,3a,7-PAPBAZ	**(76)**	−14.81	9.512	9.339	2.303
2,3a,4,5,8a-PAPBAZ	**(77)**	−14.58	9.960	9.755	2.023
1,2,3,3a,8-PAPBAZ	**(78)**	−12.86	9.816	9.526	2.025
1,2,3,3a,6-PAPBAZ	**(79)**	−10.74	9.521	9.106	2.090
1,3,3a,6,8a-PAPBAZ	**(80)**	−10.49	9.276	9.567	0.7947
1,3,3a,5,8a-PAPBAZ	**(81)**	−6.231	8.994	9.068	1.783
2,3a,4,8,8a-PAPBAZ	**(82)**	−5.008	9.374	9.698	3.773
1,3a,4,7,8a-PAPBAZ	**(83)**	−4.755	9.660	9.699	2.034
1,3a,4,6,8a-PAPBAZ	**(84)**	−4.113	9.629	9.679	1.637
1,2,5,8,8a-PAPBAZ	**(85)**	−0.4454	9.987	10.12	2.020
1,3,3a,4,5-PAPBAZ	**(86)**	0.8543	9.821	9.626	0.9044
1,3a,6,7,8a-PAPBAZ	**(87)**	1.915	9.549	9.746	4.328
1,3a,5,6,8a-PAPBAZ	**(88)**	2.261	9.374	9.836	2.690
3a,4,5,6,8-PAPBAZ	**(89)**	2.287	9.850	9.568	2.150
3a,4,5,7,8a-PAPBAZ	**(90)**	3.018	9.786	8.988	2.181
1,2,4,8,8a-PAPBAZ	**(91)**	3.857	9.354	9.389	2.965
1,2,6,8,8a-PAPBAZ	**(92)**	4.499	9.659	9.542	2.657
3a,5,6,7,8-PAPBAZ	**(93)**	5.789	9.882	9.458	0.7103
1,2,5,6,8a-PAPBAZ	**(94)**	6.129	10.11	10.12	1.540
1,2,3a,4,5-PAPBAZ	**(95)**	6.566	9.812	9.731	1.695
2,3a,4,5,6-PAPBAZ	**(96)**	8.309	9.998	9.608	1.614
1,3a,4,5,6-PAPBAZ	**(97)**	9.211	10.29	9.786	2.590
3a,5,6,7,8a-PAPBAZ	**(98)**	9.755	9.769	8.991	2.316
1,2,6,7,8a-PAPBAZ	**(99)**	11.26	9.795	9.853	2.758
1,2,4,5,8a-PAPBAZ	**(100)**	11.73	9.490	9.694	2.350
1,4,7,8,8a-PAPBAZ	**(101)**	14.93	9.705	9.000	0.7682
1,5,7,8,8a-PAPBAZ	**(102)**	17.51	9.864	9.213	2.819
3a,4,6,7,8-PAPBAZ	**(103)**	18.10	9.322	9.199	2.234
1,4,5,6,8a-PAPBAZ	**(104)**	18.57	9.889	9.333	1.573
3a,4,5,7,8-PAPBAZ	**(105)**	18.84	9.352	9.147	1.384
3a,4,6,8,8a-PAPBAZ	**(106)**	19.22	9.383	8.184	0.8849
3a,4,6,7,8a-PAPBAZ	**(107)**	23.65	9.428	8.590	2.257
1,5,6,7,8a-PAPBAZ	**(108)**	24.43	9.797	9.124	2.822
1,2,3,5,6-PAPBAZ	**(109)**	25.24	9.551	9.902	2.327
1,4,5,6,7-PAPBAZ	**(110)**	25.40	9.596	9.687	1.954
1,2,3,4,5-PAPBAZ	**(111)**	26.89	9.234	9.130	1.717
1,5,6,7,8-PAPBAZ	**(112)**	28.01	9.815	9.268	2.280
2,4,5,6,7-PAPBAZ	**(113)**	28.87	9.533	8.912	2.350
1,4,5,8,8a-PAPBAZ	**(114)**	29.62	9.268	8.600	1.601
1,2,4,5,6-PAPBAZ	**(115)**	32.27	9.655	9.650	0.9546
1,2,3a,8,8a-PAPBAZ	**(116)**	33.15	9.925	9.820	2.351
1,2,6,7,8-PAPBAZ	**(117)**	38.00	9.746	9.101	2.338
1,5,6,8,8a-PAPBAZ	**(118)**	40.30	9.346	8.854	3.898
1,2,5,6,7-PAPBAZ	**(119)**	43.65	9.504	8.767	2.349
1,3,3a,4,8a-PAPBAZ	**(120)**	43.79	9.546	9.531	2.657
1,3a,7,8,8a-PAPBAZ	**(121)**	48.67	10.44	10.12	1.948

TABLE 1 Continued

Compound[b]		Heat of Formation (kcal/mol)	Ionization Potential (eV)	LUMO − HOMO (eV)[c]	Dipole Moment (debye)
1,2,3a,4,8a-PAPBAZ	**(122)**	51.60	9.467	9.530	3.410
1,3a,4,8,8a-PAPBAZ	**(123)**	53.83	10.23	10.17	2.139
1,2,3,3a,4-PAPBAZ	**(124)**	59.52	9.476	8.693	1.684
1,3a,4,5,8a-PAPBAZ	**(125)**	63.56	9.875	9.347	1.092
1,2,7,8,8a-PAPBAZ	**(126)**	66.59	10.06	9.686	2.593
3a,4,5,6,7-PAPBAZ	**(127)**	69.37	10.21	9.946	2.363
3a,4,5,6,8a-PAPBAZ	**(128)**	71.62	10.30	9.323	2.585
3a,4,5,8,8a-PAPBAZ	**(129)**	75.60	9.867	8.960	1.242
4,5,6,7,8-PAPBAZ	**(130)**	88.69	10.14	9.366	3.833
1,6,7,8,8a-PAPBAZ	**(131)**	95.43	9.917	8.871	2.595
1,2,3,3a,8a-PAPBAZ	**(132)**	96.31	9.723	8.909	1.508

[a] All values have been arbitrarily reported to four significant figures.
[b] For molecules (**1**) and (**2**), see Ref. [1].
[c] The difference between molecular orbital number 25 (the LUMO) and molecular orbital number 24 (the HOMO).

