CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

Amine Boranes. III. Propanolysis of Pyridine Boranes[1a]

BY G. E. RYSCHKEWITSCH AND E. R. BIRNBAUM[1b]

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The solvolysis kinetics in 1-propanol of a number of alkyl-substituted pyridine boranes was studied. The reactions were first order in amine borane. Linear variation of log *k* with pK_a of the pyridinium ion was observed for groups of compounds with the same *ortho* substituents; steric enhancement of rate was attributed to 1.1 and 3.5 kcal./mole of strain relief in the transition state for one or two *o*-methyl groups, respectively. It was concluded that the solvolysis mechanism involves B–N cleavage in the slow step. It was found that the free energy of the transition state referred to the dissociation products was invariant with substitutions on the pyridine ring.

Introduction

The reaction of addition compounds of pyridine derivatives with BH_3 occurs quantitatively with alcohols according to the over-all equation

$$R'C_5H_4NBH_3 + 3ROH \longrightarrow R'C_5H_4N + B(OR)_3 + 3H_2$$

In an earlier publication[1] we presented evidence that the propanolysis of pyridine boranes proceeds by dissociation of the boron–nitrogen bond in the slow step. Recently, Kelly, *et al.*,[2] reported in an extensive study of the reaction of arylamine boranes in acidic solutions that unimolecular dissociation of the boron–nitrogen bond can occur in competition with a bimolecular reaction involving attack of a solvated proton of the amine nitrogen. The latter mechanism has also been suggested for the protolysis of trimethylamine borane in water.[3] In contrast to B–N cleavage mechanisms, the reaction of pyridine diarylboranes with water in acetonitrile proceeds by a hydride transfer from boron to the water protons.[4]

We now wish to report further evidence that boron–nitrogen bond cleavage is the rate-determining step in the solvolysis of pyridine boranes. In addition data are reported which elucidate the importance of electronic and steric effects of substituents on the pyridine ring.

Experimental

Materials.—The amines used were stirred for 8–12 hr. with calcium hydride and then distilled in a 25-plate column, taking a 1° center cut. Reagent grade 1-propanol was distilled from barium oxide, taking a 97–98° center cut. Purified grade *p*-dioxane was refluxed for several days over calcium hydride and was distilled just before use to give samples free of peroxide, as evidenced by a negative test in acidified potassium iodide.

Preparation and Purification of Amine Boranes.—Pyridine borane was obtained from the Callery Chemical Co. in lots of varying purity. Relatively pure samples were further purified by washing an ether solution with dilute sodium hydroxide. The compound was then obtained by vacuum evaporation of the ether solution. Less pure lots were placed over calcium hydride, slowly heated with continuous pumping to 70°, and then condensed onto a cold finger. The kinetic behavior of samples purified by either method was the same. It should be noted that pyridine borane refluxing at 90° in a stainless steel spinning-band column may spontaneously react with rapid gas evolution and formation of a solid.

Alkyl-substituted pyridine boranes were prepared by bubbling diborane into excess amine. Excess amine was removed by continual pumping for several hours. Solids were then recrystallized from *n*-nonane and liquids were condensed under vacuum on a cold finger.

Analyses for BH_3 hydrogen were performed by the iodate method.[5] Boron analysis was accomplished by solvolyzing a sample in concentrated HCl–methanol, distilling the resulting methyl borate–alcohol azeotrope into water, and titrating boric acid in the hydrolyzed distillate as the mannitol complex. A typical analysis for 4-methylpyridine borane is as follows. *Anal.* Calcd. for $CH_3C_5H_4NBH_3$: C, 67.37; H, 9.42; N, 13.10; B, 10.12. Found: C, 67.20; H, 9.66; N, 13.32; B, 10.31. Reducing equivalents gave typically 97–98% of the amount calculated from the equation

$$RC_5H_4NBH_3 + IO_3^- + H^+ \longrightarrow RC_5H_4NH^+ + B(OH)_3 + I^-$$

Kinetic Experiments.—Solutions of the amine boranes were made up by dissolving a weighed amount of compound in propanol in a volumetric flask. The solutions were placed in a thermostat (Sargent Thermonitor) where the temperature was held to at least ±0.005°. When working with temperatures below 30° the thermostat bath was externally cooled by immersing it in a refrigerated bath controlled to a few degrees below the desired operating temperature. Under these conditions the reaction temperature was maintained to ±0.01°.

