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ORGANOBORON COMPOUNDS

CCCXVIII. ON THE PROBLEM OF THE AROMATIC CHARACTER OF BORON HETEROCYCLIC COMPOUNDS

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Summary

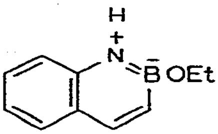
The ability of boron heterocyclic compounds to form salts was studied. 10-Hydroxy-10,9-borazarophenanthrene and 10-hydroxy-10,9-boroxarophenanthrene were found to have no qualitative difference in the formation of salts and both these compounds can behave as protonic and Lewis acids. ^{11}B NMR spectroscopy data of heterocyclic boron compounds with B—N and B—O bonds are discussed and the non-aromaticity of these compounds is shown.

Results and discussion

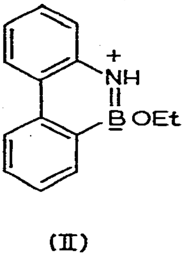
One of the most interesting problems of pure chemistry is the character of the chemical bond between boron atoms and elements containing unshared electron pairs. Coordination interaction is theoretically possible in boron compounds containing B—N, B—O, B—S and B—Hal bonds, due to the vacant *p*-orbital of boron and the *p*-electrons of the heteroatom. With complete electron transfer, the specific double bond may be formed by superposition of a π-coordination bond on a δ-bond. For boron—nitrogen compounds this is represented by the following structural formula: $>\bar{\mathrm{B}}=\overset{+}{\mathrm{N}}<$. The coordination bond may be depicted with an arrow when only partial delocalization of the unshared electron pair takes place: $>\mathrm{B}\overset{\leftarrow}{-}\mathrm{N}<$. The arrow here represents a specific donor—acceptor interaction between the π-electron donor and the *p*-orbital of boron. This is contrary to the usual complex compounds of trivalent boron; where an arrow represents a dative bond, which is formed by the sp^3-orbital of boron and the donor electrons occupying sp^3-hybridized orbitals.

The nature of the chemical bond between boron and a heteroatom has long been attracting the attention of chemists, who attempt to throw some light on the problem by studying boron—nitrogen compounds with the help of physical methods of investigation. The B—N bond in boron—nitrogen compounds is considered to be only of a partial double bond character, and therefore is usually depicted as an ordinary covalent bond [1,2,3]: $\geq$B—N$\leq$. Boron—nitrogen and boron—oxygen heterocyclic compounds are of interest in connection with the problem of the character of the boron—element bond. Dewar [4,5] considers B—N and B—O bonds in these compounds as double bonds forming an aromatic system in which $\geq\bar{B}=\overset{+}{N}\leq$ $\geq\bar{B}=\overset{+}{O}\leq$ fragments are analogous to the $\geq$C=C$\leq$ fragment. According to Dewar, the physical and chemical properties of various types of heterocyclic compounds confirm this suggestion.

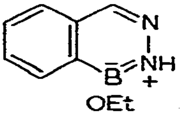
First of all, the arguments of Dewar et al. [6] should be considered on the basis of the NMR spectra of the heterocyclic boron compounds I—VIII which are represented as bipolar "aromatic" structures.



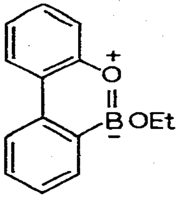
(I)
δ -29.7 ppm



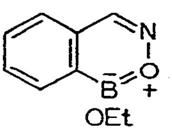
(II)
δ -26.3 ppm



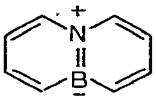
(III)
δ -30.0 ppm



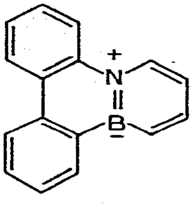
(IV)
δ -28.8 ppm



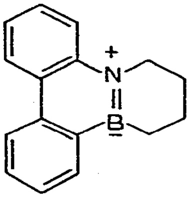
(V)
δ -30.0 ppm



(VI)
δ -28.4 ppm



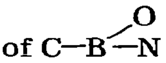
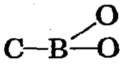
(VII)
δ -31.0 ppm

