

Comparative Borazarobenzenes Calculations Following Different Methods

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Borazarobenzenes are studied with different approaches, some treating only π electrons and others including all valence electrons. The importance of the total net electronic density for interpreting the chemical behaviour of the molecules is stressed. All methods agree in assigning fairly high values to dipole moments. Disagreeing conclusions about other properties in the different methods are analyzed.

Die Borazarobenzol-Isomeren werden mit verschiedenen Methoden untersucht, die entweder nur die π -Elektronen oder alle Valenzelektronen behandeln. Die Wichtigkeit der Gesamt-Elektronendichte für die Erklärung des chemischen Verhaltens der Moleküle wird hervorgehoben. Alle Methoden stimmen in dem Ergebnis recht hoher Werte für die Dipolmomente überein. Unterschiedliche Ergebnisse bei der Anwendung der verschiedenen Methoden werden analysiert.

On étudie les borazarobenzènes suivant de diverses méthodes; les unes traitent seulement les électrons π et les autres impliquent tous les électrons de valence. On souligne l'importance des charges nettes totales pour interpréter le comportement chimique des molécules. Toutes les méthodes s'accordent en attribuer des valeurs assez hautes au moment dipolaire. On analyse des conclusions discordantes sur d'autres propriétés prévues par les différents méthodes.

1. Introduction

Boron-nitrogen cyclic compounds deserve ever growing interest. We shall consider here the series 2,1-, 3,1- and 4,1-borazarobenzene (hereafter abbreviated as BAB), about which exist few theoretical studies [1, 2], as a first step towards a more extensive analysis of these substances. Despite the fact that derivatives of 3,1-BAB are still unknown, a number of compounds containing 2,1- and 4,1-BAB are now being synthesized and studied [3, 4], and 2,1-BAB itself has been obtained [5]. It seems to be a very reactive and chemically unstable system; and it is predicted [3] that this is the most stable of the three molecules. The lack of experimental data on them stimulates us to undertake further theoretical treat-

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ments of the BAB ring, in order to understand the chemical behaviour of its derivatives.

We think it worthwhile to attack the problem with the methods which we have found useful in calculating some properties of other molecules, and with other methods involving all valence electrons, which are being applied now to a number of conjugated systems. We have therefore calculated BAB's by the following approaches:

1) SCHMO (self-consistent Hückel molecular orbitals) [6], which is a modified ω -technique for the π systems.

2) LCAO with complete H (Hamiltonian) and S (overlap) matrices, with Kohlrausch's nuclear effective charges (LCAOK) [7].

3) EHT (extended Hückel theory) proposed by Hoffmann to include σ orbitals [2, 8], but with another expression for $H_{\mu\nu}$.

4) IEHT (iterative EHT), which consists of method 1) applied to 3) [9, 10].

5) CNDO (complete neglect of differential overlap) extending the Pariser-Parr-Pople formalism to all valence electrons [11].

Regarding the properties of BAB's, we shall compare our calculations mainly with Kaufman and Hamann's [1], who employ the Pariser-Parr-Pople method. We shall pay particular attention to all-valence-electron methods and, in order to settle parallelisms and contrasts between the IEHT and CNDO procedures, we shall take specially into account the results of Pullman *et al.* [12, 13], who apply them to biological purines and pyrimidines.

2. Methods of Calculation and Parameters

We shall briefly outline the basic suppositions and the parameters needed in each method. Even if for borazine we had adopted the supposition of B^-N^+ π polarity [14], we have chosen in this case neutral B and N, not being here so clear the way how conjugation takes place, owing to the presence of the C atoms. We realize that this is a point of controversy [1, 15], but it seems too confusing to compare several calculation methods and also two different models.

1. SCHMO. The i -th iteration is obtained from the results for the $i-1$ iteration for charges (q_μ) and distances ($r_{\mu\nu}$). Distances are in turn connected with bond orders ($p_{\mu\nu}$) by the expression given by Julg [16]. Diagonal and non-diagonal Hamiltonian elements are:

$$\alpha_\mu^{(i)} = H_{\mu\mu}^{(i)} = H_{\mu\mu}^{(i-1)} + \omega Q_\mu^{(i-1)} |Q_\mu^{(i-1)}|,$$

$$\beta_{\mu\nu} = H_{\mu\nu} = (r_0/r_{\mu\nu})^6 \beta_0.$$

Q_μ is the net charge on atom μ . $H_{\mu\nu} = 0$ if μ and ν are non neighbouring atoms. β_0 and r_0 design respectively a reference resonance integral and a reference distance. Overlap is neglected.

If β_0 is taken equal to 1 for C-C bonds, and $r_0 = 1.40 \text{ \AA}$, then

$$\beta_{CN} = 1.24; \quad \beta_{BC} = 0.54; \quad \beta_{BN} = 0.661.$$

The starting iterative parameters are

$$\omega = 1; \quad \alpha_{\text{N}}^{(0)} = 2; \quad \alpha_{\text{B}}^{(0)} = -1; \quad \alpha_{\text{C}}^{(0)} = 0$$

$$Z_{\text{N}}^* = 3.9; \quad Z_{\text{B}}^* = 2.6; \quad Z_{\text{C}}^* = 3.25.$$

$r_{\mu\nu}$ is the addition of covalent radii [17].