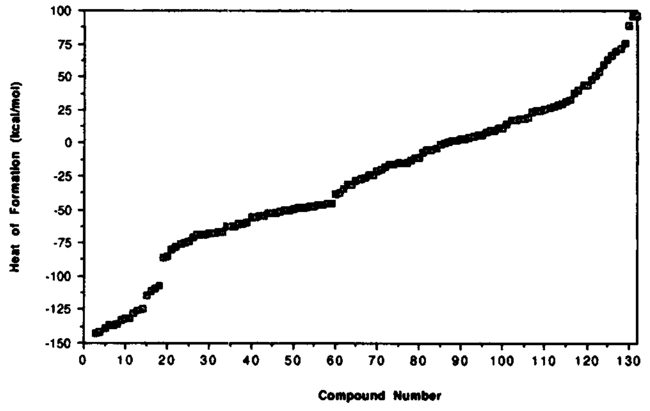


FIGURE 1 The MNDO-calculated heats of formation for molecules (**3**) through (**132**) plotted vs. compound number.

tures contribute to the stability of the molecule. Such dipolar resonance structures (see Figure 2(b)) have been used to rationalize the dipole moment of azulene (1.08 debye) [7].

The first significant discontinuity in heat of formation differences occurs between (**14**) and (**15**). Molecules (**5**) through (**14**) each contain one N–N and one B–B bond and an N–B ring fusion bond, while (**15**) is the first molecule to contain a B-B-B system. When any N–N and B–B bonds are adjacent to each other, bipolar structures may form with a charge separation distance only slightly greater than that found in those circumstances in which the bipolar system is composed of an N–B bond. Dewar [8] used the idea of minimum charge separation distance to predict that 1,2-azaborine would be more stable than 1,4-azaborine, which MNDO calculations confirmed [9]. When the N-N group is part of the seven-membered ring and bipolar resonance structures contribute to the stability of the

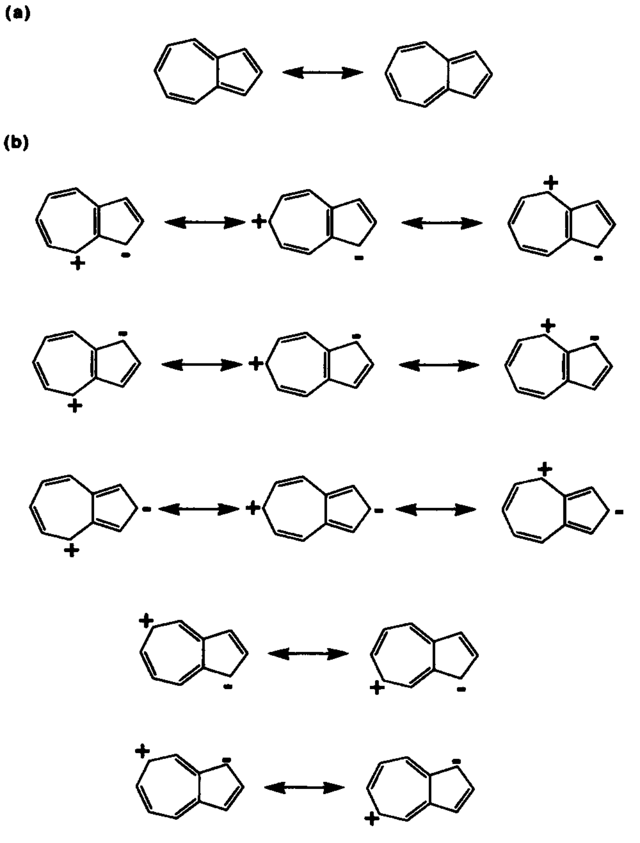


FIGURE 2 Resonance structures for azulene: (**a**) uncharged structures and (**b**) charged, bipolar structures. Only resonance structures which place the negative charge in the five-membered ring and the positive charge in the seven-membered ring have been considered.

molecule, the more electronegative nitrogen atoms appear in the ring which also contains the formal positive charge. Thus, placing the N–N bond in the seven-membered ring is expected to be destabilizing in those molecules which rely upon bipolar resonance structures for additional stability.

Molecule (**15**) contains the first example of a three-membered B-B-B system, while (**19**) contains the first example of an N-N-N system. Along with (**1**) and (**2**), the first examples of a B-B and an N-N system, respectively, it can be noted that homonuclear bonds containing boron are generally more stable than the respective systems containing nitrogen. The trend holds true for the first appearances of the B-B-B-B (**47**) and N-N-N-N (**67**) systems and for the B-B-B-B-B (**109**) and N-N-N-N-N (**116**) systems. Apparently, placing nitrogen atoms adjacent to each other, with their lone pairs of electrons interacting, is more destabilizing than placing boron atoms adjacent, other factors being equal. However, this trend strongly affects heat of formation differences only up to the B-B-B and N-N-N systems; the first appearances of the B_4, N_4, B_5, and N_5 systems do not correspond to significant discontinuities in heats of formation.

