Materials. Cyclodextrins (α-CD, β-CD, and γ-CD) were obtained from Hayashibara Biochemical Laboratories Inc. Their purities were checked by elemental analysis and optical rotation. (Arene)tricarbonylchromium complexes were prepared according to the methods described in the literature.[11] Since chromium hexacarbonyl readily sublimes, spiral stainless wire was attached to the motor in the condenser to scratch the chromium carbonyl deposited back to the reaction mixture.

Preparation of Inclusion Compounds. The β-CD–(benzene)tricarbonylchromium inclusion compound was prepared by adding finely ground crystals of (benzene)tricarbonylchromium complex (0.108 g, 0.5 mmol) to an aqueous solution of β-CD (10H_2O adduct, 0.328 g, 0.25 mmol) at 60 °C with stirring. The product was washed with water to remove any remaining CD and dried in vacuo. Nonincluded (benzene)tricarbonylchromium was removed by washing the residue with benzene. The product was recrystallized from water or aqueous alcohol to give pale yellow crystals. β-Cyclodextrin–(benzene)$Cr(CO)_3 \cdot 7H_2O$: mp 235–245 °C dec; IR (Nujol mull) $\nu_{C=O}$ 1960, 1895 cm^{-1}; ^1H NMR (DMSO-d_6, 100 MHz) δ 5.68 (s, 6 H). Anal. Calcd for $C_{51}H_{92}O_{46}Cr$: C, 41.52; H, 6.14. Found: C, 40.97; H, 5.73.

The other inclusion compounds were prepared in a similar way, and their analytical and spectral data are summarized in Tables II and III.

Instrumentation. Infrared spectra were recorded on a Hitachi 295 spectrometer and UV spectra on a Shimadzu UV-202 spectrophotometer. ^1H NMR spectra were run on a JEOL FX100 spectrometer. Circular dichroism spectra were recorded on a JASCO J-205 spectropolarimeter. Thermogravimetric analysis was made by using a Shimadzu DT-30 thermal analyzer. Atomic absorption analysis was made by using a Shimadzu A-610S atomic absorption/flame spectrophotometer.

Table III. Spectral Data of Inclusion Compounds

CD	arene	IR $\nu_{C=O}$ (cm^{-1})	^1H NMR δ, ppm (guest)
β	benzene	1895, 1960	5.5–5.8 (6 H, aromatic)
γ	benzene	1830, 1980	5.6–5.8 (6 H, aromatic)
β	toluene	1900, 1980	2.14 (3 H, methyl), 5.3–5.9 (5 H, aromatic)
γ	toluene	1890, 1975	2.14 (3 H, methyl), 5.4–5.9 (5 H, aromatic)
β	*o*-xylene	1880, 1970	2.14 (6 H, methyl), 5.5–5.8 (4 H, aromatic)
γ	*o*-xylene	1900, 1950	2.14 (6 H, methyl), 5.6–5.8 (4 H, aromatic)
β	*m*-xylene	1895, 1970	2.15 (6 H, methyl), 5.3–6.0 (4 H, aromatic)
γ	*m*-xylene	1900, 1975	2.15 (6 H, methyl), 5.3–6.0 (4 H, aromatic)
β	*p*-xylene	1900, 1975	2.07 (6 H, methyl), 5.3–5.9 (4 H, aromatic)
γ	*p*-xylene	1880, 1975	2.08 (6 H, methyl), 5.6–5.8 (4 H, aromatic)
γ	mesitylene	1875, 1950	2.15 (9 H, methyl), 5.33 (3 H, aromatic)
γ	hexamethylbenzene	1870, 1950	2.20 (18 H, methyl)
γ	methyl benzoate	1900, 1985, 1735	3.84 (3 H, methyl), 5.5–6.2 (5 H, aromatic)

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[11] For preparation, King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, pp 136–139.

Thermochemistry of Borabenzene and Borepin

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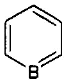
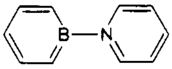
Aspects of the thermochemistry of borabenzene and borepin are studied by means of homodesmic reactions and ab initio 6-31G* SCF energies. Model compounds for these analyses include divinylborane, 3-boraheptatriene, and the pentadienyl and heptatrienyl cations.