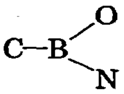
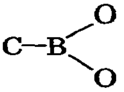


(VIII)
δ -38.1 ppm

The authors note that the chemical shifts of ^{11}B in boron—nitrogen heterocycles containing ethoxy groups at the boron atom (I, δ —29.7 ppm; II, δ —29.3 ppm and III, δ —30.0 ppm) are very close to those in the corresponding boron—oxygen compounds (IV, δ —28.8 ppm and V, δ —30.0 ppm), whereas acyclic boron—nitrogen and boron—oxygen compounds considerably differ in the degree of shielding. Thus, the chemical shifts of $C_6H_5B(NMe)_2$ and $C_6H_5B(OMe)_2$ are δ —32.4 and —28.6 ppm, respectively, while the chemical shifts of $B(NMe)_3$ and

$B(OMe)_3$ differ to an even greater extent (δ —27.1 and —18.2 ppm, respectively). This is considered as evidence of the aromaticity of boron heterocyclic compounds I—V, since resonance stabilization of molecules annihilates any differences in specific structural features of the compounds under study.

We think, however, that this argumentation is inconclusive, since it is well known that similar boron compounds have almost the same values of ^{11}B chemical shifts. One should also take into account that the nature of the substituent considerably affects the degree of shielding of the boron atom. So the fact that the ^{11}B chemical shifts of $B(NMe)_3$ differ significantly from those of $B(OMe)_3$ does not imply that compounds containing systems of  $\mathrm{C{-}\overset{O}{B}{-}N}$ (I—III) and  $\mathrm{C{-}\overset{O}{B}{-}O}$ (IV and V) should differ greatly in the degree of screening.

Compounds I—III should be compared with acyclic compounds containing  $\mathrm{C{-}B}\begin{smallmatrix}\mathrm{O}\\ \mathrm{N}\end{smallmatrix}$ bonds, for instance, with methoxydimethylaminomethylborane or with methoxydimethylaminoethylborane. These compounds have equal chemical shifts of ^{11}B (δ —31.8 ppm) [7], i.e. are very close to the chemical shifts in compounds I—III. Similarly, the ^{11}B chemical shifts of the cyclic compounds IV—V do not differ considerably from the chemical shifts of acyclic compounds with a  $\mathrm{C{-}B}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}$ group, namely, phenylboric acid (δ —28.4 ppm) and its diethyl ester (δ —28.6 ppm) [7]. At the same time, structurally similar heterocyclic compounds VI, VII and VIII containing B—N bonds in key positions should exhibit equal "aromaticity", but their chemical shifts differ considerably (δ —28.4, —31.0 and —38.1 ppm, respectively) [6]. A significant up-field shift of ^{11}B signals should be observed if compounds I—VIII had the dipolar structure that they are attributed with. It is known that coordination of trivalent boron compounds with a nitrogen ligand sharply increases the screening of boron atom. Thus, the chemical shifts of $C_2H_5NH_2 \cdot B(OC_2H_5)_3$, $N(CH_2CH_2O)_3B$ and $(CH_3)_3N \cdot B(CH_3)_3$ are δ —13.7, —10.7 and +13.7 ppm, respectively. In tetravalent compounds of negatively charged boron the chemical shifts of ^{11}B are in the higher field region; $NaB(OMe)_4$ δ —2.5, $LiB(NCH_3)_4$ —0.2 and $[C_6H_5B(OH)_3]K$ —3.15 ppm [6,7].

It follows from the above that the results of ^{11}B NMR spectroscopy do not confirm the dipolar aromatic structure of the compounds under study; on the contrary, they unambiguously show the absence of resonance stabilization and the similarity of B—N (B—O) bonds in these compounds as well as in boron acyclic compounds.

