Extended Hückel Theory. III. Compounds of Boron and Nitrogen

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Extended Hückel Theory. III. Compounds of Boron and Nitrogen

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The extended Hückel theory is applied to compounds of boron and nitrogen, with emphasis placed upon similarities and differences with isoelectronic and isosteric carbon analogs. The barrier to internal rotation in borazane is predicted to be ~1.5 kcal/mole and the torsional barrier in aminoborane~10 kcal/mole. The internal charge-transfer nature of the expected electronic transitions is stressed. The highest occupied orbitals in aminoborane and borazine are computed to be σ type, with important consequences for the reactions of these molecules. It is proposed that the accepted valence picture of borazine is incorrect and that in all B–N molecules N is more negative. Stabilization due to nonbonded electrostatic interactions is studied. Predictions are made regarding the geometry of B–N analogs of cyclobutadiene and cyclooctatetraene. Borazine is calculated to be inefficient in transmitting electronic effects. Computations of the relative stabilities of heteroaromatic B–N compounds are made.

IT was not very long ago that borazine, then passing under the name of borazole, was patronizingly described as "inorganic benzene." Things have changed very much in recent years, and the synthesis of B–N analogs of ethanes, ethylenes, cyclobutanes, cyclohexanes, butadienes, allenes, biphenyls, naphthalene, cyclobutadiene, and cyclo-octatetraene has established the largest isoelectronic sequence (B–N to C–C) in chemistry.[1] For every similarity in this series there is a difference and it is with a view toward understanding the dissimilarities in analogous compounds that a study of B–N molecules was undertaken. Since the differences are the consequence of the change to a heteropolar bond, the extended Hückel method,[2] which allows an approximate calculation of σ as well as π orbitals, is particularly well suited. The procedure utilized was identical to that in the first paper in this series—a fairly realistic molecular geometry was chosen and changes studied in charge distribution and energy as a function of various distortions of the molecule. In fact, the procedure used exactly the same model coordinates as for the hydrocarbons, i.e., B–N, B–C, and N–C 1.54 Å; B=N 1.34 Å; B–N aromatic 1.40 Å; B–H, C–H, and N–H, 1.10 Å. This was done with full awareness that B–N distances are 0.02 to 0.06 Å longer than C–C,[3] and that B–C, N–C, N–H, and B–H are quite different as well. For critical molecules the computation was repeated for many B–N distances and the calculations, detailed below, indeed showed that B–N bonds should be longer than C–C; however, the essential arguments and conclusions were not sensitive to model geometry.

The Coulomb integrals for N are a compromise set, described in Paper II: ${}^2H_{ii}(2s) = -26.0$ eV; $H_{ii}(2p) = -13.4$ eV. The choice of the B sp^2 valence state is less ambiguous, and the Coulomb integrals used were $H_{ii}(2s) = -15.2$ eV; $H_{ii}(2p) = -8.5$ eV.[4] The Slater exponents are 1.300 for B; 1.950 for N. The computations were limited to compounds of B, N, C, and H and the parameters for C and H are identical to those of the first paper.[2]

In this work the analogs of alkanes, B and N four-coordinated, are called borazanes. The B–H cyclohexane, cyclobutane is termed cyclotriborazane, cyclodiborazane. Analogs of olefins, i.e., B and N three-coordinated, are called aminoboranes. Dewar's suggestion *re* the nomenclature of the azarobenzenes,[5] heteroaromatic compounds with two carbons substituted by B and N, is adopted. Finally some compounds such as the B–N analog of cyclobutadiene or biphenyl are called just such.

In Table I are listed calculated total energies for the most stable conformation of most of the compounds studied. Conformational problems are discussed separately below.

BORAZANE

The B–N analog of ethane is the simplest donor–acceptor complex; there is also interest in the barrier to internal rotation in this molecule relative to ethane. If one carries out the absolute minimization procedure described in I, i.e., varies B–N, N–H, and B–H and torsional angle while keeping tetrahedral angles about B and N, one obtains a minimum for a staggered BH_3NH_3 at B–N, 2.10 Å; B–H, 1.25 Å; N–H, 0.85 Å. Whereas the B–N distance is unrealistically long, a

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[1] Research in the field was reviewed at the International Symposium on Boron–Nitrogen Chemistry, Durham, April 1963, where this work was presented in part. The proceedings of the Symposium are published in *Boron–Nitrogen Chemistry*, Adv. in Chem. No. 42 (American Chemical Society, Washington, D. C., 1963), hereafter referred to as BNC.

[2] R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963); **40**, 2745 (1964); hereafter referred to as I, II.