I. Introduction

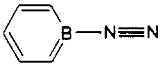
Although the 4*n* + 2 rule is successful in rationalizing the thermodynamic stability of monocyclic π systems,[1] borabenzene and borepin, two relatively simple systems with *n* = 1, still await synthesis. Borabenzene (I) does exist, however, in the form of metal complexes,[2] a pyridine adduct[3] (II, the analogue of biphenyl), the 1-phenylborabenzene anion,[4] and a dinitrogen complex of borabenzene observed at low temperature and presumed to be structure III.[5] Borabenzene adducts whose ligands are attached to boron are probably aromatic.[6]



I



II



III

In the case of borepin (IV), which is isoelectronic with tropylium cation (V), the syntheses of 1-methylborepin[7] and 1-methyl-4,5-cyclopentenoborepin[8] have been reported recently; many aryl and benzoborepins have been known for some time.[9] Ab initio studies show borepin to be

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[1] See, for example: Streitwieser, A., Jr. *Molecular Orbital Theory, for Organic Chemists*; Wiley: New York, 1961.

[2] For a review, see: Herberich, G. E.; Ohst, H. in *Advances In Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: Orlando, FL, 1986; Vol. 25, p 199.

[3] Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644.

[4] Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804.

[5] Maier, G.; Reisenauer, H. P.; Henkelmann, J.; Kliche, C. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 295.

[6] Dewar, M. J. S. in *Progress In Boron Chemistry*; Steinberg, H., McCloesky, A. C., Eds.; Pergamon: Oxford, **1964**.

[7] Nakadaira, Y.; Sato, R.; Sakuri, H. *Chem. Lett.* **1987**, 1451.

[8] Ashe, A. J., III; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879.

[9] Some examples are: (a) Leusink, A. J.; Drenth, W.; Noltes, J. G.; van der Kirk, G. J. M. *Tetrahedron Lett.* **1967**, 1263. (b) Axelrad, G.; Halpern, D. *J. Chem. Soc. D* **1971**, 291. (c) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. (d) Van Tamelen, E. E.; Brieger, G.; Untch, K. G. *Tetrahedron Lett.* **1960**, *8*, 14. (e) Jeffries, A. T., III; Gronowitz, S. *Chem. Scr.* **1973**, *4*, 183. (f) Synthesis of 1-hydroxy-4,5-cyclohexenoborepin is reported by: Halpern, D. F. Ph.D. Thesis, City University of New York, 1971.