The second of Dewar's arguments to prove the aromaticity of boron heterocyclic compounds is based on the UV and ^{11}B NMR spectroscopic study of salt formation. Organoboron acids and their esters act as Lewis acids in reactions with bases to form salts of the borate type [8—13];

$$RB(OR')_2 + R'O^- \rightarrow [RB(OR')_3]^- \qquad (1)$$

$$R_2BOH + OH^- \rightarrow [R_2B(OH)_2]^- \qquad (2)$$

$$RB(OH)_2 + OH^- \rightarrow [RB(OH)_3]^- \qquad (3)$$

With organolithium compounds in inert solvents they react as protonic acids [14]:

$$R_2BOH + LiR' \rightarrow R_2BOLi + R'H \qquad (4)$$

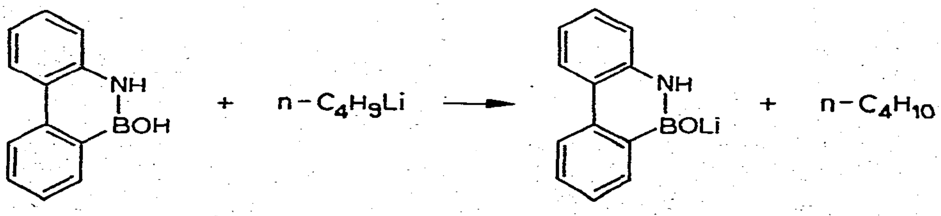
Proceeding from the identity of UV spectra, in alcohol and alcohol/alkaline solutions, of 10-hydroxy-10,9-borazarophenanthrene (IX) [15], 10-hydroxy-10,9-boroxarophenanthrene (XII) [16] and 4-hydroxy-4,3-boroxaroisoquinoline (V) [17] (OH instead of OEt), these compounds were assumed to react as protonic acids with alkalis. The difference in behavior of organoboron (eq. 2, 3) and the mentioned heterocyclic acids towards alkalis was explained by the aromaticity of the boron-containing cyclic compound which inhibits conversion of the trigonal configuration of the boron atom into the tetrahedral one.

It was thought that comparison of ^{11}B chemical shifts in neutral and alkaline media using ^{11}B NMR spectroscopy would establish the true nature of salt formation of boron heterocyclic compounds. The chemical shifts of 2-hydroxy-2,1-borazaronaphthalene (I, Et = H, δ —29.7 ppm), 4-hydroxy-4,3-borazaroisoquinoline (III, Et = H, δ —29.8 ppm) and 10-hydroxy-10,9-borazarophenanthrene (IX, δ —29.3 ppm) in 20% alcohol solution of potassium hydroxide are not displaced towards the high-field region as would be expected if these compounds acted as Lewis acids, but are observed at lowest field (δ —33.0, —33.2 and —43.9 ppm, respectively) [18]. These data were considered as evidence of the aromatic stabilization of boron-containing cyclic compounds which form salts by losing a proton, the chemical shifts of these salts being in the lower field as compared with the initial acids.

The same method applied to 4-hydroxy-4,3-boroxaroisoquinoline (V, Et = H, δ —30.0 ppm) [18] and 10-hydroxy-10,9-boroxarophenanthrene (XII, δ 28.8 ppm) [19] showed the formation of Lewis-type salts of these compounds (δ —5.0 and —5.5 ppm respectively) in 20% alcohol solution of potassium hydroxide. 6-Nitro-10-hydroxy-10,9-borazarophenanthrene (δ —36.9 ppm) and 8-nitro-10-hydroxy-10,9-borozarophenanthrene (δ —41.0 ppm) act as Lewis acids in tetrahydrofuran or dimethylsulphoxide solution containing 5% sodium hydroxide (δ —12.5 and —21.8 ppm respectively).

