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# An ab Initio Study of Potentially Aromatic and Antiaromatic Three-Membered Rings

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**Abstract:** Ab initio calculations were performed on 18 three-membered ring systems including 11 closed-shell and seven open-shell systems. The geometries of all systems were completely optimized on the RHF/6-31G** level. Both known and unknown closed-shell molecules were investigated including the cyclopropenyl cation, $C_3H_3^+$, **1**, the azirinyl cation, $C_2H_2N^+$, **2**, the diazirinyl cation, $CHN_2^+$, **3**, the triazirinyl cation, $N_3^+$, **4**, and its acyclic isomers, borirene, $C_2H_3B$, **5**, borazirene, $CH_2NB$, **6**, boradiazirine, $N_2BH$, **7**, azadiboridine, $NB_2H_3$, **8**, the borazarinyl cation, $CHNB^+$, **9**, azirene, $C_2H_3N$, **10**, and the diazaridinyl cation, $CH_3N_2^+$, **11**. Open-shell systems studied included the cyclopropenyl radical, $C_3H_3^\bullet$, **12**, the azirinyl radical cation, $C_2H_3N^{\bullet+}$, **13**, the diazirinyl radical, $CHN_2^\bullet$, **14**, the triazirinyl radical cation, $N_3H^{\bullet+}$, **15**, the borazirinyl radical, $CHNB^\bullet$, **16**, the azadiboridinyl radical cation, $NB_2H_3^{\bullet+}$, **17**, and the diaziridinyl radical $CH_3N_2^\bullet$, **18**. This series includes both potentially aromatic and potentially antiaromatic structures. The optimized structures are discussed in terms of their valence bond resonance hybrid representations. Previous theoretical and experimental results are compared with these calculations. The effect of boron and nitrogen in aromatic and nonaromatic systems is considered. Several unforseen results were found. Radicals **14** and **16** and radical cations **13**, **15**, and **17** were of interest since they might be systems with three $\pi$ electrons. However, the azirinyl, **13**, and triazirinyl, **15**, radical cations were each nonplanar with two $\pi$ electrons. The borazirinyl radical, **16**, and azadiboridinyl radical cation, **17**, were planar. Borazirinyl radical, **16**, is a two $\pi$ electron system with the unpaired electron in the $\sigma$ system largely located at the boron. **17** has a two $\pi$ electron aromatic system with a weak BB $\sigma$ bond (approximately a one-electron bond) with some BB $\pi$ overlap. Its unpaired electron is also in a $\sigma$ orbital. Only the diazirinyl radical, **14**, was found to be a three $\pi$ electron planar system in spite of any antiaromaticity associated with this structure.

## Introduction

According to simple MO theory, conjugated planar cyclic systems with $4n + 2$ $\pi$ electrons ($n = 0, 1, 2, ...$) exhibit particularly high stabilities, compared to systems with a different number of $\pi$ electrons. These systems are commonly referred to as aromatic, and the extra stabilization is associated with delocalization of the $\pi$ electrons over the ring. On the other hand, systems with $4n$ $\pi$ electrons show particularly low stability and little $\pi$-electron delocalization. These systems are referred to as antiaromatic when forced to have a planar geometry.

Three-membered rings represent the simplest potentially aromatic or antiaromatic systems. Most of these highly strained systems are expected to be short-lived; however, some have been detected or postulated as reaction intermediates.

The cyclopropenyl cation **1** with two $\pi$ electrons is, according to Hückel theory, an aromatic system and thus expected to be a relatively stable species. The *sym*-triphenylcyclopropenyl cation was synthesized in 1957 by Breslow,[1] and isolated as a stable salt. Since then several other phenyl,[2,3] substituted aryl,[4] alkyl,[5] halo,[6] and amino[7] derivatives have been prepared and isolated. Finally, in 1970 three salts of the parent $C_3H_3^+$ cation were prepared.[8] The $pK_R^+$ values for some substituted cyclopropenyl cations have been determined,[9-12] and these values indicate remarkable stabilitites of these ions, supporting the notion of resonance stabilization or aromaticity.

The crystal structures of two cyclopropenyl salts, the perchlorate salt of the *sym*-triphenylcyclopropenyl[13] and 1,2,3-tris(dimethylamino)cyclopropenyl[14] cations, have been determined. The rings' C–C bond lengths were 1.373 and 1.363 Å, respectively. Since the substituents in these cations allow significant delocalization of the positive charge out of the cyclopropenyl ring, the ring C–C bond lengths should be expected to be longer than in the parent cyclopropenyl cation. However, the experimental results for these two substituted species should give some indication of the reliability of the computational approach used in the present study on hydrogen-substituted analogues.

Even though properties of the parent species cyclopropenyl cation are known, little is known about related species where carbon atoms have been replaced by heteroatoms with the exception of the borirene, $C_2BH_3$, **5**, molecule. In an early theoretical study of this molecule,[15] it was suggested that trivalent boron had the same electronic structure as the carbocation and, based on theoretical calculations,[16] Pittman concluded that this molecule would have aromatic properties if an independent existence were possible. In 1981 borirene was found as an intermediate,[17] and in 1987 Eisch et al.[18] prepared trimesitylborirene and determined its structure by X-ray diffraction. They concluded that this molecule was highly strained, but stabilized by aromatic $\pi$ delocalization. However, they found both the CC and CB bond lengths equal to 1.416 Å. This seemed unlikely to us and stimulated calculations on the parent borirene molecule. After our calculations were completed, Eisch et al.[19] isolated the unsymmetrical substitued 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene and found the three-membered ring had bond lengths of CC, 1.380 Å, $C_1B$, 1.450 Å, and $C_2B$, 1.464 Å, based on an X-ray crystal structure. The CC bond length was 0.08 Å longer than cyclopropene's CC double-bond length,[20,21] and the CB bond length

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**Table I.** Summary of SCF/6-31G** Calculations on the Closed-Shell Species, **1–11**

