CYCLIC FOUR-COORDINATE BORON COMPOUNDS FROM 5-AMINO-1,2,4-TRIAZOLE AND AROMATIC NITRILES

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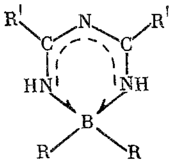
Amidines and α-aminoheterocycles (AH) are readily borylated by organoboranes [1-6]. The products obtained are characterized by their high reactivity and may be used for the synthesis of chelate type boron-containing cyclic systems. Thus borylated amidines and 2-aminothiazole are added to nitriles to form the corresponding mono- and bicyclic compounds I and II [1, 2, 6]. Although not reacting with nitriles, dialkylboryl derivatives of 2-aminopyridine were converted to chelates III by the action of formamide [7].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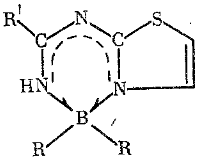
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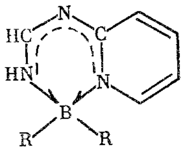
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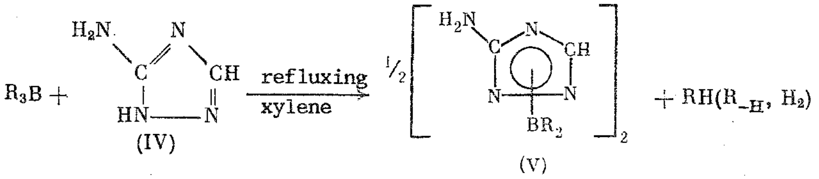
We report now the synthesis of novel compounds of four coordinate boron from 5-amino-1,2,4-triazole (IV), aromatic nitriles, and trialkylboranes.

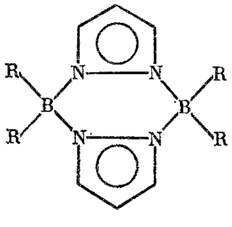
IV reacted readily with excess R_3B (R = Pr, Bu) in refluxing xylene to give dimeric compounds V in which the R_2B groups were connected to the ring N atoms. Thus IV behaves similarly to pyrazole also being borylated at the ring to form the stable dimers VI (also called pyrazaboles [8]). This distinguishes IV from the AH series (2-aminopyridine, 2-aminopyrimidine, and 2-aminothiazole) in which the R_2B diorganoboryl group is bound to the exocyclic N atom [3-6].



R = Pr(Va), Bu(Vb).

Crystalline V were readily soluble in THF and moderately in DMSO, $CHCl_3$, and hot benzene. Analogously to pyrazaboles (VI) they were stable in air and not decomposed by water.

Compounds V turn out to be a mixture of the isomers VII and VIII with the former predominating (∿85%), the PMR ring signal (CH) for VII being at lower field (8.04 ppm for VII and 7.96 ppm for VIII)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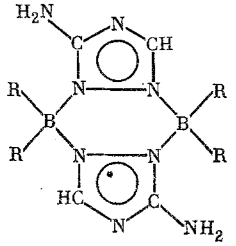
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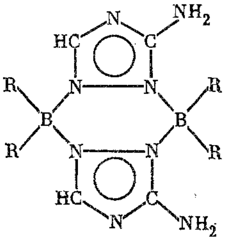
(VIII)

R = Pr(VIIa), (VIIIa), Bu(VIIb), (VIIIb).

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TABLE 1. Coordinates for Non-Hydrogen Atoms in IXa

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
N^1	0.6330(2)	0.0019(2)	0,7799(2)	C^7	0,7352(4)	0.4644(3)	1,1347(3)
N^2	0.6032(2)	0.1072(2)	0,9323(2)	C^8	0,8312(3)	0,4204(3)	1,0938(3)
N^3	0.7289(2)	0,1874(2)	0,8264(2)	C^9	0.8120(3)	0,3322(3)	1.0193(3)
N^4	0,5045(2)	−0.0721(2)	0,8776(2)	C^{10}	0.8506(3)	0.0341(3)	0,7396(3)
N^5	0,5900(2)	−0,1002(2)	0.7303(2)	C^{11}	0.9096(4)	−0.0188(4)	0,8415(3)
C^1	0,6784(3)	0,1917(3)	0,9113(2)	C^{12}	1.0330(4)	−0,0688(4)	0,8414(4)
C^2	0.5796(3)	0,0131(3)	0.8648(2)	C^{13}	0,6601(3)	0,1397(3)	0,6224(3)
C^3	0.5163(3)	−0,1381(3)	0.7917(3)	C^{14}	0.7403(4)	0.2062(3)	0,5593(3)
C^4	0,6987(3)	0.2883(3)	0.9885(2)	C^{15}	0.6749(4)	0,2547(4)	0,4568(3)
C^5	0,6026(3)	0.3342(3)	1,0298(3)	B	0.7225(3)	0.0887(3)	0.7369(3)
C^6	0.6209(3)	0,4251(3)	1,1014(3)				