Of the remaining discontinuities in heats of formation differences, all but one appear among the final 10 isomers of PAPBAZ, and that discontinuity occurs between (**59**) and (**60**). Both (**58**) and (**59**) contain an N-N-N and a B-B-B-B unit. (In the latter, the two units are connected end-end, while in the former, the terminal N is connected to an internal B, giving a branched chain). However, molecule (**60**) contains an N-N-B-B-B-N-N system. The differences here appear slight, and there appears to be a delicate balance in the relative stabilities of these types of nitrogen-boron systems which apparently causes a fairly large difference in heats of formation.

As mentioned previously, molecule (**67**) contains the first example of an N-N-N-N system. Unlike the first examples of B-B-B-B systems, however, where the boron systems were unbranched, the first N-N-N-N systems to appear are branched in a *Y*-configuration. The branched *Y*-configuration for a B-B-B-B system does not occur until molecule (**72**). Apparently, linear B-B-B-B systems are more stable than the branched counterparts, while for N-N-N-N systems, the reverse is true.

Following the pattern established for B_4- and N_4-containing systems, the B-B-B-B-B system first appears in molecule (**109**) but does not appear as a branched system until (**112**). As expected, the first appearance of an N-N-N-N-N system is as a *Y*-shaped branched system in molecule (**116**), and the N-N-N-N-N system does not appear as a linear system until (**122**).

The three remaining discontinuities in heat of formation differences occur between (**123**) and (**124**), (**129**) and (**130**), and (**130**) and (**131**). For the first pair, the difference appears to be due to a branched N_5-system in (**123**) vs. a linear system in (**124**), while for the second pair, (**130**) places more nitrogen atoms completely in the seven-membered ring than does (**129**). The final pair contrasts (**130**), which contains all nitrogen atoms in the seven-membered ring, with (**131**) containing only three nitrogen atoms in that ring.

In molecule (**130**), all of the boron atoms are in the five-membered ring, which, if bipolar resonance structures contribute to stability, is a destabilizing position. This molecule, however, is more stable by approximately 6.7 kcal/mol than (**131**), where the nitrogen and boron atoms are arranged on the top and bottom halves of the molecule, and 7.6 kcal/mol more stable than (**132**), where all of the nitrogen atoms comprise the five-membered ring. The explanation for this ordering may be that dipolar resonance structures are *not* involved in these three molecules. If this is the case and only single bonds are present in (**130**), (**131**), and (**132**), each of the nitrogen atoms must contain a lone pair of electrons and these electrons should be highly repulsive and destabilizing. The wider angles in the seven-membered ring can allow the nonadjacent nitrogen atoms to be somewhat less crowded than is possible with the narrower angles in the five-membered ring, making (**130**) slightly more stable than (**131**) and (**132**). A similar but intermediate situation might then exist for (**131**), which contains nitrogen atoms in both the five- and the seven-membered ring. Thus, for these three least stable isomers of PAPBAZ and perhaps for other isomers as well, lone pairs of electrons on nitrogen may account for the observed order of heats of formation.

Ground State Electronic Properties

Included in Table 1 are the MNDO-calculated values for the ionization potentials and the LUMO − HOMO energy differences for the nonfully B-N alternating isomers of PAPBAZ. Ionization potentials range from 8.735 eV for (**9**) to 10.88 eV for (**32**), while the LUMO − HOMO energy differences span a range from 8.184 eV for (**106**) through 11.04 eV for (**32**). (The ionization potentials for these molecules are calculated by MNDO from the energy of each HOMO.)

The ionization potentials calculated for the PAPBAZ isomers exhibit no trend when plotted vs. the heat of formation, but if the differences in energy between the LUMO and HOMO are similarly plotted, the graph in Figure 3 results. Although there is significant scatter in this graph, a definite trend toward a smaller LUMO − HOMO energy gap as the heat of formation becomes more positive is observed.

The LUMO − HOMO energy differences vs. the ionization potential for molecules (**3**) through (**132**) are plotted in Figure 4. The correlation here is still

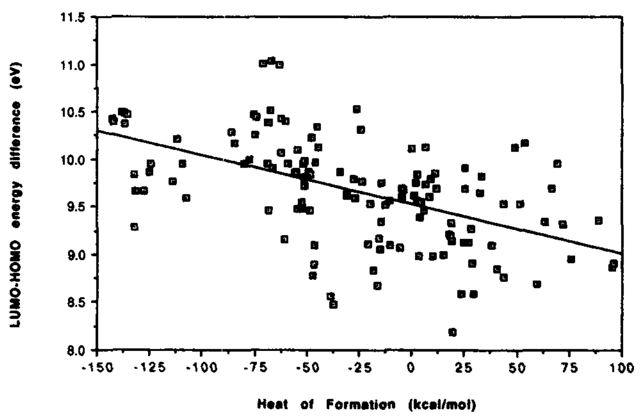
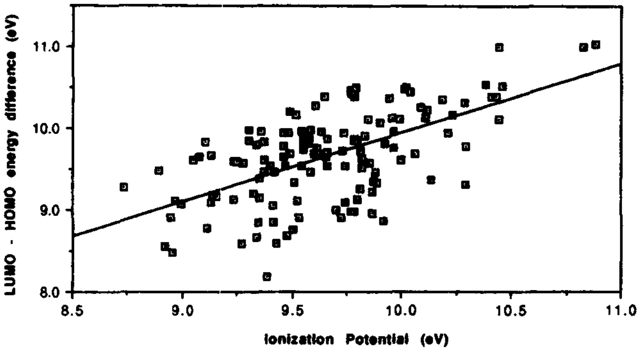


FIGURE 3 A plot of the LUMO − HOMO energy differences vs. the heat of formation for molecules (**3**) through (**132**). The equation for the best-fit linear regression line through the points is $y = 9.521 - 0.005161x$, with $R^2 = 0.272$.

weak, with an R^2 of 0.358, but the data indicate that, as the ionization potentials increase, the LUMO − HOMO energy differences also tend to increase, supporting the data in Figure 3.