[3] B–N distances have been measured in the range of 1.57–1.64 Å, B–N in borazine 1.41–1.44 Å. For a compilation of various B distances see W. N. Lipscomb, BNC.

[4] H. A. Skinner and H. O. Pritchard, Trans. Faraday Soc. **49**, 1254 (1953); H. O. Pritchard and H. A. Skinner, Chem. Rev. **55**, 745 (1955).

[5] M. J. S. Dewar, BNC.

TABLE I. Calculated total energies of some B–N compounds.

	Molecule	$-E$
BH_3NH_3	borazane	240.803
$BH_3NH_2CH_3$	N-methyl borazane	345.720
$BH_3NH(CH_3)_2$	N-dimethyl borazane	450.629
$BH_3N(CH_3)_3$	N-trimethyl borazane	555.498
$BH_2CH_3NH_3$	B-methyl borazane	344.811
$BH(CH_3)_2NH_3$	B-dimethyl borazane	448.978
$B(CH_3)_3NH_3$	B-trimethyl borazane	553.214
$BH_2CH_3NH_2CH_3$	B-methyl, N-methyl borazane	449.730
$(BH_2NH_2)_3$	cyclotriborazane	621.491
$(BH_2NH_2)_2$	cyclodiborazane	415.040
$B_3N_3H_{11}CH_3$	B-methyl cyclotriborazane	725.766
$B_3N_3H_{11}CH_3$	N-methyl cyclotriborazane	726.357
$BH_3NH_2BH_2NH_3$	B–N butane	447.874
BH_2NH_2	aminoborane	209.343
BH_2NHCH_3	(methylamino) borane	314.266
$BH_2N(CH_3)_2$	(dimethylamino) borane	419.172
$BHCH_3NH_2$	(amino) methylborane	313.734
$B(CH_3)_2NH_2$	(amino) dimethylborane	418.015
$BHCH_3NHCH_3$	*cis*-(methylamino) methyl-borane	418.503
$BHCH_3NHCH_3$	*trans*-(methylamino) methyl-borane	418.631
$(BHNH)_2$	B–N cyclobutadiene	351.375
$(BHNH)_3$	borazine	527.323
$(BHNH)_4$	B–N cyclooctatetraene	701.149
BNC_4H_6	2,1-borazarobenzene	525.686
BNC_4H_6	3,1-borazarobenzene	524.215
BNC_4H_6	4,1-borazarobenzene	524.632
$B_2N_2C_2H_6$	2,4-dibora, 1,3-diazarobenzene	525.894
$BH_2NHBHNH_2$	B–N butadiene (B=N–B=N)	385.089
$BH_2NHNHBH_2$	B–H butadiene (B=N–N=B)	384.152
$NH_2BHBHNH_2$	B–N butadiene (N=B–B=N)	381.685
$BH_2BHNHNH_2$	B–N butadiene (B=B–N=N)	379.247
CH_2NBH_2	B–N allene (C=N=B)	281.418
CH_2BNH_2	B–N allene (C=B=N)	280.031
BH_2CNH_2	B–N allene (B=C=N)	278.607
$B_3N_3H_5CH_3$	B-methyl borazine	631.617
$B_3N_3H_5CH_3$	N-methyl borazine	632.217
$B_3N_3H_4(CH_3)_2$	B,B-dimethyl borazine	735.911
$B_3N_3H_4(CH_3)_2$	N,N-dimethyl borazine	737.109
$B_3N_3H_4(CH_3)_2$	B,N-dimethyl borazine (*ortho*)	736.402
$B_3N_3H_4(CH_3)_2$	B,N-dimethyl borazine (*para*)	736.510
BNC_8H_8	2,1-borazaronaphthalene	842.068
$BNC_{12}H_{10}$	10,9-borazarophenanthrene	1157.863
BNC_4H_6	6,1-borazarofulvene	526.616
$C_5H_5NBH_3$	pyridine-borane	630.217
$C_5H_4CH_3NBH_3$	2-methylpyridine-borane	734.499
$C_5H_4CH_3NBH_3$	3-methylpyridine-borane	734.578
$C_5H_4CH_3NBH_3$	4-methylpyridine-borane	734.665

TABLE II. Some energy levels in borazane, aminoborane, and borazine. Starred levels are antibonding.