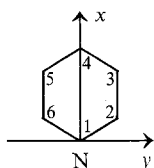
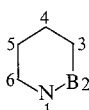
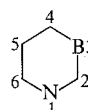
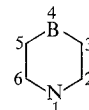


Fig. 1. Labelling and axes

Ten iterations are necessarily to attain self-consistency up to the fourth decimal of the wave function coefficients. The self-consistent distances obtained in this way are taken as data for the other methods. The resulting molecular geometry is given in Table 1 (see section 6). The X–H distances were taken as the mean of the values reported for several different molecules in Ref. [18]. For the angle calculation the procedure proposed by Gołbiewski and Nowakowski was adopted [19].

Table 1. *Molecular geometry*

			
a) Distances (Å)			
1–2	1.449	1.369	1.397
2–3	1.555	1.527	1.354
3–4	1.355	1.533	1.550
4–5	1.455	1.381	
5–6	1.358	1.411	
1–6	1.399	1.373	
Mean distance	1.429	1.432	1.434
b) Angles (degrees and decimals)			
1	118.3	126.4	130.6
2	121.5	111.5	114.8
3	114.3	123.8	125.1
4	121.8	113.6	
5	123.8	122.6	
6	120.2	122.1	

Note: The X–H distances are C–H:1.10 Å; N–H:1.02 Å and B–H:1.19 Å. They are taken over the bisector of angle X.

Putting the N atoms at the origin (Fig. 1), x is calculated as

$$x = 1/4(r_{12} + r_{34} + r_{45} + r_{16}) + 1/2(r_{23} + r_{56}).$$

Supposing that x is parallel to r_{23} and r_{56} , and that the projection of r_{12} is equal to that of r_{34} , it is possible to estimate the ring angles. As to the X-H distances, they are drawn on the bisector of the X angle.

The molecules exhibit a highly deformed structure as compared with the parent benzene ring. Nevertheless, this geometry deserves some confidence, for the same method is able to reproduce surprisingly well the interatomic distances of borazine and several other molecules [20].

Aromaticity A is calculated by the definition of Julg and François [21]:

$$A = 1 - \frac{225}{6} \sum_{(\mu\nu)} \left(1 - \frac{r_{\mu\nu}}{\bar{r}}\right)^2$$

where \bar{r} is the mean interatomic distance and μ, ν neighbouring atoms. The results for 2,1-BAB, 3,1-BAB and 4,1-BAB are, respectively,

$$0.4788; \quad 0.4563; \quad 0.2275.$$

These values, compared with 1 for benzene, and the interval 0.6–1.0 calculated for alternant and non-alternant hydrocarbons, seem quite reasonable. It is clear that 2,1-BAB should be the most aromatic of the three molecules, and this result supports the present geometry.

2. LCAOK. Kohlrausch's nuclear effective charges (Z^*) are employed to estimate the overlap matrix. The Hamiltonian elements are supposed to be

$$H_{\mu\mu} = -(I_{\mu} + A_l); \quad H_{\mu\nu} = -(A_{\mu} + A_{\nu})S_{\mu\nu};$$

$$Z_C^* = 2.03; \quad Z_B^* = 1.9; \quad Z_N^* = 2.28$$

where $I_{\mu}(A_{\mu})$ [22] is the valence-state ionization potential (electronic affinity) of atom μ , and A_l the mean valence-state electronic affinity of the atoms l neighbours of μ . q_{μ} and $p_{\mu\nu}$ are calculated following Löwdin's formalism [23].

3. EHT. As in Hoffman [8]

$$H_{\mu\mu} = -I_{\mu}.$$

The values of I_{μ} are listed in Table 2, together with the nuclear effective charges used. The values of Z^* are those given by Clementi and Raimondi [24], except the one for hydrogen, where 1.2 has been preferred to the usual 1.0 value [11] (a comparative calculation has been performed for $Z_H^* = 1.0$ and the results are shown in Table 10).

Table 2. Parameters for EHT and IEHT

	B	C	N	H
I_{1s}				13.6
I_{2s}	15.2	21.2	27.4	
I_{2p}	8.53	11.4	14.4	
Z^*	2.498	3.176	3.842	1.2

For $H_{\mu\nu}$ Cusach's approximation [25] has been taken

$$H_{\mu\nu} = 1/2(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}(2 - |S_{\mu\nu}|).$$

The Hoffman method has been shown to be equivalent, under certain conditions, to the self-consistent Hartree-Fock equations [26].

4. IEHT. We iterate method 3) as proposed by Carroll *et al.* [10], but without damping. We use the quadratic dependence between the diagonal elements and the net charges outlined by one of us [9]:

$$H_{\mu\mu}^{(i)} = -I_{\mu} + \sum_{j=1}^{i-1} Q_{\mu}^{(j)} |Q_{\mu}^{(j)}|.$$

$H_{\mu\mu}$ for each iteration is introduced in $H_{\mu\nu}$. Q_{μ} is in this case the net total charge calculated with Löwdin's formalism. This method is able to reproduce accurately experimental dipole moments [9, 27]. Ten iterations have been performed.

5. CNDO/2. The same parameters as in the original procedure have been used [11]. Slater atomic orbitals are used to calculate $S_{\mu\nu}$ (with an effective charge of 1.2 for hydrogen), and electron-repulsion integrals are obtained theoretically from valence s orbitals. The $\beta_{\mu\nu}$ are taken proportional to $S_{\mu\nu}$. Penetration terms are neglected.