According to the data in Table 1, dipole moments for the 130 PAPBAZ isomers range from 0.1004 debye for (**11**) to 4.328 debye for (**87**). The dipole moment data exhibit no correlation with heat of formation.



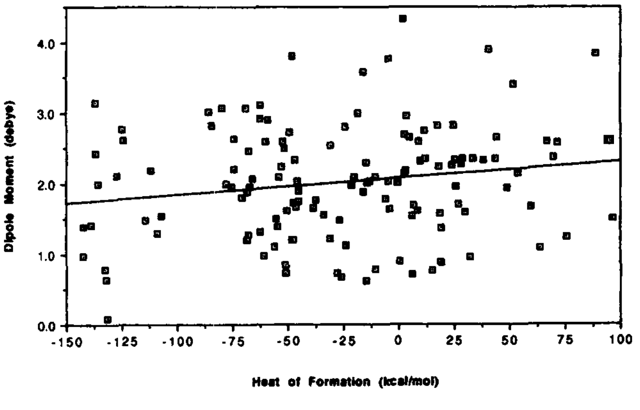


FIGURE 4 A plot of the LUMO − HOMO energy differences vs. the ionization potentials for molecules (**3**) through (**132**). The equation for the best-fit linear regression line through the points is $y = 1.535 + 0.8411x$, with $R^2 = 0.358$.

Structure: General

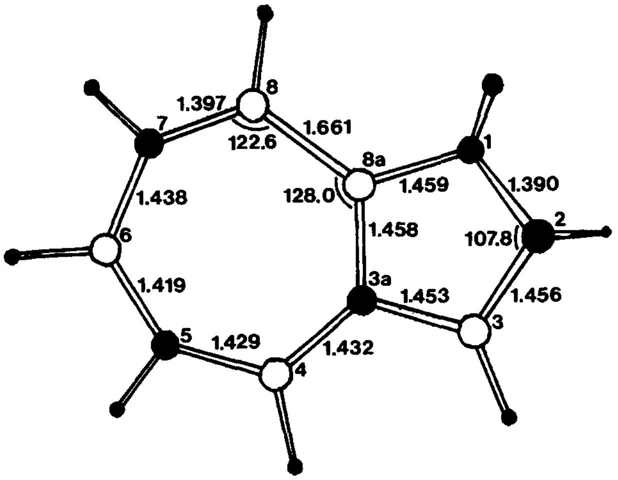
As noted earlier, each of the 130 molecules discussed in this report optimizes as a slightly to extremely nonplanar structure but remains as a system containing a seven-membered ring fused to a five-membered ring. No ring-opened structures were observed, although such a structure was observed for a diazadiborine isomer [10].

Because a discussion of the individual structures of each of the 130 different PAPBAZ isomers would be beyond the scope of this report, the structures of 16 of these molecules, each individually chosen because of a specific attribute, will be discussed. The molecules chosen are as follows: (**3**) and (**4**), the molecules which are the most thermodynamically stable; (**9**), the molecule with the lowest ionization potential; (**11**), the molecule with the lowest dipole moment; (**15**), the molecule in which the B-B-B system appears for the first time; (**19**), in which the N-N-N system appears for the first time; (**32**), the molecule with the highest ionization potential and the greatest LUMO − HOMO energy difference; (**47**), the molecule in which the B-B-B-B system first appears; (**67**), the first appearance of the N-N-N-N system; (**87**), the molecule with the highest dipole moment; (**106**), the molecule with the smallest LUMO − HOMO energy difference; (**109**), the first appearance of the B-B-B-B-B system; (**116**), the first appearance of the N-N-N-N-N system; and (**130**), (**131**), and (**132**), the isomers which are calculated to be the least stable thermodynamically.

Structure: Molecules Chosen Because of Thermodynamic Properties

Molecules (**3**) and (**4**) are the most thermodynamically stable of the 130 molecules discussed in this report, and their structures are depicted in Figure 5. These two molecules are the most nearly planar of the nonfully B-N alternating PAPBAZ isomers; each contains a planar seven-membered ring but a slightly nonplanar five-membered ring. In (**3**), atom N^2 is slightly pyramidalized, and in (**4**), atom N^3 has become somewhat pyramidal; both pyramidal nitrogen atoms are part of the N–N bond. The hydrogen atoms in both molecules also deviate from an idealized planar structure.

Bond lengths and angles in these molecules are not unusual in comparison to previous reports [1,9,10]. Bond alternation is not evident in the N–B bonds, although the N^7–B^8 bonds in (**3**) and (**4**), adjacent to the respective B–B bonds, are significantly shorter than the remaining N–B bonds. These



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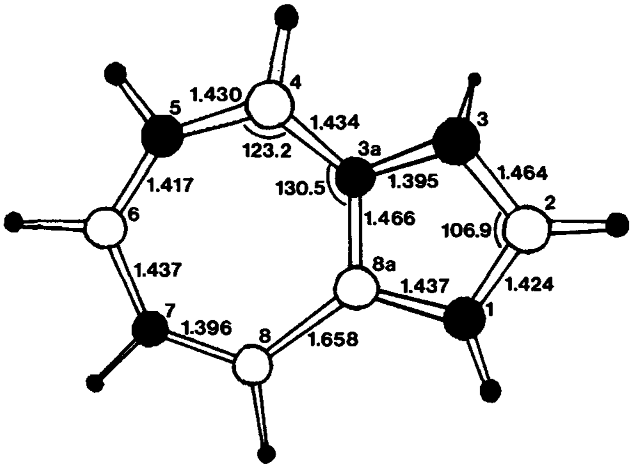
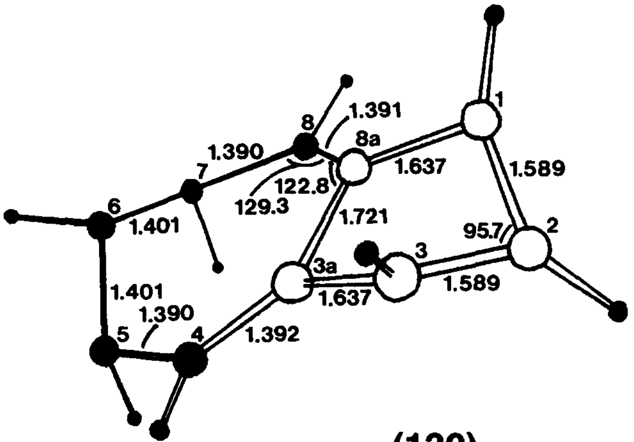