Borazane[a]		Aminoborane[b]		Borazine[c]	
e^*	13.394	b_1^*	1.929	$a_2''^*$	−4.889
e^*	6.594	(π) b_2^*	−6.949	(π) e''^*	−6.606
a_1^*	2.338	b_1	−13.112	e'	−12.860
e	−13.247	(π) b_2	−13.770	(π) e''	−13.571
a_1	−14.227	a_1	−14.457	a_2'	−14.258
e	−16.148	b_1	−16.407	(π) a_2''	−14.490
a_2	−19.639	a_1	−18.815	e'	−14.972
a_1	−28.358	a_1	−28.111	a_1'	−15.446

[a] B–N, 1.60; B–H, 1.20; N–H, 1.00.
[b] B–N, 1.34; B–H and N–H, 1.10.
[c] B–N 1.40; B–H and N–H, 1.10. 6 most bonding levels omitted.

comparison with the corresponding ethane result of 1.92 Å for C–C and 1.0 Å for C–H, does show the observed lengthening of B–N and B–H and the shortening of N–H. At B–N 1.54 Å the difference between staggered and eclipsed BH_3NH_3 is 3.0 kcal (ethane was computed as 4.0).[2] At B–N, 1.60 Å; B–H, 1.20; N–H 1.00, the result is 2.2 kcal, and the number is not too sensitive to different choices for N Coulomb integrals. Assuming a proportionality between the calculated and observed barrier as in ethane, the predicted barrier to internal rotation in BH_3NH_3 should be about 1.5 kcal/mole.

Selected energy levels are shown in Table II. The highest occupied level is mainly B–H bonding; the a_1 below is B–N bonding with 1.37 electrons on N, 0.41 on B (out of a total of 2.00). A transition corresponding to an excitation of an electron from this a_1 to a_1^*, with an electron distribution of 1.38 on B, 0.46 on N, may be termed an internal charge-transfer transition. It would be interesting to observe this band in the far uv; it may be difficult to find it since a nearby transition involves excitation of B–H bonding electrons, with probable bond fracture. Subsequent calculations indicate that the charge transfer transition should be more accessible

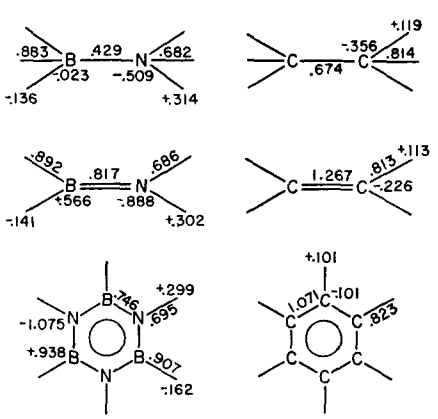


FIG. 1. Population analyses for borazane, aminoborane, and borazine compared with their hydrocarbon analogs.

in the N-methyl substituted borazanes. The charge distribution of Fig. 1 indicates transfer of 0.43 electrons from the ammonia to the borane moiety.

AMINOBORANE

The parent compound has not been synthesized nor is there a determination of the B–N distance in any aminoborane. The absolute minimization gives a planar C_{2v} BH_2NH_2 with bond lengths B–N, 1.80; B–H, 1.1; N–H, 0.75 Å. At B–N, 1.40; B–H, 1.20; N–H, 1.00 Å, the difference in energy between the planar BH_2NH_2 and a twisted form in which BH_2 and NH_2 planes are perpendicular is 10.4 kcal, and for shorter B–N the barrier is greater. The value quoted is in fortuitous agreement with measured activation energies of *cis–trans* isomerization in substituted aminoboranes[6]; however comparison with the corresponding computed energy difference for ethylene, 80.5 kcal,[2] clearly indicates that there is much less resistance to torsional motion in the B–N analog.

In the population analysis (Fig. 1) there is a total charge transfer of 0.28 electrons *from BH_2 to NH_2*. In the π system, where initially N has two electrons and B none, there has to be charge transfer to B from N. However, the greater electronegativity of N overrides this effect with still greater charge transfer in the opposite direction in the σ electrons. This point is discussed further below.

Some energy levels for BH_2NH_2 are shown in Table II. The highest occupied orbital is σ type, mostly B–H bonding; the $\sigma \rightarrow \pi^*$ transition is forbidden. The $\pi \rightarrow \pi^*$ transition is also of the internal charge transfer type. One rather interesting and probably verifiable conclusion about the geometry of the excited states of aminoborane emerged from the calculation. In ethylene the first excited state prefers a twisted D_{2d} arrangement,[7] but for aminoborane it is found that the analogous excited state arising from a $\pi \rightarrow \pi^*$ excitation still prefers to remain planar.

