Anal. Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43. Found: C, 75.10; H, 8.65.

5,6-Dimethylhydrindene-4-carboxylic Acid.—The above ketone (35 mg.) was dissolved in methanol and treated with excess potassium hypochlorite at 60–65° for thirty minutes. At this time most of the methanol had evaporated. An ether extract of the solution upon evaporation deposited an oil containing much chlorine (Beilstein test). This oil was dissolved in methanol (15 cc.) to which potassium hydroxide (3 pellets) had been added and the solvent was evaporated on a steam-bath until the volume reached 3 cc. Addition of dilute hydrochloric acid precipitated the carboxylic acid; m. p. 169–170°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.36; H, 7.72.

Tetrahydrobenz[f]indane.—To a mixture containing phosphoric acid (165 g., 85%) and phosphorus pentoxide (165 g.) was added γ-(5-hydrindenyl)-butyric acid (68.5). After being heated at 100–120° for five minutes with good stirring, the solution was poured into water (1000 cc.). The crude product was extracted with benzene and the benzene solution was washed with dilute alkali and dried. Removal of the benzene and distillation in a sausage flask gave a crude ketone which solidified on standing. Two recrystallizations from petroleum ether (b. p. 40–75°) followed by recrystallization from aqueous alcohol gave 28 g. of 6,7-cyclopentene-1-tetralone; m. p. 38–39°. Clemmensen reduction of this ketone gave pure tetrahydrobenz[f]indane; m. p. +4°. A sample prepared earlier in this Laboratory[5] melted at −3 to −5°.

Acetotetrahydrobenz(f)indane (V).—To tetrahydrobenz[f]indane (8 g., m. p. 4°) dissolved in carbon bisulfide (85 cc.) was added aluminum chloride (21 g.). Stirring was commenced and acetic anhydride (7.1 g.) was added over fifteen minutes. The entire reaction was carried out at 0° for one and three-quarters hours. After decomposition with ice and hydrochloric acid in the usual manner there was obtained a liquid ketone; wt. 6.8 g.; of b. p. 167–170° (1 mm.); $n^{25.5}_D$ 1.5610. This material could not be induced to crystallize.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.17; H, 8.44.

Summary

1. Further evidence is presented to prove that the steric effect of methylene groups in five membered rings (*i. e.*, hydrindene) is smaller than that in corresponding six-membered rings (*i. e.*, tetralin).

(5) R. Barnes, Ph.D. Thesis, University of Minnesota, 1943.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 30, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Tri-α-naphthylboron as a Highly Hindered Reference Acid; a Case of Polymorphism Ascribed to Hindered Rotation[1]

BY HERBERT C. BROWN[2] AND SEI SUJISHI[2,3]

Earlier results[4] have shown that the relative base strengths of ammonia and a given series of primary, secondary, and tertiary amines (NH_3, RNH_2, R_2NH, R_3N) are dependent upon the reference acid used to compare them. Thus the sequence in strength observed with trimethylboron as the reference acid is $NH_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$. This sequence is altered to $NH_3 < CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$, when tri-*t*-butylboron is used as the reference acid. This change in sequence has been ascribed to the increase in the steric requirements of the reference acid.[4b]

According to this interpretation, a reference acid of even greater steric requirements than tri-*t*-butylboron should cause the observed sequence to approach the theoretically possible limit, $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. It was of interest to test this conclusion.

The selection for this purpose of a triarylboron with large steric requirements was dictated by a number of considerations. Tri-*t*-butylboron is a very weak reference acid for the amines under discussion, considerably weaker than trimethylboron itself.[4a] This weakness has been attributed to the large steric requirements of the three tertiary butyl groups. Further increase in the bulk of the alkyl groups would be expected to decrease the stability of the addition compounds with the amines to the point where it would be relatively difficult experimentally to make comparisons. The available evidence strongly suggests that the replacement of alkyl groups by aryl groups markedly increases the acid strength of the boron compounds.

For a number of reasons, tri-α-naphthylboron[5] (hereafter TNB) appeared especially promising in attaining the theoretical limit sequence. It was therefore decided to prepare the addition compounds of ammonia and the three methylamines with TNB and to compare their relative stabilities by a careful study of each system. Since the addition compounds were found to be highly dissociated at temperatures at which neither TNB nor the addition compound were sensibly volatile, the problem reduced itself to measuring and comparing the pressures exerted by the only volatile component of the system—the gaseous base.

$$(\alpha\text{-}C_{10}H_7)_3B:NR_3 \text{ (solid)} \rightleftarrows (\alpha\text{-}C_{10}H_7)_3N \text{ (solid)} + NR_3 \text{ (gas)}$$

The observed pressures vary in the order $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ (*vide post*), and support the conclusion that the theoretical

---

[1] Studies in Stereochemistry. XII.

[2] Present address: Department of Chemistry, Purdue University.

[3] Ethyl Corporation Fellow at Wayne University, 1945–1947.

[4] (a) Brown, THIS JOURNAL, 67, 374 (1945); (b) 67, 378 (1945); (c) 67, 1452 (1945); (d) Brown and Pearsall, *ibid.*, 67, 1765 (1945).

[5] Krause and Nobbe, *Ber.*, 63, 934 (1930).

limit sequence of base strength, $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$, is actually under observation. In the course of these studies, some interesting and unusual instances of polymorphism were observed in the behavior of the addition compounds. It is suggested that these phenomena are the result of restricted rotation of the α-naphthyl groups in the addition compounds.