The programs have been run on a CDC 3600 computer of the Blaise Pascal Institute in Paris (during the stay of one of us (R. C.) at the "Centre de Mécanique Ondulatoire Appliquée") and on an IBM 1620 of the Engineering School of Barcelona.

3. Energy Levels for All-Valence-Electrons Methods

The main feature in Table 3 is the mixing of σ and π levels, already observed when applying this kind of methods [13, 28]. Although this intermingling may be exaggerated [12], it destroys the usual LCAO supposition that σ and π levels occur in quite separate regions. Excited π and σ levels mix up only in CNDO.

Table 3. Some σ energy levels and all the π energy levels for the EHT, IEHT and CNDO methods (in eV)

2,1-BAB			3,1-BAB			4,1-BAB		
EHT	IEHT	CNDO	EHT	IEHT	CNDO	EHT	IEHT	CNDO
- 4.63 π^*	- 4.80 π^*	6.26 σ^*	- 4.40 π^*	- 4.43 π^*	5.11 σ^*	- 4.49 π^*	- 4.55 π^*	5.53 σ^*
- 6.99 π^*	- 7.34 π^*	4.77 π^*	- 7.27 π^*	- 7.35 π^*	4.50 π^*	- 7.93 π^*	- 7.82 π^*	4.70 π^*
- 8.72 π^*	- 8.69 π^*	2.73 π^*	- 9.13 π^*	- 9.01 π^*	1.67 π^*	- 8.17 π^*	- 8.37 π^*	2.29 π^*
- 11.96 σ	- 11.94 σ	- 13.00 π	- 11.67 π	- 11.65 π	- 12.08 π	- 11.92 σ	- 11.72 σ	- 13.11 σ
- 12.10 π	- 12.06 π	- 13.45 σ	- 11.94 σ	- 11.80 σ	- 13.20 σ	- 12.34 σ	- 12.18 π	- 13.64 π
- 12.93 σ	- 12.77 σ	- 14.51 σ	- 12.28 σ	- 12.13 σ	- 13.92 σ	- 12.54 π	- 12.18 σ	- 14.27 σ
- 13.63 π	- 13.26 π	- 15.55 π	- 13.41 σ	- 13.24 π	- 15.62 π	- 12.85 π	- 12.79 π	- 14.88 π
- 13.68 π	- 13.62 σ	- 17.52 σ	- 13.42 π	- 13.35 σ	- 17.90 σ	- 13.84 σ	- 13.62 σ	- 18.07 σ
- 14.36 σ	- 14.20 σ	- 19.39 σ	- 14.53 σ	- 14.49 σ	- 19.22 σ	- 14.16 σ	- 14.00 σ	- 19.31 σ
- 14.85 σ	- 14.61 σ	- 20.49 σ	- 14.95 σ	- 14.87 σ	- 21.11 σ	- 14.84 σ	- 14.76 σ	- 20.02 σ
- 15.11 σ	- 14.92 π	- 21.42 σ	- 15.09 σ	- 15.00 σ	- 22.07 σ	- 15.06 σ	- 15.09 σ	- 21.87 σ
- 15.47 π	- 14.99 σ	- 23.12 π	- 15.76 π	- 15.71 π	- 23.76 π	- 15.77 π	- 15.54 π	- 23.56 π

Energy levels of EHT are little affected by iteration (the mean variation is 0.13%), increasing slightly. The few cases indicated by arrows show an inversion of σ and π levels due to the iteration. The σ energy levels on one hand, and the π levels on the other hand, appear fairly more separated in CNDO than in the other two methods.

4,1-BAB has a σ HOMO (highest occupied molecular orbital), 3,1-BAB a π HOMO and for 2,1-BAB the three methods do not agree as to the HOMO assignment. The first two LEMO's (lowest empty molecular orbital) seem instead to be π orbitals for all three molecules. Hoffmann [2] reports σ HOMO's for some boron-nitrogen compounds including borazine. Kuznesof and Shriver

Table 4. First transition

	2,1-BAB	3,1-BAB	4,1-BAB
EHT	3.24 eV ($\sigma \rightarrow \pi^*$)	2.54 eV ($\pi \rightarrow \pi^*$)	3.75 ($\sigma \rightarrow \pi^*$)
IEHT	3.25 eV ($\sigma \rightarrow \pi^*$)	2.64 eV ($\pi \rightarrow \pi^*$)	3.35 ($\sigma \rightarrow \pi^*$)
CNDO	15.73 eV ($\pi \rightarrow \pi^*$)	13.75 eV ($\pi \rightarrow \pi^*$)	15.40 ($\sigma \rightarrow \pi^*$)

[29] too find σ HOMO's for some methyl-substituted borazines, and argue that this is in conflict with observed trends in ionization potentials and electronic spectra. IEHT applied to biological purines and pyrimidines also assigns σ HOMO's [13]. If these molecules are calculated instead with CNDO approximation, both HOMO and LEMO have a π character [12].

For all three molecules, CNDO indicates a higher ionization potential than EHT and IEHT. The methods coincide in that the lowest ionization potential corresponds to 3,1-BAB.

The values for the first transition energies (Table 4) differ widely between the EHT-IEHT methods, and CNDO. This one assigns much higher first transitions; configuration interaction and a different parametrization should probably improve these values [30].

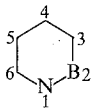
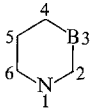
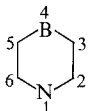
All methods predict a bathochromic shift from 2,1- and 4,1- to 3,1-BAB. For EHT and IEHT the sequence in the first transition is 4,1-BAB > 2,1-BAB > 3,1-BAB. CNDO gives instead 2,1-BAB > 4,1-BAB > 3,1-BAB. The fact that the easiest transition should be for 3,1-BAB may be related to the instability of this molecule.

