5° to a solution of 60 g (1.2 moles) of hydrazine hydrate in 1.5 l. of ethanol. The solution was evaporated at 40° (20 mm), yielding a white solid which was recrystallized from toluene. Two crops, 148 and 15 g, were obtained for a total yield of 72%. The material was purified further by sublimation and melted at 133–135°. *Anal.* Calcd for $C_5H_6F_6N_2O_2$: C, 25.0; H, 2.50; F, 47.5. Found: C, 24.9; H, 2.73; F, 47.5.

B. The above product (173 g, 0.72 mole) was melted and heated with stirring as water distilled slowly. After cessation of water evolution, the temperature rose and a material boiling at 147–149° (1 atm) came over and solidified. It melted at 84°, had an unpleasant, pungent odor, and sublimed with great ease. *Anal.* Calcd for $C_5H_2F_6N_2$: C, 29.4; H, 0.98; F, 56.0; mol wt, 204. Found: C, 29.5; H, 1.20; F, 56.2; mol wt (cryoscopic in benzene), 208.

Trimethylamine 3,5-Bis(trifluoromethyl)pyrazol-1-ylborane. A mixture of 3,5-bis(trifluoromethyl)pyrazole (20.4 g, 0.100 mole) and trimethylamine borane (7.3 g, 0.10 mole) was refluxed overnight in 150 ml of toluene. The solvent was distilled at atmospheric pressure leaving an oil. On vacuum distillation there was obtained 21.4 g (78%) of product, bp 88° (1 mm). *Anal.* Calcd for $C_8H_{12}BF_6N_3$: C, 34.9; H, 4.37; F, 41.5; N, 15.3. Found: C, 35.2; H, 4.47; F, 42.2; N, 15.2.

The infrared spectrum has a BH_2 multiplet in the 2500-cm^{-1} region. The nmr spectrum shows two singlets at τ 3.12 and 7.41 with relative intensity of about 1:9.

4,4,8,8-Tetraethyl-*sym*-triazabole. A mixture of 13.8 g of 1,2,4-triazole and 28 ml of triethylborane (both 0.2 mole) in 250 ml of xylene was stirred and refluxed overnight. The solution was evaporated to dryness, and the residue was sublimed *in vacuo.* The product was obtained, after recrystallization from heptane and resublimation, in 14-g (50%) yield. It melts at 163–164°. *Anal.* Calcd for $C_{12}H_{24}B_2N_6$: C, 52.5; H, 8.77; N, 30.7. Found: C, 52.5; H, 8.66; N, 31.2.

The nmr spectrum has a single sharp peak at τ 1.74 and a multiplet around τ 9.35 with relative intensities 1:5.

Boron–Pyrazole Chemistry. II. Poly(1-pyrazolyl)borates

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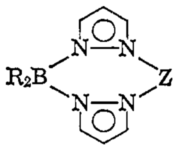
Abstract: Alkali metal dihydrobis(1-pyrazolyl)borates, hydrotris(1-pyrazolyl)borates, and tetrakis(1-pyrazolyl)borates have been prepared from alkali metal borohydrides and pyrazole. The first two are parent compounds, each representing a new class of chelating agents. Dihydrobis(1-pyrazolyl)borates are uninegative bidentate ligands and react with divalent transition metal ions forming square-planar or tetrahedral chelates, while hydrotris(1-pyrazolyl)borates are uninegative tridentates yielding octahedral coordination compounds. A study of the solvent and cation dependence in the nmr spectra of poly(1-pyrazolyl)borate ions permitted assignment of the 3-H and 5-H doublets. All alkali metal poly(1-pyrazolyl)borates can be converted to isolable free acids of moderate stability. The synthesis and properties of representative compounds are described.

It has been shown recently[1,2] that when a BR_2 group acts as a bridging unit between two pyrazole nuclei, several new classes of boron compounds are obtained, depending on the nature of the second bridging unit.[3] When that unit, Z, is BR_2, then the resulting structure is a pyrazabole (I). When Z is a metal or onium ion, the compound belongs to the class of poly(1-pyrazolyl)borates (II). Finally, when Z is a hydrogen bridge, we have the corresponding free acid (III).



I, Z = BR_2
II, Z = M
III, Z = H

Pyrazaboles (I) are neutral heterocycles that may be regarded as dimers of an intermediate dihydroborylpyrazole (for R = H) fragment. On the other hand, poly(1-pyrazolyl)borates belong to the class of uninegative tetrasubstituted boron compounds which hitherto have been known only as salts. Of these, there are only a few examples of $[BR_nR'_{4-n}]^-$ species containing a B–N bond, N being an amino, pyrrolyl, or indolyl group. None of these has displayed any unusual properties.[4–8]

By contrast, poly(1-pyrazolyl)borates not only exhibit remarkable hydrolytic and oxidative stability but are excellent chelating agents for a wide range of transition metals and provide for the first time examples of isolable, albeit hydrated, free acids, $H[BR_nR'_{4-n}]$. This paper is concerned with the synthesis and properties of the two parent ligands, dihydrobis(1-pyrazolyl)borates[9] and hydrotris(1-pyrazolyl)borates,[9] and their free acids and diverse salts and chelates derived therefrom. Although tetrakis(1-pyrazolyl)borates[9] are, in terms of coordinating ability, merely a substituted variant of tris(1-pyrazolyl)borates, they will be covered

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[1] S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

[2] S. Trofimenko, *ibid.*, **89**, 3165 (1967).

[3] One could, of course, view this field from the aspect of a bidentate pyrazolyl group acting as a bridge between two BR_2 groups or between BR_2 and a metal ion. Analogies in the former case are numerous with hydrogen, dialkylamino, alkylmercapto, and other groups acting as bridges. To the latter belong the few examples of hydrogen-bridged metal borohydrides: B. D. James, R. K. Nanda, and M. G. H. Wattbridge, *J. Chem. Soc., Sect. A*, 182 (1966), and references cited therein.

[4] C. A. Kraus and W. W. Hawes, *J. Am. Chem. Soc.*, **55**, 2776 (1933).

[5] C. A. Kraus, *Nucleus*, **13**, 213 (1936).

[6] J. E. Smith and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 2751 (1951).

[7] H. S. Turner and R. J. Warne, *Proc. Chem. Soc.*, 69 (1962).

[8] V. A. Sazonova and V. I. Karpov, *Zh. Obshch. Khim.*, **33**, 3313 (1963).

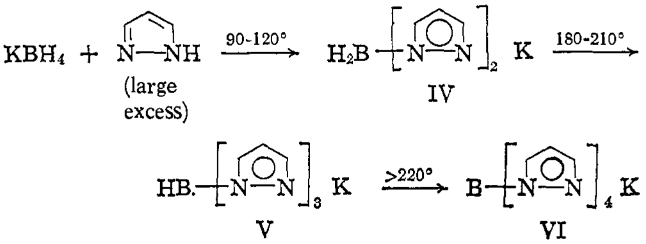
[9] For the sake of brevity the dihydrobis(1-pyrazolyl)borate, hydrotris(1-pyrazolyl)borate, and tetrakis(1-pyrazolyl)borate ions will be written as $H_2B(pz)_2^-$, $HB(pz)_3^-$, and $B(pz)_4^-$, respectively, "pz" denoting the 1-pyrazolyl fragment.

in this paper since they are preparatively related to the latter and they also fit the $[H_nB(pz)_{4-n}]^-$ formula.