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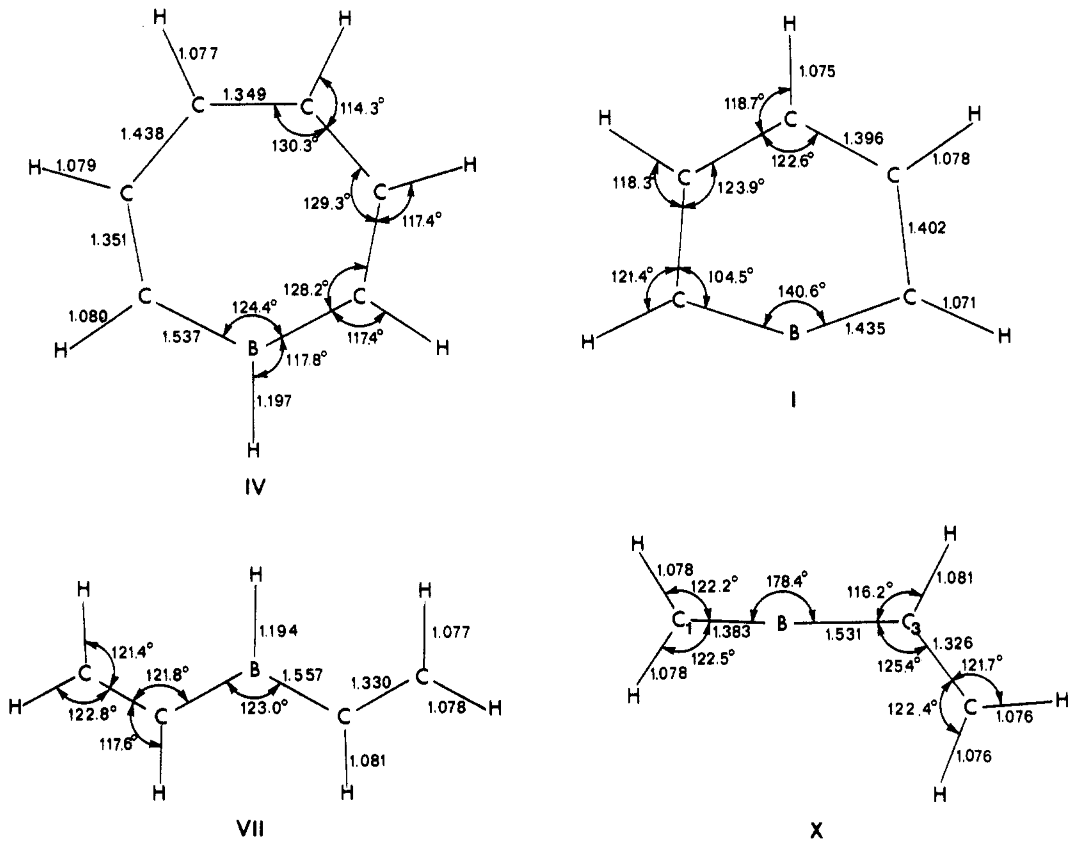
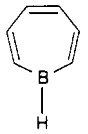
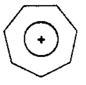
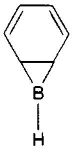
Chart I



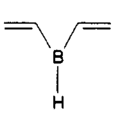
planar and markedly more stable than its valence isomer boranorcaradiene (VI).[10] This suggests that borepin has

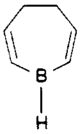

IV

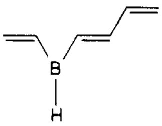

V


VI

some aromatic character, since cycloheptatriene is only ca. 6 kcal/mol more stable than norcaradiene[10b] and is not planar. The aromatic character of borepin is also supported by comparisons of the UV spectra and NMR chemical shifts of substituted borepins with those of appropriate model compounds, e.g., tropone, divinylborane (VII), dihydroborepin (1*H*-boracyclohepta-2,6-diene, VIII), and 3-borahepta-1,4,6-triene (IX).[7-9,11]


VII


VIII


IX

A recent approach to the assessment of aromatic character is the use of so-called empirical resonance energies (ERE's),[12] based upon real rather than hypothetical reference compounds. The ERE's of borabenzene and borepin are calculated here from ab initio 6-31G* SCF

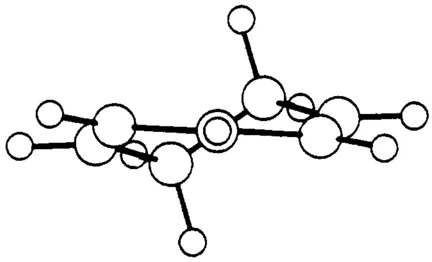


Figure 1. Perspective drawing of dihydroborepin, viewed along its twofold axis.

Table I. B–C Bond Lengths (Å) in the 6-31G* Basis Set

molecule	bond length
dimethylborane	1.581
dihydroborepin	1.558
divinylborane	1.557
3-borahepta-1,4,6-triene	1.560 (B–C_2), 1.557 (B–C_4)
2-borabuta-1,3-diene	1.531 (B–C_3), 1.383 (B–C_1)
borepin	1.537
borabenzene	1.435

energies, in the absence of experimentally determined enthalpies of formation.