Observations

TNB was prepared by the action of α-naphthylmagnesium bromide on boron trifluoride etherate in benzene–ether solution. The product was isolated in the form of white crystals containing one mole of benzene per mole of TNB. Krause and Nobbe[5] report that TNB separates from benzene solution with two moles of benzene, but repeated experiments support the conclusion that the pure material obtained in the present study contains but one mole of benzene.

After a single recrystallization from benzene, the benzene of crystallization was removed under high vacuum at 150–160°. TNB was thus conveniently obtained in pure form in over-all yields of 50–60%.

The high degree of purity of the product is indicated by the following observations. It melts sharply at 206–207° (vacuum)[6] in contrast to the previously reported value[5] of 203–205°. Moreover, Krause and Nobbe report that the substance, although remarkably stable when compared to other triarylborons, showed significant signs of oxidation after several days of exposure to air; yet samples of TNB prepared by the present procedure show no noticeable change after exposures to laboratory air for more than one year. Finally, ultimate analyses for boron and acidimetric titrations of the compounds with a standard solution of sodium ethoxide in alcohol and phenolphthalein as indicator, yield results which point to purities of better than 99.8%.

$$(\alpha\text{-}C_{10}H_7)_3B + Na^+\,OC_2H_5^- = Na^+[(\alpha\text{-}C_{10}H_7)_3B:OC_2H_5]^-$$

The titration of TNB with standard solutions of sodium methoxide, ethoxide, and isopropoxide in the corresponding alcohols proceeded very smoothly—the indicator, phenolphthalein, changed color sharply at the equivalence point. However. with sodium *t*-butoxide the end-point was indistinct and the indicator changed color considerably before the true stoichiometric quantity of base had been added. It therefore appears that the large steric requirements of the *t*-butoxide group produce a definite shift of the acid–base equilibrium toward the left.

$$(\alpha\text{-}C_{10}H_7)_3B + {}^-OC(CH_3)_3 \rightleftarrows [(\alpha\text{-}C_{10}H_7)_3B:OC(CH_3)_3]^-$$

Krause and Nobbe prepared their addition compounds by adding the base to a saturated solution of the triarylboron in ethyl ether. The addition compounds precipitated and were recovered on the filter. In order to avoid the possibility that the presence of traces of ether in the resulting compounds might affect the observed dissociation pressures, preparation of the substances in the absence of solvents was investigated.

Three methods were examined. In the first, a large excess of the liquified amine was contacted with the boron compound. After reaction was complete, the excess amine was removed under high vacuum. In the second method, the gaseous amine was passed over the solid boron compound. Absorption was very rapid and the reaction could be readily followed by noting the evolution of heat. Both methods yielded products whose composition satisfactorily agreed with the 1:1 compounds previously reported. However, the addition compounds possess a marked affinity for excess amine and it proved difficult to remove such excess amine to obtain samples as analytically pure as the studies required. Recourse was therefore had to the third procedure, which avoided this difficulty. In this method, the addition compounds were synthesized by bringing together carefully matched equivalent samples of the two components in the high vacuum apparatus used to study the dissociation pressures.

The products prepared by each of these three procedures appeared identical as regards analyses, melting points, and dissociation pressures. However, the last procedure proved so much more definite and convenient, that it was finally adopted for all preparations in the present study.

The melting points of the addition compounds showed an unusual behavior not reported by Krause and Nobbe. For example, ammonia–TNB, if heated slowly in a capillary tube, melted at 200–205°. However, if the tube were inserted in a bath at 170–172°, the substance melted, resolidified, and then remelted at the higher temperature. Monomethylamine–TNB likewise showed two melting points—a fugitive one at 150–155°, followed by resolidification, and the permanent one at 190–192°. Dimethylamine–TNB melted only at 193–196°; no other melting point was observed. All attempts to add trimethylamine to TNB by the three procedures described were unsuccessful.

Ammonia–TNB was then synthesized in the apparatus shown in Fig. 7 (attached to the main high vacuum apparatus) and the dissociation pressures measured over a range of temperatures. It

TABLE I

DISSOCIATION PRESSURE OF AMMONIA-TNB

Mole ratio Ammonia/TNB	Pressure, mm.	Mole ratio Ammonia/TNB	Pressure, mm.
A. Freshly prepared sample, at 40°		B. Heat-treated sample, at 130°	
0.30	4	0.20	4
.60	6	.40	4
.90	26	.50	4
.98	43	.98	5
1.00	62		

---

(6) All melting points were taken with capillary tubes of the usual dimensions. These tubes were evacuated and sealed after the samples had been introduced. The temperatures are corrected.

was observed that the pressure of the freshly prepared addition compound varied with the mole fraction of amine. The results of a typical experiment at 40° are summarized in Table I-A. The other amines behaved similarly.

The addition compounds were then synthesized by bringing the two components together with a slight constant deficiency of the base. It was hoped that in this way the observed pressures for the different bases would be made strictly comparable, and, moreover, that the effects of slight errors in the mole ratio of the two components would thereby be minimized. Under these conditions, the pressure of the system became sensibly constant within several minutes,[7] and the plot of log P vs. $1/T$ showed the expected linearity (Fig. 1).