Results and Discussion

When potassium borohydride is added to an excess of molten pyrazole, evolution of hydrogen commences. It continues smoothly at 90–120° and comes, essentially, to a halt when 2 equiv of hydrogen has been evolved. On pouring the melt into toluene, the salt IV, mp 171–172°, is precipitated in 74% yield. This salt may be recrystallized from anisole.

If, on the other hand, the above reaction mixture is heated further, a third equivalent of hydrogen is evolved at 180–210°, and the salt V can be isolated in 80% yield. It can be recrystallized from anisole and melts at 188–189°. Finally, on prolonged heating above 220°, a fourth equivalent of hydrogen is evolved, and the salt VI can be isolated in 98% yield. It melts, after recrystallization from ethanol, at 230–231°.



The structure of IV is consistent with the following: the stoichiometry of hydrogen evolution, elemental analysis, the infrared spectrum which shows a strong BH_2 stretch multiplet resembling that of pyrazabole at 2230–2460 cm^{-1}, and the H^1 nmr spectrum which shows the three pyrazole hydrogens as doublets at τ 2.42 (J = 1.8 cps) and 2.49 (J = 2.2 cps) and a triplet at τ 3.83 (J = 2.0 cps) in a 1:1:1 ratio. The signal arising from BH_2 hydrogens is broad and cannot be discerned, but the number of boron-bonded hydrogens can be determined as two by integration in the τ 3–9 range. The B^{11} nmr spectrum consists of a triplet (J = 96 cps) centered at +25.7 ppm.[10]

Structure V was established in similar fashion. The BH stretch appeared as a single peak at about 2470 cm^{-1}. The H^1 nmr spectrum in D_2O showed three peaks due to CH hydrogens as doublets at τ 2.43 (J = 1.8 cps) and 2.82 (J = 2.2 cps) and a triplet at τ 3.85 in a 3:3:3 ratio. The BH hydrogen of intensity 1 was found by integration over the range τ 3–9. The B^{11} nmr spectrum had a doublet (J = 105 cps) at +19.6 ppm.

The salt $KB(pz)_4$ showed no BH band in the infrared and had three nmr peaks (in D_2O): doublets at τ 2.32 ($J \sim$ 1.7 cps) and 2.62 (J = 2.3 cps) and an ill-resolved triplet at τ 3.67 in a 1:1:1 ratio. The B^{11} nmr spectrum consisted of a sharp singlet at + 17.3 ppm.

The proton nmr spectra of $H_2B(pz)_2^-$, $HB(pz)_3^-$, and $B(pz)_4^-$ ions show that all the pyrazolyl residues in each ion are identical. The triplet (resolvable into a set of overlapping doublets) was readily assigned to the 4-H. On the other hand, the data available were insufficient to assign the $J_{2.2}$ and $J_{1.8}$ doublets.[11] In a similar situation pertaining to 1-acyl-substituted pyrazoles, Williams[12] concluded, by unambiguously blocking the 5 position, that the 5-H appears at *lower* field and that it has the *higher* coupling constant of the two. The above conclusions were corroborated later and extended to 1-alkylpyrazoles by other authors.[13]

Since there was no basis to assume *a priori* that these conclusions could be equally well applied to poly(1-pyrazolyl)borates, and especially since boron is known to change the appearance of signals arising from well-known groups in unpredictable fashion,[14] the problem of assigning the 3-H and 5-H doublets in poly(1-pyrazolyl)borate ions had to be solved independently.

The approach chosen entailed studying the effect of changing the solvent and/or cation on the chemical shifts in $M[H_nB(pz)_{4-n}]$ salts. It was assumed that in solvents where ionization is suppressed and ion-pairing or, in the extreme case, chelation[15] of the cation takes place, the environment of the "outer," 3-H, would change more significantly than that of the "inner," 5-H, and suitable changes in their chemical shifts would be observed. In order to separate the differential solvent effect from the over-all solvent effect, the position of the 4-H was used as an internal standard, and changes in the distance ($\Delta_{2.2}$ and $\Delta_{1.8}$) of the two doublets $J_{2.2}$ and $J_{1.8}$ from it were measured in cycles per second. It was established that in a given system $\Delta_{2.2}$ and $\Delta_{1.8}$ are relatively independent of concentration.

When $\Delta_{2.2}$ and $\Delta_{1.8}$ were measured in water for a series of $MB(pz)_4$ salts (M = Li, Na, K, Cs, and Me_4N), values of 62 ± 1 and 82 ± 1 cps, respectively, were obtained, which is consistent with complete separation of the ions. The situation changed dramatically upon switching to acetone as solvent. There $\Delta_{1.8}$ remained relatively constant at 84 ± 2 cps, but $\Delta_{2.2}$ proved to be strongly cation dependent, and values of 45 (Li), 55 (Na), 65 (K), 72 (Cs), and 76 cps (Me_4N) were obtained. The same effect was observed in dimethylformamide and dimethyl sulfoxide. There $\Delta_{1.8}$ varied over 6–7 cps in going from the Li to the Me_4N salt, while $\Delta_{2.2}$ ranged over 30 and 38 cps, respectively.

A similar situation prevails in $M[HB(pz)_3]$ salts. There, too, $\Delta_{2.2}$ and $\Delta_{1.8}$ are relatively invariant in water (65 ± 2 and 83 ± 2 cps, respectively). On switching to acetone $\Delta_{1.8}$ remains at 84 ± 2 cps while $\Delta_{2.2}$ is again cation dependent with values of 98 (Li), 97 (Na), 93 (K), 84 (Cs), and 80 cps (Me_4N). This behavior is also noted in other solvents such as dimethylformamide, dimethyl sulfoxide, and acetonitrile, where $\Delta_{1.8}$ remains relatively constant at 83 ± 3 cps, while $\Delta_{2.2}$ values range over 12–17 cps. Since in all of these cases the $J_{2.2}$ doublet appears at either higher or lower field than the $J_{1.8}$ doublet, the hazard involved in assigning the 3- and 5-hydrogens in unsymmetrical pyrazoles on the basis of their chemical shifts alone becomes immediately obvious.

If the cation is held constant but the solvent varied,

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(10) The B^{11} nmr spectra were determined at 19.2 Mc, and the chemical shifts are referred to external trimethyl borate.

(11) The 3,5 splitting of ~0.6 cps is not always discernible.

(12) J. K. Williams, *J. Org. Chem.*, **29**, 1377 (1964).

(13) L. G. Tensmeyer and C. Ainsworth, *ibid.* **31**, 1878 (1966); I. L. Finar and E. F. Mooney, *Spectrochim. Acta*, **20**, 1269 (1964).

(14) For instance, the B-ethyl group may appear as a singlet or a triplet around τ 9 rather than the well-known triplet–quadruplet pattern: L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *Inorg. Chem.*, **4**, 1649 (1965).

(15) Formation of very tight ion pairs in systems capable of chelate formation has been demonstrated: H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc.*, **87**, 1857 (1965), and references cited therein.