| | geometry (total energy) | |
|---|---|---|
| | 1. Cyclopropenyl Cation ($D_{3h}$) | |
| *R*(CC), 1.350 | *R*(CH), 1.072 | (−115.0132914) |
| | 2. Azirinyl Cation ($C_{2v}$) | |
| *R*(CC), 1.330 | ∠CNC, 61.0 | (−130.9752942) |
| *R*(CN), 1.309 | ∠CCN, 59.5 | |
| *R*(CH), 1.075 | ∠CCH, 159.0 | |
| | 3. Diazirinyl Cation ($C_{2v}$) | |
| *R*(NN), 1.286 | ∠NCN, 59.4 | |
| *R*(CN), 1.297 | ∠NNC, 60.3 | |
| *R*(CH), 1.078 | (−146.9107751) | |
| | 4. Triazirinyl Cation ($D_{3h}$) | |
| *R*(NN), 1.275 | linear open structure | |
| (−162.8249922) | (−162.8067071) | |
| | 5. Borirene ($C_{2v}$) | |
| *R*(CB), 1.464 | ∠CBC, 54.4 | (−102.1066389) |
| *R*(CC), 1.340 | ∠CCB, 62.8 | |
| *R*(CH), 1.072 | ∠CCH, 138.8 | |
| *R*(BH), 1.174 | ∠CBH, 152.8 | |
| | 6. Borazirine ($C_s$) | |
| *R*(CB), 1.434 | ∠BCN, 62.5 | (−118.1197377) |
| *R*(CN), 1.290 | ∠CNB, 63.8 | |
| *R*(NB), 1.417 | ∠NBC, 53.8 | |
| *R*(CH), 1.075 | ∠CBH, 160.8 | |
| *R*(BH), 1.171 | ∠BCH, 167.1 | |
| | 7. Boradiazirine ($C_{2v}$) | |
| *R*(BN), 1.395 | ∠NBN, 53.9 | (−134.1061483) |
| *R*(NN), 1.264 | ∠BNN, 63.1 | |
| *R*(BH), 1.167 | ∠NBH, 153.1 | |
| | 8. Azadiboridine ($C_{2v}$) | |
| *R*(BB), 1.598 | ∠NBB, 55.0 | ∠BNH, 145.0 |
| *R*(BN), 1.394 | ∠BNB, 69.9 | (−105.5592628) |
| *R*(BH), 1.178 | ∠BBH, 168.6 | |
| | 9. Borazarinyl Cation ($C_s$) | |
| *R*(CN), 1.347 | ∠CNB, 62.8 | ∠HCB, 169.2 |
| *R*(BC), 1.387 | ∠BCN, 59.8 | (−117.1208781) |
| *R*(BN), 1.313 | ∠NBC, 57.4 | |
| *R*(CH), 1.075 | ∠HCN, 133.4 | |
| | 10. Azirene<br>nonplanar form ($C_s$)[a] | |
| *R*(CC), 1.256 | ∠CCN, 65.1 | $H_c$OUT, −4.0 |
| *R*(CN), 1.490 | ∠CNC, 49.9 | $H_n$OUT, 69.3 |
| *R*(CH), 1.065 | ∠HCC, 156.8 | (−131.7832566) |
| *R*(NH), 1.008 | ∠HCN, 137.6 | |
| | ∠HNC, 108.7 | |
| | planar form ($C_{2v}$) | |
| *R*(CC), 1.272 | ∠CCN, 52.2 | (−131.7124395) |
| *R*(CN), 1.447 | ∠CNC, 63.9 | rel energy, 44.4 |
| *R*(CH), 1.064 | ∠HCC, 155.0 | |
| *R*(NH), 0.978 | ∠HCN, 141.0 | |
| | ∠HNC, 153.9 | |
| | 11. Diaziridinyl Cation<br>nonplanar trans form ($C_2$) | |
| *R*(CN), 1.509 | ∠CNN, 54.4 | $H_c$OUT, 0.0 |
| *R*(NN), 1.296 | ∠NCN, 71.2 | $H_n$OUT, 55.5 |
| *R*(CH), 1.078 | ∠CNH, 115.2 | HNNH, 58.7 |
| *R*(NH), 1.009 | ∠NNH, 123.5 | (−148.1009102) |
| | ∠NCH, 144.4 | |
| | nonplanar cis form ($C_s$) | |
| *R*(CN), 1.539 | ∠CNN, 53.6 | $H_c$OUT, 6.2 |
| *R*(NN), 1.297 | ∠NCN, 72.8 | $H_n$OUT, 53.1 |
| *R*(CH), 1.078 | ∠CNH, 119.3 | HNNH, 0.0 |
| *R*(NH), 1.014 | ∠NNH, 124.7 | (−148.0931733) |
| | ∠NCH, 143.1 | rel energy, 4.9 |
| | planar form ($C_{2v}$) | |
| *R*(CN), 1.520 | ∠CNN, 52.2 | (−148.0547640) |
| *R*(NN), 1.268 | ∠NCN, 73.6 | rel energy, 30.0 |
| *R*(CH), 1.077 | ∠CNH, 165.7 | |
| *R*(NH), 0.998 | ∠NNH, 141.1 | |
| | ∠NCH, 143.2 | |

[a] Definition of internal coordinates describing deviation from planarity; $H_c$OUT, the angle between the CH bond and the plane of the ring; HCCH, the HCCH torsional angle.

was 0.10 Å shorter than that of trivinylborane.[22] Thus, the borirene ring system seems to be aromatic.

In the present study we have performed ab initio calculations on a series of 18 three-membered unsaturated rings systems: the cyclopropenyl cation, the cyclopropenyl radical and 16 heterocyclic species where carbon atoms have been replaced by nitrogen or boron. Complete details of these calculations can be found in ref 22. Included are 11 closed-shell species, **1–11**, and seven open-shell species, **12–18**. Systems **1–9** are potentially aromatic two $\pi$ electron systems, while **10** and **11** are potentially antiaromatic systems with four $\pi$ electrons when forced to have a planar geometry. The open-shell systems, **12–18**, could have three $\pi$ electrons in their planar form and thus are "partially" antiaromatic. The questions that will be addressed are: which of these ring systems exhibit aromatic character, and could any of these systems be stable enough to be isolated. Some of the systems studied here are potentially antiaromatic; for these systems it is interesting to see if the antiaromaticity is reflected in the geometries, or if the system distorts to avoid the unfavorable antiaromatic electronic structure. To answer these questions the calculated geometries, energies, charge distributions, and $\pi$ delocalization will be used and inversion barriers are examined.

To our knowledge no experimental information is available for these transient species with the exceptions discussed above. Some of the systems have been the subject of semiempirical (**1–6**, **8**, **10**, **12**)[15,16,23–33] and ab initio (**1–3**, **5**, **10**, **12**)[34–47] studies. However, this is the first systematic study of series of unsaturated three-membered heterocycles, and for all systems our calculations are

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**Table II.** Summary of Results for ROHF/6-31G** on the Open-Shell Systems, **12–18**