II. Methods

The geometries of I, IV–IX, 2-borabuta-1,3-diene (X), pentadienyl cation, heptatrienyl cation, and cyclohexa-1,4-diene were optimized at the 6-31G* SCF level.[13] C_{2v} structures were assumed for borabenzene, borepin, dimethylborane, divinylborane, and the pentadienyl and heptatrienyl cations. The geometry and energy of the pentadienyl cation are essentially the same as those reported recently by Schleyer et al.[14] Divinylborane was

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(10) (a) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 3785. (b) Schulman, J. M.; Disch, R. L.; Sabio, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 7696. (c) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1863.

(11) Allinger, N. L.; Siefert, J. H. *J. Chem. Soc.* **1975**, *97*, 752.

(12) (a) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. W. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.

(13) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, **1986**.

studied in both ditransoid (VII) and cisoid–transoid conformations, which are found to be equienergetic and planar. 3-Boraheptatriene (vinylbutadienylborane, IX) was assumed to be planar. Dihydroborepin (VIII) was optimized in C_2 symmetry (Figure 1). Cyclohexene and cyclohexa-1,4-diene were optimized in C_2 and D_{2h} symmetry, respectively, the minimum-energy conformations found by Saebø and Boggs.[15] The energy of the tropylium cation was computed in D_{7h} symmetry. All geometrical parameters reported in this work were obtained in the 6-31G* basis set. The B–C bond lengths are summarized in Table I; optimized structures for I, IV, VII, and X are given in Chart I.

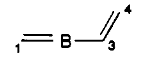
In the computation of the enthalpy changes of homodesmic reactions, small corrections for zero-point energies and thermal effects are neglected.

The perspective drawing was obtained with Chem-X, developed and distributed by Chemical Design, Ltd., Oxford, England.

III. Geometries

Borabenzene STO-3G and 4-31G structures have been reported by Raabe et al.,[16] who showed the C_{2v} structure to be kinetically stable at the 4-31G SCF level. We find a similar geometry in the 6-31G* basis (Chart I). Borabenzene has a large C–B–C angle, 140.6°, and its B–C bond length is 1.435 Å. The electric dipole moment of borabenzene is 0.76 D in the sense C→B.

An acyclic model for borabenzene is 2-borabuta-1,3-diene (X), whose C—B=C and B—C=C bond angles are 178.4° and 125.4°, respectively. The B–C_3 and B–C_1 bond lengths of X, 1.531 and 1.383 Å, bracket the value of 1.435 Å in borabenzene. The molecule has a dipole moment of 1.5 D essentially in the C=B—C direction with the sense C_1→C_3.



X

The planar C_{2v} geometry of borepin at the STO-3G level has been reported previously;[10a] the 6-31G* structure (Chart I) is very similar. The B–C bond lengths are 1.537 Å, while those of the double bonds are 1.349 and 1.351 Å.

Models for borepin that are not cyclically conjugated are divinylborane (3-borapentadiene, VII), dihydroborepin (VIII), and 3-borahepta-1,4,6-triene (IX). The divinylborane moiety of dihydroborepin has a CBCC dihedral angle of 13.7°, reflecting a balance between the planarity of the π system and angle strain at the saturated carbons, which is relieved by ring puckering. Conjugation between boron and the C–C double bond has been discussed for vinylborane,[17] while two interesting examples of homoconjugation are found in boranorbornadiene[10c] and 1,2-dihydroborete.[18] The B–C bond length of dihydroborepin, 1.558 Å, is greater than that of borepin, 1.537 Å; the C–C double bonds of dihydroborepin, 1.332 Å, are shorter than those of borepin, 1.349 and 1.351 Å. Divinylborane has B–C and C–C bond lengths of 1.557 and 1.330 Å, respectively; the B–C bond lengths in IX are 1.560 (B–C_2) and 1.557 Å (B–C_4). The combination of shortened B–C single bonds and lengthened C–C double bonds in borepin, relative to its model compounds VII, VIII, and IX, is consistent with cyclic conjugation. Nonetheless, the decrease in the B–C bond length found for borepin, 0.02 Å, is much smaller than that found in passing from borirane to borirene (0.06 Å).[19] Similarly, the lengthening of the C—C double bonds in passing from dihydroborepin to borepin (ca. 0.02 Å) is significantly smaller than the amount by which the C=C length of borirene exceeds that of cyclopropene (0.06 Å).