Table I. Compounds of Structure $M[H_2B(pz)_2]_2$

			%	C, %		H, %		N, %		M, %		Mol wt	
Color	M	Mp, °C	yield	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
White	Mn	Darkens 155,[a] 162 dec	56	41.3	42.7	4.58	4.72						
White (greenish tinge)	Fe	~130[a] dec	52	41.2	41.9	4.58	4.82	32.0	32.2				
Violet	Co	163–164[b]	87	40.8	41.1	4.53	4.61			16.7	16.6		
Orange	Ni	181–182[c]	92	40.8	40.7	4.54	4.60	31.7	31.1	16.7	16.7	352	337[d]
Lilac	Cu	134–135[c]	84	40.3	40.6	4.48	4.77			17.8	17.7	357	367[e]
White	Zn	161–162[b]	90	40.1	39.8	4.46	4.37	31.2	30.6				

[a] Sublimed. [b] Recrystallized from heptane. [c] Recrystallized from toluene. [d] Ebullioscopic in benzene. [e] Ebullioscopic in methylene chloride.

the same behavior is observed. For instance, for $LiHB(pz)_3$ $\Delta_{1.8}$ is 84 and 86 cps in water and acetone, respectively, while the corresponding $\Delta_{2.2}$ values are 64 and 98 cps. Intermediate values for $\Delta_{2.2}$ may be obtained by using water–acetone mixtures as solvent. Analogous, if less dramatic, results were obtained with other cation or solvent combinations as well as with the $M[H_2B(pz)_2]$ salts.

These results show clearly that the chemical shift of the $J_{2.2}$ doublet is much more cation and solvent dependent than that of the $J_{1.8}$ doublet. On this basis, the former is assigned to the 3-H and the latter to the 5-H.

When sodium or lithium borohydrides are used instead of potassium borohydride, the corresponding sodium and lithium poly(1-pyrazolyl)borates are obtained. It is noteworthy that $LiHB(pz)_3$, $LiB(pz)_4$, and $NaHB(pz)_3$ can be sublimed *in vacuo* without decomposition.

The oxidative and hydrolytic stability of poly(1-pyrazolyl)borates increases with decreasing number of hydrogens attached to boron. Thus, $H_2B(pz)_2^-$ is oxidized instantaneously by aqueous permanganate, $HB(pz)_3$ is oxidized slowly, while $B(pz)_4^-$ remains unaffected under these conditions. This trend is also corroborated by polarographic studies. The same order of stability is observed with regard to storage of their solutions: $B(pz)_4^-$ can be stored for long periods of time in solution without noticeable deterioration, while $HB(pz)_3^-$ is stored less well, and $H_2B(pz)_2^-$ solutions have to be used within a few days. In the solid state, however, all three salts can be stored for years at room temperature exposed to air and light.

Careful acidification of aqueous solutions of IV, V, and VI with acetic acid yields the corresponding free acids as water-insoluble solids. This is the first known instance of a stable free acid derived from a $[BR_nR'_{4-n}]^-$ species being isolated,[16] and it underscores the importance of chelation as a stabilizing factor.

The exact structure of these free acids has not been determined. They may be ion pairs or have a "chelated proton" structure. They are hydrated to varying degrees. Analysis of the free acid derived from $KH_2B(pz)_2$ fits best $H[H_2B(pz)_2]_2 \cdot 4H_2O$, which is in accord with data pertaining to hydration of a proton extracted into organic solvents.[17] On the other hand, $HB(pz)_4$ is essentially anhydrous. That these solids do indeed contain the intact $[H_nB(pz)_{4-n}]^-$ ion is indicated by the fact that they can be reconverted to salts with the same or different cation by titration with an alkali or onium hydroxide. Moveover, the free acids do react readily with transition metal ions giving the same chelates as those obtained from the salts. In fact, precipitation of $M[H_nB(pz)_{4-n}]_2$ chelates is often carried out advantageously slightly on the acid side to avoid coprecipitation of transition metal hydroxides. The free acid derived from $KHB(pz)_3$ is the least stable of the three and could not be recrystallized. Nevertheless, it too could be converted to $HB(pz)_3^-$ salts by titration with metal or onium hydroxides. All the free acids have infrared spectra generally similar to those of the salts from which they were derived. They all have broad absorption around 2000–3000 cm^{-1}, and area characteristic of intramolecular hydrogen bonding.

Coordination compounds derived from $H_2B(pz)_2^-$, $HB(pz)_3^-$, $B(pz)_4^-$, and divalent first-row transition metal ions can be prepared readily by metathesis. Since the compounds $M[H_2B(pz)_2]_2$ and $M[HB(pz)_3]_2$ are of different structural types, they will be discussed separately.

Chelates of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are precipitated immediately when aqueous solutions of $KH_2B(pz)_2$ and the appropriate metal ion are mixed. Similarly, the compounds $M[H_2B(pz)_2]_2$ are precipitated when M is Pb^{2+} or Cd^{2+}, but not when M is Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}. Ag^+, Pd^{2+}, and Hg^{2+} ions are reduced to the free metals. Compounds $M[H_2B(pz)_2]_2$ are extractable with organic solvents, particularly well with methylene chloride. They are stable to air and moisture and can be stored in the solid state for years without decomposition, with the exception of the unstable, air-sensitive $Mn[H_2B(pz)_2]_2$ and $Fe[H_2B(pz)_2]_2$. Most of them can be sublimed *in vacuo*, although sublimation is at times accompanied by decomposition to diverse products, mainly metal pyrazolide, pyrazabole, and $M[HB(pz)_3]_2$. For tths reason purification by recrystallization or by chromatography is preferred. Properties of $M[H_2B(pz)_2]_2$ compounds are summarized in Table I. Their structures were determined as follows.

From *a priori* consideration of contributing structures of the $H_2B(pz)_2^-$ ion, it is apparent that significant contributions are to be expected from structures VIIb and c.

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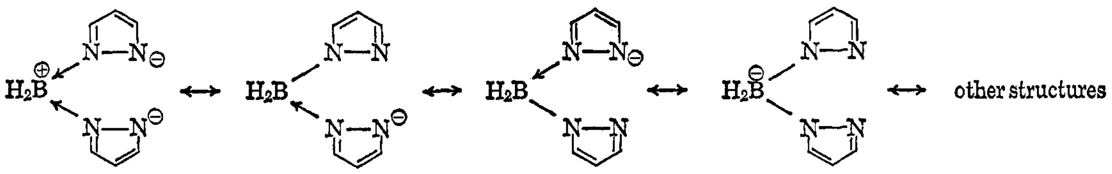
(16) The ions $[BR_nR'_{4-n}]^-$ are extremely sensitive to aqueous acid: R. Damico, *J. Org. Chem.*, **29**, 1971 (1964). Even in the case of relatively stable $B(C_6H_5)_4^-$, no evidence for the existence of a viable $HB(C_6H_5)_4$ species was found: J. H. Cooper and R. E. Powell, *J. Am. Chem. Soc.*, **85**, 1590 (1963). On the other hand, the preparation of $H[(C_6H_5)_2B(OH)_2]$, mp −35 to −33°, has been claimed: B. M. Mikhailov and V. A. Vaver, *Dokl. Akad. Nauk SSSR*, 102, 531 (1955).

(17) M. I. Tocher, D. C. Whitney, and R. M. Diamond, *J. Phys. Chem.*, **68**, 368 (1964), and references cited therein.