(4)

FIGURE 5 The MNDO-calculated structures of (**3**) and (**4**), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.



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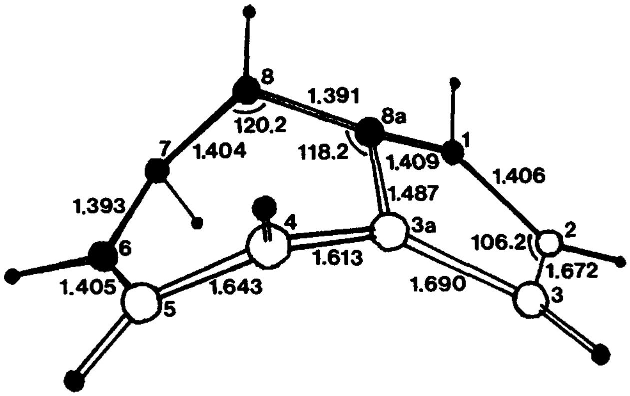

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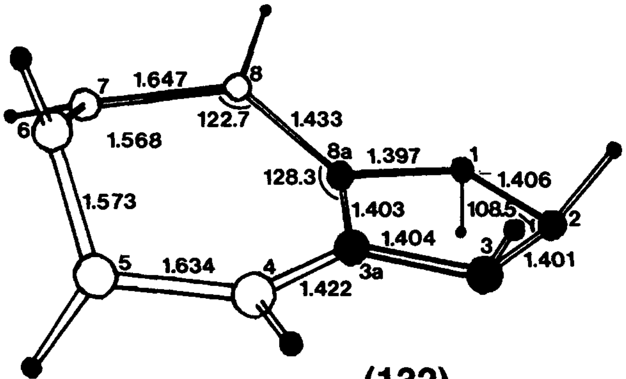


(132)

FIGURE 6 The MNDO-calculated structures of (**130**), (**131**), and (**132**), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.

short N–B bonds have the highest bond indices (>1.3), but all N–B bonds are calculated to have bond indices of 1.1 or greater. The B–B bonds are relatively long and the N–N bonds relatively short in both molecules. These bond lengths are simply a function of differing atoms, however, as both types of bonds are calculated to have bond indices of approximately 0.9, indicating single bonding is occurring.

The molecules in Figure 6, (**130**), (**131**), and (**132**), are the least thermodynamically stable of the isomers of PAPBAZ. As the drawings in the figure indicate, however, each molecule has minimized as a seven-membered ring fused to a five-membered ring and the lack of planarity of the molecules is evident. These molecules also demonstrate that, in comparison to the seven-membered ring, the five-membered ring in these molecules does not twist as radically into a nonplanar conformation.

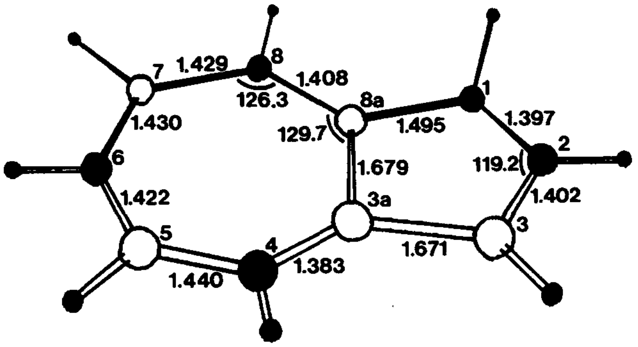
Both (**131**) and (**132**) have nearly planar five-membered rings, even though the hydrogens attached to these rings, especially in (**132**), are not in the plane of the ring. The five-membered ring of (**130**) is quite twisted; the torsion angle formed by atoms B^1-B^2-B^3-B^{3a} is 56°. The symmetry of (**130**) is also evident, as the molecule approximates C_s symmetry with a plane through B^2 and N^6 bisecting the ring fusion bond B^{3a}–B^{8a}.

Molecule (**132**) can be related to (**130**) by a simple interchange of the boron and nitrogen atoms and also might be expected to exhibit C_s symmetry. In this case, however, the hydrogen atom attached to N^3 in (**132**) points up instead of down and spoils the symmetry of the molecule. The five-membered ring in (**132**) is nearly planar, with a torsion angle formed by atoms N^1-N^2-N^3-N^{3a} of only −2.4°, but the seven-membered ring is twisted out of the plane of the five-membered ring by −32°, the torsion angle of atoms B^7-B^8-N^{8a}-N^{3a}. For comparison, equivalent torsion angles in (**130**) and (**131**) are 12° (atoms N^7-N^8-B^{8a}-B^{3a}) and −69° (atoms N^7-N^8-N^{8a}-B^{3a}), respectively.

