Notes

Is Borazine Aromatic? Unusual Parallel Behavior between Hydrocarbons and Corresponding B−N Analogues

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Introduction

The inorganic benzene, borazine, is a textbook example of a six-π-electron six-membered ring.[1] Compared to benzene, the cyclic delocalization of electrons in the borazine ring is reduced due to the large electronegativity difference between boron and nitrogen. The polarity of the BN bond causes borazine to show a reactivity pattern different from that of benzene. Understandably, the chemistry of borazine is dominated by addition reactions. However, recent experiments of Chiavarino et al. demonstrate that borazine undergoes electrophilic aromatic substitution in the gas phase much like its organic counterpart.[2] The electrophiles first attack at nitrogen centers and form the corresponding conjugate acid, $H_3B_3N_3H_3E^+$ (E = electrophile; H^+, CH_3^+, etc.), similar to the benzonium ion,[3] and, under basic conditions, substitution reactions occur.[2] This new experimental data calls for a fresh reexamination of the criteria used to understand the aromatic nature of borazine and related systems. While the nature of the σ- and π-complex in the parent system and the thermodynamic contributions to their stability are still open questions,[3] the formation of these intermediates has been an accepted characteristic of benzenoid aromatics. We present here a comparison of the energetics of σ-complex formation in borazine, benzene, and related systems.

Energetic criteria have been used to estimate the extent of the aromaticity of borazine. Early studies by Fink, Gordon, and others using homodesmotic equations came to the conclusion that borazine has a nonnegligible resonance energy (9.6 kcal/mol) which is close to half of the value for benzene (21.9 kcal/mol), indicating substantial aromaticity.[4,5a] Following the studies on benzenoid aromatics, the idea of ring current and resulting magnetic properties have been used to describe aromaticity. However, the different magnetic criteria used to understand the nature of the ring current indicate that borazine is not aromatic.[5] Neither the diamagnetic susceptibility exaltation (−1.7 for borazine and 13.7 for benzene),[5d] nor the ^{1}H chemical shifts of H(B) and H(N) (5.0 and 5.5), nor nucleus-independent chemical shift (NICS) computations (−2.1 for borazine and −11.5 for benzene) indicate the presence of appreciable ring current. Krygowski et al., in a discussion of geometric indices, observed that borazine derivatives are less aromatic compared to the benzene analogues,[6] but not nonaromatic.

Thus, the theoretical evaluations of aromaticity (magnetic, energetic, and geometric) do not go parallel to each other.[7] While the magnetic criteria are useful in describing the aromaticity of hydrocarbon systems, the reactivity criteria are more important in describing the same for more polar BN systems. There are few theoretical studies which have taken *reactivity* as a criterion of aromaticity.[8] The present computational study shows a parallel behavior of hydrocarbon systems and BN systems toward protonation and methylation. In view of the traditional emphasis of substitution rather than addition as a hallmark of aromaticity, the energetics of these reactions are important in the evaluation of aromaticity. We consider the following hydrocarbons and B−N analogues to study the energetics of protonation and methylation. Cyclobutadiene, 1,3-butadiene, benzene, 1,3,5-hexatriene, and their protonated and methylated species represented the hydrocarbon systems. For the B−N systems, the carbon atoms of the hydrocarbons were replaced by alternating B and N atoms.

Computational Details

The structures **1**−**24** were optimized at the B3LYP/6-311+G** level of theory.[9] The frequencies are evaluated at the same level. Only the minimum energy structures were included in the energy evaluations. In order to gauge the reliability of the relative energies at this level, single-point calculations at the CCSD(T)/6-31G* level were carried

