

Organic and Biological Chemistry

Boron-Pyrazole Chemistry. I. Pyrazaboles

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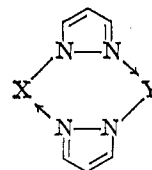
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Abstract: Boranes and borane complexes react cleanly with pyrazoles giving rise to nondissociable dimers of 1-borylpyrazoles. These compounds represent a new, remarkably stable class of boron heterocycles and have been named pyrazaboles. One-step syntheses of representative pyrazaboles are described and their properties are discussed.

In 1924 Morgan and Tunstall¹ found that a BF_2 group can replace the hydrogen bridge in acetylacetone, benzoylacetone, and dibenzoylmethane. The stability of the products has been attributed to coordination of the BF_2 group with the second heteroatom. Since that time other examples of a BR_2 group ($\text{R} = \text{F}, \text{Cl}, \text{alkoxy}, \text{alkyl}, \text{aryl}; \text{R}_2 = o\text{-phenylenedioxy}$) replacing the chelated proton in enolizable β -diketones,²⁻¹² β -keto esters,^{9b,10,13} β -ketocarboxamides,¹⁴ β -ketoimines,^{9b,10,15} 8-hydroxyquinoline,^{10,12,16-19} biguanide,²⁰ 1-amino-7-imino-1,3,5-cycloheptatrienes,²¹ bis(dimethylglyoxime)nickel²² and -cobalt,²³ as well as miscellaneous chelating agents with N and O terminals^{24,25} have appeared. The notion that a BR_2 grouping, when bonded to one heteroatom of a chelating agent and coordinated to the other, resembles in some ways a metal ion is implicit in the above results and has been mentioned by several of the authors. It is further supported by the finding that BF_2 -bridged acetylacetone

undergoes electrophilic substitution reactions²⁶ akin to those of transition metal acetylacetonates for which quasi-aromaticity has been invoked.²⁷

In all these compounds the BR_2 group forms an intramolecular bridge. We were interested in constructing resonance-stabilized cyclic structures of high symmetry based on *intermolecular* BR_2 bridges. Pyrazole was selected for this purpose since its geometry was known to favor formation of hydrogen-bonded dimers²⁸ and since both its cationic and anionic forms possess C_{2v} symmetry.²⁹ In addition this heterocyclic nucleus has great hydrolytic and oxidative stability. With pyrazole dimer as the starting point, it was assumed that this entity could be bridged by any binary combination chosen from (a) hydrogen, (b) transition metal ion, and (c) BR_2 group, the interchangeability of these in chelating systems having been amply demonstrated. Structures I-VI were arrived at in this fashion. Of these, the first two are known examples of pyrazole dimer and



- I, X = H; Y = H
 II, X = M; Y = M
 III, X = BR_2 ; Y = BR_2
 IV, X = BR_2 ; Y = H
 V, X = BR_2 ; Y = M
 VI, X = M; Y = H

- (1) G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, 125, 1963 (1924).
 (2) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, 72, 3635 (1950).
 (3) C. R. Hauser, F. L. Frostick, Jr., and E. H. Man, *ibid.*, 74, 3231 (1952).
 (4) J. F. W. McOmie and M. S. Tute, *J. Chem. Soc.*, 3226 (1958).
 (5) H. Schafer and O. Braun, *Naturwiss.*, 39, 280 (1952).
 (6) G. M. Badger and J. M. Sasse, *J. Chem. Soc.*, 746 (1961).
 (7) B. M. Mikhailov and Yu. N. Bubnov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1883 (1960).
 (8) A. T. Balaban, C. N. Rentea, and M. Bacescu-Roman, *Tetrahedron Letters*, 2049 (1964).
 (9) (a) M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, 86, 5016 (1964); (b) *J. Org. Chem.*, 30, 3857 (1965).
 (10) L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *Inorg. Chem.*, 4, 1649 (1965).
 (11) I. Bally, A. Arsene, M. Bacescu-Roman, and A. T. Balaban, *Tetrahedron Letters*, 3929 (1965).
 (12) R. Köster and G. W. Rotermond, *Ann.*, 689, 40 (1965).
 (13) W. Gerrard, M. F. Lappert, and R. Schafferman, *Chem. Ind. (London)*, 722 (1958).
 (14) J. F. Wolfe and C.-L. Mao, *J. Org. Chem.*, 31, 3069 (1966).
 (15) M. J. S. Dewar and R. C. Dougherty, *Tetrahedron Letters*, 907 (1964).
 (16) R. Neu, *Z. Anal. Chem.*, 142, 335 (1954).
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 (18) H. J. Roth and B. Miller, *Naturwiss.*, 50, 732 (1963).
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 (23) G. N. Schrauzer, *J. Am. Chem. Soc.*, 88, 3738 (1966).
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 (25) F. Umland and C. Schleyerbach, *ibid.*, 77, 169, 426 (1965).