| | geometry<br>(total energy) | |
|---|---|---|
| | 12. Cyclopropenyl Radical | |
| | nonplanar form ($C_s$) | |
| $R(\mathrm{C_2C_3})$, 1.293 | $\angle\mathrm{C_3C_1C_2}$, 52.8 | $\mathrm{H_1OUT}$[a], 45.6 |
| $R(\mathrm{C_1C_2})$, 1.454 | $\angle\mathrm{C_2C_3C_1}$, 63.6 | (−115.1955958) |
| $R(\mathrm{C_2H_2})$, 1.068 | $\angle\mathrm{H_2C_2C_3}$, 148.8 | |
| $R(\mathrm{C_1H_1})$, 1.083 | $\angle\mathrm{H_1C_1C_3}$, 147.6 | |
| | $\angle\mathrm{H_1C_1C_3}$, 128.8 | |
| | planar form ($C_{2v}$) | |
| $R(\mathrm{C_2C_3})$, 1.300 | $\angle\mathrm{C_3C_1C_2}$, 53.5 | (−115.1753217) |
| $R(\mathrm{C_1C_2})$, 1.443 | $\angle\mathrm{C_2C_3C_1}$, 63.2 | rel energy, 12.7 |
| $R(\mathrm{C_2H_2})$, 1.068 | $\angle\mathrm{H_2C_2C_3}$, 148.1 | |
| $R(\mathrm{C_1H_1})$, 1.057 | $\angle\mathrm{H_1C_1C_3}$, 153.2 | |
| | 13. Azirinyl Radical Cation | |
| | nonplanar form ($C_s$) | |
| $R$(CC), 1.295 | ∠CCN, 62.1 | $\mathrm{H_nOUT}$, 36.8 |
| $R$(CN), 1.382 | ∠CNC, 55.9 | (−131.5357127) |
| $R$(CH), 1.070 | ∠CCH, 158.2 | |
| $R$(NH), 1.011 | ∠NCH, 139.8 | |
| | ∠CNH, 135.0 | |
| | planar form ($C_{2v}$) | |
| $R$(CC), 1.298 | ∠CCN, 61.9 | (−131.5214125) |
| $R$(CN), 1.376 | ∠CNC, 56.3 | rel energy, 9.0 |
| $R$(CH), 1.069 | ∠CCH, 157.9 | |
| $R$(NH), 1.001 | ∠NCH, 140.2 | |
| | ∠CNH, 151.0 | |
| | 14. Diazirinyl Radical | |
| $R$(CN), 1.484 | ∠CNN, 54.5 | (−147.2013542) |
| $R$(NN), 1.277 | ∠NCN, 71.1 | |
| $R$(CH), 1.072 | ∠NCN, 144.5 | |
| | 15. Triazirinyl Radical Cation | |
| | nonplanar form ($C_s$) | |
| $R(\mathrm{N_2N_3})$, 1.200 | $\angle\mathrm{N_1N_2N}$, 64.0 | HOUT, 40.2 |
| $R(\mathrm{N_1N_2})$, 1.369 | $\angle\mathrm{N_3N_1N_2}$, 52.0 | (−163.4206655) |
| $R$(NH), 1.022 | ∠NNH, 132.8 | |
| | planar form ($C_{2v}$) | |
| $R(\mathrm{N_2N_3})$, 1.208 | $\angle\mathrm{N_1N_2N_3}$, 63.6 | (−163.4087814) |
| $R(\mathrm{N_1N_2})$, 1.366 | $\angle\mathrm{N_3N_2N_1}$, 52.9 | rel energy, 7.5 |
| $R$(NH), 1.017 | ∠NNH, 153.6 | |
| | 16. Borazirinyl Radical ($C_s$) | |
| $R$(CB), 1.435 | ∠NCB, 62.0 | (−117.471845) |
| $R$(CN), 1.292 | ∠BNC, 64.0 | |
| $R$(NB), 1.411 | ∠CBN, 54.0 | |
| $R$(CH), 1.074 | ∠NCH, 130.5 | |
| | ∠BCH, 167.5 | |
| | 17. Azadiboridinyl Radical Cation ($C_{2v}$) | |
| $R$(BB), 1.848 | ∠NBB, 47.3 | (−105.2754902) |
| $R$(NB), 1.364 | ∠NBN, 85.3 | |
| $R$(BH), 1.164 | ∠HNB, 137.3 | |
| $R$(NH), 1.008 | ∠NBH, 158.0 | |
| | ∠BBH, 154.6 | |
| | 18. Diaziridinyl Radical | |
| $R(\mathrm{CN_1})$, 1.396 | $\angle\mathrm{N_2N_1C}$, 57.8 | HNNH, 148.0 |
| $R(\mathrm{CN_2})$, 1.389 | $\angle\mathrm{N_1N_2C}$, 58.2 | $\mathrm{HN_1CH}$, 145.1 |
| $R$(NN), 1.475 | ∠NCN, 64.0 | $\mathrm{HN_2CH}$, 17.6 |
| $R(\mathrm{N_1H})$, 1.003 | $\angle\mathrm{N_2N_1H}$, 105.7 | $\mathrm{H_{n1}OUT}$, 68.0 |
| $R(\mathrm{N_2H})$, 1.004 | $\angle\mathrm{CN_1H}$, 111.4 | $\mathrm{H_{n2}OUT}$, −66.5 |
| $R$(CH), 1.077 | $\angle\mathrm{N_1N_2H}$, 107.0 | $\mathrm{H_cOUT}$, −46.2 |
| | $\angle\mathrm{CN_2H}$, 112.5 | (−148.3703057) |
| | $\angle\mathrm{N_1CH}$, 124.1 | |
| | $\angle\mathrm{N_2CH}$, 127.6 | |
| | cis-1 ($C_s$) | |
| $R$(CN), 1.396 | ∠CNN, 57.9 | HNNH, 0.0 |
| $R$(NN), 1.483 | ∠NCN, 64.2 | HNCH, 141.6 |
| $R$(CH), 1.076 | ∠CNH, 110.2 | $\mathrm{H_NOUT}$, −66.7 |
| $R$(NH), 1.005 | ∠NNH, 110.3 | $\mathrm{H_COUT}$, 46.9 |
| | ∠NCH, 125.4 | (−148.3608453) |
| | | rel energy, 5.9 |
| | cis-2 ($C_s$) | |
| $R$(CN), 1.393 | ∠CNN, 57.9 | HNNH, 0.0 |
| $R$(NN), 1.481 | ∠NCN, 64.2 | NNCH, −15.2 |
| $R$(NH), 1.006 | ∠CNH, 111.1 | $\mathrm{H_NOUT}$, −65.7 |
| $R$(CH), 1.077 | ∠NNH, 111.2 | $\mathrm{H_COUT}$, −45.4 |
| | ∠NCH, 126.5 | (−148.3590086) |
| | | rel energy, 7.1 |

[a] See footnote *a* of Table I for definition of out-of-plane internal coordinates.

of higher quality than reported earlier.

## Method

The 18 three-membered rings, **1–18**, were completely optimized on the Hartree–Fock level using the ab initio gradient[48,49] program TEXAS.[50] For the open-shell species (**12–18**) the spin-restricted Hartree–Fock method (ROHF) was used. For all calculations reported here, the 6-31G** basis set[51,52] was applied. This basis set has been widely used and is expected to give reliable estimates for equilibrium structures.[36]

We do not claim quantitative accuracy for the absolute values of our structural parameters; however, for a family of related molecules calculated with the same procedure using the same basis set, the predicted variations should be reliable. Experience has shown[53,54] that when bond lengths and angles are obtained in different molecules by ab initio calculations on the SCF level using a fixed and relatively modest atomic basis set (4-21G), the error is nearly the same in wide families of molecules. In the present study a polarized basis set was applied. Polarization functions are required for three-membered rings[36] and for the description of the heteroatoms[35,36] and their valence angles.

The wave functions were analyzed by Mulliken population analysis.[55] Even though a fractional partitioning of the charge to different parts of a molecule always will be somewhat arbitrary, the Mulliken scheme can provide useful information, in particular, when used in direct comparisons of related species.

Throughout this paper bond lengths are given in ångströms, angles in degrees, total energies in hartrees, and relative energies in kcal/mol. Explanations will use the language of resonance hybrid structures to assist understanding. All calculations were carried out on the UNIVAC 1174 system at Mississippi State University.

## Results and Discussion

The 18 species studied here, labeled **1** to **18**, are shown sequentially in the text. The optimized geometries, total energies, and relative energies (when applicable), for the closed-shell species, **1–11**, are given in Table I. The results for the open-shell species, **12–18**, are summarized in Table II. Preliminary calculations were also carried out with the unpolarized 6-31G basis. Some of these results are given in the text for comparison. Complete details can be found in ref 22. However, even for the cyclopropenyl cation, **1**, the bond lengths were overestimated with unpolarized basis sets (see below), illustrating the necessity of the angular flexibility provided by polarization functions to describe three-membered rings. Results from Mulliken population analysis are given in the text and only when needed for the discussion.