The statement by Dewar and Jones [18] that 10-hydroxy-10,9-borazarophenanthrene (IX) in an alcohol solution of KOH forms trigonal salts seems to be experimentally unfounded, since salts of this type, as we noted previously [14], exist only in anhydrous media, i.e. are hydrolytically unstable. To solve this question we have undertaken systematic study of the ability of compound IX to form salts. Along with IX, 10-hydroxy-10,9-boroxarophenanthrene was also studied.

The trigonal lithium salt of 10-hydroxy-10,9-borazarophenanthrene (X) was first obtained by treating IX with n-butyllithium in benzene solution. The salt was isolated and its properties studied.



(IX) (X)

TABLE 1

CHEMICAL SHIFT VALUES FOR ^{11}B IN COMPOUNDS IX, X AND XI

Compound	Temperature (°C)	Solvent	Chemical shift δ (ppm)	Width of signal (Hz)	Instrument
10-Hydroxy-10,9-borazarophenanthrene (IX)	20	C_2H_5OH	—28.0	220	A
	31.5	C_2H_5OH	—27.8	540	C
	33.5	CH_3OH	—28.0	210	C
	25	C_2H_5OH	—28.7	710	B
	20	DMFA	—28.0	370	A
	60	C_2H_5OH	—28.1	400	A
	80	C_2H_5OH	—28.1	280	A
X	20	CH_3OH	—19.7	860	B
	80	C_2H_5OH	—20.0	600	A
XI	20	CH_3OH	—2.9	350	A
	20	C_2H_5OH	—2.6	240	A
	33.5	CH_3OH	—4.3	214	C
	20	DMSO	—1.7	375	B
	20	HMP	—1.7	500	B
IX	90	H_2O + 20% KOH	—29.5	710	B
IX	80	C_2H_5OH + 20% KOH	—27.0	600	A
IX	90	H_2O + 10% KOH	—28.7	417	B
IX [a]	80	H_2O	—2.5	67	A
IX [b]	25	C_2H_5OH	—29.3	221	[6]
	25	C_2H_5OH + 20% KOH	—43.9	>2500	[18]

[a] After heating with 20% KOH at 110—120°C. [b] According to Dewar.

Salt X, similar to salts of borinic acids [14], is stable only in a dry atmosphere and is readily hydrolyzed in water-containing solvents. The chemical shift of ^{11}B in X in methanol solution at 20°C is δ —19.7 ppm whereas that of IX varies from δ —27.8 to —28.7 ppm depending on the solvent, temperature and type of spectrometer (Table 1).

Although the ^{11}B chemical shift of IX in 20% ethanol solution of potassium hydroxide was reported in [18] to be equal to δ —43.9 ppm, at width signal of 2500 Hz, our measurements showed it to be δ —27.0 ppm at a signal width of 600 Hz, thus indicating that IX does not form trigonal salts in alkaline/alcohol solutions.

Further, we investigated the behavior of IX towards alkalis in aqueous solution. It was found that IX does not react with aqueous solutions of LiOH or KOH at room temperature. When heated to 80—90°C for 5—15 min the acid dissolves; after cooling it precipitates in the initial form. Heating IX at 100—120°C for 30—40 min leads to partial decomposition of the acid with B—N bond breaking (elemental analysis and IR spectroscopic data).

Although IX is a weak acid with respect to hydrolysis of alkali metals, it is able to form tetrahedral (Lewis) type salts with tetramethylammonium hydroxide. XI was isolated from benzene/methanol solution in a pure state. The

TABLE 2

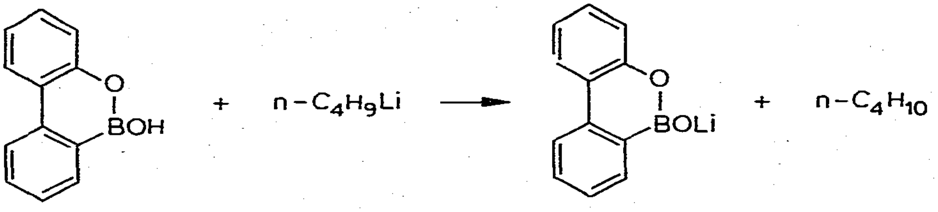
CHEMICAL SHIFT VALUES FOR ^{11}B IN COMPOUNDS XII, XIII AND XIV