- (26) A. P. Skoldinov and P. N. Shigorin, *Zh. Obshch. Khim.*, 33, 3110 (1963); *J. Gen. Chem. USSR*, 33, 3037 (1963).

- (27) J. P. Collman, *Angew. Chem. Intern. Ed. Engl.*, 4, 132 (1965); "The Chemistry of Quasiaromatic Metal Chelates," *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p 78.

- (28) (a) W. Hüchel, J. Datow, and E. Simmersbach, *Z. Physik. Chem. (Leipzig)*, 186A, 129 (1940); (b) W. Hüchel and Jahneitz, *Ber.*, 75, 1438 (1942); (c) H. Hayes and L. Hunter, *J. Chem. Soc.*, 1 (1941); (d) L. Hunter, *ibid.*, 806 (1945); (e) D. M. W. Anderson, J. L. Duncan, F. J. C. Rossotti, *ibid.*, 140, 4201 (1961); (f) S. N. Vinogradov, *Can. J. Chem.*, 41, 2719 (1963).

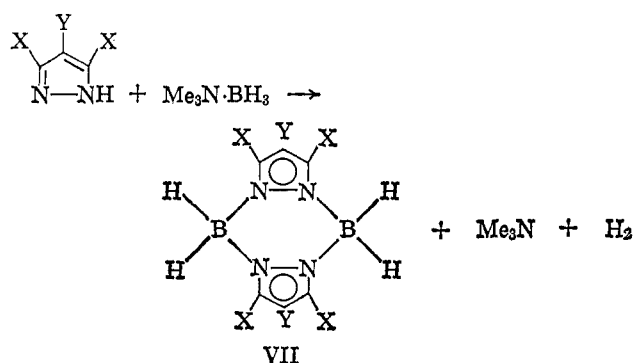
- (29) See, for instance, "Physical Methods in Heterocyclic Chemistry," Vol. I, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, p 45.

transition metal compounds with pyrazole,³⁰ respectively. Compounds IV and V are hydrogen and metal poly(1-pyrazolyl)borates³¹ and are dealt with elsewhere.³²

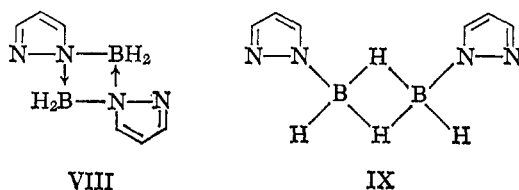
This paper is concerned with compounds of type III which, because of their unusual features, stability, and wealth of derivatives, were given the trivial name "pyrazabole" with numbering as shown in structure X.

Results and Discussion

Refluxing equimolar amounts of pyrazole and trimethylamine borane in toluene resulted in rapid evolution of hydrogen and trimethylamine (eq 1, X = Y = H). A crystalline, sublimable solid of camphoraceous odor, mp 80–81°, was isolated in good yield. It was a dimer of 1-dihydroborylpyrazole as established by elemental analysis, molecular weight determination, the presence of a strong BH₂ multiplet around 2400–2500 cm⁻¹ in the infrared, and the degradation of this compound by boiling hydrochloric acid to pyrazole and boric acid.



Of the three *a priori* possible structures, VII (X = Y = H), VIII, and IX, one would immediately tend to select VII for electronic and steric reasons.³³ Support for this structure was obtained from H¹ nmr which had



only two C–H peaks: a doublet at τ 2.49 and a triplet at τ 3.83 ($J = 2.0$ cps) in a 2:1 ratio. This is obviously incompatible with structures VIII and IX, both of which should display spectra characteristic of asymmetrically substituted pyrazole.³⁴ The nmr spectrum of pyraza-

(30) M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 627 (1965).