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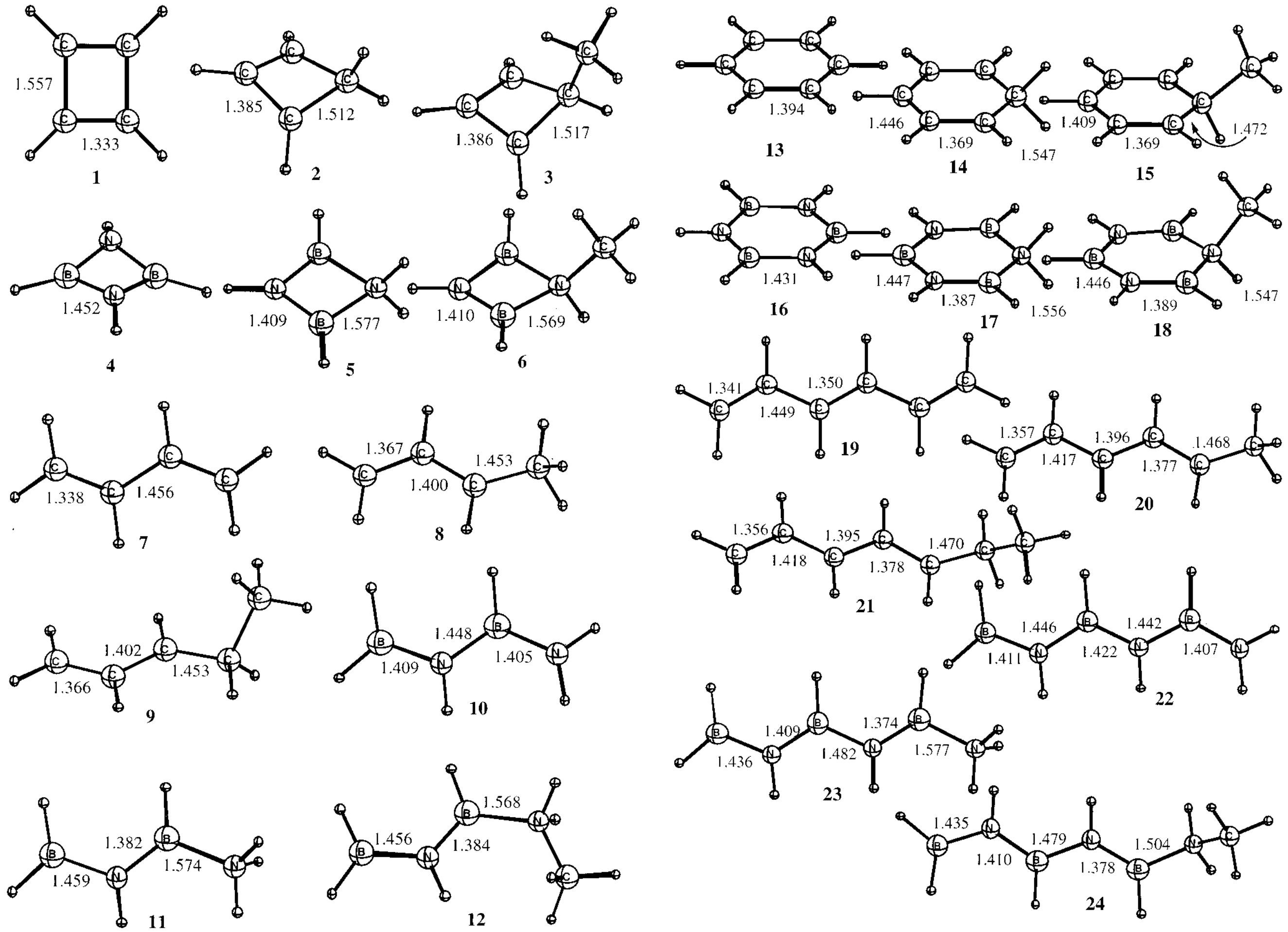

Figure 1. Optimized (B3LYP/6-311+G**) structures (**1**−**24**) along with important bond lengths (Å).

out. NICS computations were done at the HF/6-31+G*//B3LYP/6-311+G** level on selected ring systems. All the calculations of the structures **1**−**24** (Figure 1) were carried out using the Gaussian 94 suite of programs.[10]

Results and Discussion

The protonation and methylation energies were evaluated using eqs 1−8, Scheme 1. Though isolated protonation energies are not helpful in understanding the delocalized nature of electrons, useful comparisons can be made with open-chain and antiaromatic systems. This provides a clear picture of the stabilities and reactivities of the systems involved. The magnitude of protonation energy is an indication of the stability of the polyene; the lower the magnitude, the more stable is the polyene. Obviously, the lowest value of protonation energies is calculated for benzene. This is lower than that of hexatriene by 24.5 kcal/mol, a reflection of the lack of aromatic stabilization. Butadiene with two π-electrons has less delocalization energy.