BORAZINE

The calculation shows that in the π system of borazine 0.27 electrons are transferred to B (Fig. 1). The σ effect is decidedly in the opposite direction, so that in the total charge distribution, N is quite negative. As in aminoborane, the highest occupied orbital is σ type (Table II), with a charge distribution in the doubly degenerate orbital of H_B, 0.30; H_N, 0.02; B, 0.31; N 0.70. I believe that many of the differences in the reactions of unsaturated and conjugated hydrocarbons and their B–N analogs are a consequence of the greater accessibility of σ electrons in the latter. It would seem that the ease of addition reactions in the borazines could be explained in this manner; however, one must be cautious about reactivity conclusions not based on detailed examination of the electronic structure of the transition state.

THE POLARITY OF THE B–N BOND

In the above section charge distributions were presented which indicated that (1) in BH_3NH_3 there is charge transfer from NH_3 to BH_3; (2) in BH_2NH_2 and borazine there is π charge transfer from N to B, but σ transfer from B to N, with the latter effect dominant; (3) in each case the nitrogen carries a larger negative net charge, even in BH_3NH_3, where onto the B^-N^+ polarity there is superimposed B^+–H^- and N^-–H^+.

Now if one writes down aminoborane with a B=N double bond, or one of the Kekule structures of borazine, one is compelled by the formalism of ordinary valence theory to put a formal positive charge on N and a negative one on B. The general tendency has been to attribute reality to these formal charges. Present calculations indicate that the charges imposed by valence theory are here grossly misleading and that in fact the actual charge distribution is opposite to that usually assumed.

A few workers have recognized the possibility of this: Becher,[8] Goubeau,[9] Coates and Livingstone,[10] and Parry.[11] For instance, Becher concluded on the basis of a study of the dipole moments of some substituted borazanes and aminoboranes that the aminoborane B–N bond moment was close to zero. The calculations reported here actually assign to this moment the direction B→N, but our conclusions agree in that in all B–N compounds the nitrogen is more negative. It should be stressed that the charges calculated here should, in view of the approximations made and the arbitrariness of any division of electrons among atoms, be viewed as giving only a qualitative picture of the electronic distribution.

OTHER BORAZANES

The compounds studied were the methyl-substituted borazanes, and the boron–nitrogen analogs of *n*-butane, cyclobutane, and cyclohexane. The general observation was made that $=BH_2$ or BH_3 groups will cause greater steric problems than $=CH_2$ or $-CH_3$ which in turn will be greater than those of $=NH_2$ or $-NH_3$. The BH_3 group is bulkier since not only are B–H bonds longer, but due to the ordering of electronegativities one has the polarity B^+–H^-, and the hydrogens appear "larger".

For N-methyl, B-methyl borazane the energy difference between the *gauche* and *trans* arrangements is calculated as 0.255 eV, similar to the computed value for *n*-butane[2]; the potential maximum corresponding to B-methyl eclipsing N–H came out much higher in the

[6] W. S. Brey, Jr., M. E. Fuller II, G. E. Ryschkewitsch, and A. Saji, BNC.

[7] R. S. Mulliken and C. C. J. Roothaan, Chem. Rev. **41,** 219 (1947).

[8] H. J. Becher, Z. Anorg. Allgem. Chem. **270,** 273 (1952).

[9] J. Goubeau, Naturwiss. **35,** 246 (1948).

[10] G. E. Coates and J. G. Livingstone, J. Chem. Soc. **1961,** 1000. I am indebted to M. F. Lappert for bringing this reference to my attention.

[11] R. W. Parry (private communication).

B–N compound than in the hydrocarbon. The results of the population analysis for the methyl substituted borazanes are shown in Fig. 2.

It has been suggested that the boat–chair equilibrium in cyclotriborazane might not be as unfavorable to the boat form as it is in cyclohexane, since as a result of the B–N polarity there might be some additional stabilization due to nonbonded attraction across the boat.[12] These calculations confirm such an effect; the boat form is calculated as less stable by 0.385 eV, compared to 0.768 eV for cyclohexane.[2] The magnitudes are in themselves again much too large, but the relative order is significant. Axial and equatorial isomers of *B*-methyl and *N*-methyl cyclotriborazane were examined. The *a–e* difference (favoring equatorial) was 0.220 eV for N methyl, 0.762 eV for *B* methyl, 0.529 eV for methyl cyclohexane.[2] The conclusion that the *N*-methyl *a–e* difference is less than for *C*-methyl agrees with some recent experimental measurements,[12,13] the prediction that the *B*-methyl difference is greater remains to be tested. In cyclodiborazane any out-of-plane deformation would on similar grounds be expected to lead to destabilization, and the calculations do indicate that this B–N analog will be more resistant to distortions from planarity than cyclobutane.