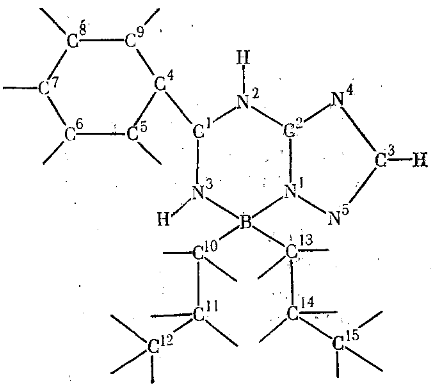
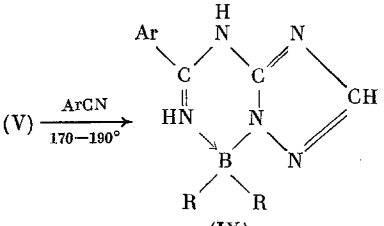


Fig. 1. Schematic representation and numbering of atoms in IXa.

Pure VII was obtained by recrystallization from dioxan and preliminary X-ray investigation confirmed the structure VIIa.

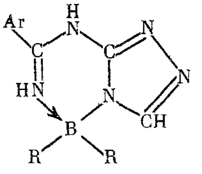
Mass spectra of VII and VIII showed intense ion peaks corresponding to loss of one alkyl group from the dimer (up to 90% of total ion current). The ^{11}B NMR shifts in VII and VIII were practically identical thus V showed just a singlet at $\delta \sim 1$-2 ppm in the region for four coordinate boron. The IR spectra of both isomers were also the same and V showed sharp, characteristic NH_2 group absorptions at 3520 (ν_{as}) and 3420 cm^{-1} (ν_s). The dimers V did not measureably dissociate in neutral media at $t < 120$-130°C, thus they were stable to refluxing EtOH and to refluxing with aliphatic nitriles of the series $C_nH_{2n+1}CN$ (where $n = 1$ to 4). However V did react with aromatic nitriles at 170-190°C to form chelates IX in which the ligands are the deprotonated 1,2,4-triazol-5-yl-amidines.



(IX)

R = Pr, Ar = Ph(IXa); R = Bu, Ar = Ph(IXb); R = Pr, Ar = p-MeC$_6$H$_4$(IXc); R = Bu, Ar = p-MeC$_6$H$_4$(IXd); R = Pr, Ar = o-MeC$_6$H$_4$(IXe); R = Bu, Ar = o-MeC$_6$H$_4$(IXf).

The structures of the synthesized bicycles could only be proved by x-ray analysis because spectral data did not allow an unambiguous choice of structural formula IX so far as other possible isomers or tautomers X-XII were concerned (other possible structural variants could be directly rejected by IR spectral data).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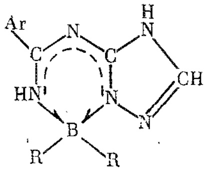
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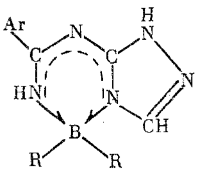

(XII)

The molecular structure of the reaction product of Va with PhCN is given in Fig. 1 and corresponds to IXa with the H atoms localized on N^2 and N^3. Atomic coordinates are given in Table 1. Values of the interatomic distances, valency angles, and temperature factors can be obtained from the authors.

The bicyclic system of the molecule is planar within the limit 0.031(3) Å. The B atom is in a distorted tetrahedron with the N^1, N^2, and N^3 atoms planar. The phenyl ring is not coplanar with the bicycle being turned by 42.9° relative to the C^1—C^4 bond. The C—N distances in IXa were significantly different inter alia. The greatest of these (1.387 Å for C^2—N^2) considerably exceeds the length of the exocyclic C—N bond in IV (1.342 Å [9]). Distances in the $N^3C^1N^2$ fragment were typical of amidine coordinated to B at the C=N group (cf. [10]).

