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Structural Aspects of the Aromaticity of Cyclic π-electron Systems with BN Bonds

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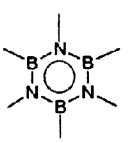
Abstract An extension of the HOMA model and Bird's I_6 model for systems with B-N bonds is given. Analysis of the aromatic character of 11 pairs of borazine derivatives and their benzene analogues is done based on Cambridge Structural Database (CSD) release using HOMA and I_6 indices. Borazine derivatives exhibit less aromatic character than their benzene analogues and are much less sensitive to the chemical and topological effects from the environment of the rings in question. In contrast to cyclooctatetraene, 1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetraazatetraborocine does not exhibit antiaromatic character.

Introduction

Aromaticity of heterocyclic π-electron systems is a subject of great interest.[1-5] Quantitative measures of aromaticity permit one to study how structural changes in π-electron systems may affect their aromaticity in both, the local and overall meanings.[6,7] A very interesting group of heterocyclic systems are those which contain B-N and B-C bonds.[8] In this report we concentrate on π-electron systems with B-N bonds.

The cyclic borazine[9,10] (–BH–NH–)$_3$ and its derivatives form one of the largest classes of boron-nitrogen compounds.[11] The parent compound is described in the literature as „inorganic benzene"[8-11] which is justified, at least partly, due to the same number of valence electrons and comparable sums of electronegativities as well as atomic radii in the BN and CC units. Additionally B-N bonds in borazines are of the same length,[10] which resembles the situation in benzene.[12] Its similarity to benzene is also visible in some physical (eg. density, surface tension)[11] and some chemical properties (eg. hexahapto ligands[13] in organometallic complexes), similar to those observed for benzenoid hydrocarbons.[14] On the other hand these compounds reveal distinct reactivity differences, eg. no electrophilic substitution under reaction conditions corresponding to benzenoids,[11] which is usually attributed to a significant difference between the electronegativities of boron and nitrogen atoms. Moreover, recent studies on energetics of borazine and other „benzene-like" molecules in agreement with the older ones[15] revealed that borazine has about half[16] or even less than one third[17] of the ASE value of that for benzene. Magnetic properties of borazine also locate it as moderately aromatic[18] or even non-aromatic.[17]

Analogously to benzene derivatives, borazines contain a planar B_3N_3 ring and are illustrated schematically as



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representing delocalization of the formal nitrogen lone pairs. This picture may be somewhat misleading since following the latest analyses,[16,17] equality of bond lengths may result from the localization of π-electrons at strongly electronegative nitrogen atoms.[19]

The purpose of this paper is to discuss the analogies and differences in aromatic character of borazine derivatives in comparison with the appropriate benzenoid systems. In order to do so, an extension of the HOMA model[1] and Bird's I_6 model[2] for systems with B-N bonds is presented.

Extension of the HOMA model for π-electron systems with B-N bonds

The HOMA index is defined as follows:[1]

$$HOMA = 1 - \left[\frac{\alpha}{N}\sum\left(R_{opt} - R_i\right)^2\right] \qquad (1)$$

where N is the number of bonds taken into summation and α is an empirical constant fixed in a way to get HOMA = 0 for the Kekulé[20] structure with alternate single and double bonds for typical aromatic system, and equal to 1 for the system with all bonds equal to the optimal value R_{opt}. In order to define empirical constants for the B-N bond, the well defined single and double B-N bond lengths between relevant atoms, R(1) and R(2) respectively, are needed. For this purpose we have chosen bond lengths from H_3B–NH_3[8] and $(^iPr)_2N$=B=$C(SiMe_3)_2$[21] respectively and applied formula (2) for obtaining the value of R_{opt}:[1]