Table II. SCF Total Energies in the 6-31G* Basis Set (au)[a,b]

molecule	energy
borabenzene	−216.8638
borepin	−255.9350
tropylium ion	−268.8974
dihydroborepin	−257.0973
2-borabutadiene (optimized)	−141.1135
2-borabutadiene (bent)	−141.0890
3-boraheptatriene	−257.0760
divinylborane	−180.1881
pentadienyl cation	−193.1159
heptatrienyl cation	−270.0246
cyclohexa-1,4-diene	−231.8336
dimethylborane	−104.4925

[a] Tabulated energies correspond to structures optimized at the 6-31G* SCF level. [b] For the energies of ethylene, butadiene, and benzene see ref 21b. The energies of cycloheptatriene, norcaradiene, and boranorcaradiene are given in ref 10b.

Table III. Empirical Resonance Energies (kcal/mol)

molecule	empirical resonance energy
benzene	24.7
borabenzene	19.2
pyridine	25.4
borepin	12.7

The dipole moment of dihydroborepin is 1.9 D, with its positive end pointing away from the boron, is surprisingly similar to that of borepin, 2.0 D in the same sense.

IV. The Aromatic Character of Borabenzene and Borepin

A. Borabenzene. George et al.[12] define the empirical resonance energy of benzene as the enthalpy change of reaction 1,

$$3\,\text{ethylene} + \text{benzene} \rightarrow 3\,\textit{trans}\text{-butadiene} \quad (1)$$

which balances similar structural elements in the σ systems of reactants and products. It is preferable to comparing the heat of perhydrogenation of benzene with 3 times that of cyclohexene, a scheme which ascribes the same strengths to C–C bonds formed from sp^2 and sp^3 hybrids. Benzene ERE values are 24.8[20] and 24.7[21] kcal/mol at the SCF level in the 6-31G*(5D) and 6-31G* basis sets, respectively. The experimental value, which includes zero-point and thermal effects of ca. 0.2 kcal/mol, is 21.2. These same authors point out that were a butadiene having a 90° $C_1C_2C_3C_4$ dihedral angle employed as the reference compound in

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(14) Schleyer, P. v. R.; Bentley, T. W.; Koch, W.; Kos, A. J.; Schwarz, A. *J. Chem. Soc.* **1987**, *109*, 6953.

(15) Saebø, S.; Boggs, J. E. *J. Mol. Struct. (THEOCHEM)* **1981**, *73*, 137.

(16) (a) Raabe, G.; Heyne, E.; Schleker, W.; Fleishhauer, J. *Z. Naturforsch.* **1984**, *A39*, 678. (b) Raabe, G.; Schleker, W.; Heyne, E.; Fleishhauer, J. *Z. Naturforsch.* **1987**, *A42*, 352.

(17) Williams, J. E., Jr.; Streitwieser, A., Jr. *Tetrahedron Lett.* **1973**, 5041.

(18) Cremer, D.; Gauss, J.; Schleyer, P. v. R.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 370.

(19) (a) Budzelaar, P. H. M.; Kraka, E.; Cremer, D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 561. (b) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589. (c) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics*, **1985**, *4*, 429.

(20) George, P.; Bock, C. W.; Trachtman, M. *Tetrahedron Lett.* **1985**, *26*, 5667.

(21) (a) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. (b) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

reaction 1, the calculated ERE would increase by ca. 3 × 7.2 = 22 kcal/mol.[22] However, *trans*-buta-1,3-diene is used here: we measure aromatic character by the further stabilization of the cyclically conjugated system beyond the linearly conjugated reference, with appropriate correction for angle strain. (Strictly speaking, these resonance energies are not empirical in that they are based upon hypothetical strain-free molecules.)