VIIa VIIb VIIc VIId

These structures have electronic and geometric features (a formal negative charge and an available electron pair, located at the termini of the N-N-B-N-N sequence, which can exchange places by way of resonance) very similar to those of the anion derived from an enolizable 1,3-dicarbonyl compound or its imine analogs. Hence, as a first approximation, structures analogous to metal acetylacetonates would be expected.

It will be noted, however, that (a) the 3-CH group is fairly close to the metal atom, thus shielding it, especially in tetrahedral chelates, and (b) both nitrogen atoms in pyrazole are involved in bond formation or coordination and hence are expected to be unreactive. For these reasons formation of associated species, such as those encountered in various nickel(II) and cobalt(II) diketonates,[18] would not be anticipated. Indeed, all $M[H_2B(pz)_2]_2$ compounds show no evidence of self-association or planar–tetrahedral equilibrium and are monomeric.

The infrared spectra of $Mn[H_2B(pz)_2]_2$, $Fe[H_2B(pz)_2]_2$, $Co[H_2B(pz)_2]_2$, $Ni[H_2B(pz)_2]_2$, $Cu[H_2B(pz)_2]$, and $Zn[H_2B(pz)_2]$ are all very similar. Closer examination reveals that these compounds can be divided into two groups, the spectra within each group being identical. To the first group (A) belong $Ni[H_2B(pz)_2]_2$ and $Cu[H_2B(pz)_2]_2$; to the other (B), $Mn[H_2B(pz)_2]_2$, $Fe[H_2B(pz)_2]$, $Co[H_2B(pz)_2]$, and $Zn[H_2B(pz)_2]_2$. There are three regions of the spectrum where differences are apparent: (1) the fine structure in the BH_2 stretch region (see Figure 1) where the second strongest band in group B is shifted toward lower frequency and the strongest band is resolved into a doublet, compared with group A; (2) the band around 1060 cm^{-1} is a doublet in group B but a singlet in group A; and (3) the 850–950-cm^{-1} region is distinctly different in each group.

As the same ligand is involved in all these compounds, and the ionic radii of the metal ions are comparable, the observed spectral differences are ascribed to differences in molecular geometry. Since zinc forms almost exclusively tetrahedral complexes, group B must consist of tetrahedral chelates while those of group A are likely to be square planar. In accord with this, $Ni[H_2B(pz)_2]_2$ is orange-red and diamagnetic. The BH_2 region in the infrared spectra of $Ni[H_2B(pz)_2]$ and $Cu[H_2B(pz)_2]_2$ is more similar to that of pyrazabole, which is consistent with molecular models which indicate that the environment of the BH_2 in the above compounds resembles that found in pyrazabole rather than that of chelates from group B.

Proton nmr spectra of the diamagnetic chelates $Ni[H_2B(pz)_2]_2$ and $Zn[H_2B(pz)_2]_2$ each consisted of two doublets and a triplet (made up of two overlapping doublets) in a 1:1:1 ratio. They were at τ 2.38 (J = 2.1 cps), 3.17 (2.1), and 3.87 (2.1) for $Ni[H_2B(pz)_2]_2$ and at τ 2.29 (J = 2.3 cps), 2.46 (2.3 cps), and 3.80 (2.3 cps) for $Zn[H_2B(pz)_2]$ again implying fundamentally different molecular geometries.

Definitive evidence for the structure of all these chelates was obtained from magnetic data, electronic spectra, and nmr studies of the paramagnetic chelates.[19]

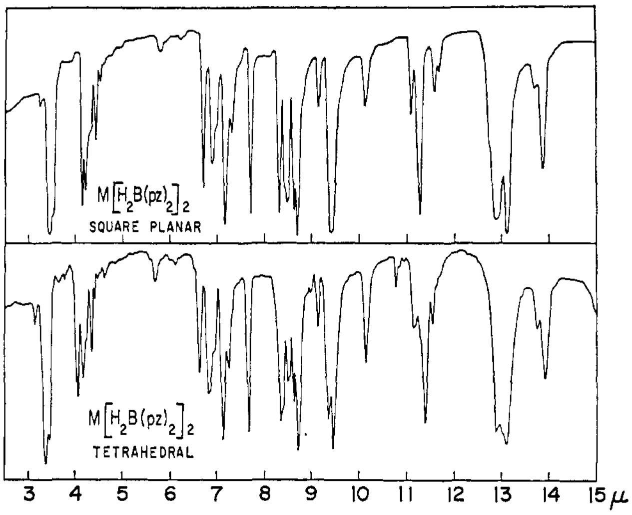


Figure 1. Infrared spectra of $M[H_2B(pz)_2]_2$ compounds.

Compounds of structure $M[HB(pz)_3]_2$ are precipitated immediately upon mixing solutions of an alkali or onium hydrotris(1-pyrazolyl)borate and of a divalent transition metal ion. In addition, such compounds are also precipitated with Mg^{2+}, Pb^{2+}, Cd^{2+}, and Pd^{2+} ions. Using Ag^+ ion, the compound $AgHB(pz)_3$ is obtained. The Ag as well as the Pd compounds decompose readily on heating with formation of the free metal. Besides Mg^{2+}, Ca^{2+} is also precipitated by the $HB(pz)_3^-$ ion but from more concentrated solutions. The solubility in water of alkaline earth hydrotris(1-polypyrazolyl)borates increases in the order Mg $\ll$ Ca $<$ Sr $<$ Ba. The strontium and barium compounds are salt-like and, like the alkali salts, may serve as starting materials for the preparation of transition metal compounds. The calcium compound behaves in some ways like a salt and in others like a chelate, although $Mg[HB(pz)_3]_2$ behaves like one of the transition metal compounds in terms of physical properties. Despite their high solubility in water, $Sr[HB(pz)_3]_2$ and $Ba[HB(pz)_3]_2$ can be extracted with organic solvents, *e.g.*, methylene chloride, and $Sr[HB(pz)_3]_2$ can be sublimed *in vacuo* without decomposition.

The transition metal compounds $M[HB(pz)_3]_2$ are all high-melting solids, sublimable *in vacuo*. They are sparingly soluble in polar solvents such as alcohols or acetone but dissolve readily in halocarbons and aromatic hydrocarbons from which they may be conven-

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[18] See, for instance, F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965); G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961), and references cited therein.

[19] J. P. Jesson, S. Trofimenko, and D. Eaton, *J. Am. Chem. Soc.*, **89**, 3148 (1967).

Table II. Compounds of Structure $M[HB(pz)_3]_2$

Color	M	Mp, °C	% yield	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	M, % Calcd	M, % Found	Mol wt Calcd	Mol wt Found
White	Mg[a]	284–285	71	48.0	48.3	4.45	4.40						
White	Ca	269–271	92	46.9	46.9	4.29	4.53	36.1	35.7				
White	Mn	283–284	100	44.9	45.1	4.17	4.33			11.4	10.9	481	496
Wine-red	Fe	265–269	96	44.9	45.1	4.16	4.24			11.6	11.7	482	479[b]
Yellow	Co	277–278	93	44.6	44.8	4.13	4.21			12.2	12.0		
Lilac	Ni	280–281	100	44.6	44.6	4.13	3.92			12.1	11.9		
Blue	Cu	245–247	96	44.2	44.2	4.08	4.18						
White	Zn	282–284	94	44.0	44.4	4.08	4.38			13.3	13.3		
White	Cd	285–286	75	40.2	40.0	3.72	3.64	31.2	31.3				
White	Pb	220–222	93	34.1	33.9	3.16	3.34	26.5	26.5	32.7	32.7		

[a] All samples were recrystallized from toluene. [b] By vapor-pressure osmometry in chloroform.

iently recrystallized. Some properties of $M[HB(pz)_3]_2$ are summarized in Table II.