New phenomena made their appearance at higher temperatures. The curve showed a definite deviation from linearity, and the observed pressures, particularly in the higher ranges (120° and above) declined noticeably with time. The decrease was very rapid at 140°. In one experiment at this temperature the pressure dropped from a value of 450 mm to 20 mm. within one hour. However, the rate of pressure decrease then diminished, and the pressure at this temperature became constant at a new low value, 10 mm., only after a period of twenty hours.

The behavior of the product obtained in this way was then investigated. A new series of pressure values at elevated temperatures were recorded. These values were much lower than the first series of measurements, they were easily reproducible, and yielded only the second series of pressure measurements, without evidence of any tendency to revert to the original high values.

In contrast to the original material, the dissociation pressures of which were highly dependent on the mole ratio of the components (Table I-A), the dissociation pressures of the heat-treated material were essentially independent of composition (Table I-B).

That these phenomena were not due to some irreversible change in the TNB component was demonstrated by a number of experiments. A sample of the heated compound was maintained at 130°. The gas evolved was pure ammonia; the amount corresponded exactly to the original quantity of ammonia used in the synthesis. The residual solid melted at 205–206° and caused no depression in melting point when mixed with a sample of the original material. Moreover, the product formed by recombining the recovered ammonia and TNB possessed the same characteristic high dissociation pressures as the original preparation and exhibited the same behavior on heating. It may therefore be concluded that the recovered TNB is chemically indistinguishable from the original material.

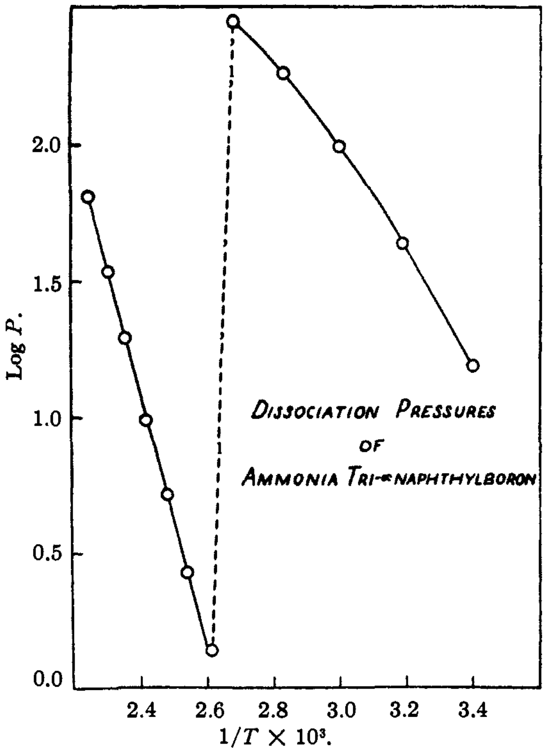


Fig. 1.—Dissociation pressures exhibited by a freshly prepared sample of ammonia-tri-α-naphthylboron as the temperature is raised.

The curves for the log P vs. $1/T$ plots of the corresponding monomethylamine and dimethylamine compounds with TNB showed the same general characteristics. The entire curve (*i. e.*, the two sections which describe the behavior of the freshly prepared substance and of the heat-altered product) for the methylamine compound lies above the curve for the ammonia derivative; the curve for dimethylamine is higher still.[8] Trimethylamine did not add to TNB under these conditions.

It was concluded that the observed pressures of the freshly prepared compounds are dependent not only on the mole fraction (particularly so in the region of equimolar ratios), but are also dependent upon time (particularly in the higher temperature ranges.) It was therefore decided that little could be gained by further refining the measurements of the variable pressures exhibited by these materials. Instead, attention was focused on the highly reproducible dissociation pressures exhibited by the addition compounds after prior heat treatment at 100–140°.

---

(7) Although the pressure of the system apparently reached an equilibrium value within several minutes, it was noted that the observed pressure tended to drift to lower values over periods of several hours duration. Moreover, samples of the addition compound which had been stored at room temperature for several weeks yielded considerably lower values of the dissociation pressure than freshly synthesized samples.

(8) The dissociation pressure curve definitely established the existence of two forms of the dimethylamine derivative. Failure to observe a "fugitive" melting point, as in the case of the other two addition compounds, is believed to be due to a more rapid transformation of the dimethylamine derivative near its melting point into the higher melting form.

TABLE II

DISSOCIATION PRESSURES OF THE HEAT ALTERED FORMS OF THE ADDITION COMPOUNDS OF TNB WITH AMINES

Ammonia, $\log P = -4762/T + 12.525$

Temp., °C.	110	120	130	140	150	160	170
Press., mm.	1.4	2.7	5.3	10.0	20.0	34.5	65.5

Methylamine. $\log P = -4666/T + 12.863$

Temp., °C.	103	110	119	130	140	150
Press., mm.	2.7	5.3	10.7	19.9	39.1	72.1

Dimethylamine, $\log P = -4296/T + 13.71$

Temp., °C.	50	60	70	80	90	100
Press., mm.	4.0	7.4	15.2	34.8	71.3	164

The observed dissociation pressures for the heat-treated products are listed in Table II, and the values are represented graphically in Fig. 2.