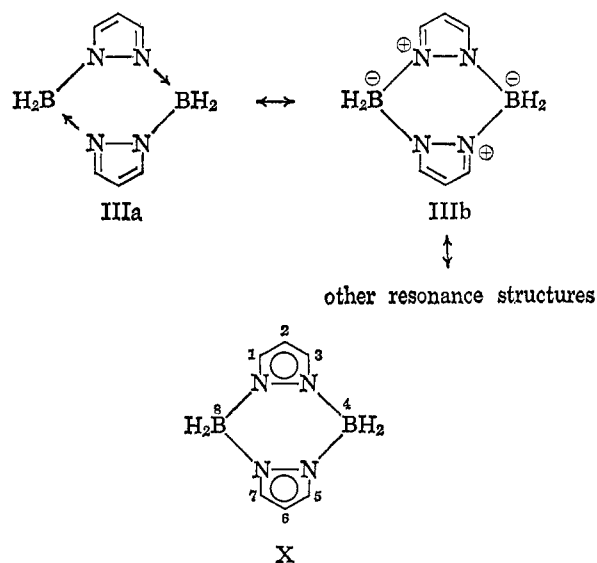
(31) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

(32) S. Trofimenko, *ibid.*, **89**, 3170 (1967).

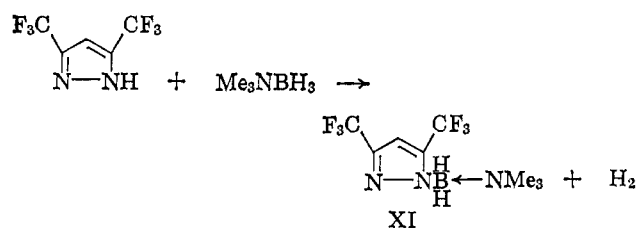
(33) As far as VIII is concerned, no precedent is known for electron donation by the substituted nitrogen in 1-alkylpyrazoles. Reactions such as quaternization invariably take place at the 2 position, thus maintaining resonance in the pyrazole ring which would otherwise be lost. Values for the resonance energy of pyrazole range, depending on the method used, were from 27 to 41 kcal/mole: H. Zimmerman and H. Geisenfelder, *Z. Elektrochem.*, **65**, 368 (1961); A. F. Bedford, P. B. Edmondson, and C. T. Mortimer, *J. Chem. Soc.*, 2927 (1962). Moreover, VII should be favored over VIII by some additional 26 kcal/mole from strain considerations, using the thermochemical strain energy for cyclobutane of 26.2 kcal/mole: S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952). With regard to IX, no precedent is known for a simple aminoborane containing hydrogen bridges; such bridges are always broken in the presence of donor atoms.

(34) Proton nmr was shown to be a reliable and discriminating tool for establishing the type of substitution in pyrazole. See, for instance, L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966), and

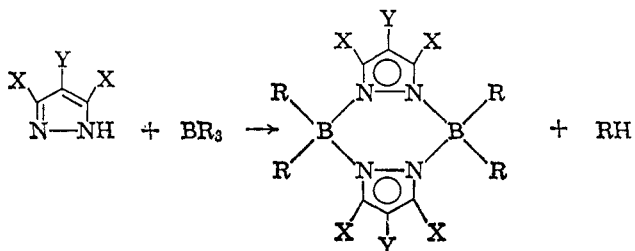
bole indicates equivalence of positions 1, 3, 5, 7. This spectroscopic equivalence persists in all pyrazabole derivatives and is indicative of a structure such as X containing tetrahedral boron in a symmetrical environment. This structure would contain positive charges delocalized in the ligand and negative charges on boron much like the analogous β -diketonates, which is consistent with the inertness of pyrazabole to sodium hydroxide and other nucleophiles.³⁵



When substituted pyrazoles were used instead of pyrazole, the reaction proceeded analogously and C-substituted pyrazaboles were obtained (Table I). Pyrazoles with strong electron-withdrawing substituents reacted at a slower rate, commensurate with the reduced nucleophilicity of the 2-nitrogen. In the case of 3,5-bis(trifluoromethyl)pyrazole the product was trimethylamine 3,5-bis(trifluoromethyl)pyrazol-1-ylborane (XI), which could be distilled without decomposition. 1,2,3,5,6,7-hexabromopyrazabole (as well as 1,2,3,5,6,7-hexabromopyrazabole) was prepared by using tetrahydrofuran-borane complex instead of trimethylamine borane.