**Cyclopropenyl Cation 1.** Ab initio calculations[34] show that the cyclopropenyl cation is the most stable species on the $C_3H_3^+$ energy

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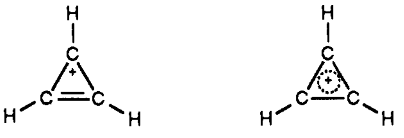


**1**

surface. It is about 30 kcal/mol below the propargyl cation system.[34] The relatively high stability of this ion, rationalized by aromatic stabilization, has also been confirmed experimentally.[56–58]

This system has two $\pi$ electrons and represents the simplest aromatic system according to Hückel's rules. For this reason the cyclopropenyl cation has been the subject of several semiempirical[16,23–29] and ab initio[34–40] studies. Consistent with previous studies, our calculations predict that the cyclopropenyl cation is a perfect equilateral triangle with the two $\pi$ electrons delocalized over the ring. Our calculated C–C bond lengths of 1.350 Å are somewhat shorter than the ones obtained with smaller basis sets and shorter than the corresponding C–C ring bond lengths of 1.373 and 1.363 Å for the *sym*-triphenylcyclopropenyl[13] and the 1,2,3-tris(dimethylamino)cyclopropenyl[14] cations, respectively, as expected. Our calculated value of 1.350 Å seems reasonable for the parent cyclopropenyl cation.

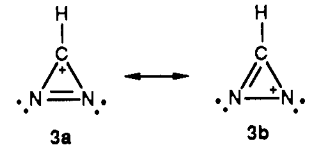
Employing the 6-31G basis set (this work) gave 1.365 Å for the CC bond lengths. Other calculations have given 1.418 Å (CNDO/2),[35] 1.380 Å (INDO),[33] 1.377 Å (STO-3G),[36] and 1.381 (3-21G).[35] The atomic charges were 0.028 and 0.306 for carbon and hydrogen, respectively.

**Azirinyl Cation 2.** The azirinyl cation, $C_2NH_2^+$, **2**, is isoelectronic with the cyclopropenyl cation with two $\pi$ electrons. Semiempirical calculations[16] showed that this system exhibited aromatic properties, and ab initio calculations[42] showed that the azirinyl cation was the most stable among the possible $C_2H_2N^+$ species.

**2a** **2b**

The cyclopropenyl cation **1** and triazirinyl cation **4** (see below) are both perfectly aromatic systems, and, based on the optimized geometries for these systems, a CN bond length should be about 1.310 Å in an aromatic three-membered ring cation. Polarization toward the more electronegative nitrogen atom would result in a shortening of the CN bond and a lengthening of the CC bond. The calculated optimized bond lengths were 1.330 and 1.309 Å for the CC and CN bonds, respectively. Thus considerable CN double-bond character is expected (resonance structure **2b**), and this is confirmed by the $\pi$ bond orders of 0.594 (CC) and 0.703 (CN). These implicate strong $\pi$ polarization toward nitrogen (e.g., hybrid **2b**). Ring strain favors an equilateral triangle-like geometry, further contributing to a short CC bond.

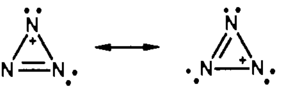
**Diazirinyl Cation 3.** The diazirinyl cation, $CN_2H^+$, **3**, has also been studied by semiempirical[16,28] and by ab initio calculations[42] with a smaller basis set than the one used in the present study. Our calculations predict the diazirinyl cation to be an almost perfect equilateral triangle with NN and CN lengths of 1.286 and 1.297 Å, respectively. These bond lengths are markedly shorter than the values of 1.324 and 1.320 Å obtained using the 6-31G basis set. Previous INDO calculations[16] predicted a more isosceles triangle-like geometry. The $\pi$ electrons are delocalized over the three ring-atoms, though polarized toward the nitrogen atoms as indicated by the NN (0.734) and CN (0.633) $\pi$ bond orders and by electron populations of 0.73 and 0.53 in the $p_z$ orbitals of N and C, respectively. These results indicate significant contribution from hybrid **3b**. Based on resonance alone, the NN bond should be a little shorter than the NN bond in the triazirinyl **4** cation and the CN bond longer than in the azirinyl cation **2**. Our results show the opposite trend, indicating the importance of ring strain for the geometries of three-membered rings.



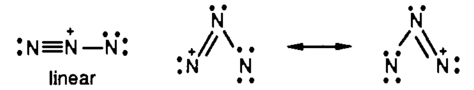
**3a** **3b**

Both azirinyl **2** and diazirinyl **3** cations clearly exhibit aromatic properties, and they have geometries close to equilateral triangles. Even though these species are highly strained, independent existence could be possible in nonnucleophilic media.

**Triazirinyl Cation 4.** The cyclic $N_3^+$ isomer, triazirinyl cation, **4**, has two $\pi$ electrons and should, according to the Hückel theory, be an aromatic species. This has also been indicated by semiempirical calculations.[23] However, no previous ab initio calculations or experimental geometry determination has appeared. Our calculations show that the triazirinyl cation is the minimum energy structure on the $N_3^+$ singlet potential surface occurring about 11 kcal mol$^{-1}$ below the lowest energy open-chain form (linear symmetrical). The cyclic ion is perfectly aromatic with $D_{3h}$ symmetry, NN bond lengths of 1.275 Å, and a $\pi$ bond order of 2/3. Archibald, et al.[39] predicted the triplet form of the linear structure to be 43.8 kcal mol$^{-1}$ more stable than the bent geometry.



**4a** **4b**

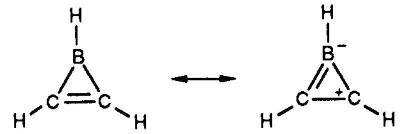


linear

bent

The triazirinyl cation, with maximum resonance stabilization, is expected to be a relatively stable cation. Since the cyclopropenyl cation has been detected, we expect that also the triazirenyl cation could be detected.

**Borirene 5.** In an early theoretical discussion[15] of the possible aromatic character of this molecule, it was concluded that trivalent boron possessed the same configuration as a carbocation. Experimental work on **5** was summarized in the Introduction. Both semiempirical[16] and ab initio[44] calculations with STO-3G and 4-31G basis sets showed that this molecule has a delocalized $\pi$ system and that an independent existence of this molecule was conceivable. Our calculations showed that the molecule is planar ($C_{2v}$) with CB bond lengths of 1.464 and a CC bond length of 1.340 Å. The covalent radius of boron is 0.11 Å larger than that of carbon, and the calculated bond lengths are as expected for this system assuming a delocalized $\pi$ system. The $\pi$ donation to the empty $p_z$ orbital on boron is 0.34 electron and the $\pi$ bond orders are 0.59 and 0.83 for the CB and CC bonds, respectively. Thus this molecule possesses a delocalized $\pi$-electron system, but **5b** does not contribute as strongly as **5a**. While the $\pi$ electrons are delocalized toward boron, the calculated charges of −0.250 at C and +0.258 at B show $\sigma$ polarization toward carbon. Thus bulky groups are needed as substituents to prevent the borirene ring from reacting. The parent system should be a challenge to isolate owing to its expected reactivity.