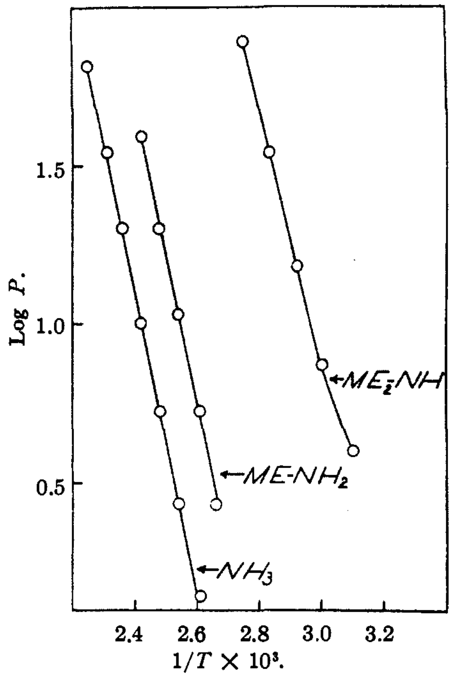


Fig. 2.—Dissociation pressures of the heat-treated ("stable") forms of the addition compounds of tri-α-naphthylboron with ammonia, methylamine and dimethylamine.

Discussion

In this investigation the pressure of the gaseous amine above a mixture of the solid TNB and solid addition compound has been taken as a measure of the stability of the latter.

$$(\alpha\text{-}C_{10}H_7)_3B\text{:}NR_3 \text{ (solid)} \rightleftarrows (\alpha\text{-}C_{10}H_7)_3B \text{ (solid)} + NR_3 \text{ (gas)}$$

This interpretation of the data apparently ignores such complications as may be caused by the crystal lattice energies of the solid compounds. Fortunately, there are reasons for believing that the differences between the crystal lattice energies of TNB on the one hand and each of the addition compounds on the other are relatively small and sensibly constant.

First, TNB and the three addition compounds (the heat stable forms) all melt at approximately the same temperatures. This observation suggests that the stabilities of the crystal lattices are of the same order of magnitude. Second, the molecular dimensions of the amines used are quite small compared to the TNB component. It therefore appears probable that the attractive forces between individual molecules of the addition compounds are largely due to the TNB portion of the molecule. This suggests that the difference between the lattice energy of any given addition compound and that of TNB itself should not be large. Finally, the amine component is so small and must be buried so deeply within the relatively huge masses of the three α-naphthyl groups that the attractive forces between individual molecules of the addition compounds should not be markedly affected by the particular amine present. It therefore appears not unreasonable to assume that, in the present instances, the differences in the crystal lattice energies of the individual compounds are relatively small and their effects are relatively minor compared with the effects of F-strain.

If this assumption is valid, it may be concluded that the relative stabilities of the addition compounds decrease in the order, $NH_3 > CH_3NH_2 > (CH_3)_2NH > > (CH_3)_3N$, and the apparent strengths of the four bases decrease in the same order, $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. This is obviously the order predicted by the F-strain hypothesis for a reference acid with an exceedingly high F-strain factor.

There remain to be considered the phenomena observed in the course of preparing the addition compounds and measuring their dissociation pressures. It is suggested that these phenomena are due to the existence of two polymorphic forms of the solid addition compounds. Furthermore, the existence of these polymorphic forms is ascribed to the restricted rotation of the three α-naphthyl groups in the addition compounds about the carbon to boron bonds.

The observations requiring explanation may be briefly summarized as follows:

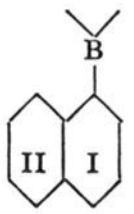
1. Solid TNB absorbs the gaseous bases with avidity to form only the lower melting, metastable form of the addition compound. For convenience, this substance will be referred to hereafter as the "metastable" form of the addition compound.
2. The metastable form of the addition compound is converted to another form, the "heat-altered" or "stable" form, slowly at room temperature and rapidly above 100°.
3. The dissociation pressures exhibited by the metastable form are much higher than those exhibited by the corresponding stable form.
4. The dissociation pressures of the metastable form are strongly dependent upon the relative

mole ratios of the two components; the dissociation pressures of the stable form do not exhibit such dependence.

5. The dissociation pressures of the metastable form are dependent upon the age of the sample and decrease with time, slowly at room temperature and more rapidly at higher temperatures. The corresponding pressures of the stable form are not dependent upon these factors.

6. Removal of the base from either form of the addition compound yields apparently identical samples of TNB.

For the ensuing discussion it will be convenient to distinguish between the two fused rings of the α-naphthyl groups. Accordingly, that ring which is directly attached to the boron atom will be designated by the numeral I; the other by the numeral II.



Presumably, the boron atom in TNB will be similar to the boron atom in trimethylboron[9] with its three bonds coplanar, making equal angles of 120° with each other. For convenience this plane, defined by the three bonds of the boron atom, will be referred to simply as the plane of reference or reference plane of the molecule.

Examination of the Fisher–Hirschfelder model of TNB indicates that the three α-naphthyl groups can be arranged about the central boron atom in two different ways. In one of these arrangements, the three α-naphthyl groups are relatively symmetrically fixed, with the three II-rings all pointing in the same direction away from the reference plane (the "symmetrical" arrangement or form, Fig. 3). In the other possible form, one of the α-naphthyl groups is so fixed that its II-ring is pointed in a direction from the plane of reference opposite to that of the other two α-naphthyl groups (the "unsymmetrical" arrangement or form, Fig. 4).[10]

These two forms would be readily interconvertible were it possible to rotate one of the α-naphthyl rings about the boron-to-carbon bond through the reference plane. However, the model suggests that such a rotation would be difficult and would involve the simultaneous rotation of all three groups at a carefully controlled rate in order to effect the transformation without excessive distortion of the model.