As to total energies, EHT predicts that the stabilities decrease in the order (2,1-BAB; 4,1-BAB; 3,1-BAB), agreeing with Dewar's prevision [3] and with other theoretical estimations [2]. But iteration inverts the sequence, contradicting both predictions and experimental evidence for derivatives of BAB's. CNDO assigns practically the same energy to the three molecules. The EHT energy calculated simply as twice the addition of the occupied energy levels, is subject to the objections common to this kind of estimations. CNDO is in this sense more reliable, taking into account electronic interaction [11].

As the errors involved in the calculations are likely to be larger than the energy differences which can be obtained supporting a certain molecule (which are at most of 2 eV in more than 500 eV, that is 0.4%), we do not think that it is

appropriate to draw from them conclusions about stability. From our calculations with all valence electrons, we could only say that none of the three molecules seems to have a preferential stability.

Table 5. π electronic charges following different methods

Molecule	pos.	SCHMO	LCAOK	EHT	IEHT	CNDO	PPP-I
	1	1.836	1.719	1.653	1.476	1.498	1.403
	2	0.148	0.840	0.343	0.530	0.548	0.705
	3	0.988	0.845	1.117	0.967	1.010	1.120
	4	0.988	0.765	0.888	0.961	0.884	0.889
	5	1.025	0.752	1.137	1.066	1.098	1.090
	6	1.015	1.078	0.862	1.000	0.962	0.792
	1	1.737	1.738	1.459	1.457	1.377	
	2	1.016	1.131	1.014	1.010	0.981	
	3	0.201	0.669	0.509	0.555	0.714	
	4	1.012	0.705	1.050	0.942	0.872	
	5	1.003	0.810	0.980	1.010	0.987	
	6	1.032	0.947	0.988	1.026	1.068	
	1	1.833	1.683	1.624	1.554	1.602	
	2	1.000	1.027	0.848	0.996	0.924	
	3	1.019	0.869	1.156	1.006	1.024	
	4	0.130	0.525	0.369	0.445	0.500	

4. Electronic Density

Let us see the π distribution predicted by the different calculation methods (Table 5). For SCHMO, q_C is near to 1 in the three molecules, and a large polarity is concentrated on the BN bond, with very low π charge displacement from nitrogen to boron. The other methods assign, in different ways, more conjugation to BAB's. The LCAOK shows the least uniform distribution, which seems peculiar to this kind of parametrization [7]. Iteration in EHT tends, as expected, to smooth out the charge distribution. It is curious that, despite iteration produces a very small change in the energy levels, the mean charge variation is about 12%. Comparing CNDO and Pariser-Parr-Pople approximation model I (PPP-I)¹ [1] suggests that the introduction of all valence electrons decreases π transfer between the different positions.

Among the methods taking into account all valence electrons, CNDO and IEHT give similar values for 2,1- and 4,1-BAB, but not for 3,1-BAB.

The σ distribution (Table 6) is similar for all methods, the signs of the individual charges being the same in almost all cases. The only method which differs from the others in this sense is CNDO, and this could mean that the introduction of overlap represents for σ bonds a qualitative difference. It has been remarked as a charac-

¹ Kaufman and Hamann [1] use two models: model I is the same as ours, with neutral B and N; model II (referred to here as PPP-II) supposes B^-N^+ .

Table 6. σ net charges following different methods

Molecule	Pos.	LCAOK		EHT		IEHT		CNDO	
		Ring atoms	Hydrogen atoms	Ring atoms	Hydrogen atoms	Ring atoms	Hydrogen atoms	Ring atoms	Hydrogen atoms
	1	-1.631	+0.463	-0.922	+0.305	-0.702	+0.202	-0.590	+0.113
	2	+1.630	-0.259	+0.883	-0.227	+0.674	-0.151	+0.600	-0.110
	3	-0.737	+0.211	-0.277	+0.036	-0.164	+0.003	-0.091	+0.003
	4	-0.294	+0.258	-0.021	+0.019	-0.041	+0.020	-0.018	-0.019
	5	-0.614	+0.265	-0.026	+0.027	+0.001	+0.020	+0.036	+0.002
	6	+0.626	+0.082	+0.188	+0.022	+0.095	+0.041	+0.077	-0.002
	1	-1.125	+0.451	-0.677	+0.291	-0.617	+0.241	-0.568	+0.109
	2	-0.023	+0.057	-0.088	+0.042	-0.072	+0.036	-0.011	+0.016
	3	+1.162	-0.216	+0.701	-0.237	+0.633	-0.202	+0.549	-0.104
	4	-0.953	+0.293	-0.273	+0.042	-0.201	+0.009	-0.127	-0.001
	5	-0.249	+0.231	-0.010	+0.018	-0.016	+0.018	+0.018	-0.012
	6	+0.221	+0.151	+0.175	+0.018	+0.140	+0.031	+0.122	+0.008
	1	-0.971	+0.486	-0.710	+0.294	-0.581	+0.225	-0.465	+0.093
	2	+0.219	+0.107	+0.179	+0.024	+0.094	+0.044	+0.073	+0.006
	3	-0.598	+0.197	-0.229	+0.027	-0.129	-0.008	-0.076	-0.010
	4	+0.813	-0.179	+0.641	-0.232	+0.538	-0.184	+0.476	-0.092

teristic of the CNDO method the appearance of negatively charged hydrogens bound to carbon atoms [12].