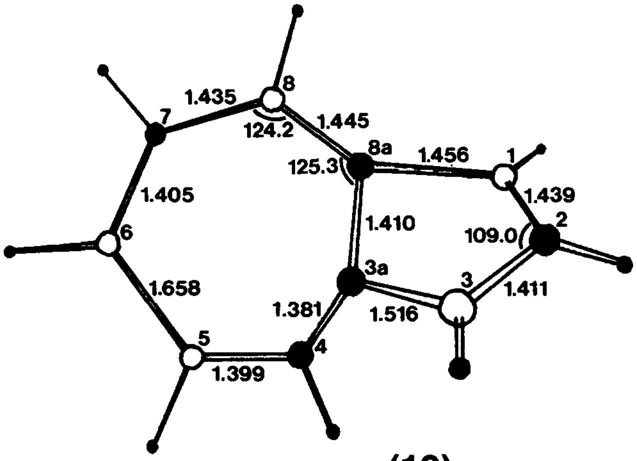
Structure: Molecules Chosen Because of Structural Properties

Molecules (**15**) and (**19**), drawn in Figure 7, represent the first appearances of the B-B-B and N-N-N groups, respectively. Molecule (**15**), even though containing a B-B-B system, minimizes as a remarkably planar system similar to molecules (**3**) and (**4**). The seven-membered ring is, to within torsion angles of less than 2°, planar, and the hydrogen atoms also do not deviate markedly from the plane of the ring. The five-membered ring contains a pyramidalized nitrogen atom (N^1), with an N^1-N^2-B^3-B^{3a} torsion angle of −6.0°.

The presence of an N-N-N group in molecule (**19**) causes a great deal more distortion than the B-B-B group. Both the seven- and the five-membered rings are twisted out of planarity individually and with respect to each other. The seven-membered ring is twisted approximately 11° with respect to the five-membered ring, and each of the three nitrogen atoms which are part of the five-membered ring (N^2, N^{3a}, and N^{8a}) is pyramidalized (torsion angles of −4.5° for B^1-N^2-B^3-N^{3a} and 136.0° for N^2-B^3-N^{3a}-N^4). The B–B bond lengths in both (**15**) and (**19**) are greater than 1.6 Å; B–N bonds adjacent to B–B systems, whether diatomic or triatomic, are shorter than the other B–N bonds in the molecules.



(15)

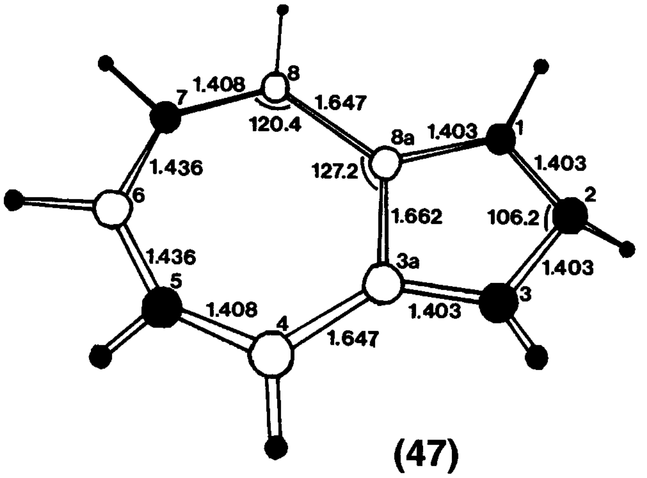


(19)

FIGURE 7 The MNDO-calculated structures of (**15**) and (**19**), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.

A four-membered B-B-B-B system first appears in the symmetrical molecule (**47**), and the N-N-N-N system, in a *Y*-shape, first appears in (**67**); the structures of these two molecules are reproduced in Figure 8. The C_s symmetry of (**47**) is very nearly complete: bond lengths are mirrored across the plane which contains atoms N^2 and N^6 and which bisects the bond B^{3a}–B^{8a}, and bond angles differ by less than 0.5°.

The four bond lengths of 1.403 Å in the five-membered ring are only coincidentally equal in length: bond order calculations indicate that bonds N^1–N^2 and N^2–N^3 are single, with bond indices of 0.967, while bonds N^1–B^{8a} and N^3–B^{3a} are calculated to each have a bond index of 1.364. Thus, no bond delocalization in this ring is indicated. How-



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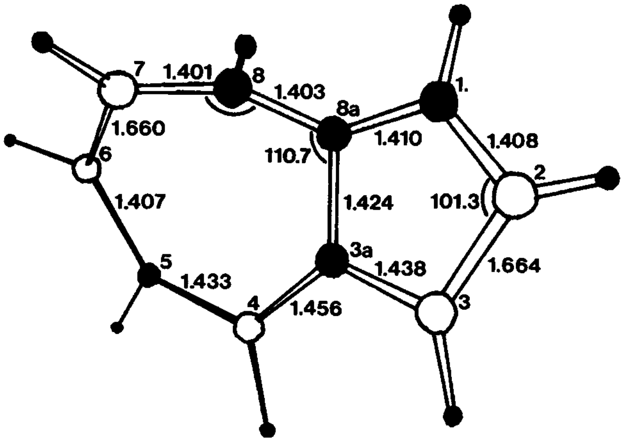
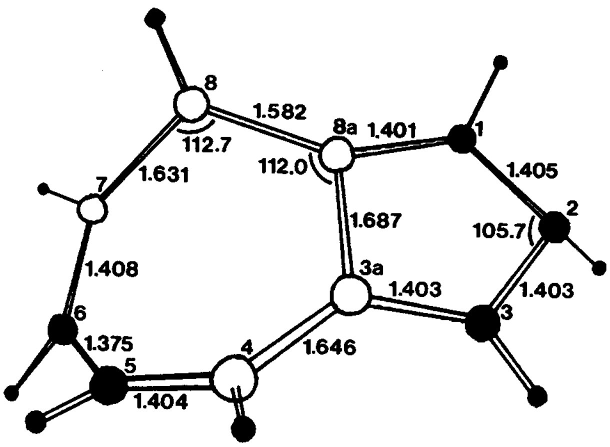
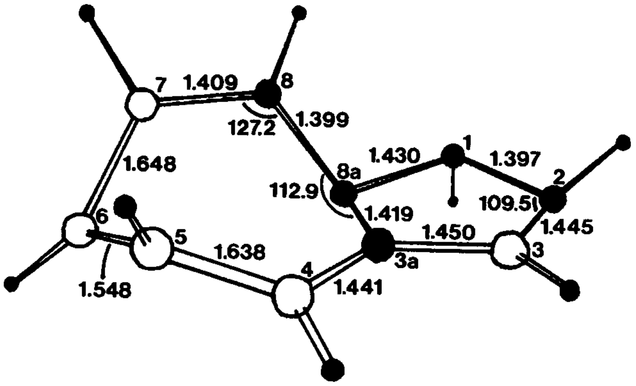