The progress of the reaction was followed by periodically withdrawing 5-ml. aliquots and oxidizing the sample with standard KIO_3 to which KI and acid had been added. Excess iodine was then back-titrated with standard sodium arsenite. In this way unreacted amine borane was determined.

The reaction rates were in all instances first order in amine borane concentration over several half-lives of reaction. The data gave excellent fit by the least-squares method and are presented in Table I. At least two runs were made at different concentrations (0.05–0.1 *M*) for each temperature. The rate constants agreed to 1% or better and were only slightly increased in 0.4 *M* pyridine due to dielectric effects.

The temperature variation of the first-order rate constants gave excellent fit to the Arrhenius equation, $\log k = A - B/T$.

First-order rate constants extrapolated to 30° from the Arrhenius equation are listed in Table II. Activation enthalpies and entropies at 30° were calculated from the Arrhenius parameters by means of the relations $\Delta H^* = 2.303RB - RT$ and $\Delta S^* =$

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[1] (a) Paper II: G. E. Ryschkewitsch and E. R. Birnbaum, *J. Phys. Chem.*, **65**, 1087 (1961). (b) Based on the Ph.D. dissertation by E. R. Birnbaum, University of Florida, 1961. Portions of this dissertation were presented at the International Symposium on Boron–Nitrogen Chemistry, Durham, N. C., April 1963; Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 53.

[2] H. C. Kelly, F. R. Marchelli, and M. B. Giusto, *Inorg. Chem.*, **3**, 431, (1964).

[3] G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **82**, 3290 (1960).

[4] M. F. Hawthorne and E. S. Lewis, *ibid.*, **80**, 4296 (1958).

[5] D. A. Little, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

TABLE I

FIRST-ORDER RATE CONSTANTS FOR PROPANOLYSIS OF PYRIDINE BORANES

Pyridine							
H-	T, °C.	43.12	45.49	47.63	50.00	52.43	54.26
	k^a	0.83	1.12	1.44	1.88	2.40	2.98
2-Methyl-	T, °C.	39.67	41.80	43.95	46.44	48.84	
	k^a	1.40	1.84	2.37	3.13	4.15	
3-Methyl-	T, °C.	52.70	55.20	57.47	59.97	62.07	
	k^a	1.59	2.07	2 76	3.57	4.44	
4-Methyl-	T, °C.	58.20	60.10	62.00	64.94	66.43	
	k^a	1.91	2.49	3.22	4.17	5.00	
2-Ethyl-	T, °C.	30.00	32.50	34.78	37.27	39.77	
	k^a	1.11	1.52	2.10	2.83	3.75	
2,4-Dimethyl-	T, °C.	48.49	50.95	53.35	55.87	58.37	
	k^a	1.70	2.16	2.92	3.87	5.18	
2,6-Dimethyl-	T, °C.	10.00	14.00	17.08	19.60	22.10	
	k^a	0.62	1.11	1.68	2.21	3.02	
2,4,6-Trimethyl-	T, °C.	30.00					
	k^a	2.88					

[a] $\times 10^5$, sec.$^{-1}$.

TABLE II

RATE CONSTANTS, ACTIVATION ENTHALPIES, AND ACTIVATION ENTROPIES AT 30°

Pyridine borane	k (sec.$^{-1}$) $\times 10^6$	ΔH^*, kcal./mole	$-\Delta S^*$, e.u.
H-	1.70	22.7 ± 0.1	9.9 ± 0.4
2-Methyl-	4.27	22.9 ± 0.2	7.5 ± 0.5
3-Methyl-	0.96	23.7 ± 0.5	7.9 ± 1.6
4-Methyl-	0.55	24.9 ± 1.3	5.1 ± 3.8
2-Ethyl-	11.0	23.4 ± 0.5	4.2 ± 1.8
2,4-Dimethyl-	1.70	23.2 ± 0.6	8.3 ± 1.9
2,6-Dimethyl-	79	20.9 ± 0.6	8.3 ± 1.8
2,4,6-Trimethyl-	28.8	. . .	. . .