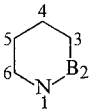
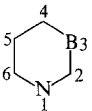
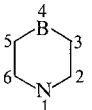
The contributions to the total σ electronic charges from the ring atomic orbitals of 2,1-BAB, calculated for the CNDO approximation (Table 7) shows clearly the trigonal hybridization. The trend is common to the three molecules, and to EHT and IEHT. There is a slight tendency to increase the s character (the hybridization ratio best showing this feature is boron's $s^{0.86}p^{1.54}$), except for the carbon atoms next to boron, where there is instead a decrease in s character: for example carbon-4 in 3,1-BAB is $s^{1.02}p^{2.10}$.

The σ LCAOK distribution is deduced from Sanderson's electronegativity equalization principle [31], which has recently been justified from the point of view of Molecular Orbital theory, analyzing its limitations and relationship to other electronegativity equalization formalisms [32]. Furthermore, electronegativity variation due to the π charges is taken into account [7]. The calculation leads to exaggerated values of the σ charges (see Table 6). When computing the

Table 7. Contributions to the total σ electronic charges from the ring atomic orbitals of 2,1-BAB as calculated in the CNDO approximation

	2s	2p _x	2p _y
1	1.196	1.113	1.281
2	0.859	0.807	0.733
3	1.015	1.096	0.981
4	1.019	0.976	1.042
5	1.007	0.994	0.963
6	1.024	1.005	0.893

Table 8. Net electronic charges following different methods

Molecule	Pos.	LCAOK		EHT		IEHT		CNDO	
		Ring atoms	Hydrogen atoms	Ring atoms	Hydrogen atoms	Ring atoms	Hydrogen atoms	Ring atoms	Hydrogen atoms
	1	-1.350	+0.463	-0.575	+0.305	-0.178	+0.202	-0.088	+0.113
	2	+0.790	-0.259	+0.540	-0.227	+0.144	-0.151	+0.052	-0.110
	3	-0.582	+0.211	-0.394	+0.036	-0.131	+0.003	-0.101	+0.003
	4	-0.059	+0.258	+0.091	+0.019	-0.002	+0.020	+0.098	-0.019
	5	-0.366	+0.265	-0.163	+0.027	-0.065	+0.020	-0.062	+0.002
	6	+0.548	+0.082	+0.320	+0.022	+0.095	+0.041	+0.115	-0.002
	1	-0.864	+0.451	-0.136	+0.291	-0.074	+0.241	+0.055	+0.109
	2	-0.154	+0.057	-0.102	+0.042	-0.082	+0.036	+0.008	+0.016
	3	+0.493	-0.216	+0.192	-0.237	+0.078	-0.202	-0.165	-0.104
	4	-0.658	+0.293	-0.323	+0.042	-0.143	+0.009	+0.001	-0.001
	5	-0.059	+0.231	+0.010	+0.018	-0.026	+0.018	+0.031	-0.012
	6	+0.274	+0.151	+0.187	+0.018	+0.114	+0.031	+0.054	+0.008
	1	-0.654	+0.486	-0.334	+0.294	-0.135	+0.225	-0.067	+0.093
	2	+0.192	+0.107	+0.331	+0.024	+0.098	+0.044	+0.148	+0.006
	3	-0.467	+0.197	-0.385	+0.027	-0.135	-0.008	-0.100	-0.010
	4	+0.288	-0.179	+0.277	-0.232	+0.093	-0.184	-0.024	-0.092

σ charge transference owing to the electronegativity difference, it should be considered that the transferences in the different bonds related to a certain atom are not independent, and this should appreciably lower the transferences obtained.

Net total charges are shown in Table 8. Again, the methods generally agree concerning the polarity of each position, except CNDO, and this is particularly striking looking at the BN polarity in 3,1- and 4,1-BAB. For the three molecules, the B-N polarity is B^-N^+ as regards the π part (Table 5), but it is inverted in the σ skeleton. The total polarity is thus likely to be B^+N^- (due to the greater electronegativity of nitrogen), which is consistent with the chemistry of this kind of molecules, and with previous calculations [5, 8, 29].

Even if the methods differ regarding the weight of the BN polarity, they all agree in assigning importance to the X-H bonds. Let us remember that the dipole moment in borazane has been ascribed to the respectively negative and positive charges of the hydrogen atoms bonded to boron and nitrogen [33].

Fig. 2 visualizes the characteristics of the different methods regarding net total charges. There is clearly a tendency towards a uniform distribution in the order LCAOK \rightarrow EHT \rightarrow CNDO. It is thus confirmed that the extension of the ω -technique to all-valence electrons calculations (IEHT) can take care of the excessive charge accumulation on the more electronegative atoms, which arises in EHT [27].