Nothing has been said thus far about the structure of these compounds. Since chelates $M[H_2B(pz)_2]_2$ are, in terms of geometry and symmetry, similar to transition metal acetylacetonates or to the BR_2-bridged bis(dimethylglyoxime)nickel(II)[20] and its cobalt analog,[21] one might expect a similar structure in $M[HB(pz)_3]_2$ compounds except for the 1-pyrazolyl group replacing a hydrogen. That this is not the case became apparent.

For one thing, the colors of the iron, cobalt, nickel, and copper compounds are all different from those in the corresponding $M[H_2B(pz)_2]_2$ compounds and essentially identical with those of the corresponding complexes with the isosteric and isoelectronic ligand, 1,1,1-tripyrazolylmethane.[22] Molecular models[23] show that the 2-nitrogen of the third pyrazolyl group is in such close proximity to the metal ion that it can form a coordinate bond with it, thus giving rise to a compact structure of D_{3d} symmetry.

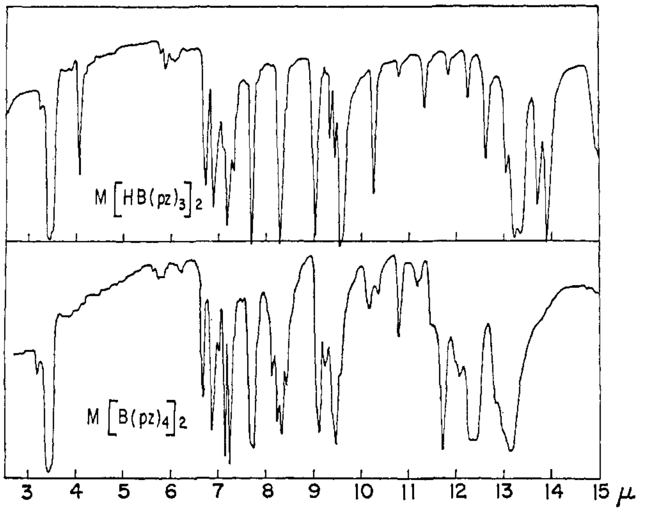

Figure 2. Infrared spectra of $M[HB(pz)_3]_2$ and $M[B(pz)_4]_2$ compounds.

Compounds $M[HB(pz)_3]_2$ have the simplest infrared spectra (Figure 2) among poly(1-pyrazolyl)borates, all containing a BH singlet.[24] The $Cu[HB(pz)_3]_2$ is significantly different in having several of the peaks that are singlets in other $M[HB(pz)_3]_2$ compounds appear as doublets. The nmr spectra of $M[HB(pz)_3]_2$ compounds discern only one kind of pyrazolyl group. The octahedral nature of these compounds is also confirmed by electronic spectra, magnetic data, and nmr studies of paramagnetic compounds.[19] An interesting case of spin equilibrium between high- and low-spin forms has been found in $Fe[HB(pz)_3]$.[25]

Compounds $M[B(pz)_4]_3$, which have the same octahedrally coordinated structure around the metal ion as $M[HB(pz)_3]_2$, are, nevertheless, in some ways different. They are prepared by metathesis and have the same colors as their $M[HB(pz)_3]_2$ counterparts. They, too, are sublimable but are higher melting, more thermally stable, and less soluble in organic solvents. However, the presence of two additional 1-pyrazolyl groups per molecule makes $M[B(pz)_4]_2$ compounds soluble in aqueous mineral acids from which they can be recovered on basification. In addition to divalent first-row transition metal ions, Cd^{2+}, Pd^{2+}, Hg^{2+}, and Ag^+ are precipitated, and of these all but the silver compound can be purified by recrystallization. In the alkaline earth group Mg^{2+} is precipitated readily, Ca^{2+} less readily, and Sr^{+2} and Ba^{+2} are too soluble to be precipitated except from very concentrated solutions. The infrared spectra of all $M[B(pz)_4]$ compounds are similar (Figure 2) and devoid of BH absorption. Their properties are shown in Table III.

Convincing proof that one of the four 1-pyrazolyl groups attached to boron is different from the other three is provided by the nmr spectrum of the paramagnetic $Co[B(pz)_4]_2$ compound where protons due to three identical and one different 1-pyrazolyl groups per ligand are discerned, the signals covering a range of over 12,000 cycles due to spin–contact interactions.[19]

At this point it is pertinent to touch on the mechanism of the reaction of pyrazole with the tetrahedral borohydride ion. While some work has been done in the area of displacement reactions on tetrahedral boron,[26] mainly relating to solvolytic and displacement reactions of borane complexes, the situation is by no means as clear as in the case of substitution on carbon.

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(20) G. N. Schrauzer, *Ber.*, **95**, 1438 (1962).

(21) G. N. Schrauzer, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

(22) S. Trofimenko, unpublished results.

(23) While the exact dimensions of the pyrazole ring are not known, the Stuart–Briegleb models provide a good qualitative picture of the molecular structure.

(24) At higher resolution this is seen to consist of two peaks at 2460 and 2474 cm^{-1} assigned, on the basis of their intensities, to the BH stretch of the B^{11} and B^{10} isotopes.

(25) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3158 (1967).

(26) G. E. Ryschkievitsch and E. R. Birnbaum, *Inorg. Chem.*, **4**, 575 (1965); *J. Phys. Chem.*, **65**, 1087 (1961); M. F. Hawthorne, W. L. Budde, and D. Walnisky, *J. Am. Chem. Soc.*, **86**, 5337 (1964); M. F. Hawthorne and W. L. Budde, *ibid.*, **86**, 5337 (1964).

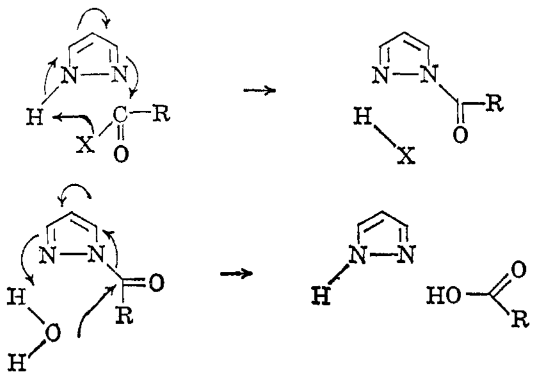
Table III. Compounds of Structure $M[B(pz)_4]_2$