For borabenzene, we employ the reaction

3 ethylene + borabenzene →
2 *trans*-butadiene + 2-borabutadiene (2)
X

The relevant 6-31G* energies are given in Table II and ERE values in Table III. Reaction 2 has a calculated ΔH of 3.8 kcal/mol. This small value is due in part to angle strain at the boron atom, which offsets the effect of aromatic stabilization. Dicoordinate boron prefers a linear C=B—C arrangement, as in X; because of this, the C—B—C angle in borabenzene, 140.6°, is unusually large for a cyclic structure. An equivalent view of the strain energy is that the vacant lone-pair orbital has s character "borrowed" from the bonding B→C hybrids, which are thereby weakened. The s character of this vacant orbital of borabenzene accounts in part for its being a strong Lewis acid, capable of coordinating a nitrogen molecule.

The strain energy of borabenzene can be estimated by computing the energy of a bent form of X in which all parameters are optimized except for the C=B—C angle, which is fixed at the borabenzene value, 140.6°; the energy of X is found to increase by 15.4 kcal/mol. This implies that the ERE of borabenzene should be taken to be 15.4 + 3.8 = 19.2 kcal/mol.

The ERE of borabenzene can be compared with those of other hetero-cyclic benzenes. For pyridine, the reaction

3 ethylene + pyridine →
2 *trans*-butadiene + 2-azabutadiene (3)

furnishes an ERE of 25.4 kcal/mol in the 6-31G*(5D) basis.[20] Thus, benzene and pyridine have comparable empirical resonance energies, while that of borabenzene is ca. 25% smaller. ERE's for other group V and group IV heterobenzenes (without corrections for angle strain) have been determined by Baldridge and Gordon;[23] stannabenzene has the lowest value, 12.2 kcal/mol.

B. Borepin. From the energies of Table II, the ΔH of reaction 4 is 1.6 kcal/mol. A similar ΔH, 1.7 kcal/mol,

borepin + 3 ethylene →
2 *trans*-butadiene + divinylborane (4)

is obtained for reaction 5, in which boron is contained in an array of seven conjugated atoms in both reactants and products. The small enthalpy changes of reactions 4 and

borepin + 2 ethylene →
trans-butadiene + 3-boraheptatriene (5)
IX

5, which compare borepin to essentially unstrained linearly conjugated systems, show that there is little resonance energy in borepin in excess of its strain energy.

In order to obtain the ERE of borepin, the enthalpy changes of reactions 4 and 5 must be corrected for the strain energy of its σ system, whose average internal ring angle is 128.6°. This is a model-dependent problem for which cyclohepta-1,3,5-triene can serve as a point of reference. MMP2 calculations[24] on a cycloheptatriene having a planar carbon framework with alternating C–C bond lengths furnish a σ strain energy of ca. 11 kcal/mol. While this estimate is perhaps slightly low (equivalent to only 1.57 kcal/mol per ring atom), the trigonal boron of borepin is less strained than the saturated carbon of planar cycloheptatriene. The ERE of borepin is then estimated to be 12.7 kcal/mol, from the strain energy and the enthalpy changes of (4) and (5).

The heats of hydrogenation of linearly conjugated olefinic double bonds are in the range −15 to −25 kcal/mol,[25] depending upon factors such as strain and retention of conjugation in the product; because of its large resonance stabilization, the experimental heat of hydrogenation of benzene to cyclohexadiene is +5.6 kcal/mol.[26] Consider the following hydrogen-transfer reaction between benzene and borepin:

benzene + dihydroborepin →
cyclohexadiene + borepin (6)

(The choice of 1,3- or 1,4-cyclohexadiene is immaterial, since experiment[25] and calculation[15] show them to be nearly equienergetic.) From the calculated ΔH of reaction 6, 20.0 kcal/mol, and the experimental hydrogenation energy of benzene, we obtain the value 5.6 − 20.0 = −14.4 kcal/mol for the monohydrogenation energy of borepin. Alternatively, using the group-equivalent scheme developed by Ibrahim et al.[27] to obtain hydrogenation energies from the ab initio SCF energies of an olefin and its hydrogenated product, we obtain the value −10.9 kcal/mol. The agreement with the value of −14.4 kcal/mol is reasonable, since the group-equivalent method evidently gives hydrogenation energies for aromatics which are algebraically too large, e.g., by 3.5 kcal/mol in the case of benzene. Borepin, then, is predicted to resemble other conjugated olefins in having a negative heat of monohydrogenation, with a value at the algebraically high end of the range. The hydrogenation energy of borepin, −14.4 kcal/mol, is essentially the same as that of cycloheptatriene to cyclohepta-1,4-diene.[25]