Simplified line drawings of the two postulated forms of TNB are shown in Figs. 5 and 6. In

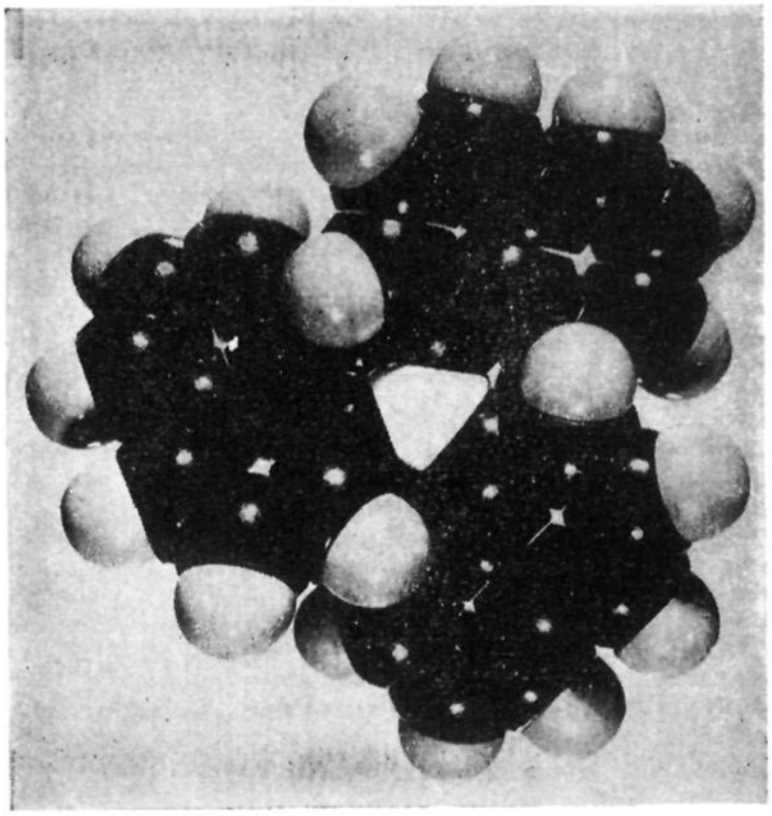


Fig. 3.—Molecular model of tri-α-naphthylboron–symmetrical arrangement.

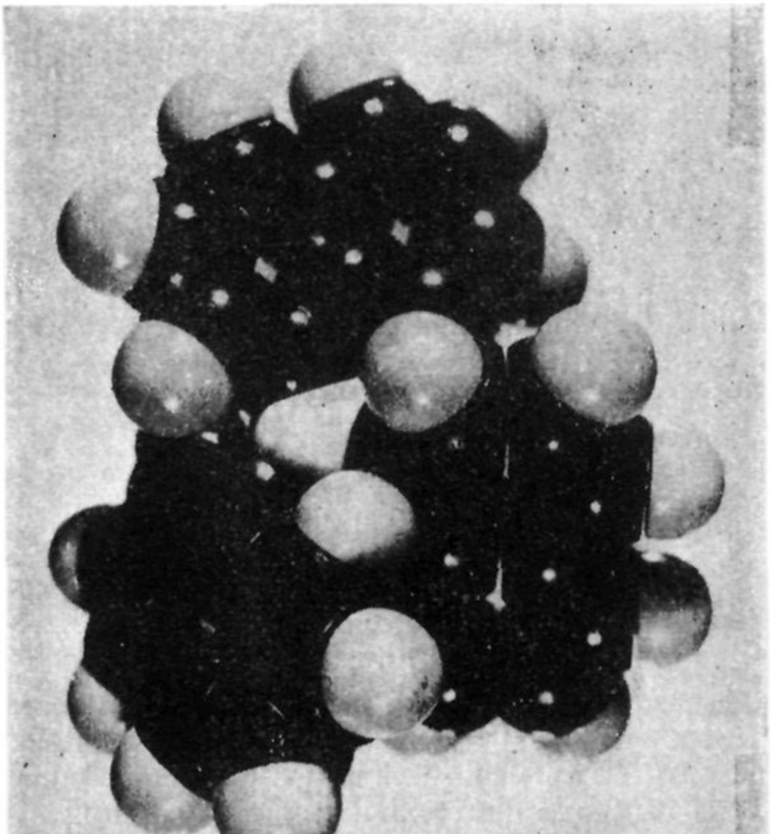


Fig. 4.—Molecular model of tri-α-naphthylboron–unsymmetrical arrangement.

---

(9) Levy and Brockway, THIS JOURNAL, **59**, 2085 (1947).

(10) It has been suggested already [Lewis, Magel and Lipkin, *ibid.*, **64**, 1774 (1942)] that triphenylmethyl and related compounds exist in two isomeric forms, one in which the three rings face in the same direction, similar to the blades of a propeller, the other containing one ring facing in a direction opposed to the other two. At first sight the isomerism proposed in the present paper may seem to be related to that proposed by G. N. Lewis. However, the latter is independent of the symmetry of the rings involved; the former could only be observed if the rings attached to the central atom were unsymmetrical, as with the α-naphthyl groups of the present investigation. Indeed, the consideration of the molecular models indicates that the large II-ring makes the type of isomerism proposed for triphenylmethyl impossible in the case of TNB.