$2.303R(A - \log kT/h) - R$. Table II lists these data and their standard errors.

Experiments in 1-propanol–water mixtures and 1-propanol–dioxane mixtures were carried out under similar conditions and showed an increase in rate with a decrease in dielectric constant. These data have been reported previously.[1a] Values for the dielectric constants of propanol–water mixtures were interpolated from the data given by Åkerlof.[6]

Discussion

The reaction rate is first order in pyridine borane and not retarded by added pyridine. This indicates that a preliminary dissociation equilibrium is not established. The excellent fit to a first-order law over several half-lives implies that reaction intermediates are not accumulating.

Rate data for dioxane–propanol and water–propanol mixtures have been reported in an earlier communicatin.[1a] The rates of reaction increased on addition of dioxane and decreased on addition of water. Thus, the rate changes cannot be interpreted in terms of alcohol concentration alone. In fact, only the first-order rate constants give a linear Kirkwood relation.[7] Such variation of solvolysis rate with dielectric constant is typical of a reaction where the transition state has a lesser polarity than the ground state and is consistent with a mechanism where the B–N dipole is destroyed in the rate-determining step through cleavage of the boron–nitrogen bond. Constants calculated by assuming a first-order dependence on alcohol concentration only give a curvilinear Kirkwood plot. It thus would appear that the reaction is zero order in alcohol.

The mechanism therefore appears to be slow dissociation of amine borane in the solvent, followed by rapid reaction of the BH_3 fragment with propanol to give the final product.

$$\text{py}\cdot\text{BH}_3 \longrightarrow \text{py} + \text{BH}_3\text{, slow}$$

$$\text{BH}_3 + \text{alcohol} \longrightarrow \text{products, rapid}$$

Comparisons of the rate constants at 30° listed in Table II reveal variations in the reaction rates related to steric and electronic effects of the substituents. Substitution of one methyl group in the 2 position adjacent to the nitrogen atom increases the rate about threefold; an additional methyl group in the 6 position produces an additional 17-fold increase in rate. Methyl substitution in the 4 position of the ring reduces the solvolysis rate to about one-third of the value for the pyridine adduct not substituted in this position. The latter variation is in accord with the B–N cleavage mechanism since one would expect an increase in electron density on the donor nitrogen and strengthening of the boron–nitrogen bond in these cases through the hyperconjugative and inductive effect of the methyl group. Methyl substitution in the 3 position has a smaller retarding effect on the rate since here only the inductive effect can operate strongly.

If boron–nitrogen bond cleavage is the rate-determining step there should be a correlation between the base strength of the pyridine and the rate of the reaction. Figure 1 is a plot of log k *vs.* the pK_a of the pyridinium ions[8,9] as a measure of base strength. The data (excepting 2-ethylpyridine borane) form three groups of parallel relations, the groups differing in the number of methyl substituents in the *ortho* position. In each group the expected decrease in rate with increasing base strength is evident. If hydride loss were the rate-determining step one would expect the opposite correlation since a strengthening of the nitrogen-to-boron dative bond should increase the electron density on boron and thus facilitate hydride loss. The magnitude of the observed steric effects also argues against a hydride loss mechanism. In accord with the proposed mechanism, the pyridine boranes highly substituted in the *ortho* position give the largest solvolysis rates. This can be interpreted as due to a relief of steric strain as the boron–nitrogen bond is stretched in the transition state.

It is noteworthy that all the data for the methyl-substituted pyridine boranes will give a linear log k *vs.* pK_a relation if one assumes that each *o*-methyl group contributes a constant increment to the free energy of activation. The lowest line in Figure 1 is thus obtained under the assumption that one *o*-methyl group reduces the free energy of strain by 1.1 kcal. and that two methyl groups produce 3.5 kcal. in strain relief.