**5a** **5b**

**Borazirene 6.** No experimental study of borazirene or any of its derivatives has been reported. The only theoretical study of this system is a semiempirical calculation.[32]

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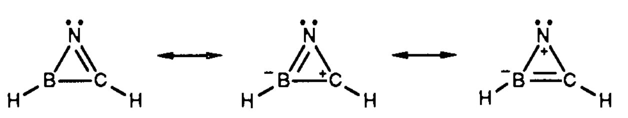
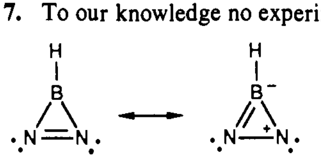
We found that this molecule is planar, and the CB, BN, and CN bond lengths were determined to be 1.434, 1.427, and 1.290 Å, respectively. The lengths suggest **6a** as the major hybrid contributor. The distribution of the two π electrons on the three atoms is 0.74 electron on C, 0.95 on N, and 0.31 on B. This indicates a significant π donation onto boron with the major loss of π density from carbon; e.g., **6b** contributes more than **6c**. Such aromatic delocalization is also illustrated by the π bond orders for CB (0.53), BN (0.67), and CN (0.71) which further emphasizes contributions by hybrid structures **6b** and **6c**. The atomic charges are B (+0.30), C (−0.05), N (−0.39), B–*H* (−0.03), and C–*H* (+0.16). These show that, despite the existing π donation toward boron, the σ framework is polarized toward nitrogen.



**6a** **6b** **6c**

The more highly polar nature of borazirene could increase its reactivity toward nucleophiles and electrophiles relative to borirene.

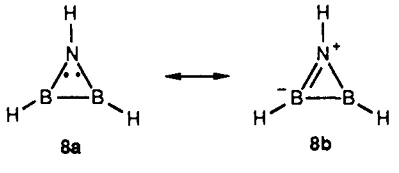
**Boradiazirine 7.** To our knowledge no experimental or theoretical studies of this molecule have been reported. It is formally a two π electron system, isoelectronic with the diazirinyl cation **3**. We found that this molecule is planar with a NN bond length of 1.264 Å and BN bond length of 1.395 Å. The difference between the BN and CN bond lengths of 0.13 Å is somewhat smaller than the difference between tabulated covalent radii of 0.18 Å. Furthermore, the BN bond length is shorter than in the borazirene molecule, **6**. The NN bond is 0.26 Å shorter than the CN bond in borazirene, while the difference in the covalent radii for C and N is 0.07 Å. Significant π donation to the boron atom contributes 0.28 electron to boron's $p_z$ orbital which illustrates aromatic delocalization within this molecule. The π bond orders of 0.57 (BN) and 0.86 (NN) and the π donation to boron indicate that both resonance hybrids **7a** and **7b** contribute significantly, although **7b** contributes less strongly to **7** than **3b** to **3**. The 0.032-Å shortening of the BN bond in **7** compared to the BN bond in the borazirene molecule, **6**, may be explained by the minimization of angle strain which occurs as the geometry of **7** tries to approximate an equilateral triangle. The NBN angle (54°) is significantly smaller than the BNN angle (63°). The π bond order in the BN bond of borazirine (0.71) is significantly larger than the value of 0.57 in boradiazirine despite the fact that the BN bond in boradiazirine is 0.032 Å shorter. With only one nitrogen atom to π-donate electrons back to boron, the larger order in borazirine makes sense. The shorter BN length in boradiazirine is the result of the nitrogen's high electronegativity.



**7a** **7b**

The boradiazirene molecule is highly strained and partly stabilized by an aromatic-type resonance. Given trivalent boron's typical instability and tendency to dimerize (which would destroy the aromaticity that exists), the isolation of **7** seems a difficult task.

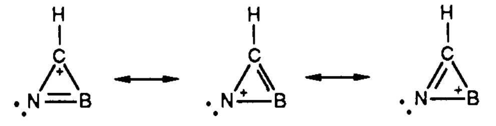
**Azadiboridine 8.** In its planar form, azadiboridine **8** would be a potentially aromatic delocalized two π electron system. No experimental results have been reported for this molecule or its derivatives. Two semiempirical studies[32,33] showed that this molecule would be most stable in its planar form stabilized by π donation to the boron atoms.



**8a** **8b**

We also find this molecule to be planar ($C_{2v}$). The optimized planar form had a BB bond length of 1.598 and BN bond lengths of 1.394 Å. The difference between the BB and BN bond lengths is somewhat larger than the difference in covalent radii of boron and nitrogen. The π bond order is very high for the BN bond (0.87) and fairly low for the BB bond (0.26). The relatively short BN bond lengths are similar to the bond lengths in the boradiazirene molecule **7**. π donation to each boron atom from nitrogen places 0.26 electron in each boron $p_z$ orbital, leaving 1.49 π electrons on nitrogen. Despite the π polarization toward boron, there is a strong σ polarization toward the more electronegative nitrogen atom. This is illustrated by Mulliken population analysis which predicts charges of +0.21 on boron and −0.64 for nitrogen. The charges in resonance hybrid **8b** are a manifestation of the valence bond language applied to the π system, and the calculated atomic charges should not be interpreted as being evidence against the contribution of **8b**. Since the double bond character in the BB bond is low (π bond order 0.26), the molecule should not be considered truly aromatic.

**Borazarinyl Cation 9.** Removal of $H^-$ from boron in the borazirine molecule, **6**, leaves the 18-electron boraziriny1 cation, **9**.

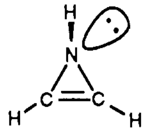


**9a** **9b** **9c**

No experimental or theoretical studies for this species have been reported. It is included in our study since, in its planar form, it would be a potentially aromatic two π electron system.

Calculations showed the planar geometry was more stable than all nonplanar forms. It exhibits aromatic properties. The NB, BC, and NC bond lengths are 1.313, 1.387, and 1.347 Å, respectively, and the corresponding π bond orders are 0.69, 0.54, and 0.78. Thus, each bond in the ring has significant double-bond character. The π electrons are highly delocalized. The ring is almost an equilateral triangle, and the π populations are 0.91, 0.64, 0.45 electron on N, C, and B, respectively. Taken together, these data illustrate strong contributions from hybrid structures **9a**, **9b**, and 9c. Most of the positive charge (+0.64) is carried by the electropositive boron atom (strong BN σ polarization toward nitrogen and weak N-to-B π polarization contribute to this charge), which may explain the significant differences between this ion and the borazirine molecule. These calculations suggest that the borazarinyl cation might possibly be an isolatable species.

**Azirene 10.** This molecule is a 22-electron system, and its planar form would have four π electrons. Thus it is a potentially antiaromatic system. Both semiempirical[24] and ab initio[46,47] studies have been reported for this molecule.