Compound	Temperature (°C)	Solvent	Chemical shift δ (ppm)	Width of signal (Hz)	Instrument
10-Hydroxy-10,9-boroxarophenanthrene (XII)	20	C_2H_5OH	—30.0	240	A [a]
	60	DMSO	—30.5	585	A
	110	diglyme	—26.2	140	A
XIII	60	DMSO	—27.7	520	A
	80	DMSO	—28.8	390	A
	100	DMSO	—28.7	560	A
XIV (· $3H_2O$), M = Li	20	CH_3OH	—4.2	105	B [b]
	20	H_2O	—4.5	140	C [c]
	20	DMSO	—5.0	417	B
	60	C_2H_5OH	—3.8	180	A
	100	diglyme	—4.1	160	A
XIV (· H_2O), M = K	20	C_2H_5OH	—2.9	270	A
	80	diglyme	—2.9	170	A
	120	diglyme	—3.5	170	A
XIV, M = $N(CH_3)_4$	60	C_2H_5OH	—5.2	260	A
	80	C_2H_5OH	—5.4	165	A
XII	25	C_2H_5OH	—28.8	233	[6]
XIV [d], M = K	25	C_2H_5OH + 5% KOH	—5.5	162	[6]

[a] RS-56 SCB IOCh spectrometer. [b] Brüker HX-90. [c] Varian HA-100 D. [d] According to Dewar.

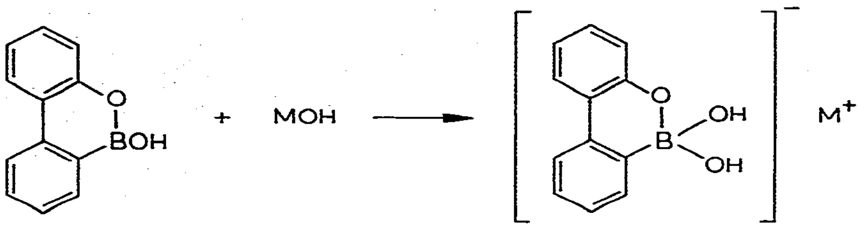
chemical shift of XI varies from δ —1.7 to 4.3 ppm, depending on the solvent and the type of spectrometer (Table 1). XI is easily hydrolyzed to form the initial IX. IX does not form salts with ammonium hydroxide. Thus the ability of IX to form salts of the tetrahydral (borate) type depends on the nature of the cation.

10-Hydroxy-10,9-boroxarophenanthrene (XII) reacts with n-butyllithium in benzene solution to yield a trigonal-type lithium salt XIII. The chemical shift of XIII in DMSO is slightly displaced towards higher field (δ —27.7 ppm) as compared with the acid (δ —30.5 ppm) (Table 2). XIII is very sensitive to traces of



(XII) (XIII)

water and is easily converted to Lewis-type salts. XII is a stronger acid than IX with respect to hydroxides of alkali metals, forming Lewis-type salts (XIV) in aqueous solutions.



(XII) M = Li,K,$(CH_3)_4N$ (XIV)

Lithium, potassium and tetramethylammonium salts were isolated in the pure state. The lithium salt crystallizes from aqueous solutions in the form of colourless crystals and contains three molecules of water in its composition. When heated in a vacuum at 50—70°C for 8 h the salt converts into a monohydrate. The potassium salt crystallizes from water in the form of a monohydrate. The ^{11}B chemical shifts of XIV are in the high-field region (Table 2).