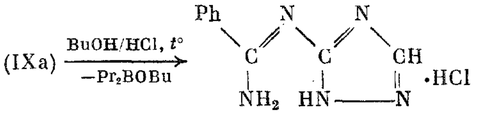
Thus the investigated compound was different in the boron containing ring structure from its related chelates I-III where the ligands were correspondingly imidoylamidines, N-(thiazol-2-yl)amidines and N-(pyrid-2-yl)foramidine. On the orbitals of the five atom fragment NCNCN in I-III there were six delocalized π-electrons with equal C—N bonds; this being confirmed by spectral data [1, 2, 6, 7] and x-ray analysis (III) [11] (this type of chelate system corresponding to the structural formula, XI).

Crystalline IXa showed strong hydrogen bonds $N^2H...N^4$ (2.903(4) Å) holding the molecule in centrosymmetric dimers and very weak $N^3H...N^5$ (3.348(4) Å) in a chain sprially twisted around the 2_1 axis.

Chelates IXa-f were colorless, crystalline compounds readily soluble in THF and slightly in DMSO, $CHCl_3$, and C_6H_6. The ^{11}B NMR spectra of IXa-f showed signals for four coordinate boron. The mass spectra showed patterns typical of chelated compounds with a dialkylboryl group [12]. The molecular ion peak was virtually absent and the most intenst peak was that for the ion $[M-R]^+$. Three further fragmentations were seen: splitting off of alkene C_nH_{2n} (from R = C_nH_{2n+1}), loss of the $C_{n-1}H_{2n-1}$ radical, and elimination of alkane $C_{n-2}H_{2n-2}$.

In contrast to the chelates with delocalized multiple bonds (I-III) compounds IXa-f had an IR band for C=N in the usual region of 1630-1640 cm^{-1}. As shown above, crystalline IXa has two types of intermolecular NH...N bonds. In $CHCl_3$ solutions H bonds with the participation of the BNH fragment were readily dissociated (IR absorption bands in the region 3390-3400 cm^{-1}). On the other hand, the H bridges in the centrosymmetric dimers of the chelates IX were distinguished by unusual stability and were not dissociated, even upon addition of powerful H-acids (decachlorocarborane or p-fluorophenol) giving broad peaks with several maxima in the region 2400-3300 cm^{-1}.

Chelates IXa-f were not decomposed by water or refluxing with ethanol. In contrast to I-III they did not form salts with HCl in ether. However, refluxing IXa in BuOH/HCl did yield the hydrochloride of N-(1,2,4-triazol-5-yl)benzamidine XIII.



(XIII)

The structure of XIII was confirmed by spectral data. Attempts to prepare XIII by an independent synthesis from IV and PhCN with $AlCl_3$ were unsuccessful.

EXPERIMENTAL

Operations with organoboron compounds were carried out under dry argon. PMR spectra were recorded on a Bruker WM-250 (δ, ppm), and ^{11}B NMR spectra on a Bruker WP-200SY instrument (δ, ppm). IR spectra were taken on a UR-20 (ν, cm^{-1}) and UV spectra on a Specord UV-VIS (λ_{max}, nm). Mass spectra (m/z) were recorded on a Varian MAT CH-6 with direct introduction of the sample into the ion source (sample temperature 150-200°C). The solvents used were: DMSO-d_6 for NMR, EtOH for UV, and $CHCl_3$ for IR unless otherwise stated.

Dimer of Dipropylboryl-5-amino-1,2,4-triazole (Va). A mixture of IV (3.3 g), Pr_3B (11.5 g) and xylene (20 ml) was refluxed until gas evolution ceased (propane, propylene, H_2). Volatile products were distilled in vacuo at ∿100°C, ethanol (4 ml) and hexane (40 ml) were added to the residue, and the product was refluxed for 0.5 h. The precipitated solid was filtered off, washed with hot hexane and dried to give 5.02 g (72%). Found: C 53.18; H 9.51; B 6.17; N 31.53%. $C_{16}H_{34}N_8B_2$ Calculated: C 53.36; H 9.52; B 6.00; N 31.52%. Mass spectrum 317 $[M-Pr]^+$. PMR Spectrum: 8.04 s and 7.96 s (triazole ring, H, ratio 6:1), 6.09 s and 6.05 s (NH_2, ratio 1:5.7). ^{11}B NMR spectrum: 1.3 s. UV spectrum: 234 (7120). IR spectrum: 3520, 3421 (NH_2).