However, butadiene has a lower protonation energy than hexatriene. This is due to an additional factor that controls protonation energy. The cation generated by protonation of butadiene is less favorable because of the size effect. A larger molecule can accommodate a charge better. For this reason, protonation energies of molecules of widely varying sizes cannot be used directly for drawing general inferences. Comparison between molecules of similar size, however, helps in understanding relative stabilities. The large magnitude of the antiaromaticity of cyclobutadiene is gauged by comparing its protonation energy with that of butadiene. Borazine, as anticipated, has the lowest protonation energy. The hexatriene equivalent, $B_3N_3H_8$ (**22**), has a relative protonation energy of −10.6 kcal/mol. Obviously, the stabilization in the cyclic π-electron system, $B_3N_3H_6$, is considerably lower than that in benzene. The antiaromaticity in $B_2N_2H_4$ (**4**), the cyclobutadiene equivalent, is also low as indicated by the relative protonation energy. It was found that protonation at boron centers is less favorable and therefore not considered here.

A graphical representation of the relative protonation and methylation energies (Figures 2 and 3) shows a striking similarity between the carbon and the B−N analogues. The changes observed are only in the quantitative detail. The aromaticity of benzene and the antiaromaticity of cyclobutadiene are reflected in their B−N analogues, albeit to a lower extent. Thus, in terms of the stability of the σ-complex, an acknowledged indicator of aromatic systems, both benzene and borazine behave similarly, and the differences are only in quantitative detail.

The reaction energies can also be used to estimate aromatic stabilization energies (ASE). For example, the ASE of benzene is the difference in protonation energy between **13**+**20** and **19**+**14** (26.9 kcal/mol). The ASE is close to the earlier estimates

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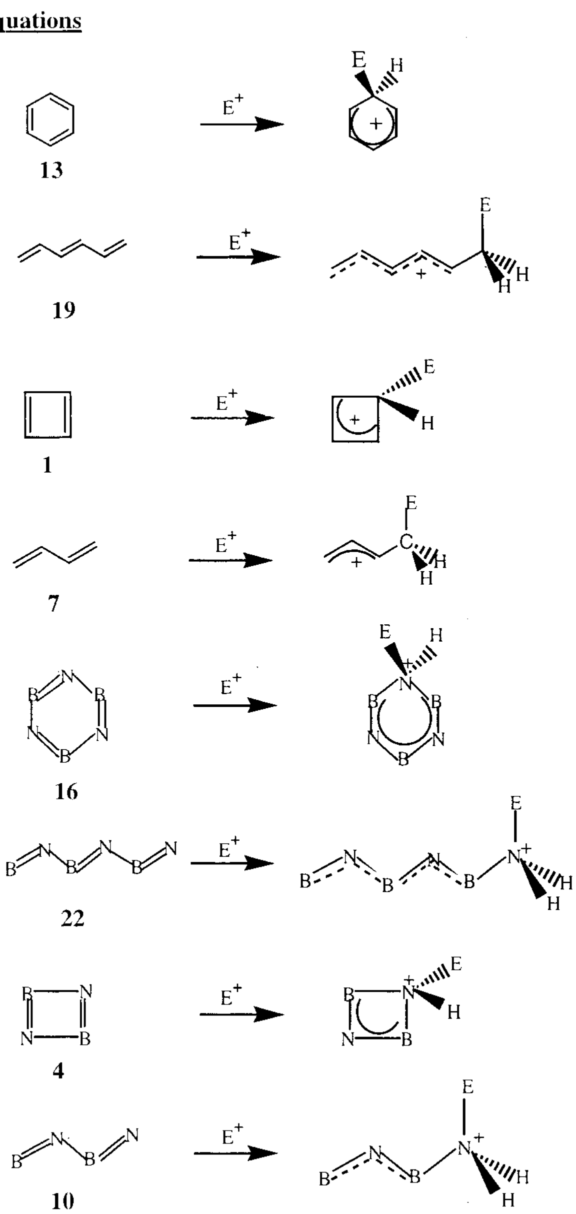
Scheme 1