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(6) G. Åkerlof, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1961, p. 140.

(8) H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955).

(9) E. A. Braude and F. C. Nachod, Ed., "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955, p. 594.

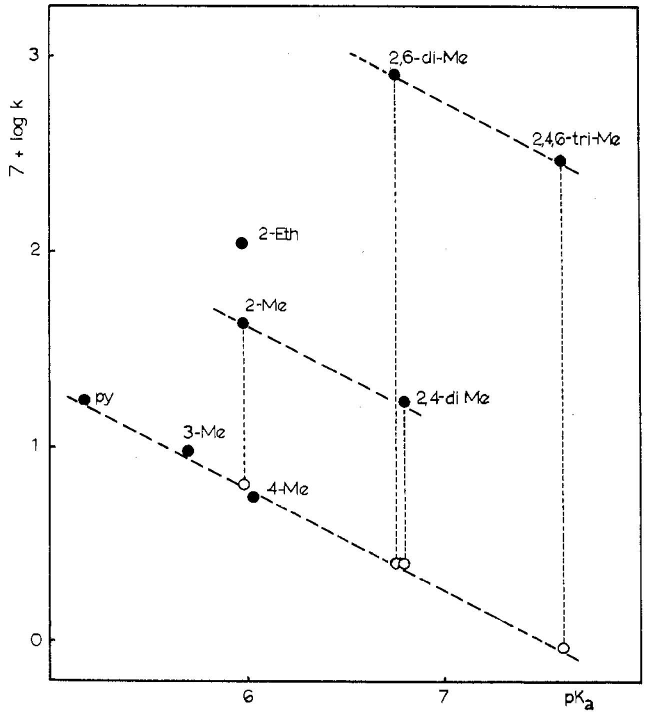

Figure 1.—Correlation between solvolysis rate and base strength (30°): ●, experimental points; ○, expected in the absence of strain.

The resulting line would thus define the solvolysis rates expected from changes in base strength alone and would reflect essentially only the electronic effects of substitution. Rates of 2-methyl derivatives are then sterically increased by a factor of about seven and rates of 2,6-dimethyl derivatives by a factor of about 300. 2-Ethyl substitution would produce steric enhancement of rate intermediate between these factors (18 times for 2-ethylpyridine borane).

A detailed examination of the experimental activation enthalpies provides a further test for the correctness of the reaction mechanism. A partially stretched boron–nitrogen bond should produce steric strains intermediate between the strain present at the shorter interatomic distance in the ground state and an essentially unstrained addition compound, such as the pyridinium ion. As mentioned previously,[1] a plot of the activation enthalpies *vs.* the dissociation enthalpies of the amine borane, calculated from the data of Brown[10] and Bauer,[11] is consistent with this view. Sterically unhindered pyridine boranes follow a linear trend but those with *ortho* substituents exhibit an activation enthalpy larger than expected from the linear trend. The vertical deviation from the trend toward higher activation enthalpies is attributable to the greater strain destabilization of the ground-state borane relative to the transition state If the activation enthalpy is plotted *vs.* the enthalpy change of a proton loss from pyridinium ions[12] a linear trend is again observed for the unhindered compounds, but here the experimental activation enthalpies of the *ortho*-substituted compounds are *smaller* than expected from the trend; this indicates that the steric interaction of the leaving BH_3 group with the ring substituents in the stretched state is indeed intermediate between those of $pyBH_3$ and pyH^+. In this analysis we essentially follow the line of arguments advanced by Brown, *et al.*, concerning linear strain energy relations.[13]

The kinetic data given here are somewhat unique since they present an opportunity not only to relate transition-state energies to ground-state energies but also to relate both energy quantities to a common reference state. This is so because data are available on the enthalpies of formation of various pyridine boranes from diborane and the respective pyridines.[10] We therefore can calculate enthalpies and free energies of the transition states relative to BH_3 and free pyridine. The results are given in Table III and are based on the following data and assumptions.