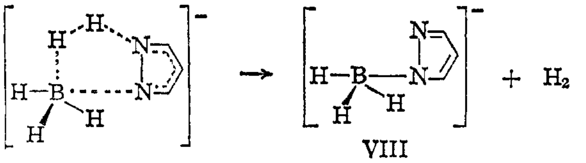
Color	M	Mp, °C	Yield, %	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	M, % Calcd	M, % Found	Mol wt Calcd	Mol wt Found
White	Mg	358–359[a]	71	49.6	49.2	4.13	3.79			4.18	4.10		
White	Ca	310–311[a]	80	48.1	48.0	4.02	4.06	37.5	37.5				
White	Sr	343–346 dec[b]	60	44.6	44.1	3.72	3.91	34.7	34.1				
White	Ba	316–318[c]	72	41.4	39.8[d]	3.45	4.08	32.2	30.8				
White	Mn	342–343[a]	88	47.0	47.2	3.92	3.85			8.95	8.93	613	643[e]
Pale wine-red	Fe	352–360 dec[a]	86	46.9	47.1	3.91	4.04	36.5	35.9	9.12	9.05	614 3.52 % B	614[f] 3.75 % B
Yellow	Co	364–365[a]	88	46.8	46.8	3.89	3.91	36.3	36.4	9.57	9.59		
Lilac	Ni	371–372[a]	88	46.8	47.1	3.89	4.22			9.49	9.48		
Blue	Cu	310–312[a]	86	47.1	46.6	4.11	3.86			10.2	10.4		
White	Zn	322–323[a]	92	46.2	46.3	3.85	3.62			10.5	10.5		
White	Cd	328–329[a]	75	43.0	43.1	3.58	3.61	33.4	33.1				
White	Pb	230–232[a]	79	37.6	37.5	3.14	3.13	29.3	28.9	27.1	27.0		
White	Hg	216–220	71	37.9	37.5	3.16	3.66	29.5	28.7				

[a] Recrystallized from toluene. [b] Sublimed. [c] Recrystallized from water. [d] Calculated for dihydrate: C, 39.4; H, 3.82; N, 30.6. [e] Ebullioscopic in toluene. [f] Osmometric in chloroform.

In our case, the reaction of borohydride ion with pyrazole is thought to proceed in a manner that combines some features of SN1 and SN2 reactions. This mechanism is probably also operating in the reaction of trimethylamine borane with pyrazole.

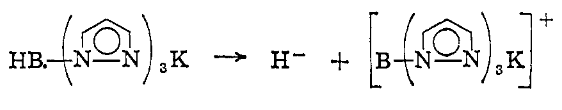
The main feature of this mechanism is a cyclic low-energy transition state with a geometry resembling that in SN2 substitution. However, while in SN2 reactions the departing and the attacking groups are at the apices of a trigonal bipyramid, in the case of pyrazole and borohydride ion the evolution of hydrogen proceeds concertedly through a cyclic five-center transition state[27] and involves equatorial rather than apical hydrogen. Here, both B-N bond forming and B-H bond breaking are facilitated by the "push-pull" effect of pyrazole approaching as a 1,3 dipole. The intermediate VIII could then again undergo the same type of reaction to reach a resonance-stabilized form as the potassium chelate IV. Alternatively, the same stage could be reached by coordination of 1-dihydroborylpyrazole (obtained from VIII *via* loss of hydride ion) with pyrazole, present in large excess, to yield the free acid $H[H_2B(pz)_2]$ directly. This acid, in a basic medium, would be converted to the $[H_2B(pz)_2]^-$ ion, as the potassium chelate. It should be noted that there is no noticeable break in hydrogen evolution until two pyrazole molecules per BH_4^- have reacted. The third pyrazolyl group is attached less readily, probably for steric reasons, and also because of possible orientation of the noncoordinating nitrogen in the transition state toward the potassium ion rather than toward the hydrogen to be eliminated.



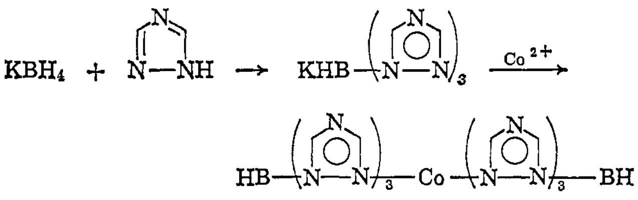


VIII

The fourth pyrazolyl group is introduced very slowly as, by now, the access to the boron atom is quite obstructed. Possibly, a direct SN1, dissociation may occur with the slow step being followed by rapid reaction of IX with pyrazole or pyrazolide ion.



When potassium borohydride is heated in excess 1,2,4-triazole, the hydrotris(1,2,4-triazol-1-yl)borate ion is formed, as proved by the formation of compound X when the reaction product was treated with Co^{2+} ion. This compound is yellow just like $Co[HB(pz)_3]_2$. In contrast to $Co[HB(pz)_3]_2$, however, it is soluble in and can be recrystallized from water. This solubility is attributable to the presence of six additional nitrogens in the molecule.



X

Experimental Section

Potassium Dihydrobis(1-pyrazolyl)borate. Potassium borohydride (54 g, 1 mole) was mixed with 272 g (4 moles) of pyrazole in a 1-l. flask attached through an air condenser to a gas meter. The pyrazole was carefully melted by means of an oil bath at 90°. When the contents of the flask was sufficiently molten to allow magnetic stirring, the mixture was stirred and heated at tempera-

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[27] This cyclic five-center transition state is probably characteristic of all pyrazole reactions with dipolarophiles AB; it is just as applicable to, *e.g.*, acylation of pyrazoles as to hydrolysis of acylpyrazoles.

tures not exceeding 115°. Potassium borohydride dissolved slowly with evolution of hydrogen, and the progress of the reaction was followed on the gas meter. After 20 hr, 2 moles (*ca.* 50 l.) of hydrogen had evolved and only a few small particles of KBH_4 were still floating in the melt. These were removed mechanically. The melt was poured into 500 ml of toluene; the resulting mixture was stirred until it cooled to room temperature and was then filtered. The filter cake was washed twice with 150-ml portions of hot toluene and then air-dried, yielding 137 g (74%) of a solid, mp 171–172°. The analytical sample was recrystallized from anisole. The infrared spectrum of the product has a complex BH pattern at 2250–2420 cm.$^{1-}$ *Anal.* Calcd for $C_6H_8BN_4K$: C, 38.7; H, 4.30; N, 30.1. Found: C, 38.9; H, 4.36; N, 29.9.

Potassium Hydrotris(1-pyrazolyl)borate. A mixture of 272 g (4.0 moles) of pyrazole and 54 g (1.0 mole) of potassium borohydride was heated with stirring in a 1-l. flask, connected *via* an air-cooled condenser to a gas meter, until about 75 l. (3 moles) of hydrogen had been evolved. The melt was poured slowly into 600 ml of stirred toluene, whereupon a solid precipitated. The mixture was filtered and the product was washed with hot toluene, then with hexane, and air-dried. There was obtained 190 g (79%) of white solid, mp 185–190°. The solid was recrystallized from anisole and obtained as fine needles, mp 188–189°. *Anal.* Calcd for $C_9H_{10}BKN_6$: C, 42.8; H, 3.97; N, 33.3. Found: C, 42.9; H, 4.23; N, 33.4.

Lithium Hydrotris(1-pyrazolylborate). This compound was prepared by the above method and obtained, after recrystallization from toluene, as needles, mp 264–265°. It is readily sublimable at 240° (2 mm). *Anal.* Calcd for $C_9H_{10}BLiN_6$: C, 49.1; H, 4.55; N, 38.2. Found: C, 48.8; H, 4.84; N, 38.2. This lithium salt is very soluble in water, acetone, alcohols, and tetrahydrofuran, moderately soluble in chloroform, and sparingly soluble in cold toluene.