**10**

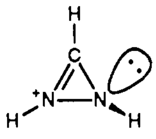
In agreement with the earlier theoretical studies, we found that this molecule prefers a nonplanar geometry with the hydrogen, bound to the pyramidal nitrogen atom, tilted 69.3° out of the plane of the ring. Ab initio calculations with the 6-31G* basis, without polarization functions on the hydrogen atoms, gave a tilt angle of 72.1°.[46] The optimized nonplanar structure is 44.6 kcal $mol^{-1}$ more stable than the optimized planar geometry. The optimized planar structure represents the transition state for nitrogen inversion, so a 44.6-kcal/mol barrier to nitrogen inversion is predicted. The short CC bond length (1.256 Å) and the long CN bond lengths (1.490 Å) clearly show that the valence bond structure of this molecule is best represented as **10** with a CC double bond and CN single bonds.

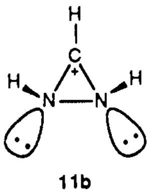
Finally, when forced into a planar structure, the CC length increases only slightly to 1.272 Å and the CN lengths are 1.447

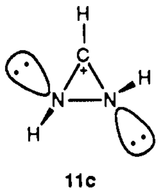
Å. This substantial CN versus CC bond-length difference in the planar geometry is a manifestation of the molecule avoiding the delocalized antiaromatic four $\pi$-electron structure. This agrees with the remarkably large energetic bias for nonplanarity and is consistent with antiaromatic destabilization.

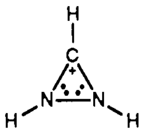
It should be possible to construct substituted azirenes and resolve enantiomers due to the large inversion barrier at nitrogen. Substituted aziridines have been resolved and do not interconvert at room temperature.[59,60] Based on the antiaromatic nature of azirene, it would be expected to have a higher inversion barrier than aziridines.

**Diazaridinyl Cation 11.** This ion is isoelectronic with the azirene molecule **10**, and would be an antiaromatic four $\pi$-electron system in its planar form. Our calculations represent the first study of this system. There are four cyclic geometries of importance including the all-planar system (both nitrogen atoms sp$^2$ hybridized) and three nonplanar systems: **11a**, one nitrogen sp$^2$-hybridized and one sp$^3$; **11b**, both nitrogens sp$^3$ with the hydrogens on the nitrogens cis; and **11c**, with both nitrogens sp$^3$ with the hydrogens on the two NH bonds trans. When the molecule was optimized without symmetry restrictions using the 6-31G** basis set, it converged to **11c** ($C_2$ symmetry). This is called the nonplanar trans form in Table I and lies only 4.9 kcal mol$^{-1}$ below structure **11b** (called the nonplanar cis form in Table I). This energy difference can be explained by the unfavorable repulsion of the two nitrogen lone pairs in the cis form. Structure **11a** is not a minimum on the 6-31G** potential surface. Upon geometry relaxation, **11a** converged to **11c**.


**11a**


**11b**


**11c**


**11d**

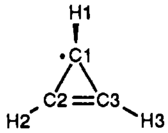
Complete geometry optimization was also carried out for the planar $C_{2v}$ form, **11d**. This geometry has four $\pi$ electrons (antiaromatic) and proved to be very unstable, lying 30 kcal above **11c**, the predicted equilibrium geometry. Thus, the diazaridinyl cation, like azirene **10**, strongly preferred the nonplanar structure to avoid the unfavorable antiaromatic electronic configuration. In contrast to the results using the 6-31G** basis set, the lowest energy geometry using the 6-31G basis set was **11a** which lies 3.8 kcal below **11c**. Structure **11a** has one planar and one pyramidal nitrogen. This allows a single C=N bond to form, fostering delocalization of charge onto nitrogen while avoiding the unfavorable antiaromatic four $\pi$-electron configuration.

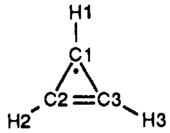
The low-energy form **11c** (6-31G** basis) exhibits some interesting features. The major part of the positive charge is carried by the carbon (+0.57) and hydrogens, N-*H* (+0.41), C-*H* (+0.34), versus nitrogen (−0.37). Based on this and both the long NN bond (1.51 Å) and the short CN bonds (1.30 Å), it appears that lone-pair–lone-pair repulsion operates. That structure **11a** is not predicted to be more stable than **11c** is perhaps a surprise to some organic chemists, and it is in contrast to the 1,3-oxazolinium cation[61] where the nitrogens are planar. The diazaridinyl cation geometry, **11c**, indicates that it is highly strained and the introduction of the N = C bond (e.g., **11a**) is counteracted by angle strain in attempting to force the sp$^2$-hybridized nitrogen into a triangle. There is no evidence of resonance stabilization. The diazaridinyl cation should be very reactive, and its isolation, should it be capable of independent existence, would be very difficult.

**Summary of Closed-Shell Systems.** The results presented above indicate that the Hückel rules work well for three-membered heterocyclic rings. We found that all two $\pi$-electron systems (**1–9**) preferred planar geometries. In all these systems significant delocalization of the $\pi$ electrons was predicted. The potentially antiaromatic systems (**10**, **11**) preferred nonplanar geometries to avoid the unfavorable antiaromatic electronic configurations. Where planar geometries are forced, distortion toward an isosceles triangle occurs within the plane to remove one $\pi$ electron pair away from the other double bond. For the nonplanar forms of these systems, our calculations indicated that there was little or no $\pi$-electron delocalization.

**Open-Shell Systems.** The open-shell species considered here, **12–18**, have an odd number of electrons, and the completely optimized geometries, total energies, and relative energies are given in Table II. In these systems, for which an uneven number of $\pi$ electrons is possible, the simple Hückel rule cannot be applied. However, for three-membered rings, it is expected that systems with one or two $\pi$ electrons have aromatic properties, and systems with more than two $\pi$ electrons are potentially antiaromatic.

**Cyclopropenyl Radical 12.** This species has three $\pi$ electrons in its planar form and is thus potentially antiaromatic. However, semiempirical[25,30] and ab initio[38] calculations predicted this radical to be planar. More recently, ab initio gradient calculations with STO-3G and 4-21G basis sets predicted that the nonplanar form is preferred.[41]


**12a**

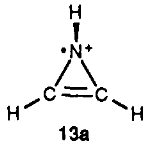

**12b**

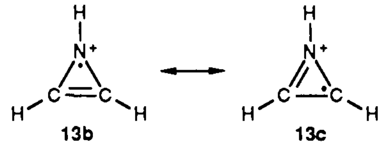
Nonplanar geometry, **12a**, lies 12.7 kcal below the planar geometry, **12b**. The latter has three $\pi$ electrons, and this unfavorable antiaromatic electronic configuration is avoided by bending one of the CH bonds 45.6° out of the plane of the ring to give **12a**. In cyclopropene this angle is 56°;[21] the smaller angle in the cyclopropenyl radical can be explained with the smaller repulsion between a bonding pair and a single electron than between two bonding pairs. The three carbon atoms form an isosceles triangle with one short (1.293 Å) and two long (1.454) CC bonds. The CC double bond is shorter than in the cyclopropene molecule and considerably shorter than the CC bonds (1.350 Å) of the aromatic cyclopropenyl cation **1**. Clearly, there is very little $\pi$ electron delocalization in **12a**, and the electronic structure of this system is well described by the valence bond structure **12a**.

In the planar form, **12b**, which is probably the transition state for interconversion of the two equivalent nonplanar forms, there is a slight lenghening of the double bond (1.300 Å) and a shortening of the single bonds (1.443 Å), indicating perhaps a very small degree of $\pi$ delocalization.