Equations	H ΔE	H ΔE_{rel}	CH_3 ΔE	CH_3 ΔE_{rel}
(1).	-181.9 (-182.6)	0.0 (0.0)	-79.7 (-81.9)	0.0 (0.0)
(2).	-208.8 (-207.1)	-26.9 (-24.5)	-106.6 (-105.6)	-26.9 (-23.7)
(3).	-226.2 (-227.9)	-44.3 (-45.3)	-128.6 (-131.6)	-48.9 (-49.2)
(4).	191.7 (-190.8)	-9.8 (-8.2)	-90.2 (-90.0)	-10.5 (-8.1)
(5).	-190.1 (-193.9)	0.0 (0.0)	-83.7 (-89.8)	0.0 (0.0)
(6).	-198.4 (-204.5)	-8.3 (-10.6)	-94.1 (-101.6)	-10.4 (-11.8)
(7).	-206.5 (-210.0)	-16.4 (-16.1)	-102.1 (-107.5)	-18.4 (-17.7)
(8).	-193.7 (-199.2)	-3.6 (-5.3)	-89.1 (-96.0)	-5.4 (-6.2)

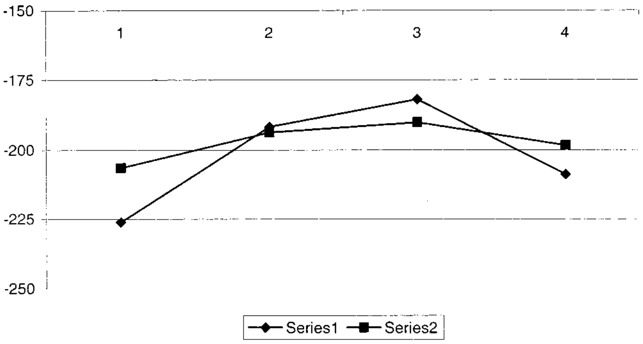


Figure 2. Protonation energies (kcal/mol) of CH and BN systems **1**−**4**. Series 1 indicates the hydrocarbon sytems, and series 2 indicates the corresponding B−N systems. The molecules considered were cyclobutadiene (**1**), 1,3-butadiene (**2**), benzene (**3**), and 1,3,5-hexatriene (**4**) and their B−N analogues.

that had employed different reference molecules. Similarly, for borazine, the ASE is 8.2 kcal/mol (from **16**+**23** and **17**+**22**), which is very close to the other estimates. The antiaromatic destabilization energy (ADE) of C_4H_4 is −34.5 kcal/mol (**1**+**8** and **2**+**7**), and for $B_2N_2H_4$, the ADE is −12.8 kcal/mol (**4**+**11** and **5**+**10**). The reaction energies considered here confirm that borazine is less aromatic than benzene, but sufficiently aromatic to show a similar gas phase reactivity pattern. Similarly, the antiaromaticity in $B_2N_2H_4$ is one-third of that in cyclobutadiene.

The parallel behavior observed in reaction energies of CH and BN systems is reflected in the geometries as well. Protonation or methylation of all systems results in a chain of alternating single and double bonds starting from the site of the electrophile attack. The extent of variation in the bond lengths before and after protonation is shown in Figure 4. As observed in the case of energies, the bond length variations of CH and BN systems also go in parallel. With the exception of antiaromatic molecules, both open-chain and aromatic molecules have similar geometrical features. C_4H_4 is planar with localized single (1.557 Å) and double bonds (1.333 Å), but $B_2N_2H_4$ is puckered (C_{2v}) with equal bond lengths (1.452 Å). The puckering in $B_2N_2H_4$ is due to the pyramidalization of the two