The B–N analog of *n*-butane also showed some evidence of stabilization in conformations where BH_3 and NH_3 were close to each other.[14] Thus, while the *trans* isomer was still most stable, the relative energy of the *gauche* form was significantly improved, being 0.169 eV above *trans*. The energy of the potential maximum for $-BH_3$ and $-NH_3$ eclipsed was also improved.

SUBSTITUTED AMINOBORANES AND RELATED COMPOUNDS

Barriers to internal rotation in (methylamino)borane and (amino)methylborane were small; 0.025 eV in favor of the conformation in which a hydrogen eclipses the double bond in the latter, 0.011 eV in favor of the *opposite conformation* in the former.

From Table I it may be seen that the isomerization energy of *cis* to *trans* (methylamino)methylborane is similar to that computed for *cis* to *trans*-butene-2.[2] Other conclusions about isomerization energies are uncertain since B–C and N–C distances will vary; tentatively then the heat of formation of (amino)dimethylborane should be close to that of *cis*-(methylamino)-methylborane, while the (dimethylamino)–*trans*(methylamino)methylborane isomerization energy should exceed that of the isobutylene-*trans*-butene–2 pair.[2]

Calculations were also performed for *cis* and *trans* conformations of isomeric analogs of butadiene, arranged in order of calculated decreasing stability (somewhat uncertain, for the same reasons as detailed in the above paragraph), from left to right

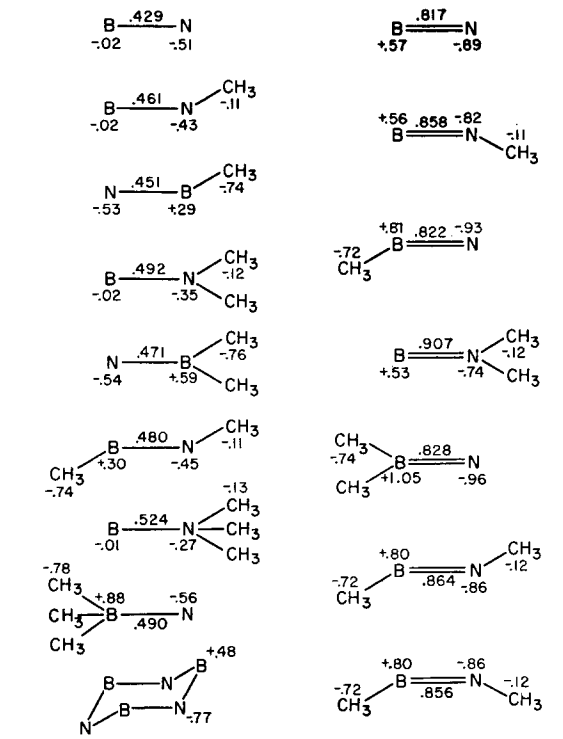
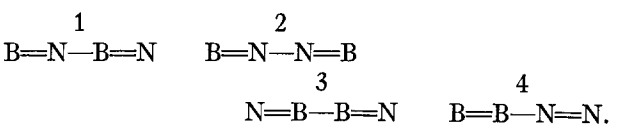
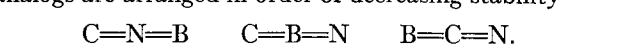


FIG. 2. Charge distributions and B–N overlap populations in some borazanes and aminoboranes. CH_3 charge refers to carbon atom only.



The *trans* configurations are favored by 0.130, 0.913, 0.022, and 0.245 eV, respectively; as expected from a simple charge interaction model the energy difference is less than in butadiene[2] (0.330) for 1 and 4, more for 2. Surprisingly the calculation shows a small energy difference between the *cis* and *trans* forms of 3. Large gaps between occupied and empty orbitals, similar to that in butadiene, are found in 1, 2, smaller in 3, 4. One interesting quantity is the π overlap population in the central bond, which in butadiene is 0.073; in 1, 2, 3, 4 are 0.078, −0.017, 0.018, and 0.179, respectively. Derivatives of 1, 2, 3 are known. The following allene analogs are arranged in order of decreasing stability



Isocyanate boranes can be considered derivatives of the first of these.

THE B–N ANALOGS OF CYCLOBUTADIENE AND CYCLO-OCTATETRAENE

Recently, the syntheses of these compounds have been reported.[15,16] Since the carbon analogs have been

[12] R. O. Buttlar, D. F. Gaines, and R. Schaeffer, BNC.
[13] D. F. Gaines and R. Schaeffer, J. Am. Chem. Soc. **85,** 395 (1963).
[14] This was suggested by R. Schaeffer, see Ref. 1.
[15] M. F. Lappert and M. K. Majumdar, Proc. Chem. Soc. **1963,** 88.
[16] H. S. Turner and R. J. Warne, BNC; H. S. Turner and R. J. Warne, Proc. Chem. Soc. **1962,** 69.