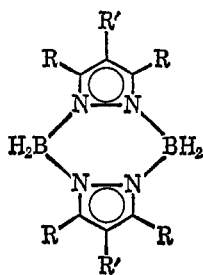
Trialkylboranes react with pyrazoles on heating to 120–150° with evolution of the appropriate hydrocarbon and formation of 4,4,8,8-tetraalkylpyrazaboles (Table



references cited therein, as well as V. F. Bystrov, I. I. Grandberg, and G. I. Sharova, *Zh. Obshch. Khim.*, **35**, 293 (1965).

(35) Part III: S. Trofimenko, submitted for publication.

Table I. Compounds of Structure



R	R'	Mp, °C	Yield, %	C, %		H, %		N, %		X, %		H ¹ nmr ^g	B ¹¹ nmr ^g	Miscellany
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found			
H	H	80–81 ^a	90	45.2	45.4	6.27	6.09	35.1	35.1	B, 13.5 Mol wt, 160	B, 13.7 Mol wt, 166	d, 2.49 (2) t, 3.83 (1) (J = 2.0 cps) s, 2.43	t, 27.1 (J = 108 cps)	Ultraviolet, end absorption 213 mμ (ε 1130)
H	Cl	119–120 ^b	74	31.4	31.3	3.49	3.49	24.2	24.2	Mol wt, 318	Mol wt, 313	s, 2.40	t, 27.6 (J = 94 cps)	Ultraviolet, λ _{max} 233 mμ (ε 7060)
H	Br	144–145 ^b	99	22.6	22.8	2.54	2.51	17.6	17.7			s, 2.46		
H	CH ₃	81–82 ^a	70	51.1	51.6		7.46					s, 2.64 (2) s, 7.95 (3)		
H	CN	290–300 dec	95	45.8	46.6	3.81	3.98	40.0	39.8			s, 0.95	t, unresolved 27.3	Ultraviolet, end absorption only; infrared, 2500 and 2470 cm ⁻¹ (BH ₂), 2260 cm ⁻¹ (CN)
H	NO ₂	202–203	96	28.8	29.4	3.20	3.12					s, 1.15		Photosensitive, turns orange on exposure to light
H	CF(CF ₃) ₂	49–50 ^a Bp 70–78 (2 mm)	66	29.0	29.5	1.61	1.88			Mol wt, 496	Mol wt, 526	s, 1.91	t, unresolved 27.2	Very unpleasant, penetrating odor
CH ₃	H	184–185 ^c	58	55.6	55.8	8.33	8.38	25.9	25.9	Mol wt, 216	Mol wt, 210		t, 31.2 (J = 103 cps)	
C ₆ H ₅	H	203 ^d sinters 232–242 dec	29	77.6	77.6	5.70	5.69	12.1	12.3					Ultraviolet, λ _{max} 248 mμ (ε 53,000)
CF ₃	H	88–89 ^a	93	27.8	27.7	1.37	1.58	12.9	12.8	F, 52.8 Mol wt, 432	F, 53.3 Mol wt, 489		t, unresolved 27.7	
CH ₃	CH ₃	173–174 ^e	99	59.0	59.2	9.02	9.06	22.9	23.1			s, 7.67 (2) s, 8.10 (1)		
Br	Br	280 ^d sinters 285–290 dec	90	11.3	11.0	0.63	0.50	8.83	8.78					

^a Recrystallized from hexane. ^b Recrystallized from heptane. ^c Recrystallized from toluene. ^d Recrystallized from xylene. ^e Distilled. ^f Molecular weights determined osmotically in chloroform. High volatility of perfluoroalkylpyrazaboles would lead to high values. ^g The H¹ nmr data show multiplicity, chemical shift in τ, and relative areas. The B¹¹ nmr data are given in parts per million and referred to external methyl borate

II), while triphenylborane yields 4,4,8,8-tetraphenylpyrazabole.