$$BH_3(g) \longrightarrow {}^1/_2B_2H_6(g) \qquad \Delta H_1 = -14.0 \text{ kcal.}^{11}$$

$$^1/_2B_2H_6(g) + \text{py (nitrobenzene)} \longrightarrow pyBH_3 \text{ (nitrobenzene)} \qquad \Delta H_2{}^{10}$$

$$pyBH_3 \text{ (nitrobenzene)} \longrightarrow pyBH_3 \text{ (1-propanol)} \qquad \Delta H_3$$

$$\text{py (1-propanol)} \longrightarrow \text{py (nitrobenzene)} \qquad \Delta H_4$$

$$pyBH_3 \text{ (nitrobenzene)} \longrightarrow [pyBH_3]^* \text{ (1-propanol)} \qquad \Delta H^*$$

$$BH_3(g) + \text{py (1-propanol)} \longrightarrow [pyBH_3]^* \text{ (1-propanol)}$$
$$\Delta H = \Delta H_2 + \Delta H^* + \Delta H_3 + \Delta H_4 - 14.0$$

ΔH is consequently the enthalpy of formation of the transition state from borane and pyridine and would represent the activation enthalpy of the association reaction. The quantity $\Delta H_3 + \Delta H_4$ represents the difference in the enthalpies of transferring a pyridine or its borane adduct from nitrobenzene to 1-propanol. We consider it very unlikely that this difference is sensitive to substitution on the pyridine. (The more stringent requirement that the enthalpies are completely unaffected by solvent changes has already been demonstrated in a related reaction system.[12]) Therefore the quantities $\Delta H_2 + \Delta H^*$ differ from the true enthalpies of the transition states, ΔH, only by a constant increment. It is seen from Table III that in the sequence pyridine, 3-methylpyridine, 4-methylpyridine the transition state grows (linearly) *less* stable with respect to BH_3 and pyridine as the strength of the pyridine base increases; *ortho* substitutents again introduce a deviation from this trend. The former result is rather surprising but can be reconciled in a straightforward manner by considering the free energies of the transition states referred to BH_3 and pyridine.

In Table III we have presented the sum of the free energy of activation and the enthalpy of formation of the addition compounds from diborane and the appropriate pyridine derivative, $\Delta G^* + \Delta H_2$. The data clearly show that this quantity is a constant, invariant

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[10] H. C. Brown and L. Domash, *J. Am. Chem. Soc.*, **78**, 5384 (1956).

[11] A. Shepp and S. H. Bauer, *ibid.*, **76**, 265 (1954).

[12] H. C. Brown and R. R. Holmes, *ibid.*, **77**, 1727 (1955). Enthalpies for the reaction $pyH^+ + CH_3SO_3^- \rightarrow py + CH_3SO_3H$.

[13] H. C. Brown, D. Gintis, and L. Domash, *ibid.*, **78**, 5387 (1956).

TABLE III

RELATIVE VALUES OF TRANSITION STATE THERMODYNAMIC QUANTITIES ABOVE THE DISSOCIATION PRODUCTS (kcal./mole, 30°)

Substituent	ΔG^{*a}	$-\Delta H_2{}^b$	$\Delta H^* + \Delta H_2{}^b$	$\Delta G^{*a} + \Delta H_2{}^b$
2-Ethyl	24.6	16.9	6.5	7.7
4-Methyl	26.4	18.5	6.4	7.9
2-Methyl	25.2	17.2	5.7	8.0
3-Methyl	26.1	18.2	5.5	7.9
2,4-Dimethyl	25.7	17.7[c]	5.5	8.0
H	25.8	17.9	4.8	7.9
2,6-Dimethyl	23.4	16.3	4.6	7.1
2,4,6-Trimethyl	24.2	16.8[c]	...	7.4