The open-shell spin densities for the nonplanar geometry, **12a**, were 0.53 for $C_1$, 0.19 for $C_2$ and $C_3$, 0.07 for $H_1$, and 0.01 for $H_2$ and $H_3$ (see above for labeling of the atoms). A larger hyperfine ESR coupling is expected for $H_1$. For planar **12b**, the spin densities were 0.58, 0.21, 0.0, and 0.0, respectively. Surprisingly, most of the spin density remains on $C_1$, and $C_1$ seems to be remarkably isolated from $C_2$ and $C_3$.

**Azirinyl Radical Cation 13.** No experimental or theoretical studies have been reported for the azirinyl cation, **13**, which is isoelectronic with the cyclopropenyl radical, **12**. Our calculations show that **13** has a similar electronic structure to **12**. We found the nonplanar form, **13a**, to be 9.0 kcal/mol more stable than the planar form, **13b**. In the nonplanar form the NH bond forms a 36.8° angle with the plane of the ring. It has a relatively short CC double bond (1.295 Å) and long CN bonds (1.382 Å). The spin densities are 0.34, 0.29, 0.00, and 0.03 for C, N, *H*-C, and *H*-N, respectively.


**13a**


**13b** **13c**

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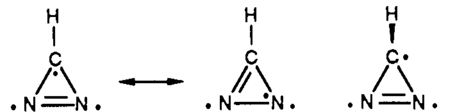
In its planar form, **13b**, the CC double bond is slightly longer and the CN bonds slightly shorter than in its equilibrium geometry, **13a**. The spin densities in **13a** are 0.25, and 0.50 for the C and N atoms, respectively.

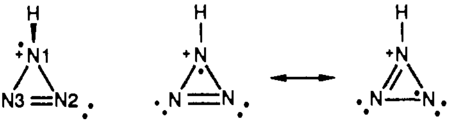
**Diazirinyl Radical 14.** The present work is, to our knowledge, the first study of the diazirinyl radical, **14**, which is also isoelectronic with the cyclopropenyl radical, **12**. We found that this system has a rather unusual electronic structure, and, unexpectedly, the most stable geometry was planar. Thus a system with three $\pi$ electrons, **14a–b**, was preferred in spite of the antiaromaticity associated with such an electronic configuration. The NN bond was calculated to be 1.484 Å which is surprisingly long, while the CN bonds are rather short at 1.277 Å. For comparison, the NN bond was 1.286 Å and the CN bonds were 1.297 Å in the diazirinyl cation, **3**, which has one less electron. Thus, the presence of the third $\pi$ electron causes the ring size to expand, but the NN bond lengthens much more than the CN bonds.



**14a** **14b** **14c**

The distribution of $\pi$ electrons was interesting. The doubly occupied $\pi$ orbital is delocalized over the ring with a slight polarization toward the carbon atom. The unpaired $\pi$ electron is localized on the two nitrogen atoms, and the open-shell spin densities are 0.0 and 0.5 for carbon and nitrogen, respectively. Thus, valence bond structure **14b** is a better representation than **14a** since it illustrates the short CN bond and the spin distribution. This radical has an unfavorable antiaromatic electronic configuration, and, based on the optimized geometry, it would be highly strained. It is thus unlikely that this radical could be isolated.

**Triazirinyl Radical Cation 15.** No experimental or theoretical studies have been reported for the triazirinyl radical cation, **15**. It is isoelectronic with all the open-shell systems **12–14** discussed above. Two cyclic structures can be considered: the nonplanar, two $\pi$ electron geometry, **15a**, and the planar, three $\pi$ electron geometry, **15b** and **15c**. The nonplanar form **15a** was more stable by 7.5 kcal mol$^{-1}$. Thus, the triazirinyl radical cation **15** is similar to the azirinyl radical cation, **13**, since it avoids the unfavorable, antiaromatic, 3-$\pi$ electron configuration demanded by the planar form. However, the barrier to ring inversion (7.5 kcal mol$^{-1}$) was somewhat smaller for **15** than for **13**.

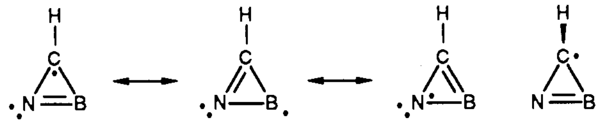


**15a** **15b** **15c**

The NH bond of **15** is tilted 40.8° from the plane of the ring, and the three nitrogen atoms form an isoceles triangle with two long (1.369) and one short (1.200) NN bond. The open-shell spin densities of 0.59 (*N*-H), 0.18 (N), and 0.05 (H) show concentration of the unpaired electron on the sp$^3$-like nitrogen (*N*-H) at the top of the isosceles triangle. Altogether these results strongly suggest that the electronic structure of the triazarinyl radical cation is best represented as valence bond structure **15a**.

When the system is forced to have a planar geometry, the $N_2$ to $N_3$ bond becomes slightly longer (1.208) and the $N_2$ to $N_1$ ($N_3$ to $N_1$) bonds slightly shorter (1.356) compared to the nonplanar form. The $p_z$ populations for the doubly occupied $\pi$ orbital are 0.8 for the two equivalent nitrogens and 0.4 for the nitrogen bonded to hydrogen. The spin densities are 0.62 ($N_1$) and 0.19 ($N_2$ and $N_3$). Thus, other than decreasing the out-of-plane NH bond angle, little structural change occurs going from the nonplanar to planar geometry, and hybrid structure **15b** is the best representation. There is very little $\pi$ delocalization in the planar geometry.

**Borazirinyl Radical 16.** The borazirinyl radical, BCHN$^{\bullet}$, **16**, has not been studied experimentally or theoretically. It might exist in either the planar, **16a–c**, or nonplanar, **16d**, geometry.

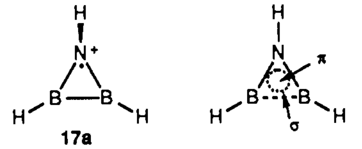


**16a** **16b** **16c** **16d**

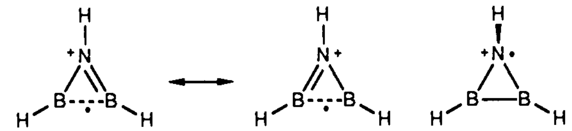
This radical can be generated by adding an electron to the borazirinyl cation **9**, and it is a 19-electron system. Our calculations indicated that the planar form was preferred. Resonance hybrid **16b** is the best valence bond description of this radical. This is illustrated by the bond lengths of 1.291, 1.435, and 1.411 Å, for CN, CB, and NB, respectively. The open-shell spin densities 0.69 (B), 0.13 (N), 0.18 (C), and 0.01 (H) also agree with **16b**. For comparison, the bond lengths in the borazirinyl cation, **9**, are 1.347, 1.386, and 1.313 Å, respectively. In the borazirinyl radical ***the unpaired electron*** concentrated on boron ***is not a $\pi$ electron***, but it belongs to the $\sigma$ system. The molecule has only two $\pi$ electrons. The $\pi$ donation to the empty $p_z$ orbital on boron is 0.37 electron, leaving 0.87 $\pi$ electron on N and 0.75 $\pi$ electron on C. This is an indication of aromatic delocalization. The $\pi$ bond orders were 0.62 (NB), 0.81 (CN), and 0.56 (CB) in accord with shorter CN bond and hybrid **16b**.