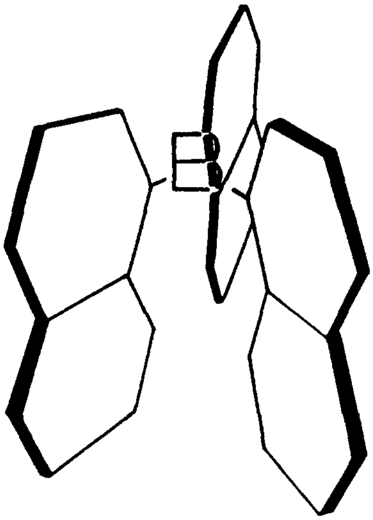


Fig. 5.—Symmetrical arrangement of tri-α-naphthylboron.

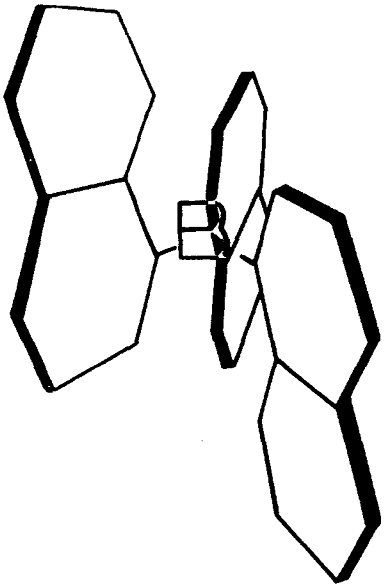


Fig. 6.—Unsymmetrical arrangement of tri-α-naphthylboron.

these figures the three α-naphthyl groups are represented with the plane of each ring lying perpendicular to the plane of reference of the molecule. It is highly probable that the three α-naphthyl groups are tilted to a greater or lesser degree from this idealized position, as indicated in Figs. 3 and 4. However, use of the idealized line drawings will facilitate the discussion without affecting the conclusions.

It is proposed that the unsymmetrical arrangement of TNB (Figs. 4 and 6) is the more stable of the two possible arrangements and that the crystalline TNB prepared in the present study consists of this unsymmetrical form. Addition of an amine to a molecule with this configuration could conceivably occur in two ways. The base could unite with the boron atom by approaching it either from above the reference plane, or from below. However, the latter path is considerably more hindered than the former. In approaching from below, the amine molecule must contend with two *peri* positions blocking the line of approach; from above, there is but one *peri* position in its path. It is therefore postulated that the base adds to the unsymmetrical form of TNB and that the addition occurs from above to give the less strained of the two possible configurations derived from the unsymmetrical form of TNB. It is further suggested that the projection of the one *peri* position of the inverted α-naphthyl group into the region occupied by the amine molecule leads to a condition of considerable strain—strain which is not present in the free TNB molecule. This strain is largely relieved by rotation of the offending α-naphthyl group so that all three *peri* positions lie below the reference plane, on the other side from the attached amine. The resulting addition compound is now configurationally related to the symmetrical arrangement of TNB and theoretically may be considered as being derived from this arrangement (Fig. 5) by addition to the boron atom from above the reference plane.

This hypothesis permits a simple interpretation of the observed phenomena. 1. Addition of the base to TNB yields the metastable or *strained* form of the addition compound.

2. The metastable or *strained* form is converted to the stable or *unstrained* form[11] slowly at room temperature, rapidly at 100°. Conversion requires rotation of one α-naphthyl group and ininvolves an appreciable energy of activation.

3. The dissociation pressures of the metastable form are high because of the strain which results from projection of the *peri* position of the odd α-naphthyl group into the region occupied by the amine molecule. The stable form exhibits much lower dissociation pressures because the offending *peri* position has been moved below the plane of the molecule, away from the added amine. (In other words, the unsymmetrical form of TNB has a higher F-strain factor[4] than the symmetrical form.)

4. Addition of the amine to the unsymmetrical form of TNB is not accompanied by any marked changes in the configuration or in the size of the molecule. Therefore the metastable form of the addition compound and TNB form a series of solid solutions and the dissociation pressures depend on the mole ratio of the two substances. On the other hand, formation of the stable form is accompanied by a marked change in the molecular configuration and the crystal lattice of TNB (the more stable, unsymmetrical form) is no longer able to accommodate the molecules of the addition compound (stable form). Accordingly, solid solution phenomena no longer occur, and the dis-

---

[11] It probably would be more precise to describe it as "less strained" rather than "unstrained," since there must be considerable F-strain present even in the stable form.

sociation pressures are no longer dependent on mole ratio.

5. Transformation of the metastable form to the stable form, slow at room temperature and rapid at higher temperatures, in effect removes equimolar quantities of the two compounds (amine and TNB) from the reaction mixture. If the amine and TNB are not present in exactly equivalent amounts at the start, the slow transformation of the metastable to the stable form will bring about a gradual change in the mole ratio of "available" TNB and amine. The observed pressure will then show a gradual change with time.[12]

6. Removal by volatilization of the amine from the stable forms of the addition compounds requires elevated temperatures (100–140°) and proceeds relatively slowly. It is probable that the symmetrical form of TNB is the first product of the dissociation, but at the elevated temperatures used it must be rapidly converted into the more stable unsymmetrical form. It is therefore not too surprising that removal of the amine from the metastable form of the addition compound at relatively low temperatures and removal of the amine from the stable form at elevated temperatures yield samples of TNB that appear to be identical.