(67)

FIGURE 8 The MNDO-calculated structures of (47) and (67), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.



(109)



(116)

FIGURE 9 The MNDO-calculated structures of (109) and (116), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.

ever, in the seven-membered ring, although each of the B–B bonds is single, the remaining bonds are calculated to exhibit some delocalization. Bonds B^4–N^5 and N^7–B^8 each have a bond index of 1.281, while bonds N^5–B^6 and B^6–N^7 each have a bond index of 1.139. The delocalization in these atoms is on the order of that calculated for (**1**) and (**2**) [1].

Both (**47**) and (**67**) are nonplanar. In (**47**), atoms B^4, N^5, B^6, N^7, and B^8, whose bonds exhibit delocalization, form a plane, but the seven-membered ring is twisted out of the plane formed by atoms N^1, B^{8a}, B^{3a}, and N^3 by approximately 8°. Atom N^2 in the five-membered ring is twisted out of that same plane by approximately −7°. In (**67**), the tetra-atomic N_5 system imparts significant distortion to the molecule, as did the N-N-N system in (**19**). Here, however, the distortion is in the seven-membered ring: The torsion angle formed by atoms B^7-N^8-N^{8a}-N^{3a} is −72°. The five-membered ring is much more nearly planar, with a torsion angle N^1-B^2-B^3-N^{3a} of less than 2°.

Figure 9 illustrates the structures of (**109**) and (**116**), containing, respectively, the linear B-B-B-B-B system and the *Y*-shaped N-N-N-N-N system. In both molecules, the seven-membered ring is decidedly nonplanar and the five-membered ring is more nearly planar. (Torsion angles for atoms 1-2-3-3a in the five-membered ring are approximately −12° and 5.6° for (**109**) and (**116**), respectively, while for atoms 7-8-8a-3a, the torsion angles are approximately −58° and −78°, respectively.)

Molecule (**109**), like molecule (**47**) (Figure 8), contains a five-membered ring composed of three nitrogen and two boron atoms in the arrangement N^1-N^2-N^3-B^{3a}-B^{8a}, and the bond distances in the five-membered rings in these two molecules are remarkably similar. Again, as was the case with (**47**), no delocalization in bond order is noted in the five-membered ring of (**109**), even though the bond lengths are all approximately the 1.403 Å observed in (**47**). Unlike (**47**), (**109**) has no delocalized bond area in its seven-membered ring: the MNDO-calculated bond indices for B^4–N^5, N^5–N^6, and N^6–B^7 are 1.361, 0.948, and 1.333, respectively, indicating the alternation of partial N–B double bonds with an N–N single bond.

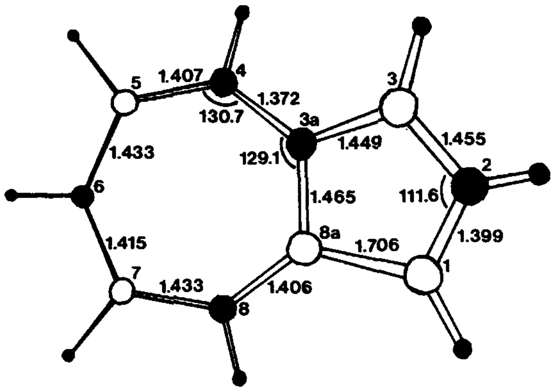
The planarity of the five-membered ring in (**116**) is offset by the pyramidal nature of the nitrogen atoms, as evidenced by the nonplanarity of the attached hydrogen atoms. The N–N bond indices (0.932 for N^{3a}–N^{8a}, 0.977 for N^1–N^{8a}, and 0.974 for N^1–N^2) indicate single bonding is occurring. However, the B–H bond is in the plane of the five-membered ring, and, here, the bond indices are slightly greater than unity (1.164 for N^2–B^3 and 1.115 for B^3–N^{3a}). This multiple bonding, albeit slight, apparently forces this local planarity to occur.

Structure: Molecules Chosen Because of Electronic Properties

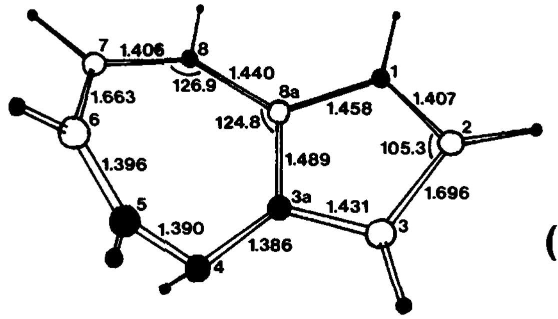
Figure 10 illustrates the MNDO-calculated structures of molecules (**9**), (**32**), and (**106**). These molecules exhibit the extremes in range for ionization potential ((**9**), low and (**32**), high) and LUMO − HOMO energy difference ((**106**), low and (**32**), high).