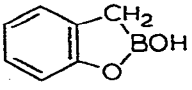
The greater ability of XII to form complexes as compared to IX can not be explained by the fact that the boron—oxygen compound is less aromatic than the boron—nitrogen one [19], since ^{11}B NMR spectra showed that both these compounds are not aromatic. Thus, the greater ability to form complexes must be due to other reasons. We suggest that the high Lewis acidity of XII is explained by the fact that the oxygen-containing compound is more readily distorted during salt formation due to an increase of $\angle COB$ which in turn leads to a decrease of $\angle CBO$ and thus favours the transition of the boron atom from a trigonal to a tetrahedral valent state. It is known that in certain oxygen compounds, for instance, in di-*p*-bromophenyl ether, $\angle COC$ is 123°, whereas in ammonia derivatives $\angle CNC$ never reaches such a value. Heterocyclic boron compounds are usually more stable to hydrolysis than acyclic nitrogen- and oxygen-containing compounds. This is explained by resonance stabilization and "aromaticity" of the boron-containing cyclic compounds [4].

In accordance with the fore-mentioned "aromaticity" of boron-containing cyclic compounds, other reasons for their chemical properties should be found. One can assume that the relative stability of boron heterocyclic compounds can be explained by the larger angles of the heteroatom bonds in the cyclic compounds (in accordance with the geometry of penta- and hexa-gons) in comparison with bond angles of nitrogen or oxygen atoms in acyclic boron compounds. Naturally, any bond angles in the cyclic compound may be distorted, but the increasing inner angle of the nitrogen (oxygen) atoms will be greater.

An increase of this angle means an increase in the *s*-character of the nitrogen (oxygen) atomic orbitals towards the adjacent atoms of the cyclic compound which leads to a more complete overlapping of the orbitals and thus increases the energy of the B—N (B—O) bond. The effect of the increase of the *s*-character on the strength of B—element bonds may be estimated from the mean values of dissociation energy of boron—carbon bonds in trimethylborane and triphenylborane; which are 88.1 and 106.0 kcal/mol respectively [21]. In our case the dissociation energy increased by 18 kcal/mol from the $C(sp^3)$—B bond to the $C(sp^2)$—B bond. This difference between dissociation energies cannot be accounted for by the increase in the π-order of the boron—carbon bond in $(C_6H_5)_3B$ since the study of rotation barriers around the boron—carbon bond in diarylboranes has shown that π-bonding is insignificant [22] and cannot essentially affect the parameters of the B—C bond.

Modification of the s-character of the orbitals in a boron-containing cyclic compound is naturally not so great as in the above-mentioned example but can lead to considerable changes in the energies of B—element bonds, which is exhibited in the relative chemical stability of heterocyclic boron compounds. According to the picturesque expression [23] "Slight hybridization leads to serious consequences".

It should be noted that many organoboron heterocyclic compounds which, due to specific structural features cannot be considered "aromatic" are chemically quite stable, for instance, benzo-1,2-oxaboralane (XV), ("boronophtalide")



(XV)

synthesized and studied by Snyder [24,25]. This compound does not oxidize in air, is not changed by treating with SeO_2, does not hydrolyze when boiled with 10% hydrochloric acid for 3 h and withstands boiling with 15% aqueous solution of potassium hydroxide for 3 h. XV is nitrated in the *meta*-position by nitric acid without "deboronation". Thus, this compound is as stable as 10-hydroxy-borazarophenanthrene or -borazaronaphthalene.

Experimental

The initial 10-hydroxy-10,9-borazarophenanthrene (IX) and 10-hydroxy-10,9-boroxarophenanthrene (XII) were obtained according to [15,16]. The compounds were identified by melting points, analysis, IR and ^{11}B NMR spectra. ^{11}B NMR spectra were recorded on a RS-56 SKV IOH (Akad. Nauk SSSR) (A), frequency 19.06 MHz; on a Brüker HX-90 (B), frequency 28.89 MHz and on a Varian HA-100 D (C), frequency 32.08 MHz. The chemical shifts are presented in δ (ppm), external standard was boron trifluoride etherate. The width of the lines was measured at half-height of the signal. IR spectra were recorded on a UR-10 absorption spectrograph, solid samples were recorded in pressed disks with KBr.