All pyrazaboles thus prepared are colorless, sublimable solids except for 4,4,8,8-tetrabutylpyrazabole which is a liquid. They are unaffected by air and water and have been stored for over 3 years without any apparent deterioration, although 2,6-dinitropyrazabole is photosensitive.

Such extraordinary stability is even more noteworthy if one considers that none of the other chelating systems has yielded isolable BH₂-bridged species despite several attempts at their preparation.^{12,22} This stability (thermodynamic as well as kinetic) may be rationalized as follows. (A) Molecular models³⁶ show that the nitrogen and boron atoms (the prospective targets of electrophilic and nucleophilic attack, respectively) in pyrazabole are much better shielded than the BR₂ group and the corresponding heteroatoms in, for instance, analogous acetylacetone derivatives. The im-

(36) While Stuart-Breigleb models may not give an accurate picture of the molecular structure, they are useful in supplying qualitative data. An unstrained model of pyrazabole is puckered in the boat form, whereas one would expect the molecule to be planar if coplanarity of the B-N bonds and tetrahedral angles around boron are preserved. Such a model may be also constructed, but it entails considerable strain.

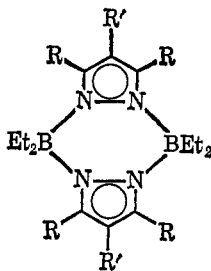
portance of steric factors in B-N coordination chemistry is well known.³⁷ (B) While there are four nonexcited resonance structures based on charge separation in BR₂-bridged acetylacetone, there are 16 structures such as IIIa in pyrazabole with attendant stabilization of the ground state. (C) The pyrazole nucleus is much more resistant to reduction than an enolizable 1,3-dione system.

A characteristic feature in the infrared spectra of B-unsubstituted pyrazaboles is the strong absorption due to BH stretch (Figure 1). It is most complex in pyrazabole itself and consists of peaks at 2470, 2430, 2410, 2370, 2310, 2280, 2250, and 2240 cm⁻¹. The strongest peak is at 2470 cm⁻¹, and the remaining ones are of gradually decreasing intensity, except for the 2310, 2280 cm⁻¹ pair where the higher frequency peak is the weaker of the two.³⁸ Most C-substituted pyrazaboles have a strong sharp doublet in the 2400–

(37) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, 1, 132 (1964), and references cited therein.

(38) This spectrum was measured in Nujol mull. The BH₂ band remained complex even in CCl₄ solution: 2440 (s), 2415 (s), 2345 (m), 2280 (w), 2265 (w), and 2220 (w) cm⁻¹. This complexity of the BH stretch is inconsistent with a planar model of essentially D_{2h} symmetry and supports a puckered structure as indicated by molecular models.

Table II. Compounds of Structure



R	R	Mp, °C	Yield, %	C, %		H, %		X, %		H ¹ nmr ^f	B ¹¹ nmr ^f
				Calcd	Found	Calcd	Found	Calcd	Found		
H	H	106-107 ^a	94	61.8	61.7	9.56	9.35	B, 7.94	B, 7.90	d, 2.41 (2) t, 3.60 (1) m, 9.5 (10) (<i>J</i> = 2.3 cps)	s, +16.1
H	Cl	117-118 ^a	85	49.0	49.3	7.00	7.18	N, 16.9	N, 16.5	s, 2.38 (1) m, 9.4 (5)	s, +15.0
H	Br	127-128 ^a	95	39.1	39.0	5.59	5.91	Br, 37.2 Mol wt, 430	Br, 37.2 Mol wt, 447 ^e	s, 2.32 (1) m, 9.4 (5)	s, +15.6
H	CN	264-265 ^b	93	59.7	60.0	7.46	7.41	N, 26.1	N, 26.0	s, 1.97 (1) m, 9.4 (5)	s, +15.4
H	NO ₂	186-189 ^b dec	46	46.4	45.0	6.63	6.70	N, 23.2	N, 23.9	s, 1.70 (1) m, 9.3 (5)	s, +13.8
CH ₃	H	156-157 ^c	86	65.8	65.9	10.4	10.6			s, 4.03 (1) s, 7.60 (6) m, 9.08-9.75 (10)	s, +14.3
CH ₃	CH ₃	173-174 ^c	99	67.4	67.4	10.7	10.7	N, 15.7	N, 15.9	s, 7.57 (6) s, 7.88 (3) m, 9.4 (10)	s, +13.8
Br	Br	~210 dec	94	22.5	23.0	2.68	2.79			q, 8.73 (2) t, 9.52 (3) (<i>J</i> = 8.0 cps)	s, +13.8
H	CF(CF ₃) ₂	63-64 ^d	69	39.5	39.5	3.95	3.96	N, 9.21	N, 9.79		s, +13.8