The borazirinyl radical is thus a two $\pi$-electron system with significant aromatic delocalization, even though the bond lengths and the spin densities indicate that resonance hybrid **16b** contributes more to its structure than **16a** and **16c**. Because of the unpaired electron located mainly on the boron atom, it is not likely that this radical can be isolated as a monomer.

**Azadiboridinyl Radical Cation 17.** The present work is the first study of the azadiboridinyl radical cation, $B_2NH^{\bullet+}$, **17**. It may be derived by removal of one electron from the azadiboridene molecule **8**. This is an interesting system because its planar geometry would have one $\pi$ electron with possible aromatic delocalization.



**17a** **17b**



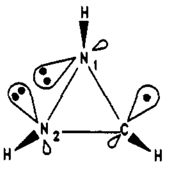
**17c** **17d** **17e**

Trivalent nitrogens are normally pyramidal but, with a single electron replacing the lone pair, the out-of-plane bias would be reduced. Any delocalization of a $p_z$ electron on nitrogen would favor a planar geometry. Our calculations showed that the planar form **17a–d** indeed was the preferred geometry. The BB, BN, BH, and NH bond lengths were 1.848, 1.364, 1.164, and 1.008 Å, respectively. Thus the BB length is very long and the BNB angle large. This might suggest that the BB bond is a $\sigma$ bond with only one electron. The unpaired spin densities were 0.32 (B), 0.23 (N), 0.03 (*H*–N), and 0.07 (*H*–B) which does suggest a BB $\sigma$ bond with only one electron. For comparison the BB bond in the azadiboridene molecule, **8**, is 1.598 Å. The BN bond of **17** (1.364 Å) can be compared to 1.394 Å in the azadiboridene molecule, **8**. The $\pi$ bond orders in **17** are 0.833 for NB and 0.344 for BB, indicating a significant $\pi$ delocalization in this system. The picture which emerges is that **17** has a weak BB $\sigma$ bond with some BB $\pi$ overlap. Furthermore, ***the unpaired electron is not a $\pi$ electron***. It is found in a $\sigma$ orbital which is the HOMO for this system. Thus **17** is a two $\pi$ electron aromatic system with a weak BB $\sigma$ bond (which approximates a one-electron $\sigma$ bond) and fractional BB $\pi$ bond.

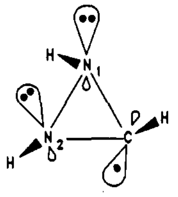
This rather unconventional electronic structure is accompanied by reduced angle strain. The long BB distance opens the BNB angle and reduces the angle strain significantly. On the other hand, since there is no true BB $\sigma$ bond, the NBB angle strain appears to be of little importance. This system cannot be represented well by **17a** or by any pure valence bond structure. It is probably best described by structures **17c** and **17d** which unfortunately leave out the $\pi$ bonding between the borons.

Despite the fact that **17** is predicted to be a two $\pi$-electron three-membered ring radical with complete conjugation, the rather weak BB $\pi$ overlap and the weak BB $\sigma$ bond suggest this radical cation will be very difficult to isolate.

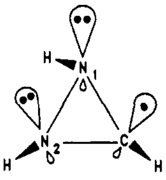
**Diaziridinyl Radical 18.** No experimental or theoretical studies have been reported for the diaziridinyl radical, **18**, which is obtained by adding one electron to the diazirinyl cation, **11**. The diaziridinyl cation, **11** (above), would have four $\pi$ electrons when forced into a planar geometry, and we found that nonplanar geometries were preferred by about 30 kcal mol$^{-1}$ compared to the unfavorable antiaromatic planar form. The bias toward the nonplanar form in the diaziridinyl cation, **18**, would obviously be even greater than for the diaziridinyl cation, **11**. Therefore, no attempts were made to optimize this system restricted to a planar form which would have five $\pi$ electrons.



**18-trans**



**18-cis-1**



**18-cis-2**

Three geometries were considered for this system: one trans form, which has no symmetry and where the two NH bonds and the two nitrogen lone pairs each have a substantial dihedral angle between them and two cis forms, each with eclipsed nitrogen lone pairs. When the diaziridinyl radical, **18**, was optimized without symmetry restrictions, the geometry converged to the trans form which is predicted to lie 6.0 kcal/mol below the cis-1 form and 7.0 kcal/mol below the cis-2 form.

The energy minimum of **18** has no symmetry with all three ring atoms sp$^3$ hybridized. The CH bond is tilted 46.1° out of the plane of the ring, while the NH bonds are 68.2°, and 66.8°, respectively, on opposite sides of the plane of the ring. The two CN and single NN bond lengths in **18** were 1.394, 1.388, and 1.472 Å, respectively. The two CN bond lengths are different for the trans form owing to their different chemical environments; an eclipsed lone-pair–lone-electron arrangement leads to a slightly longer CN bond (0.006 Å) compared to the CN bond where the lone electron eclipsed the NH bond. The geometry of **18** is very different from the geometry of the diaziridinyl cation, **11**, which had a short NN bond (1.296 Å) and long CN bonds (1.509 Å). The geometries of the two cis forms of **18** are similar to that of the trans form; however, the lone-pair–lone-pair repulsion of the cis forms makes the NN bond about 0.01 Å longer then the trans geometry.

The spin densities are 0.15 for N, 0.56 for C, 0.04 for *H*–N, and 0.06 for *H*–C for the minimum energy trans form. Thus the unpaired electron is largely localized on the carbon atom.

## Concluding Remarks

Some interesting trends emerge from this study. All systems with two $\pi$ electrons, (**1**, **9**, **16**, **17**) clearly exhibit aromatic delocalization as predicted by Hückel's rule. The remaining systems with more than two $\pi$ electrons distort from planar geometries to avoid the unfavorable antiaromatic electronic configuration. The only exception is the diazirinyl radical, **14**, which prefers a planar structure with three $\pi$ electrons.

All three-membered cyclic systems are strained. However, boron substitution could potentially reduce the angle strain since sub-70° valence angles are observed in many stable boron compounds. Nitrogen substitution is expected to have the opposite effect. These considerations are particularly important for three-membered rings for which the valence angles are determined by the bond lengths. For all the "aromatic" systems the valence angles at boron are several degrees smaller than the carbon angles which in turn are about 1° smaller than for nitrogen. Interestingly, this trend is reversed for most "antiaromatic" compounds. In these systems the bond lengths (and therefore the valence angles) are clearly dictated by the antiaromatic electronic structures. It is therefore unlikely that any three-membered cyclic system with more than two $\pi$ electrons ever will be isolated.

Boron and/or nitrogen substitutions do not destroy the aromaticity of three-membered rings. Considerable $\pi$ delocalization is observed when the vacant p orbital on boron is attached to $\pi$ donors like nitrogen or carbon. Reasonable charge distribution is conserved by $\sigma$ donation in the opposite direction. This is most clearly observed when boron is bonded to nitrogen which is a strong $\pi$ donor and $\sigma$ acceptor. The results presented here may suggest extension of the concept of aromaticity to more "inorganic-like" systems. Cyclic S–N compounds have recently received attention.[62] These compounds are electron rich and destabilized by partly filled antibonding orbitals; however, these problems are not shared by cyclic BN or BC compounds.

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