It should be possible either to isolate or to obtain some definite evidence on the existence of the symmetrical form of TNB by removing the base from the addition compound at relatively low temperatures by chemical means. An investigation of this problem is under way.

There remain to be considered certain discrepancies between the results of the present investigation and those previously reported by Krause and Nobbe.[5] These authors report that TNB is "moderately" soluble in ether. They prepared the compound by the action of α-naphthylmagnesium bromide on boron trifluoride in ether solution. After the reaction was complete, water was added. The ether layer was dried and *concentrated*, then poured into a crystallizing dish where a mass of fine crystalline needles separated. In the present investigation, addition of water to the Grignard reaction mixture caused an immediate precipitate of TNB. In order to avoid such precipitation it was necessary to add large quantities of benzene to the reaction mixture. Experiment revealed that the solubility of TNB thus obtained is relatively small, 1.6 g. per 100 ml. of ether at 25°, and is practically constant over a wide temperature range. In their preparations of triarylborons Krause and Nobbe report that they used one mole of Grignard reagent in a 1-liter reaction flask. Assuming yields similar to those we obtained, a quantity of ether from 3 to 5 liters should have been required to dissolve the product, instead of the concentration of the ether layer reported by the authors.

Krause and Nobbe prepared their amine addition compound by treating a solution of the triarylboron in ether with the base. The addition compounds precipitated immediately and were recovered by filtration. Although they do not report any details on the preparation of ammonia–TNB, presumably the technique was similar to that which they had used for other such compounds reported in their paper. In the present investigation, a saturated solution of TNB in anhydrous ether was treated with an equivalent quantity of ammonia in the same solvent. However, no precipitate was observed. At the end of several hours a small quantity of precipitate was noted, but the quantity was not increased by cooling the solution to the neighborhood of −80°. The precipitate was collected and tested—its dissociation pressures corresponded to the *stable* form of ammonia–TNB. The ether solution was allowed to stand for an additional ten days at room temperature. In the course of this time the quantity of crystalline precipitate continued to grow.

This experiment is of interest not only because of the discrepancy between our observations and those of Krause and Nobbe, but also because it suggests that the formation of the stable form of ammonia–TNB from the metastable form is a relatively slow process, even in solution at room temperature, so that the two forms of the addition compound are true geometrical isomers whose existence does not depend on crystal lattice forces. Further experimental studies along this line are underway.

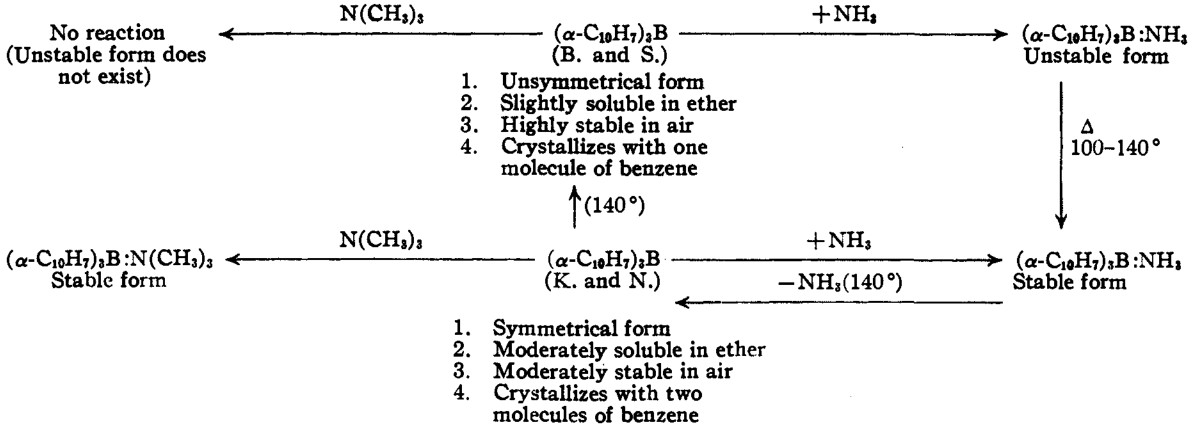
Krause and Nobbe further report that trimethylamine–TNB precipitates immediately upon bringing the components together in ether solution. Even though they report that the compound is measurably dissociated at room temperature, their ability to make the two components unite is remarkable in view of our numerous failures along this line.

The relative instability toward oxidation of TNB reported by Krause and Nobbe may also be contrasted with the high stability shown by our product. The difference in the number of molecules of benzene of crystallization in the two investigations is also worthy of comment.