Sodium Hydrotris(1-pyrazolyl)borate. This compound was prepared by the above method and obtained in 91% yield. It was purified by recrystallization from 1,2-dimethoxyethane and then by sublimation at 210–215° (2 mm), mp 222–223°. *Anal.* Calcd for $C_9H_{10}BN_6Na$: C, 45.7; H, 4.24; N, 35.5. Found: C, 45.5; H, 4.26; N, 35.2.

Potassium Tetrakis(1-pyrazolyl)borate. Potassium borohydride (54 g, 1 mole) and pyrazole (340 g, 5 moles) were heated together until about 100 l. of hydrogen (4 moles) was evolved. The melt was cooled until it became viscous and then was poured into 1.5 l. of stirred toluene. The mixture was filtered and the cake washed with successive portions of hot toluene, benzene, and ether. The solid was air-dried to give 310 g (98% yield). The analytical sample was recrystallized from ethanol and dried at 130° (2 mm), mp 253–254. *Anal.* Calcd for $C_{12}H_{12}BKN_8$: C, 45.3; H, 3.78; N, 35.2. Found: C, 45.1; H, 3.79; N, 35.2.

Preparation of Poly(1-pyrazolyl)borate Salts by Neutralization of the Free Acids. General Procedure. The free acids were prepared by adding an equimolar amount of acetic acid to a fairly concentrated aqueous solution of the appropriate potassium poly(1-pyrazolyl)borate. The precipitated free acid was isolated by filtration and washed thoroughly with water. It was then stirred with a stoichiometric amount of the appropriate alkali metal or quaternary ammonium hydroxide with additional methanol, as necessary, to effect homogeneity. The solutions were decolorized with Darco and evaporated at reduced pressure. The solid residues were recrystallized from an appropriate solvent, usually with substantial solubility losses.

Tetramethylammonium Tetrakis(1-pyrazolyl)borate. This compound was recrystallized from 1,2-dimethoxyethane and obtained in 93% yield. It decomposes with evolution of trimethylamine at 219–220°. *Anal.* Calcd for $C_{16}H_{24}BN_9$: C, 54.4; H, 6.81; N, 35.7. Found: C, 54.4; H, 7.02: N, 36.0. The nmr spectrum (D_2O) has doublets at τ 2.33 ($J < 2.0$ cps) and 2.62 ($\sim$2.3), a triplet at 3.67 ($\sim$1.9), and a singlet at 6.92 in exactly a 1:1:1:3 ratio.

Lithium Tetrakis(1-pyrazolyl)borate. This compound was obtained in 89% yield and was recrystallized from water. It was purified further by sublimation at 300° (2 mm), mp 394–395°. *Anal.* Calcd for $C_{12}H_{12}BLiN_8$: C, 50.3; H, 4.19; N, 39.2. Found: C, 50.3; H, 4.36; N, 38.8. The nmr (D_2O) has an unresolved doublet at τ 2.26, a doublet (J $\sim$2.2 cps) at τ 2.58, and an unresolved triplet at τ 3.60 in a 1:1:1 ratio.

Sodium Tetrakis(1-pyrazolyl)borate. This compound was obtained in 80% yield after recrystallization from ethanol, mp 238–239°. *Anal.* Calcd for $C_{12}H_{12}N_8BNa$: C, 47.7; H, 3.97; N, 37.1. Found: C, 47.0; H, 3.87; N, 36.3.

Cesium Tetrakis(1-pyrazolyl)borate. This salt was obtained in 47% yield after recrystallization from ethanol, mp 243–244°. *Anal.* Calcd for $C_{12}H_{12}BCsN_8$: C, 35.0; H, 2.92; N, 27.2. Found: C, 34.9; H, 2.85; N, 26.6.

Tetramethylammonium Dihydrobis(1-pyrazolyl)borate. This salt was obtained in 58% yield after recrystallization from 1,2-dimethoxyethane, mp 107–108°. *Anal.* Calcd for $C_{10}H_{20}BN_5$: C, 54.2; H, 9.05; N, 31.7. Found: C, 54.0; H, 9.44; N, 31.3.

Tetramethylammonium Hydrotris(1-pyrazolyl)borate. This compound was obtained in 46% yield after recrystallization from 1,2-dimethoxyethane, mp 96–97°. *Anal.* Calcd for $C_{13}H_{22}BN_7$: C, 54.4; H, 7.67; N, 34.1. Found: C, 53.9; H, 7.38; N, 33.5.

Hydrogen Dihydrobis(1-pyrazolyl)borate. To a solution of 19 g (0.1 mole) of $KH_2B(pz)_2$ in 200 ml of water was added 6.0 g (0.1 mole) of acetic acid. The precipitated solid was filtered, washed with water, and obtained, after air-drying, in 15.3-g yield.

Recrystallization from chloroform gave white crystals, mp 128–129°, with gas evolution. *Anal.* Calcd for $C_6H_9BN_4$ (anhydrous acid): C, 48.7; H, 6.08; N, 37.9. Calcd for $C_6H_{17}BN_4O_4$ (tetrahydrate): C, 32.7; H, 7.73; N, 25.5. Found: C, 33.6; H, 5.95; N, 25.5. The infrared spectrum of this material had, apart from the complex BH_2 sketch, broad and intense absorption characteristic of intramolecular hydrogen bonding at 1700–3000 cm^{-1}.

Hydrogen Hydrotris(1-pyrazolyl)borate. This compound was prepared as above and obtained as a solid which decomposed on attempted recrystallization.

Hydrogen Tetrakis(1-pyrazolyl)borate. To a stirred solution of 159 g (0.5 mole) of potassium tetrakis(1-pyrazolyl)borate in 1 l. of water was added 30 g (0.5 mole) of acetic acid. The precipitated solid was separated by filtration, washed thoroughly with water and then ethanol, and air-dried overnight. It was purified further by dissolution in a minimum amount of methylene chloride and concentration under reduced pressure at 30–35° to a thick slurry. It was stirred with 500 ml of ether and filtered, and the solid was dried in a stream of warm nitrogen. There was obtained 27 g of material, mp 70–71°. *Anal.* Calcd for $C_{12}H_{13}BN_8$: C, 51.4; H, 4.64; N, 40.0. Found: C, 52.1; H, 4.69; N, 40.4.

Preparation of Metal Dihydrobis(1-pyrazolyl)borates. Compounds of this type were prepared by adding an aqueous solution of 1 equiv of the appropriate metal ion to an aqueous solution of 2 equiv of potassium dihydrobis(1-pyrazolyl)borate. The chelates precipitated immediately. In the case of the air-sensitive chelates of Mn(II) and Fe(II), the addition and subsequent manipulations had to be done in an inert atmosphere. The products were isolated either by filtration or by extraction with methylene chloride. While they could be sublimed with care, such sublimation was at times attended by pyrolysis to metal pyrazolide and pyrazabole, hence recrystallization from toluene or heptane was preferred. The properties of metal dihydrobis(1-pyrazolyl)borates are summarized in Table I.

Preparation of Metal Hydrotris(1-pyrazolyl)borates. Compounds of this type were prepared by adding a solution of 1 equiv of the appropriate metal ion to a stirred solution of 2 equiv of potassium hydrotris(1-pyrazolyl)borate. The precipitated product was either extracted with methylene chloride or filtered and purified further by recrystallization from xylene and/or sublimation. Some products were purified by chromatography on acid-washed alumina. The properties of metal hydrotris(1-pyrazolyl)borates are listed in Table II.