Of the three structures, (**9**) is the most nearly planar, with heavy atom torsion angles of less than 1°. The B^1–B^{8a} bond is relatively long, at 1.706 Å, and is calculated to have a bond index of 0.876, making the bond somewhat weaker than most other B–B bonds in the PAPBAZ molecules. Structure (**32**), with the greatest ionization potential and the greatest LUMO − HOMO energy difference, contains a nearly planar five-membered ring fused to a twisted seven-membered ring.

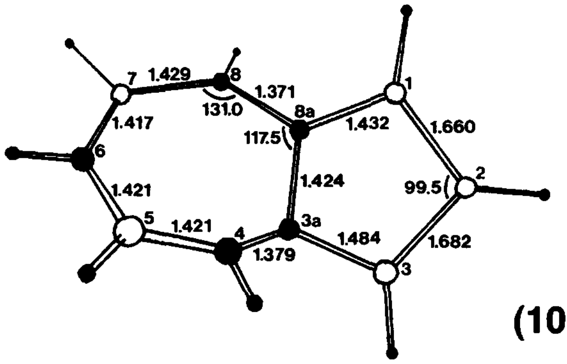
The HOMOs for (**9**) and (**32**), from which the ionization potentials are calculated, are bonding orbitals. In (**9**), the HOMO is strongly bonding at the N^{3a}–N^4 bond, while in (**32**), the HOMO is distributed more about the complete molecule. The primary bonding in the molecular orbital, however, is at the N^{3a}-N^4-N^5 position.



(9)



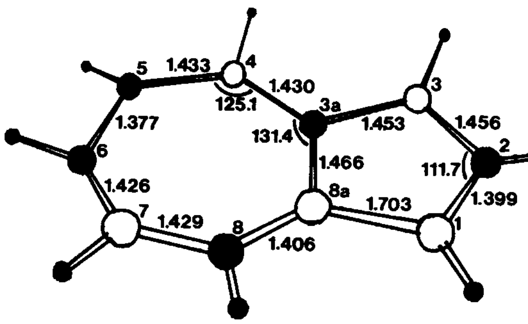
(32)



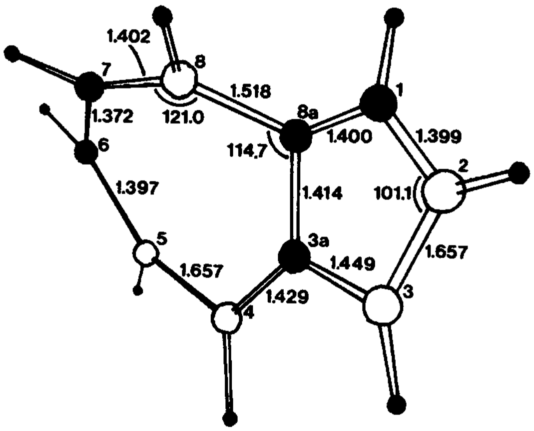
(106)

FIGURE 10 The MNDO-calculated structures of (**9**), (**32**), and (**106**), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.

The molecule with the smallest LUMO − HOMO energy difference, (**106**), is superficially symmetrical in the arrangement of atoms. However, the molecule optimizes as a strongly twisted system, but one in which the five- and seven-membered rings are, to as great an extent as possible, individually planar. The point of ring fusion, at N^{3a}–N^{8a}, is apparently a position of relatively high strain. The N–N bond length of 1.424 Å is quite long and



(11)



(87)

FIGURE 11 The MNDO-calculated structures of (**11**) and (**87**), with selected bond distances (in Ångstroms) and angles (in degrees), as depicted by the NAMODI routine of the program DRAW. Open circles represent boron atoms, large solid circles represent nitrogen atoms, and the terminally located, small solid circles represent hydrogen atoms.

is calculated to have a bond index of 0.889, making the bond a weak one.

The final molecules to be discussed are (**11**) and (**87**), the least and most polar structures, respectively (Figure 11). As might be expected for an only slightly polar molecule, (**11**) contains a nearly planar five-membered ring (torsion angles of <1°) but a distorted seven-membered ring (torsion angles of 10° or greater). The negative end of the dipole in (**11**) is near atoms N^5 and N^6 of the seven-membered ring.

With a dipole moment of more than 4.3 debye, (**87**) would be expected to be a strongly distorted molecule. That expectation is seen in the MNDO-optimized structure, although bond lengths are unremarkable. The negative end of the dipole is again, as in (**11**), in the seven-membered ring near atoms N^6 and N^7.

CONCLUSIONS

The ground state properties of all 130 possible nonfully boron-nitrogen alternating isomers of PAPBAZ have been examined using the semiempirical computational method MNDO. Many of the isomers are calculated to have strongly exothermic heats of formation, and, often, the structures optimized by MNDO are nearly planar or contain a nearly planar five- or seven-membered ring.

The synthesis of these isomeric molecules has apparently not been attempted, for no reports, save our previous publication [1] and one other computational study [2] on the two fully boron-nitrogen alternating isomers (**1**) and (**2**), have been published. In light of the increasing interest in novel precursors to boron-nitrogen-containing and boron nitride ceramic materials [11] and the apparent thermodynamic stability of many of these boron-nitrogen analogs of azulene, these compounds, if synthesized, might find uses as precursors to such materials. Further, in view of the continuing interest in inorganic ring systems [12], it is hoped that these computational results concerning the 132 isomers of PAPBAZ will spark renewed interest in this large family of molecules and their derivatives.

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SUPPLEMENTARY MATERIAL AVAILABLE

Charts 1 through 11 containing idealized drawings of all of the isomers of PAPBAZ and tables of final atomic coordinates and molecular orbital energies for molecules (**3**) through (**132**) (169 pages) may be obtained from one of the authors (RWZ) on written request.

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