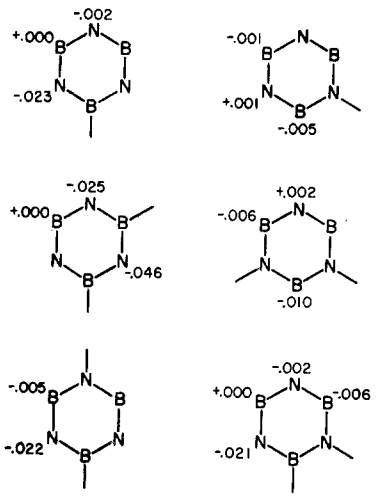


FIG. 3. Difference charge distributions for methylborazines and dimethylborazines relative to borazine.

of considerable interest to experimentalists and theoreticians alike, a series of calculations of $(BHNH)_2$ and $(BHNH)_4$ was undertaken. It is found that $(BHNH)_2$ prefers a planar geometry with little deviation, if any at all, from a square arrangement of B and N nuclei. The two levels which are degenerate in cyclobutadiene are split considerably; the charge-transfer transition involving the excitation of an electron from the bonding to the antibonding member of the pair is forbidden. However, two other allowed $\pi \rightarrow \pi^*$ transitions, close in energy, should be observed. Since the actual derivative synthesized has amino substituents on the ring borons, it may be that the structural conclusions outlined above are not applicable.

For C_8H_8 and $(BHNH)_4$ five conformations were examined: chair, tub, crown, planar, cubical. In each case the tub geometry was preferred, in agreement with structural conclusions; relative to this most stable arrangement the cubane structure was less unfavorable for $(BHNH)_4$ than for C_8H_8, as would be expected from the electrostatic model. For the anion and dianion of C_8H_8 the planar form was found to be favored over the tub, but for $(BHNH)_4$ negative ions the calculation leads to the interesting prediction that in the anion the tub geometry is still best, while in the dianion the tub and planar forms are of very nearly equal energy, the latter slightly more stable.

ELECTRONIC EFFECTS IN BORAZINE

How aromatic is borazine? All too precise specifications are bound to be misleading since the very concept of aromaticity is not amenable to quantification. Borazine is obviously quite different from benzene in stability and reactions. It is characterized by the presence of diamagnetic anisotropy indicating delocalization of electrons in π orbitals but of magnitude smaller than in benzene.[17] Still another attribute of aromaticity is the propagation of electronic effects far from the site of substitution. Experimentally the study of such effects is complicated by the presence of B–N polarization and the consequent difficulty of preparing all possible substitutional isomers and effecting all reactions. To study the effect theoretically, a calculation was performed on the two methyl borazines and four dimethyl borazines. In Fig. 3 are shown *differences* between the calculated charges in borazine and those at the unsubstituted sites of the above molecules. Comparison with toluene and xylenes, described in I,[2] shows that borazine is relatively ineffective at transmitting electronic effects, particularly for methyl substitution at N.

HETEROAROMATIC B–N COMPOUNDS

We have performed LCAO-MO calculations for both the σ and π electron systems of benzene, the 3 borazarobenzenes, 11 diboradiazarobenzenes, and the 3 triboratriazarobenzenes. In general, the energy of the σ electrons emerged as a function only of the number of various bonds involved, while the π energy varied considerably. Dewar's conjecture regarding the relative stabilities of the borazarobenzenes[5] is confirmed, i.e., in order of decreasing thermochemical stability we have 2,1-, 4,1-, 3,1-borazarobenzene. The most stable of the

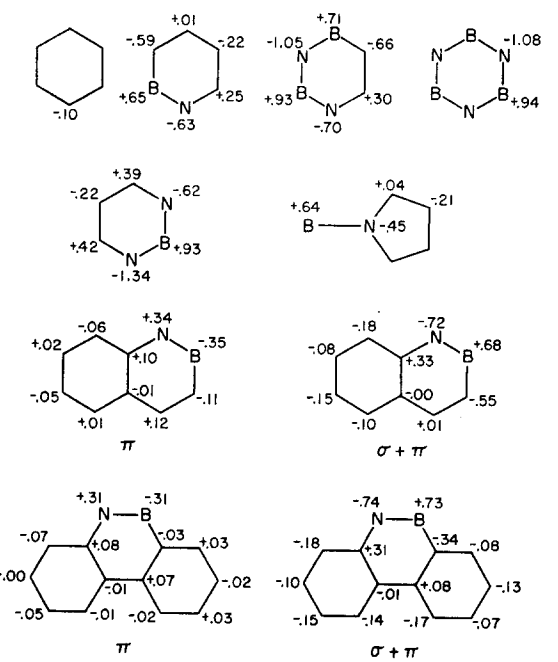


FIG. 4. Charge distribution in some heteroaromatic B–N compounds.