It has been argued, from electronegativity considerations, that positions 3 and 5 of 2,1-BAB favour the electrophilic attack [1, 3]. While from the localization energies Kaufman and Hamann obtain for these two positions different predictions with models I and II, their π -charge densities agree for both models in favouring position 3. Comparison of Tables 5 and 8 shows that, although it is not possible for us to decide between both positions from the sole consideration of π charges, the net total charges decide for position 3. As to nucleophilic attack,

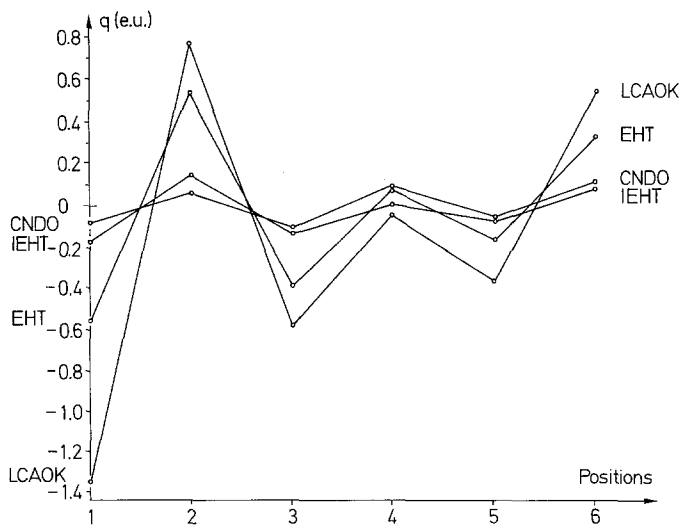


Fig. 2. Net total charges on the 2,1-BAB ring. 1 is N and 2 is B

total charges indicate position 6 to be most favoured; π charges are instead more ambiguous, and only PPP-I points at position 6.

We have shown in Table 9 the reactivity indices given by superdelocalizability [34], following SCHMO. For 2,1-BAB, the results are in complete agreement with what we just pointed for the total charges, as they are for 4,1-BAB. It is instead interesting that for 3,1-BAB superdelocalizability predicts that position 2 would be much more reactive than the others to electrophilic, nucleophilic and radical attack. This could be an indication for searching derivatives of 3,1-BAB.

Table 10 compares Chirgwin and Coulson's [35] with Löwdin's [22] charge definitions for 2,1-BAB as calculated in the IEHT method. Even if π charges are

Table 9. Superdelocalizability for SCHMO

Molecule	Position	Electrophilic	Nucleophilic	Radical
	1	0.7461	0.1408	0.4434
	2	0.1272	1.1924	0.6598
	3	0.9431	0.8771	0.9101
	4	0.7443	0.8264	0.7854
	5	0.9022	0.7315	0.8168
	6	0.8952	0.9011	0.8982
	1	0.4727	0.5598	0.5162
	2	2.9825	2.0215	2.5020
	3	0.6583	0.9045	0.7814
	4	1.8931	1.3397	1.6164
	5	0.7203	0.7369	0.7286
	6	2.1576	1.4458	1.8017
	1	0.8175	0.1530	0.4853
	2	0.7489	0.8589	0.8039
	3	0.9645	0.7385	0.8515
	4	0.7489	1.3829	0.7629

Table 10. Comparison of Chirgwin-Coulson's and Löwdin's net charges for 2,1-BAB (IEHT). The last ones are also shown supposing for hydrogen nuclear effective charge 1.0

	Atom	Ring atoms			Hydrogen atoms
		π	σ	total	
Chirgwin-Coulson ($Z_{\text{H}}^* = 1.2$)	1	+0.506	-0.996	-0.490	+0.285
	2	-0.508	+0.997	+0.489	-0.194
	3	+0.031	-0.280	-0.249	+0.031
	4	+0.034	-0.113	-0.079	+0.063
	5	-0.063	-0.021	-0.084	+0.059
	6	+0.002	+0.075	+0.077	+0.094
Löwdin ($Z_{\text{H}}^* = 1.2$)	1	+0.524	-0.702	-0.178	+0.202
	2	-0.530	+0.694	+0.144	-0.151
	3	+0.033	-0.164	-0.131	+0.003
	4	+0.039	-0.041	-0.002	+0.020
	5	-0.066	+0.001	-0.065	+0.021
	6	+0.001	+0.094	+0.095	+0.041
Löwdin ($Z_{\text{H}}^* = 1.0$)	1	+0.542	-0.741	-0.199	+0.231
	2	-0.533	+0.660	+0.127	-0.124
	3	+0.051	-0.203	-0.152	+0.041
	4	+0.014	-0.095	-0.081	+0.067
	5	-0.066	-0.040	-0.106	+0.063
	6	-0.008	+0.062	+0.054	+0.077

very similar, σ charges are not. This is not surprising, for both definitions differ in the second order in the commutator $[H, S]$ [36], whose σ part must be larger than the π part, because σ overlap is bigger than π overlap. Calculation of the dipole moment yields a difference of 10%, Chirgwin and Coulson's being lower.




For the sake of comparison, Löwdin's charge distribution has been also calculated for $Z_{\text{H}}^* = 1.0$. It is seen that the differences with the results for $Z_{\text{H}}^* = 1.2$ are less than those between Chirgwin-Coulson and Löwdin's definitions.

5. Dipole Moments

In order to estimate the dipole moment μ (Table 11), we consider the ring as a regular hexagon of side equal to the mean interatomic distance, a hypothesis which has little influence on the results. In LCAOK, EHT and IEHT we calculated μ following the point-charge approximation; this supposition is of course susceptible to criticism, but it has not prevented us, in other cases, from obtaining a good agreement with experiment [7, 9]. For CNDO we follow Pople and Segal [11] adding the contributions from the net atomic charge densities and that of the atomic polarization resulting from mixing $2s$ and $2p$ orbitals. There has been recently proposed a way to introduce the homopolar dipole contribution in CNDO [37]; however, it gives worse results, so that we shall suppose that all homopolar moments cancel out.