Lithium salt of 10-hydroxy-10,9-borazarophenanthrene (X)

9 ml (0.01 mol) of benzene solution of n-butyllithium were added to a hot solution of 1.95 g of IX in 20 ml of absolute benzene in an atmosphere of dry nitrogen. A voluminous precipitate was immediately formed. It was filtered, washed with benzene and placed in a vacuum at 20°C until constant weight was attained. Yield 1.27 g (65%). Found: C, 71.45; H, 4.31; B, 5.11; Li, 3.26. $C_{12}H_9NOLi$ calcd.: C, 71.72; H, 4.51; B, 5.38; Li, 3.45%. The salt dissolves in methanol, dimethylformamide (DMFA) and dimethylsulphoxide (DMSO) and is easily hydrolized.

Tetramethylammonium 10,10-dihydroxy-10,9-borazarophenanthrene (XI)

32.4 ml (0.005 mol) of a freshly prepared benzene/methanol solution of

$(CH_3)_4NOH$, obtained according to [26], were added in a nitrogen atmosphere at 20° C to 0.98 g (0.005 mol) of IX. While adding the base, a transparent, slightly fluorescent solution was formed. The solvents were distilled for 1 h in the vacuum of a water-jet pump, the residue was washed with absolute benzene and placed in a vacuum at 20° C until constant weight was reached. Yield 1.4 g of XI (99%). Found: C, 66.85; H, 8.58; B, 3.66. $C_{16}H_{23}BN_2O_2$ calcd.: C, 67.15; H, 8.10; B, 3.78%. The substance is easily dissolved in methanol, DMFA, DMSO and hexamethapol (HMP); it does not dissolve in benzene. The salt does not change after exposure to air for 24 h.

Hydrolysis of XI. 1.4 g of XI were agitated with 25 ml of distilled water at 20° C for 30 min. The white precipitate was filtered, washed with water and dried under vacuum. 1.3 g of 10-hydroxy-10,9-borazarophenanthrene were obtained, identified by analysis and IR spectrum.

Interaction of alcohol and aqueous solutions of alkalis with 10-hydroxy-10,9-borazarophenanthrene

(a) 0.47 g (0.025 mol) of IX were dissolved in 1 ml of freshly prepared 20% KOH solution in absolute ethanol and the ^{11}B NMR spectrum was immediately measured at 20 and 80° C (Table 1). The solution darkened after the spectrum had been recorded. In 1.5 h the alcohol solution was diluted with 10 ml of water; at pH 11.0 the solution became turbid. It was then acidified with HCl up to pH 7.0, the precipitate was filtered, thoroughly washed with water and dried. 0.4 g of initial IX was obtained.

(b) 14 ml of 20% aqueous solution of KOH (0.05 mol) were added to 0.95 g (0.005 mol) of IX. The precipitate did not dissolve during 2 h at 20° C. A yellow solution was obtained after heating the mixture for 30 min on a water bath (85—90° C). After cooling a precipitate appeared, it was filtered, washed with water and dried. 0.9 g of unconverted IX was obtained.

(c) To measure the ^{11}B NMR spectra, 0.5 g of IX and 2 ml of 10% aqueous solution of LiOH were taken. The substance only partially dissolved even when heated.

Lithium salt of 10-hydroxy-10,9-boroxarophenanthrene (XIII)

7.5 ml of benzene solution of n-butyllithium (0.67 g, 0.011 mol) were added to a hot solution of XII (1.96 g, 0.01 mol) in 15 ml of absolute benzene in a nitrogen atmosphere. A light white precipitate was formed immediately. It was filtered, washed with benzene and placed in vacuum until constant weight was reached. The yield of XIII was 2.03 g (99%). Found: C, 71.26; H, 4.62; B, 5.05; Li, 3.24. $C_{12}H_8BO_2Li$ calcd.: C, 71.29; H, 3.96; B, 5.44; Li, 3.45%. The salt dissolves in DMSO, DMFA, methanol and ethanol, slowly dissolved in hexametapol forming a viscous solution; does not dissolve in diglyme, dimethoxyethane and benzene at 20° C. XIII easily hydrolyzes in air to give XIV.