[17] K. Lonsdale, Nature **184,** Suppl. 4, 1060 (1959); H. Watanabe, K. Ito, and M. Kubo, J. Am. Chem. Soc. **82,** 3294 (1960).

diboradiazarobenzenes is the isomer 2,4-dibora-1,3-diazarobenzene, followed by 4,6-dibora-1,3-diazarobenzene. The order of stabilities was not affected by a more realistic set of distances. In general, isomers with B–B or N–N bonds are unfavored. Of the triboratriazarobenzenes borazine is easily the most stable. Total charge distributions are shown for the most stable isomer of each class in Fig. 4. The calculation shows also that borazarene and 2,4-dibora-1,3-diazarobenzene are much less stable than either borazine or benzene. One general principle emerges: B and N "like" to come adjacent into a molecule, and if a molecule already has positions of alternating negative and positive charge density, a very stable B–N compound would be one with a nitrogen in what was originally the most negative site in the molecule, and a boron in an adjacent most positive location. Thus calculated energies for some of the hypothetical borazaropyridines in which B and N are adjacent are

2,3 borazaropyridine	−535.978 eV
4,3 borazaropyridine	−534.642 eV
3,4 borazaropyridine	−534.089 eV.

In the molecules discussed discussed above the π electron energy varies with σ sum. This is no longer true in compounds with two or more rings. Thus for some

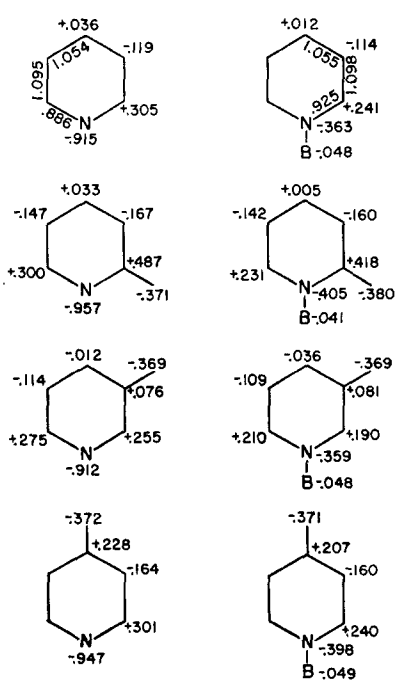


FIG. 5. Population analysis for pyridine, the picolines, and their borane adducts.

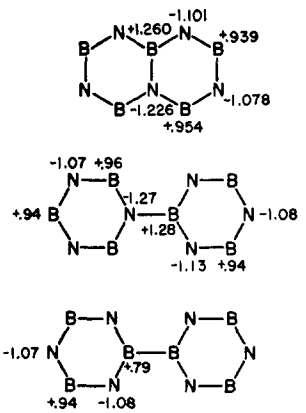


FIG. 6. Charge distribution in the B–N naphthalene and B–N biphenyls.

borazaronaphthalenes

B	N	$-E_\pi$	$-E_{\text{total}}$
2	1	134.380	842.068
1	2	134.326	841.847
1	9	133.856	842.165
9	1	133.980	841.219
9	10	133.738	841.671
2	3	134.158	841.499.

The qualitative features of the charge distributions are in agreement with those calculated by Dewar.[5] For 2,1-borazaronaphthalene and 10,9-borazaraphenanthrene these are also shown in Fig. 4. Some differences arise—for example, note the large negative population at Site 4 in the phenanthrene.

Becher has synthesized a 6,1-borazarofulvene,[18] whose calculated charge distribution is shown in Fig. 4. It is interesting to note that while fulvene is about 30 kcal/mole less stable than benzene, the borazarofulvene is calculated to be about 25 kcal/mole more stable than the isomeric borazarene.