Preparation of Metal Tetrakis(1-pyrazolyl)borates. These compounds were prepared as described above. Metal tetrakis(1-pyrazolyl)borates were, as a rule, less soluble than the tris analogs; hence, filtration was preferred to extraction. The properties of metal tetrakis(1-pyrazolyl)borates are summarized in Table III.

Hydrotris(1,2,4-triazol-1-yl)boratecobalt(II). A mixture of 5.4 g of potassium borohydride and 27 g of 1,2,4-triazole (0.1 and 0.4 mole, respectively) was heated until 7.5 l. (0.3 mole) of hydrogen was evolved. The melt was dissolved in 800 ml of hot water (90°) and was treated with 100 ml of 0.5 M cobaltous acetate solution. A precipitate formed which was insoluble in methylene chloride and was recrystallized from 800 ml of boiling water to give 3.9 g (16% yield) of well-shaped yellow crystals. The material darkens from 390° up but is still solid at 450°. *Anal.* Calcd for $C_{12}H_{14}B_2CoN_{18}$: C, 29.3; H, 2.85; N, 51.3. Found: C, 29.5; H, 2.93; N, 51.4.

Polarographic Studies. All the samples were dissolved in acetonitrile, except for the iron compounds which were dissolved in dimethyl sulfoxide. The solutions were 0.1 M in tetrabutylammonium perchlorate, used as supporting electrolyte. The dropping mercury electrode *vs.* sec was used with $Cu[H_2B(pz)_2]_2$, Cu[B-

$(pz)_4]_2$, $Co[H_2B(pz)_2]_2$, and $Co[HB(pz)_3]_2$. The rotating platinum electrode *vs.* sce was used for $Fe[HB(pz)_3]_2$ and $Fe[B(pz)_4]_2$.

Both $Cu[H_2B(pz)_2]_2$ and $Cu[B(pz)_4]_2$ were found to undergo reversible one-electron reduction at about $\epsilon_{1/2} = 0.29$ v. The cobalt compounds, $Co[H_2B(pz)_2]_2$ and $Co[HB(pz)_3]_2$, were oxidized (one electron) at +0.2 and −0.09 v, respectively. $Co[HB(pz)_3]_2$ underwent a two-electron reduction at −2.13 v, while its Fe(II) counterpart could not be reduced in the +0.34- to −2.75-v range. $Fe[HB(pz)_3]_2$ and $Fe[B(pz)_4]_2$ underwent one-electron oxidation at +0.27 and 0.37 v, respectively.

Acknowledgment. The author wishes to thank Miss Lucille E. Williams who carried out the polarographic studies.

Cyanonitrene. Reaction with Saturated Hydrocarbons[1]

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Abstract: Cyanonitrene was generated thermally from cyanogen azide, and its intermediacy in reactions with saturated hydrocarbons was established by means of isotopic labeling. The nitrene exhibits pronounced selectivity in insertions into C–H bonds, which in the absence of a solvent occur in a stereospecific manner. Mechanisms are discussed.

In contrast to the well-documented chemistry of carbenes,[3] their nitrogen counterparts (nitrenes)[4] have received serious attention by organic chemists only recently.[5] In 1962, Barton and Morgan[6] reported the first examples of intramolecular C–H insertions[7] of alkylnitrenes to afford either five- or three-membered rings, and Lwowski and Mattingly[8] presented the first case of an intermolecular insertion[7] in the reaction of carbethoxynitrene with cyclohexane.

The recent synthesis of cyanogen azide (N_3CN)[9] has provided a direct route for the generation of the highly symmetrical molecule NCN, "cyanonitrene." In the present paper we report on the thermal generation of NCN and on the mechanism of its reactions with saturated hydrocarbons.

Results and Discussion

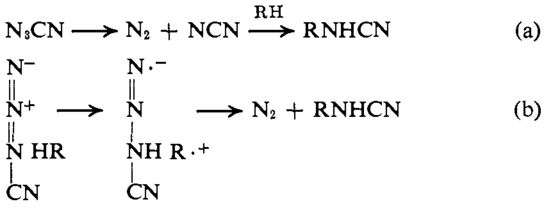
Unlike most organic azides which require temperatures in excess of 100° for fragmentation to the corresponding nitrenes,[4] cyanogen azide smoothly evolves nitrogen when heated to 40–50°. Kinetics have not been studied in detail but the rate of nitrogen evolution appears to be first order in dilute solutions. In addition the rate of nitrogen evolution depends on the polarity of the solvent employed, being more rapid in nonpolar media (hydrocarbons) than in polar media (ethyl acetate, acetonitrile). These facts are consistent with unimolecular fragmentation of the highly polar azide to two nonpolar species. When the decomposition of the azide is conducted in a paraffinic hydrocarbon, alkylcyanamides **1** are formed in yields of 55–70%.

$$N_3CN + RH \xrightarrow[40\text{–}50^\circ]{} N_2 + \underset{\mathbf{1}}{RNHCN}$$

For example, thermolysis of a 1% solution of N_3CN[10] in cyclohexane at 50° afforded cyclohexylcyanamide (**1**, R = C_6H_{11}) in 57% yield. The product showed strong infrared absorption at 3200 (NH) and 2210 (C≡N) and nmr signals at τ 4.3 (doublet, 1 H), 7.0 (multiplet, 1 H), and 7.9–9.0 (multiplet, 10 H); cyclohexylcyanamide was characterized by hydrolysis to cyclohexylurea on boiling with 10% sulfuric acid.

Isotopic Labeling Experiments. In photolytic or thermolytic reactions of azides with saturated hydrocarbons to yield insertion products, a likely mechanism involves unimolecular fragmentation of the azide to the corresponding nitrene and nitrogen followed by insertion[7] of the nitrene into C–H bonds. Although this is the most reasonable sequence of events, there usually is no unequivocal experimental evidence excluding an alternative mechanism in which the azide itself reacts with the hydrocarbon. The two possible mechanisms are depicted in Scheme I.[11]

Scheme I



$$N_3CN \longrightarrow N_2 + NCN \xrightarrow{RH} RNHCN \qquad (a)$$

$$\begin{matrix} N^- \\ \| \\ N^+ \\ \| \\ N\,HR \\ | \\ CN \end{matrix} \longrightarrow \begin{matrix} N\cdot^- \\ \| \\ N \\ | \\ NH\,R\cdot^+ \\ | \\ CN \end{matrix} \longrightarrow N_2 + RNHCN \qquad (b)$$

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(1) This work was described in preliminary form: A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *J. Am. Chem. Soc.*, **87**, 2296 (1965).

(2) To whom inquiries may be addressed at the Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210.

(3) For an excellent account see W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(4) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(5) The term nitrene is used here to indicate a monovalent nitrogen species which adds to double bonds and inserts into C–H bonds.

(6) D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962). See, however, D. H. R. Barton and A. N. Starratt, *J. Chem. Soc.*, 2444 (1965).

(7) The term insertion is used here to indicate end result rather than mechanistic detail.

(8) W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962).

(9) F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

(10) This experiment was first carried out by Dr. F. D. Marsh.

(11) In Scheme Ib the dipolar intermediate is supposed to be associated with singlet N_3CN and the diradical species with triplet N_3CN. Thus, abstraction of hydrogen might occur as either hydride ion or as a hydrogen atom.