The outstanding feature in the table is a fairly satisfactory agreement between the different calculation methods. For 2,1-BAB the LCAOK method gives a higher value than the other methods, but for 3,1- and 4,1-BAB it is the EHT which departs most appreciably from the others. The agreement is particularly striking

Table 11. Dipolar moments (in D) following different methods

Molecule	Method	μ_σ	μ_π	$\mu_{x\text{tot}}$	$\mu_{y\text{tot}}$	μ_{tot}	Orientation
	LCAOK	1.81	6.62	-2.71	4.11	4.92	123°,4
	EHT	0.049	3.314	2.09	2.63	3.36	51°,5
	IEHT	0.23	3.06	1.64	2.32	2.84	54°,7
	CNDO	0.91	3.90	1.02	2.81	2.99	70°
	LCAOK	1.54	6.32	2.16	5.05	5.49	66°,8
	EHT	0.32	6.59	5.44	3.12	6.27	29°,8
	IEHT	0.42	5.82	4.56	2.88	5.40	32°,3
	CNDO	1.98	7.72	4.64	3.37	5.73	36°
	LCAOK	0.24	4.70	4.94	—	4.94	0°
	EHT	0.22	7.05	6.83	—	6.83	0°
	IEHT	0.61	6.14	5.53	—	5.53	0°
	CNDO	1.09	6.82	5.73	—	5.73	0°

between IEHT and CNDO, where the mean difference is 5%, with $\mu_{\text{CNDO}} > \mu_{\text{IEHT}}$. In the parallel calculations on purines and pyrimidines following these last two methods, Pullman *et al.* [12, 13] find differences of more than 50%, with $\mu_{\text{CNDO}} < \mu_{\text{IEHT}}$. These authors include the hybrid moments in the IEHT, evaluated separately as in the CNDO method. Our orientation as predicted by the methods with all valence electrons is in good agreement, as found by them.

Let us separate the μ_{sp} contribution in CNDO, which may be described in this case as a "deformation moment" relative to the regular structure. For, even if we have supposed a regular ring in the dipole moment calculation, the deformation was given by the starting data.

$$\begin{array}{lll}
 2,1\text{-BAB} & (\mu_{sp})_x = -0.30 & (\mu_{sp})_y = -1.07 & (\mu_{sp})_{\text{total}} = 1.11 \\
 3,1\text{-BAB} & (\mu_{sp})_x = -1.58 & (\mu_{sp})_y = -0.99 & (\mu_{sp})_{\text{total}} = 1.60 \\
 4,1\text{-BAB} & & \mu_{sp} = -1.92 &
 \end{array}$$

It is seen that the contribution increases in the order 2,1-; 3,1-; 4,1-BAB.

It is worthwhile to remark what seems a characteristic of the polarization of the σ skeleton due to the π distribution, as calculated in the LCAOK method. This effect in monocyclic azines [7] always decreased the dipole moment value (as for 2,1- and 3,1-BAB). For fulvene instead [38] the allowance of this effect increases the dipole moment, as for 4,1-BAB. In any case, this very simple fashion of taking into account $\sigma-\pi$ interaction substantially improves the theoretical results. Here, it brings the LCAOK values nearer to those calculated taking into account all valence electrons, which deserve more confidence. Besides, for borazine, the consideration of this polarization effect permitted a good agreement with experimental infrared absorption bands [14]².

The lack of experimental data makes it difficult to decide between the individual results. Nevertheless, the fairly high values predicted may be related with the high one for other B-N containing compounds [33].

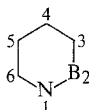
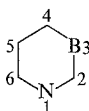
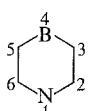
² Dr. H. D. B. Jenkins kindly remarked to us a numerical error in the energy levels of paper [14]. On correcting them, the qualitative conclusions remain the same, as q_π change slightly and the infrared absorption bands intensity relation in borazine becomes 2.5 (instead of 2.0), in better agreement with the experimental value of 3.5.

6. π Bond Orders and Distances

Section A of Table 12 displays the $p_{\mu\nu}$ values obtained in this work, while section B reproduces those reported by Kaufman and Hamann [1].

LCAOK and SCHMO have quite different results. Considering the $p_{\mu\nu}$ values that may be compared directly, in 2,1-BAB we see that in the C–C bonds, to the sequence $p_{34} > p_{56} > p_{45}$ for SCHMO, there corresponds the LCAOK sequence $p_{56} > p_{34} > p_{45}$. The same thing happens for the C–C and C–N bonds in 3,1-BAB. The LCAOK $p_{\mu\nu}$'s are somewhat similar to Hückel's and PPP-I's. Those of SCHMO seem to be more similar to PPP-II.