[a] Free energy of activation. [b] Reference 10; enthalpy for the reaction $^1/_2B_2H_6 + py \rightarrow pyBH_3$. [c] The enthalpy of reaction without steric effects is estimated by interpolation of the linear relation between enthalpy of borane adduct formation and the enthalpy of neutralization by H^+ (ref. 12), giving ΔH(2,4-dimethyl) = -19.0 kcal./mole and ΔH(2,4,6-trimethyl) = 19.5 kcal./mole. Strain energies of 1.3 kcal. for one and 2.7 kcal. for two *o*-methyl groups are added, respectively, to give the final answer (ref. 10).

with substitution. It is noteworthy that even the introduction of two *ortho* substituents does not change this result. This is indeed surprising and carries with it the strong implication that the free energy of producing the transition state from the dissociated product is also a constant, *i.e.*, the activation free energies for the reverse of dissociation are constant. This interpretation is most plausible since, by an argument similar to the one made for the enthalpies, one would expect entropy changes of transfer from one solution to another to be invariant on substitution on the pyridine. Moreover, it has been demonstrated for pyridine adducts of $B(CH_3)_3$ that the entropies for the reaction py (sol) + $B(CH_3)_3 \rightarrow pyB(CH_3)_3$ (sol) do not vary with substitution.[14] Making a similar assumption for formation of BH_3 adducts we arrive at the conclusion that the quantities $\Delta G^* + \Delta H_2$ differ from the free energies of the transition state by only a constant amount and that constancy of one in a series of related reactions implies constancy of the other.

Thus, in the present reaction, the boron–nitrogen bond is stretched to a constant free energy above the products. Stronger bases will necessitate longer interatomic distances to achieve this. In fact, as is evident from the enthalpy trend in Table III, the remaining B–N bond energy may actually be less for the stronger base, since the increased freedom of motion in a more highly stretched state will contribute a stabilizing and compensating increase in the entropy of the transition state.

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[14] H. C. Brown and D. Gintis, *J. Am. Chem. Soc.*, **78**, 5378 (1956).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

The Reactions of Borazanaphthalene and Borazine with Anhydrous Hydrogen Bromide and Hydrogen Chloride[1]

BY A. W. LAUBENGAYER, O. T. BEACHLEY, JR.,[2] AND RICHARD F. PORTER

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The reactions of borazanaphthalene, $B_5N_5H_8$, and borazine, $B_3N_3H_6$,[3] with anhydrous hydrogen bromide and hydrogen chloride and the subsequent pyrolysis of the addition products have been examined. Regardless of the reactant mole ratio used, only materials of empirical compositions $B_5N_5H_8 \cdot 5HBr$, $B_5N_5H_8 \cdot 5HCl$, $B_3N_3H_6 \cdot 3HBr$, and $B_3N_3H_6 \cdot 3HCl$ are formed. The infrared spectra of these addition compounds are consistent with covalent rather than ionic behavior and with the conclusion that the hydrohalides add across the B–N bonds to form additional B–X and N–H bonds. When these adducts are heated at 100 to 130° with or without continued removal of the volatile products, the principal reaction is dissociation to barazanaphthalene or borazine and the hydrogen halide, with small and variable amounts of hydrogen and a nonvolatile residue also forming. Deuterium chloride addition compounds yield N-deuterioborazanaphthalene or -borazine and hydrogen chloride when pyrolyzed. The compounds 2,4,5,7-tetrahaloborazanaphthalene and 2,4,6-trihaloborazine were never observed as products in these experiments.

The addition of polar molecules, such as HCl, to borazine to form adducts of the type $B_3N_3H_6 \cdot 3HCl$ has long been known.[4,5] It has been suggested that such polar molecules add across the B–N bonds, the more electronegative group bonding to boron and the less elec-

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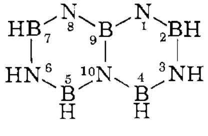
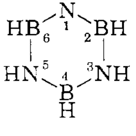
[1] Presented before the Inorganic Division at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 10, 1963, and abstracted from a thesis submitted to the Graduate School of Cornell University by O. T. Beachley, Jr., Sept. 1963.

[2] Gulf Research and Development Company Fellow, 1961–1962; NSF Research Fellow, 1962–1963.

[3] The following numbering systems will be used in this paper.



borazanaphthalene



borazine