^a Recrystallized from ethanol. ^b Recrystallized from xylene. ^c Recrystallized from heptane. ^d Distilled, bp 94-98° (4.5 mm). ^e Molecular weights determined osmometrically in chloroform. The H¹ nmr spectra show: multiplicity, chemical shift in τ , and relative areas. The B¹¹ nmr data are given in parts per million and referred to external methyl borate.

2500-cm⁻¹ range, separated by 10-100 cm⁻¹, and additional weaker and less well-defined bands in the 2250-2400-cm⁻¹ range. Other functional groups attached to carbon in pyrazaboles absorb normally. For instance,

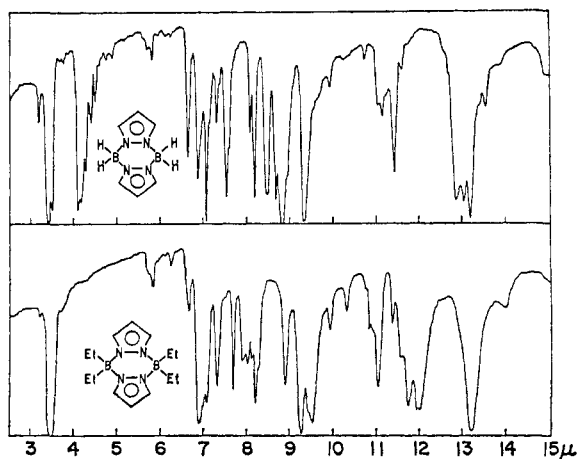


Figure 1. Infrared spectra of pyrazabole and 4,4,8,8-tetraethylpyrazabole.

2,6-pyrazabole dicarbonitrile contains the CN band at 2260 cm⁻¹, as does 4-pyrazole carbonitrile. Many 4,4,8,8-tetraethylpyrazaboles have characteristic strong

absorption in the 840-880-cm⁻¹ range and a weaker band at about 910 cm⁻¹.

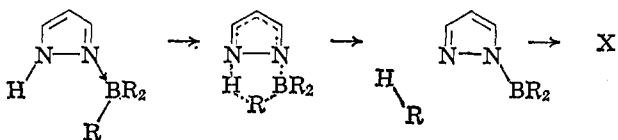
The H¹ nmr spectra of pyrazaboles were most useful in structure assignment. They invariably indicated equivalence of the 1,3,5,7 and 2,6 positions, respectively. The chemical shift of the 1,3,5,7-hydrogens in 2,6-disubstituted pyrazaboles ranges from τ 0.95 (*Y* = CN) to 2.64 (*Y* = CH₃) and seems to parallel the inductive effect of the substituents. The same trend is noted, but to a lesser extent, in 2,6-disubstituted 4,4,8,8-tetraethylpyrazaboles. Ethyl groups in the latter compounds appear as a relatively narrow triplet (half-height width 10-12 cps) around τ 9.30-9.40, the methylene hydrogens coinciding with the methyl group (Figure 2). In 1,3,5,7-tetramethyl-4,4,8,8-tetraethylpyrazabole and 1,2,3,5,6,7-hexamethyl-4,4,8,8-tetraethylpyrazabole, the methylene and methyl peaks appear as an ill-defined multiplet in the τ 9.0-9.8 range. 1,2,3,5,6,7-Hexabromo-4,4,8,8-tetraethylpyrazabole is the only compound having the normal quadruplet-triplet pattern for its ethyl groups. The hydrogens of the BH₂ group in pyrazaboles appear as an exceedingly broad (300 cps) band, but their presence and ratio to other hydrogens is easily established by integration.