Table 12. π bond orders; (A) this work; (B) reported by Kaufman and Hamann [1]

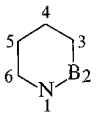
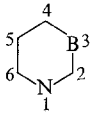
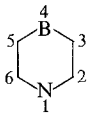
Molecule	Bond	SCHMO	LCAOK	EHT	IEHT	CNDO	Hückel	PPP	
								Model I	Model II
	1–2	0.3966	0.4481	0.5223	0.6302	0.6557	0.5114	0.5574	0.2119
	2–3	0.2475	0.7062	0.4578	0.5213	0.5138	0.6724	0.7084	0.3636
	3–4	0.9157	0.6040	0.7981	0.7713	0.8003	0.6421	0.6206	0.7986
	4–5	0.3560	0.5685	0.5132	0.5356	0.4685	0.6455	0.6782	0.5137
	5–6	0.9004	0.7410	0.7923	0.7798	0.8298	0.7083	0.6646	0.7889
	1–6	0.2940	0.3500	0.4655	0.5126	0.4602	0.5725	0.6362	0.2140
	1–2	0.4664	0.3311	0.5948	0.5885	0.6037		B	
	2–3	0.3958	0.7907	0.5748	0.6029	0.6618			
	3–4	0.3660	0.4986	0.5751	0.5767	0.6065			
	4–5	0.7704	0.5277	0.7004	0.6917	0.6697			
	5–6	0.6086	0.7962	0.6465	0.6577	0.6743			
	1–6	0.4427	0.4054	0.5958	0.5919	0.6081			
	1–2	0.3059	0.4089	0.4911	0.5116	0.4911			
	2–3	0.9218	0.8163	0.7983	0.7883	0.7962			
	3–4	0.2740	0.4968	0.4878	0.5100	0.5291			

The all-valence-electrons methods present, as a whole, a certain similarity. The mean variation which arises from iterating EHT is of 4%. The $p_{\mu\nu}$ of EHT are somewhat like PPP-II, p_{34} , p_{45} and p_{56} being practically the same. For these three $p_{\mu\nu}$'s, the IEHT and CNDO methods give also values fairly alike to those of PPP-II, not being so for the other three.

All methods employed in this work coincide in assigning positive values to certain bond orders between non-neighbouring atoms: p_{24} in the three molecules (of the order of magnitude of 0.2), p_{35} in 3,1- and 4,1-BAB (~ 0.15).

Due to the mentioned $p_{\mu\nu}$ values, the EHT, IEHT and CNDO methods should give similar interatomic distances. We have calculated them (Table 13) with Julg's formula [16], bearing in mind that: (1) it is valid on neglecting overlap; (2) and for the region 1.33–1.50 Å; (3) the dependence upon the nuclear effective charges is not clear [39]. The first point does not seem important, for the differences between EHT and IEHT on one hand, and the CNDO and Hückel methods on the other, remain within the limits of usual experimental errors. Point 3 seems more significant, and for this reason we do not report distances in this way for LCAOK

Table 13. *Interatomic distances (in Å) calculated with data of Table 12. (A) all-valence-electron methods; (B) with the data of Ref. [1]*

Molecule	Bond	EHT	IEHT	CNDO	Hückel	PPP-I
	1-2	1.423	1.404	1.399	1.425	1.417
	2-3	1.512	1.500	1.501	1.471	1.464
	3-4	1.373	1.378	1.373	1.401	1.405
	4-5	1.425	1.421	1.433	1.401	1.395
	5-6	1.374	1.377	1.368	1.390	1.397
	1-6	1.367	1.358	1.367	1.348	1.337
		1-2	1.344	1.345	1.343	
2-3		1.490	1.484	1.473		
3-4		1.490	1.489	1.484		
4-5		1.391	1.392	1.396		
5-6		1.401	1.399	1.396		
1-6		1.344	1.345	1.342		
		1-2	1.362	1.359	1.362	
	2-3	1.373	1.375	1.374		
	3-4	1.506	1.502	1.498		

and PPP-II. Results are reasonable for homonuclear distances, but they could be contradictory with the $p_{\mu\nu}$ values for some heteronuclear distances (for instance in the case of B-C bonds).

As it could be expected, Hückel and PPP-I distance values are very similar; they are instead appreciably different from those employed in this work, obtained with the SCHMO, giving a less deformed geometry.

The question opens which are the most reliable distances. On one hand SCHMO, as we have already argued, has proven useful in reproducing experimental distances in a series of molecules. We have seen that it gives reasonable values for the aromaticity. Let us remark that Hückel's distances predict an aromaticity of 0.84, which seems much too high. Besides, the low SCHMO $p_{\mu\nu}$ values for the B-N, B-C and N-C bonds in 2,1-BAB agree with those calculated by Dewar for these bonds in its derivatives 2,1-borazaronaphthalene and 10,9-borazarophenantrene. The large $p_{\mu\nu}$ variation for two neighbouring C-C bonds is also obtained in Dewar's calculation of 2,1-borazaronaphthalene. The SCHMO charges in B and N also agree with Dewar's.

Comparative calculations of dipole moments with the SCHMO geometry, and with that supposing for the rings regular hexagons with sides equal to the mean distance, lead to differences of only 2%. Geometry seems therefore irrelevant, at least in this sense [2].

7. Conclusions

Net charges allow coincident conclusions for all methods as to reactivities, but CNDO disagrees with the others which predict a polarity B^+-N^- in the three molecules.

These molecules should have fairly high dipole moments, whose values should lie between the following limits (in Debyes): 3 and 4.9 for 2,1-BAB; 5.4 and 6.3 for 3,1-BAB; 4.9 and 6.8 for 4,1-BAB.

The question remains open as to the molecular geometry.

The first transition is $\sigma \rightarrow \pi^*$ for 4,1-BAB, $\pi \rightarrow \pi^*$ for 3,1-BAB, and the methods differ regarding the assignment of this band for 2,1-BAB.

The all-valence-electrons methods, as they have been used here, do not predict a preferential stability (from the point of view of total energy) for any one of the three molecules.

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