Recrystallization of Va (1.53 g) from dioxan (10 ml) gave VIIa (0.98 g) with mp 228-235°C. Found: C 53.47; H 9.54; B 6.08; N 31.33%. PMR spectrum: 8.4 s (triazole ring H), 6.06 s (NH_2). The mother liquor was evaporated to give a residue which crystallized from dioxan to give VIIIa (mixed with VIIa). PMR spectrum: 8.04 s and 7.96 s (triazole ring H, ratio 1:5.7), 6.10 s and 6.06 s (NH_2, ratio 4.5:1). Elemental analysis was satisfactory.

Dimer of Dibutylboryl-5-amino-1,2,4-triazole (Vb), was obtained similarly to Va from Bu_3B and IV in 74% yield. Found: C 57.40; H 10.06; B 5.20; N 27.41%. $C_{20}H_{42}N_8B_2$ Calculated: C 57.71; H 10.17; B 5.19; N 26.92%. Mass spectrum: 359 $[M-Bu]^+$. PMR spectrum: 8.04 s and 7.96 s (triazole ring H, ratio of signals 5.7:1), 6.08 s and 6.04 s (NH_2, ratio 1:5). ^{11}B NMR spectrum in THF: 1.7 s. UV spectrum: 234 (9000). IR spectrum in $CHCl_3$: 3520, 3421 (NH_2). Recrystallization of 1.37 g of Vb from dioxan (10 ml) gave VIIb (0.85 g) with mp 230-235°C. PMR spectrum; 8.04 s (triazole ring), 6.04 s (NH_2), 1.22-0.38 m (butyl group). Elemental analysis was satisfactory.

VIIIb (mixed with VIIb) was obtained analogously from the mother liquors. PMR spectrum: 8.04 s and 7.96 s (triazole ring H, ratio of signals 1:4.8), 6.07 s and 6.03 s (NH_2, ratio 4.1:1). Elemental analysis was satisfactory.

Dialkylboryl-[(1,2,4-triazol-5-yl)amidinates](IXa-f). Va,b (0.01-0.02 mole) solution in a 3-5 times excess of the corresponding nitrile was refluxed for 1-2 h, the unreacted nitrile removed by distillation in vacuo and the dry residue washed with hexane and then recrystallized from benzene to give the following.

Dipropylboryl-[(1,2,4-triazol-5-yl)benzamidinate] (IXa) from Va and PhCN in 68% yield with mp 169-173°C. Found: C 63.45; H 7.67; B 3.82; N 24.47%. $C_{15}H_{22}N_5B$ Calculated: C 63.62; H 7.83; B 3.82; N 24.73%. Mass spectrum: 240 $[M-Pr]^+$. PMR spectrum: 12.03 br s and 8.93 s (2 NH), 7.87-7.42 m (Ph), 7.70 s (triazole ring H), 1.27-0.24 m (2 Pr). UV spectrum: 239 (13700), 300 sh (1960). IR spectrum: 3398 (NH), 1639 (C=N).

Dibutylboryl-[(1,2,4-triazol-5-yl)benzamidinate](IXb) from Vb and PhCN in 77% yield with mp 180-186°C. Found: C 65.42; H 8.40; B 3.62; N 22.56%. $C_{17}H_{26}N_5B$ Calculated: C 65.60; H 8.42; B 3.47; N 22.51%. Mass spectrum: 254 $[M-Bu]^+$. PMR spectrum: 12.08 br s and 8.95 s (2 NH), 7.89-7.52 m (Ph), 7.70 m (triazole ring CH), 1.32-0.31 m (2 Bu). UV spectrum: 239 (18000), 300 sh (1950). IR spectrum: 3399 (NH), 1637 (C=N).

Dipropylboryl-[(1,2,4-triazol-5-yl)p-toluamidinate](IXc) from Va and p-MeC_6H_4CN in 74% yield with mp 186-189°C. Found: C 64.64; H 8.03; B 3.84; N 23.50%. $C_{16}H_{24}N_5B$ Calculated: C 64.64; H 8.14; B 3.64; N 23.56%. Mass spectrum: 254 $[M-Pr]^+$. PMR spectrum: 11.93 br s and 8.88 s (2 NH), 7.72 d and 7.38 d (C_6H_4), 7.68 s (triazole ring H), 2.40 s (Me), 1.26-0.25 m (2 Pr). UV spectrum: 248 (22,650), 301 sh (2450). IR spectrum: 3397 (NH), 1633 (C=N).