The B¹¹ nmr spectra of pyrazaboles show the expected 1:2:1 triplet in the 27-31-ppm range.³⁹ In some cases

(39) This is close to the range reported for trimethylamine borane: D. F. Gaines and R. Schaefer, *J. Am. Chem. Soc.*, 86, 1505 (1964).

these are well resolved with coupling constants around 100 cps; in others the triplets are ill defined. In 4,4,8,8-tetraethylpyrazaboles the boron resonance appears as a singlet in the 15–17-ppm range, which is about 13 ppm higher than for the BEt_2 -bridged acetylacetonates,⁶ but about 18 ppm lower than in tetraethylborate ion.⁴⁰

With regard to the mechanism of pyrazabole formation two situations may be distinguished. Before considering these, one should note that the geometry of pyrazole is favorable to a cyclic five-center transition state. If one assumes coordination at the 2 position to precede any bond breaking, the 1-hydrogen should be sufficiently close to an R group to permit intramolecular departure of RH. Such proximity may be inferred⁴¹ from the facile formation of a pyrazole formaldehyde adduct⁴² possessing an intramolecular hydrogen



bridge and the ease of intramolecular quaternization of 1-(2,3-dibromopropyl)pyrazole.⁴³ The reaction course as shown above is the most plausible path for trialkylboranes, triarylboranes, and tetrahydrofuran-borane where uncontested B–N coordination takes place, as manifested by heat evolution and dissolving of pyrazoles suspended in xylene upon addition of trialkylborane. The 1-dialkylborylpyrazole fragment may, apart from dimerizing, react with pyrazole to form IV. It has been shown,³⁵ however, that hydrogen poly-(1-pyrazolyl)borates disproportionate irreversibly at elevated temperatures to pyrazaboles and pyrazole. Moreover, the electrophilicity of a BR_2 group ought to surpass that of pyrazole hydrogen, and hence the possible formation of IV is of minor significance. The intramolecular activation by coordination suggested above has its analogy in the reaction of boranes with carboxylic acids, the mechanism of which has been proposed by Brown⁴⁴ and confirmed by Toporcer, Dessy, and Green.⁴⁵ While the transition state in borane–pyrazole reaction involves a five-membered ring, electrons are relayed along pyrazole's π system and in that sense an eight-membered ring is involved in the transition state.

A different situation obviously exists when pyrazoles react with trimethylamine borane where a strong donor molecule is involved. Probably an equilibrium involving trimethylamine 1-pyrazolylborane is established, the reaction being driven to completion by removal of trimethylamine from the system and irreversible formation of pyrazabole.

The reaction of 1,2,4-triazole with triethylborane yielded the analogous 4,4,8,8-tetraethyl-*sym*-triazabole. This compound was obtained in lower yield than the corresponding pyrazabole, which is not surprising

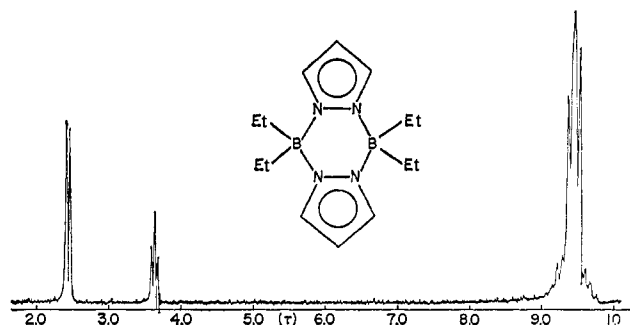


Figure 2. Nmr spectrum of 4,4,8,8-tetraethylpyrazabole.

in view of the additional nitrogen atom than can interact in the coordinating stage of the reaction.

Experimental Section

Pyrazole, 3,5-dimethylpyrazole, 1,2,4-triazole, triethylborane, tributylborane, triphenylborane, and trimethylamine borane are commercially available. They were used without further purification. 4-Chloropyrazole,⁴⁶ 4-bromopyrazole,⁴⁷ 4-methylpyrazole,⁴⁸ 4-pyrazolecarbonitrile,⁴⁹ 4-nitropyrazole,⁵⁰ 3,4,5-trimethylpyrazole,⁵¹ and 3,4,5-tribromopyrazole⁵² were prepared by published methods.