$$R_{opt} = \left[R(1) + wR(2)\right]/(1+w) \qquad (2)$$

In most applications until now it was accepted that w = k(2)/k(1) = 2, as empirically this quantity for most bonds was usually close to this value.[22] In the case of B-N bonds the situation is definitely different. B-N bonds are strongly polar and accepting the same rule as in the case of typically covalent bonds seems not to be justified. In order to investigate this problem, *ab-initio* calculations[23] at the level of HF/6-311G** and B3LYP/6-311G** for ethane, ethene, BH_3-NH_3 and BH_2=NH_2 were calculated to get force constants for the stretching motion of C-C, C=C, B-N and B=N bonds. The calculations were based upon the single point energies for five points: stretched by 0.01, 0.005A, the optimized geometry, and compressed by 0.05 and 0.01A, for which the curvature (*i.e.* force constant) was calculated from the parabolic approximation of the Morse curve.

The resulting ratio of force constants for ethane and ethene, k(2)/k(1) = 2.35, is close to 2, within a margin of experimental precision. This ratio for B-N bonds is markedly greater and amounts to w = 4.2. This value is accepted in further study of aromaticity of π-electron systems with B-N bonds.

Table 1. Structural and empirical parameters of HOMA index for B-N bond containing molecules

bond	R(1)	R(2)	R_{opt}	w	α
B-N	1.564	1.363	1.402	4.2	72.03

The HOMA index is usually compared with Bird I_6 or I_5 indices[2] which are based principally on the value of variance calculated from the bond orders obtained *via* the Gordy[24] formula, and hence they represent aromatic character due only to the geometric features. Since we have used another pair of B-N and B=N bonds for definition of reference bonds in HOMA, we have applied the same B-N bond lengths for estimating the empirical constants of Bird's I_6 index,[2] rather

than those originally used by Gordy.[24]

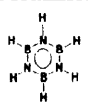
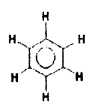
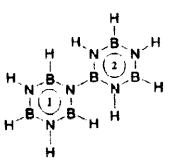
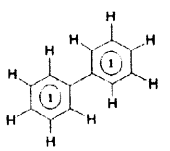
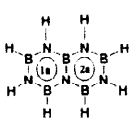
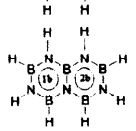
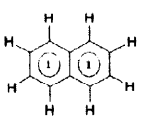
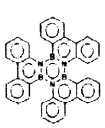
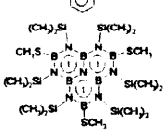
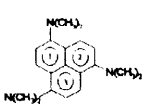
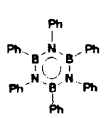
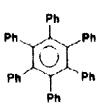
Table 2. Empirical constants of Bird's I_6 index[2]: *a, b* original Bird's values, a', b' modified values.

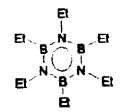
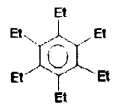
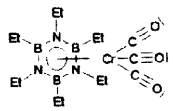
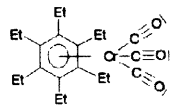
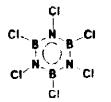
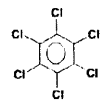
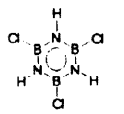
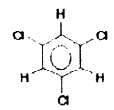
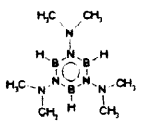
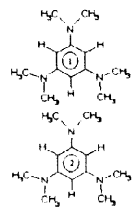
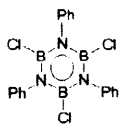
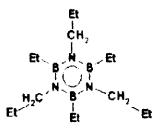
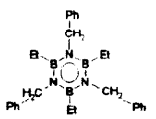
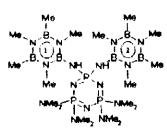
bond	*a*	*b*	a'	b'
C-C	6.80	–1.71	11.79	–4.48
B-N	7.15	–2.10	7.72	–2.16

Results and Discussion

In many cases borazine derivatives have very close analogues in the family of benzenoid hydrocarbons. In order to show analogies and differences between derivatives of borazine and carbocyclic six membered π-electron systems, results for both families of molecules are presented in Chart I.