Lithium 10, 10-dihydroxy-10,9-boroxarophenanthrene (XIV, $M = Li$)

11.5 ml of 0.9 *N* aqueous solution of LiOH were added to a hot solution of XII (2 g) in 15 ml of benzene and stirred for 10 min. Two transparent layers were formed. After cooling and separating the layers, the aqueous one was concentrated to 3 ml at 30° C 10 mmHg. XIV crystallized in the form of a trihydrate from the cooled solution. Yield 2.15 g (78%), m.p. 63—64° C. Found: C, 52.54; H, 5.84; B, 3.91; Li, 2.51. $C_{12}H_{10}BO_3Li \cdot 3H_2O$ calcd.: C, 52.60; H, 5.89; B, 3.95; Li, 2.53%. The salt was heated in 10 mmHg vacuum for 3 h at 52—55° C, then for 5.5 h at 70° C until constant weight was reached. 1.8 g of XIV monohydrate was obtained. The last molecule of water was not eliminated in these conditions. Found: C, 60.09; H, 5.02; B, 4.72; Li, 3.03. $C_{12}H_{10}BO_3Li \cdot H_2O$ calcd.: C, 60.55; H, 5.08; B, 4.55; Li, 2.92%. The salt is readily soluble in water, alcohol, DMSO, DMFA; in diglyme when heated but not at all in ether and benzene.

Potassium 10, 10-dihydroxy-10,9-boroxarophenanthrene (XIV, M = K)

6 ml of 1 *N* aqueous KOH (0.005 mol) were added to 1 g of XII at 20° C. A transparent colourless solution was formed. The water was distilled in the vacuum of a water-jet pump to the volume of 1.5—2 ml, after cooling crystals were separated. Yield 1.4 g (96%), m.p. 93—95° C. Found: C, 53.37; H, 4.34; B, 4.11; K, 14.84. $C_{12}H_{10}BO_3K \cdot H_2O$ calcd.: C, 53.35; H, 4.48; B, 4.00; K, 14.47%. The salt readily dissolves in water and alcohol, in diglyme when heated; but not in ether and benzene.

Tetramethylammonium 10, 10-dihydroxy-10,9-boroxarophenanthrene (XIV, M = N(CH₃)₄)

31 ml (0.43 g) of a benzene/methanol solution of $(CH_3)_4NOH$ were added to 1 g of XII. The solvents were distilled from the transparent solution in the vacuum of a water-jet pump. The residue was washed with benzene and placed in vacuum until constant weight was reached. 1.42 g (99%) of colourless crystalline XIV (M = $N(CH_3)_4$) was obtained, m.p. 82—84° C. Found: C, 65.64; H, 8.31; B, 3.33; N, 4.86. $C_{16}H_{22}BNO_3$ calcd.: C, 66.92; H, 7.72; B, 3.77; N, 4.88%. The salt readily dissolves in water, alcohol, acetone, DMSO, sparingly dissolves in ether and benzene but does not dissolve in petroleum ether.

Conclusions

1. Data of ^{11}B NMR spectroscopy demonstrate that heterocyclic boron compounds with B—N or B—O bonds do not possess aromaticity. Thus depicting them as dipolar structures is unjustified.
2. The salt-forming ability of boron heterocyclic compounds does not confirm their aromatic structure. The ability of 10-hydroxy-10,9-borazarophenanthrene and 10-hydroxy-10,9-boroxarophenanthrene to form salts does not differ qualitatively. Both these compounds can behave as protonic and as Lewis acids.
3. The relative hydrolitic stability of boron heterocyclic compounds is explained not by their aromaticity but by the strengthening of B—N (B—O) bonds due to rehydridisation of the heteroatom orbitals.

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