General Method for Preparing Pyrazaboles. Equimolar amounts of the appropriate pyrazole and trimethylamine borane were refluxed in toluene (about 1 l./mole). The emanating gases were conducted through a -80° trap to a wet-test meter or other suitable volumetric device. The progress of the reaction was followed by measuring the amount of hydrogen evolved. In most instances the reaction was complete within a few hours. The solvent was distilled under aspirator vacuum, and the residue was purified by recrystallization and sublimation (see Table I). In the cases of 3,5-bis(trifluoromethyl)pyrazole and 3,4,5-tribromopyrazole, their tetrahydrofuran solutions were added, under nitrogen, to an equivalent amount of borane in tetrahydrofuran. The theoretical amount of hydrogen was evolved rapidly. The solutions were then processed as above.

General Method for Preparing 4,4,8,8-Tetraethylpyrazaboles. Equimolar amounts of the appropriate pyrazole and triethylborane were stirred and refluxed in xylene (about 1 l./mole) until the theoretical amount of ethane, as measured by a wet-test meter, was evolved. The solvent was evaporated and the residue purified by recrystallization and sublimation (see Table II).

4,4,8,8-Tetraethylpyrazabole. A mixture of 13.6 g of pyrazole and 50 ml of tributylborane (both 0.2 mole) was stirred and refluxed in 250 ml of xylene until about 5 l. of butane was evolved. The solvent was evaporated at reduced pressure, and the residual oil was distilled *in vacuo*. There was obtained 34.2 g (89.0%) of material, bp 190° (4.6 mm), n_D^{20} 1.4948. *Anal.* Calcd for $\text{C}_{22}\text{H}_{42}\text{B}_2\text{N}_4$: C, 68.8; H, 10.9. Found: C, 69.0; H, 10.9.

The nmr spectrum consists of a doublet at τ 2.42 ($J = 2.5$ cps), a triplet at 3.62 ($J = 2.5$ cps), and a multiplet around 9.2 in 2:1:18 ratio.

4,4,8,8-Tetraphenylpyrazabole. A mixture of 22.6 g (0.0935 mole) of triphenylborane and 68 g (1.0 mole) of pyrazole was heated to reflux until benzene ceased to distill. The melt was poured into 800 ml of water and stirred for 2 days. The mixture was filtered, and the solid was air dried and recrystallized from 200 ml of boiling toluene. It was washed with ether and air dried. There was obtained 15.7 g (72.4%) of a material melting at $273-274^\circ$. *Anal.* Calcd for $\text{C}_{30}\text{H}_{26}\text{B}_2\text{N}_4$: C, 77.6; H, 5.60; N, 12.0. Found: C, 77.9; H, 5.40; N, 11.6.

3,5-Bis(trifluoromethyl)pyrazole. A. Adduct of 1,1,1,5,5,5-Hexafluoropentane-2,4-dione with Hydrazine. 1,1,1,5,5,5-Hexafluoropentane-2,4-dione (208 g, 1.00 mole) was added slowly at

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(41) The bond angles and distances in pyrazole have not been determined.

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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 $C_6H_2F_6N_2$: 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 over-

night 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 $C_6H_{12}BF_6N_2$: 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

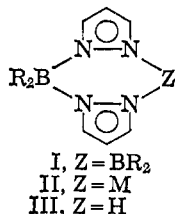
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Abstract: Alkali metal dihydrobis(1-pyrazolyl)borates, hydrotris(1-pyrazolyl)borates, and tetrakis(1-pyrazolyl)borates have been prepared from alkali metal borohydrides and pyrazole. The first two are parent compounds, each representing a new class 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).



Pyrazaboles (I) are neutral heterocycles that may be regarded as dimers of an intermediate dihydroborylpyrazole (for $R = H$) fragment. On the other hand,

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(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.

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)borates⁹ and hydrotris(1-pyrazolyl)borates,⁹ and their free acids and diverse salts and chelates derived therefrom. Although tetrakis(1-pyrazolyl)borates⁹ are, in terms of coordinating ability, merely a substituted variant of tris(1-pyrazolyl)borates, they will be covered

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(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.