The ΔH of 1.6 kcal/mol for reaction 4 can be compared with that of reaction 7 for the tropylium ion.

tropylium cation + 3 ethylene →
2 *trans*-butadiene + pentadienyl cation (7)

Use of the energies given in Table II furnishes 23.3 kcal/mol; the experimental value, calculated from the heats of formation of the tropylium[28a] and pentadienyl[28b] cations, is 24.7 kcal/mol.

An alternative model reaction for the tropylium cation is (8), the analogue of (5), which uses a linear cationic chain of seven carbon atoms. The ΔH of (8) is calculated to be

tropylium cation + 2 ethylene →
trans-butadiene + heptadienyl cation (8)

10.4 kcal/mol, substantially lower than that of (7), presumably due to a greater degree of delocalization of the positive charge. It is not clear whether reaction 7 or 8 furnishes the best model for electron delocalization in the

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[22] George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 1357.

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tropylium cation: if its positive charge resides on both carbon and hydrogen, reactions 7 and 8 are limiting cases, heptatrienyl and pentadienyl cations having seven carbons and seven hydrogens, respectively. In any event, the values of ΔH for reactions 7 and 8 are both substantially greater than their analogues for borepin (reactions 4 and 5), 1.6 and 1.7 kcal/mol, respectively. Moreover, since borepin and tropylium cation should have similar strain energies, the differences in ΔH (reactions 4 and 5 versus reactions 7 and 8) can be equated to differences in their ERE's.

We have commented upon the fact that borepin is much more stable than boranorcaradiene, while cycloheptatriene is only ca. 6 kcal/mol more stable than norcaradiene; e.g., the reaction

$$\text{norcaradiene} + \text{borepin} \rightarrow \text{cycloheptatriene} + \text{boranorcaradiene} \quad (9)$$

has a ΔH of 32.7 kcal/mol. The endothermicity of reaction 9 arises in part from the fact that the strain energy of boranorcaradiene exceeds that of norcaradiene due to the presence of an sp^2 boron in a three-membered ring. This strain effect can be estimated from ΔH for the reaction

$$\text{norcaradiene} + \text{dimethylborane} \rightarrow \text{boranorcaradiene} + \text{propane} \quad (10)$$

whose value, 17.3 kcal/mol, accounts for more than half of the endothermicity of reaction 9. The remainder can be ascribed to the relative resonance and strain energies of borepin and cycloheptatriene.

V. Conclusion

The substantial resonance energies of borabenzene and pyridine confirm that the presence of a heteroatom in the π system does not preclude a large resonance stabilization. On the other hand, the smaller borepin ERE value, together with comparisons of its monohydrogenation energy with those of benzene and cycloheptatriene, show that the $4n + 2$ rule does not per se lead to large amounts of resonance and thermodynamic stabilization. One further illustration of these points is perhaps worthwhile. The reaction

$$\text{borirene} + \text{dihydroborepin} \rightarrow \text{borirane} + \text{borepin}$$

is nearly thermoneutral ($\Delta H = 1.6$ kcal/mol). Judging from the relative strain energies of cyclopropene and cyclopropane, the strain energy of borirene exceeds that of borirane by ca. 25 kcal/mol; it is certainly much more than the amount by which the strain energy of borepin exceeds that of dihydroborepin. Thus, borirene must have a large resonance energy; it has been estimated to be 47.5 kcal/mol.[19] Even when account is taken of the fact that the ERE of borepin (12.7 kcal/mol) is referred to linearly conjugated reference molecules,[29] while that of borirene is referred to cyclopropene, the ERE of borirene is still much larger than that of borepin, although both are $4n + 2$ systems.

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[29] Twisting the vinyl groups of divinylborane out of plane by 90° increases the total energy by 13.8 kcal/mol.