Dibutylboryl-[(1,2,4-triazol-5-yl)-p-toluamidinate](IXd) from Vb and p-MeC_6H_4CN in 64% yield with mp 179-182°C. Found: C 66.42; H 8.48; B 3.68; N 21.56%. $C_{18}H_{28}N_5B$ Calculated: C 66.47; H 8.68; B 3.32]; N 21.53%. Mass spectrum: 268 $[M-Bu]^+$. PMR spectrum: 11.90 br s and 8.86 s (2 NH), 7.73 d and 7.38 d (C_6H_4), 7.68 s (triazole ring H), 2.40 s (Me), 1.30-0.30 m (2 Bu). UV spectrum: 248 (6610), 301 sh (715). IR spectrum 3396 (NH), 1632 (C=N).

Dipropylboryl-[(1,2,4-triazol-5-yl)-o-toluamidinate](IXe) from Va and o-MeC_6H_4CN in 68% yield with mp 203-207°C. Found: C 65.06; H 8.23; B 3.63%. $C_{16}H_{24}N_5B$ Calculated: C 64.66; H 8.14; B 3.64%. Mass spectrum 254 $[M-Pr]^+$. PMR spectrum: 11.76 br s and 9.13 s (2 NH), 7.60 s (triazole ring H), 7.56-7.30 m (C_6H_4), 2.38 s (Me), 1.32-0.25 m (2 Pr). UV spectrum: 228 sh (3500), 274 (2010). IR spectrum: 3392 (NH), 1641 (C=N).

Dibutylboryl-[(1,2,4-triazole-5-yl)o-toluamidinate](IXf) from Vb and o-Me_6H_4CN in 66% yield with mp 185-188°C. Found: C 66.19; H 8.75; B 3.58; N 21.44%. $C_{18}H_{28}N_5B$ Calculated:

C 66.47; H 8.68; B 3.32; N 21.53%. Mass spectrum: 268 [M-Bu]$^+$. PMR spectrum: 11.80 br s and 9.14 s (2NH), 7.58 s (triazole ring H), 7.55-7.32 m (C_6H_4), 2.38 s (Me), 1.29-0.26 m (2 Bu). UV spectrum: 228 sh (11,030), 274 (3050). IR spectrum: 3391 (NH), 1641 (C=N).

N-(1,2,4-Triazol-5-yl)benzamidine Hydrochloride (XIII). A mixture of IXa (2.4 g) and a solution of 6 N HCl (10 ml) in BuOH were refluxed for 2 h. The precipitated solid was filtered, washed with ether, and dried to give XIII (0.8 g, 42%) with mp 253-256°C (EtOH). Found: C 48.18; H 4.70; N 30.97; Cl 15.63%. $C_9H_{10}N_5Cl$. Calculated: C 48.33; H 4.51; N 31.31; Cl 15.85%. Mass spectrum: 186 [M-HCl-H]$^+$. PMR spectrum: 8.80 (triazole ring H). 7.96-7.55 m (Ph).

X-ray Crystallographic Analysis of (IXa). After recrystallization from MeCN a crystal of dimensions 1.0 × 0.8 × 1.1 mm was selected. Experimental data was obtained on a CAD-4 automatic diffractometer (Mo radiation, ω/θ scanning). In the θ range 0 to 25° 3028 reflections were registered with 1763 reflections involved in the refinement with $I > 3\sigma(I)$. Crystals were monoclinic with a = 11.303 (13), b = 11.570 (7), and c = 12.748 (6) Å; β = 98.84 (7); space group $P2_1/n$, Z = 4. Calculations were performed using the complex ENX-SDP program on a PDP-11/55t computer. The structure was solved by a direct method (MULTAN). The optimum model was refined from E synthesis. After several cycles of isotropic and anisotropic refinement of non-hydrogen atoms in difference synthesis all of the H atoms were localized. In the full matrix refinement all non-hydrogen atoms (anisotropic approximation) and the atoms HN^2, HN^3, and HC^3 (isotropic) were included. The remaining H atoms were included with fixed thermal factors. The final refinement with introduction of individual weighting and based on secondary extinction led to R = 0.052, R_w = 0.052, c = 7.8 (3)·10^7, and S = 0.959.

CONCLUSIONS

1. A new series of cyclic compounds of four coordinate boron- the dialkylboryl-[(1,2,4-triazol-5-yl)amidinates] (IX)- has been synthesized from 5-amino-1,2,4-triazole, aromatic nitriles, and trialkylboranes.

2. In the crystalline, dimeric dialkylboryl derivatives of 5-amino-1,2,4-triazole the Alk_2B groups are bonded to the ring N atoms.

3. The crystalline and molecular structure of dipropylboryl[(1,2,4-triazol-5-yl)benzamidinate] (IXa) have been determined by X-ray crystallography.

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