Chart 1 HOMA (H), and Bird's I_6 indices (original Bird's values in italics) for all actually available borazine derivatives and for some their appropriate benzenoid analogues.[25]

No.	borazines	HOMA	I_6	ref.	benzenoids	HOMA	I_6	ref.
1		H = 0.942	99.1 *99.3*	[8]		H = 0.998	97.9 *96.0*	[12]
2		H1= 0.963 H2 = 0.970	86.4 *87.0* 86.4 *89.0*	[26]		H = 0.994	96.5 *93.3*	[27]
3	 	H1a = 0.936 H2a = 0.927 H1b = 0.925; H2b = 0.930	82.5 *85.9* 87.5 *90.0* 81.6 *85.2* 82.4 *85.9*	[26]		H = 0.817	80.4 *61.0*	[28]
4		H = 0.703	68.8 *75.4*	[29]		H1 = 0.061	73.5 *40.0*	[30]
5		H = 0.837	88.9 *91.2*	[31]		H1 = 0.744 H2 = 0.722 H3 = 0.753	78.3 *55.7* 76.6 *52.3* 77.3 *54.1*	[32]
6		H = 0.890	90.7 *92.6*	[33]		H = 0.884	87.4 *74.8*	[34]

7		H = 0.961	92.4 [35] *93.9*		H = 0.946	97.0 [36] *94.0*
8		H = 0.769	57.4 [12] *66.0*		H = 0.717	96.2 [37] *92.1*
9		H = 0.955	87.8 [38] *90.2*		H = 0.992	98.6 [39] *97.2*
10		H = 0.981	90.5 [40] *92.3*		H = 0.949	88.3 [41] *77.6*
11		H = 0.931	97.8 [42] *98.2*		H1 = 0.973 H2 = 0.986	94.2 [43] *88.6* 96.1 *92.3*
12		H = 0.950	99.5 [44] *99.6*			
13		H = 0.908	93.6 [45] *94.9*			
14		H = 0.846	92.3 [45] *93.9*			
15		H1 = 0.920 H2 = 0.911	90.4 [46] *92.3* 86.3 *89.0*			

From the data of Chart I it is immediately clear that, except in a few cases, HOMA values for the borazine unit are always lower than those for analogous benzene rings. Two cases need some comments. (i) There is a substantial difference between naphthalene and its BN analogue. Naphthalene has HOMA = 0.817, *i.e.* significantly less than benzene whereas its BN–analogue has values between 0.925 and 0.966 (four independent geometries of the molecule) comparing to 0.942 for borazine itself. It means that fusion of two rings in naphthalene decreases its aromatic character by 0.18 units, whereas in the BN analogue there is no such effect. (ii) A still more dramatic difference in HOMA values is observed for the central ring of 1,2.3,4.5,6-tris(*o,o'*-biphenylene)borazine which may be compared to the central ring in triphenylene (entry 4). They are equal to 0.703 and 0.061, respectively. This ring in benzenoid hydrocarbons is in the Clar classification[47] described as „empty" *i.e.* containing less π-electrons. Its dearomatization is due mostly to the EN term (*i.e.* to the elongation of C-C bonds in the ring) of the extended HOMA model.[6] In both cases it is observed that geometry of the borazine ring involved in similar interactions with a molecular environment as the benzene ring changes much less and hence its aromatic character is less lowered. 1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetramethyl-1,3,5,7,2,4,6,8-tetra-azatetraborocine is a BN analogue of

cyclooctatetraene. Its geometry was precisely determined[48] and the resulting HOMA value is 0.532 comparing to –0.225 for cyclooctatetraene.[49] Again, the BN analogue of the hydrocarbon exhibits much less sensitivity to structural perturbation than the parent system.

The equalization of B-N bond lengths in borazine is attributed to the π-electron localization at strongly electronegative nitrogen atoms, the mechanism of which however does not work in the case of BN analogue of cyclooctatetraene. Again the Huckel rule[50] seems to work, even if borazine is said to be weakly aromatic[17] and the BN analogue of cyclooctatetraene is less affected by the 4N number of p-electrons than the parent hydrocarbon.

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