Calculations were carried out for some substituted pyridine boranes. Charge distributions in these compounds, as well as in the pyridines, are shown in Fig. 5. The calculations show that of the picolines, 2-methyl pyridine is most stable, followed by 4-, 3-, while in the adduct the 4-methyl pyridine borane is favored, followed by 3-, 2-. On examination of the reaction forming the pyridine boranes, the net result is that the heat of formation of the 2-methyl pyridine adduct is substantially greater than that of the 3- or 4-methyl isomer—in agreement with the measured heats of Brown and Domash.[19]

In the charge distribution for pyridine borane note that the charge on Carbons 3, 4, 5 is changed little from

[18] H. J. Becher, Z. Anorg. Allgem. Chem. **289,** 262 (1957).
[19] H. C. Brown and L. Domash, J. Am. Chem. Soc. **78,** 5384 (1956).

pyridine, while Positions 2, 6 become more negative. Thus in this calculation, coordination with BH_3 not only produces charge transfer from N to B but also from N to neighboring carbons (N–C overlap population also is greater in $PyBH_3$). This could be an artifact of a computation which uses the same Coulomb integrals for N regardless of environment. On the other hand one can construct an explanation for the anomalous $PyBH_3$ hydrogen chemical shifts reported by Brey *et al.*[6] by superimposing upon this charge distribution the effect of increasing ring currents.

The B,N naphthalene[20] and B,N biphenyl linked via either B–B[21] or B–N[20] have also been examined. In the naphthalene analog, the gap between filled and unfilled orbitals is large and only slightly smaller than in borazine. This situation, quite different from the benzene, naphthalene progression, indicates the trend which culminates in a colorless hexagonal boron nitride. The B–N linked biphenyl analog prefers to be slightly twisted, while the B–B linked compound should be planar. (The N hydrogens which are the source of steric difficulties in the planar form are positively charged and thus "smaller.") The total charge distributions which are shown in Fig. 6 may be of some interest when the NMR spectra of these compounds are examined.

[20] A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, J. Am. Chem. Soc. **83**, 1337 (1961).

[21] R. J. Brotherton, L. L. Peterson, and A. L. McCloskey, Abstracts, 144th Meeting, American Chemical Society, Los Angeles, 1963.

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Extended Hückel Theory. IV. Carbonium Ions

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The conformations, relative stabilities, and electronic distribution of a sample of the more important carbonium ions and positively charged hypothetical transition states are examined. The species studied include the methyl, ethyl, isopropyl, tertiary butyl, and higher alkyl carbonium ions; protonated ethylene, acetylene, benzene, cyclopropane; the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl carbinyl, allyl, and benzyl cations; the carbonium ions based on norbornane, norbornene, norbornadiene. Significant charge delocalization for a classical carbonium ion geometry is observed—the extent of this phenomenon is wider than anticipated. For the alkyl carbonium ions it is shown that the order of stabilities may be obtained from a calculation in which the polarity of the C–H bond is C^-–H^+. Protonated ethylene and acetylene show local minima for a symmetrical complex, but with rearrangement to an unsymmetrical cation favored. Protonated cyclopropane prefers an unsymmetrical three-center bonded structure, protonated benzene stabilizes in the familiar benzenium. The orientation of the empty carbonium p orbital with respect to other π-type orbitals determines the conformation in cyclopropyl carbinyl, benzyl, and allyl. The peculiar nature of the cyclopropane electron distribution is studied. The carbonium ions based on the bicyclo[2.2.1]-heptane structure show some nonclassical features; confirming experimental conclusions, the unusual 7-norbornadienyl cation is calculated to prefer an unsymmetrical geometry. Difficulties in applying the extended Hückel theory to charged species make some of the conclusions from the calculations less certain.

THE theoretical literature on carbonium ions is almost exclusively limited to conjugated molecules[1]; the experimental literature on the other hand abounds with speculations regarding positively charged species of every possible variety.[1,2] In part, the more speculative aspects of various structural proposals are due to the fact that the ions are such transitory and elusive entities that only indirect evidence, amenable to many interpretations, is available; in part, they have been almost encouraged by the absence of a guiding theoretical framework. The problem is difficult—carbonium ions are electron-deficient compounds and their structural variety and problems will be similar to the hardly simple boron hydrides.[3]

In this contribution, the extended Hückel theory, described in the first paper of this series,[4] is applied to

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[1] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* (John Wiley & Sons, Inc., New York, 1961), Chap. 12.

[2] (a) *The Transition State*, Special Publication No. 16 (The Chemical Society, London, 1962); (b) Extensive work by S. Winstein and J. D. Roberts and co-workers; see list of references on p. 387 of Ref. 1; (c) J. A. Berson in *Molecular Rearrangements*, edited by P. de Mayo (Interscience Publishers, Inc., New York, 1963), p. 111; (d) F. W. McLafferty, *Mass Spectrometry of Organic Ions* (Academic Press Inc., New York, 1963), Chap. 7.

[3] W. N. Lipscomb, *Boron Hydrides* (W. A. Benjamin, Inc., New York, 1963).

[4] R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963).