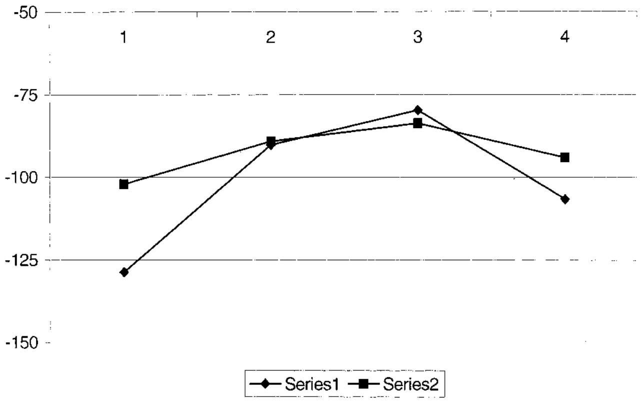


Figure 3. Methylation energies (kcal/mol) of CH and BN systems **1**−**4**. Series 1 indicates the hydrocarbon sytems, and series 2 indicates the corresponding B−N systems. The molecules considered were cyclobutadiene (**1**), 1,3-butadiene (**2**), benzene (**3**), and 1,3,5-hexatriene (**4**) and their B−N analogues.

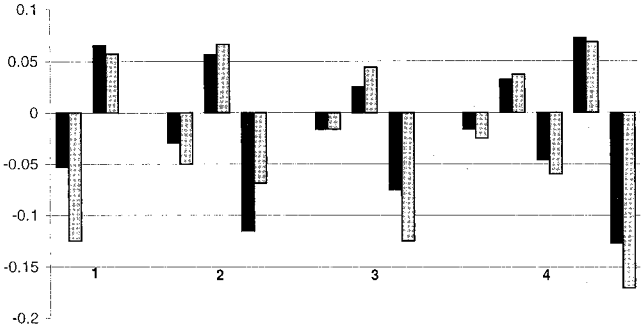


Figure 4. Variation in the bond lengths of hydrocarbon systems (dark) and the corresponding B−N systems (shaded) for molecules **1**−**4**.

lone pairs on nitrogen atoms and, by symmetry, shows equal bond lengths. This also reduces the antibonding π-interaction. Such an option is not available for cyclobutadiene. Reaction with electrophiles reverses the geometrical features. While protonated cyclobutadiene is puckered, developing a 1−3 interaction (C1−C3 = 1.77 Å, Wiberg bond index = 0.41, an indication of developing homoaromaticity[11]), the BN analogue is planar. The apparent dichotomy of geometrical features of C_4H_4 and $B_2N_2H_4$ is the result of the tendency of the nitrogen lone pair to pyramidalize when not involved in stabilizing delocalization. All observations made here are applicable to methylation energies with minor variations.

The observations from the energetic and geometric behavior of CH and BN systems differ from the conclusion obtained from magnetic criteria which point out that borazine is not aromatic. Anomalous magnetic properties associated with aromatic molecules are mainly due to the cyclic π-electrons. However, the structure, energy, and reactivity are determined by both σ- and π-electrons.[12] Localized lone pairs in borazine do not generate any ring current, but the stabilized B−N bonds, as shown by 9 kcal/mol resonance energy, does play a role in reactivity. Aromaticity and ring current are often used interchangeably. Aromaticity is a concept and best represented by a cluster of properties: energetics, structure, reactivity, magnetic properties, etc. Aromatic molecules exhibit anomalous behavior compared to the nonaromatic molecules in the above-said properties. The ring current represents only magnetic peculiarities of aromatic molecules. The failure to recognize adequately other criteria of aromaticity made the ring current model the fingerprint of aromaticity. Though it is difficult to uniquely define resonance energy, we emphasize that the energetic criterion is equally important in understanding the aromatic nature of a given molecule.

Conclusion

The protonation and methylation energies of C_6H_6, C_4H_4, $B_3N_3H_6$, and $B_2N_2H_4$ are calculated theoretically. The results show that the stability of the σ-complex obtained from protonation or methylation is a good indicator of aromaticity. Even though there are quantitative differences between hydrocarbons and the B−N analogues, the general trends show that $B_3N_3H_6$ is a stable species in the context of σ-complex. While the contribution of the σ- and π-electrons to the stability of the σ-complex cannot be separated easily, this stabilization is a characteristic, useful in estimating aromaticity. According to this, $B_3N_3H_6$ is to be considered aromatic, though its aromaticity is about half that of benzene which is in agreement with earlier theoretical results.[4]

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Supporting Information Available: The total energy and Cartesian coordinate of the optimized geometries of **1**−**24** at the B3LYP/6-311+G** level. The material is available free of charge via the Internet at http://pubs.acs.org.

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