There is a possible explanation which could resolve these differences. If the product isolated by Krause and Nobbe were the symmetrical form of TNB. the higher reactivity of their product to-

---

(12) This point may be clarified by an illustration. Assume that the reaction mixture at the start of the experiment consists of one mole of TNB and 0.5 mole of ammonia. The dissociation pressure exhibited by this mixture at a suitable temperature, 40° for example, would be that of a solid solution of 0.5 mole fraction of TNB and ammonia–TNB (metastable form). If the temperature is maintained at 40°, the metastable form will slowly change over to the stable form. At the point where the change is 50% complete, the reaction mixture will consist of 0.25 mole of ammonia–TNB (stable form), 0.25 mole of ammonia–TNB (metastable form) and 0.5 mole of free TNB. Since the pressure of the stable form is negligible at 40°, the pressure exerted by the mixture would be that of a solid solution of 0.33 mole fraction of the addition compound and 0.67 mole fraction of the free boron component. It is obvious that it should be possible to use the observed dissociation pressure to analyze a given mixture of the two forms and to follow the rate of the transformation.



ward ammonia and trimethylamine could be understood. Moreover, the symmetrical form would presumably be the less stable of the two crystalline forms of TNB, so that its crystal lattice energy would be less than that of the unsymmetrical form and a higher solubility would be anticipated. Differences in the stability toward oxidation and in the number of molecules of benzene of crystallization between their product and ours would then offer no difficulty.

In this case the various interconversions and reactions could be interpreted as shown in the chart.

Several of the proposed transformations are, of course, highly hypothetical and require experimental verification. Experimental studies to resolve the discrepancies and difficulties raised by the present study are now under way.

Experimental Part

Preparation and Purification of Intermediates.—The preparation of ammonia and the methylamines in pure form has been previously described.[4] Other intermediates used were largely Eastman Kodak Company products and were purified by standard methods.

Preparation of TNB.—Because of the discrepancies between the product obtained in the present investigation and that obtained by Krause and Nobbe, the preparation of TNB will be described in detail.[5]

A standard 1-liter 3-necked flask, fitted by standard-taper glass joints to a condenser, gland-sealed stirrer, and dropping funnel, was used. In the flask were placed 24.3 g. (1 g. atom) of magnesium turnings and a crystal of iodine. The flask was flushed out with nitrogen and then gently heated until the iodine had partially sublimed. The flask and its contents were allowed to cool to room temperature and a mixture of 100 ml. of anhydrous ether and 10 ml. of α-bromonaphthalene (b. p. 143° at 14 mm.) was added. Meanwhile 130 ml. of α-bromonaphthalene (making a total of 1 mole) was dissolved in an additional 400 ml. of anhydrous ether. One-half of this solution was then slowly added through the dropping funnel at such a rate as to keep the ether gently refluxing. The reaction mixture became brown during the addition and toward the end of the addition the Grignard reagent began to separate. Benzene, 100 ml., was added to dissolve the Grignard reagent and the remainder of the ether–halide mixture added. A total of three hours was required to add the halide. The reaction mixture was then heated under reflux for a further period of one-half to one hour to ensure completion of the reaction.

The flask was next cooled in ice, the ice-bath removed, and a solution of 32 ml. (0.25 mole) of boron trifluoride-etherate (b. p. 125°) in 150 ml. of benzene was added to the Grignard reagent over a period of approximately one hour. After all of the reagent had been added, the reaction mixture was heated under gentle reflux for an additional hour. The reaction mixture was then forced under nitrogen pressure through a glass tube into a 2-liter flask filled with crushed ice and containing 50 ml. of concentrated hydrochloric acid. The upper organic layer was yellow in color and contained a small quantity of brownish solid suspended near the interface; the lower aqueous layer was greyish-brown in color.

No attempt was made to separate the layers at this stage. The flask was stoppered and put aside overnight to allow time for the crystallization of the benzene addition compound of TNB. The organic layer was then decanted from the aqueous layer and suspended solid. The solid was recovered on a Buchner funnel (without filter paper) by pouring the gelatinous aqueous layer and suspended solid into the funnel under slight suction. The brownish-appearing residue was washed repeatedly with water and then with alcohol. The crude product was dissolved in 300 ml. of refluxing benzene (nitrogen atmosphere) and quickly poured through a prewarmed Buchner funnel (with filter paper) into a 1-l. Erlenmeyer flask. White crystals immediately began to separate from the filtrate. The flask was stoppered and placed in a refrigerator overnight (6–8°).

The next day the bottom and walls of the flask were covered with an adhering crust of white large crystals. The supernatant liquid was poured off and the solid broken up with a stirring rod. The crystals were washed with several small portions of cold benzene and then transferred to a weighed flask and the adherent solvent removed by volatilization under high vacuum to constant weight.

In a typical preparation 63 g. of the pure product, $(\alpha\text{-}C_{10}H_7)_3B\cdot C_6H_6$, was obtained, a yield of 54% based on the boron trifluoride-etherate used.

The benzene of crystallization was removed by heating the flask and its contents to a temperature of 150–160° at pressures of less than one millimeter. After the flask had reached constant weight (weighings were made only after the flask and its contents had reached room temperature to avoid exposure of the hot triarylboron to oxygen), the product weighed 51.8 g. Thus the product lost 11.2 g. compared with 10.5 g. of benzene calculated for the 1:1 compound.

The product was analyzed for boron by treating it with hot concentrated sulfuric acid followed by distillation of the boron as methyl borate and titration as boric acid in the presence of mannitol.[13]

Calcd. for $C_{30}H_{21}B$: B, 2.71. Found: B, 2.75.

Titration of TNB.—G. N. Lewis[14] has frequently pointed out the similarity between the behavior of the "proton" acids and electron acceptors such as the trialkyl- and triarylborons. It was of interest to determine whether

---

[13] Fowler and Kraus, This Journal, 62, 1143 (1940).

[14] Lewis, *J. Franklin Inst.*, 226, 293 (1938).

TNB could be analyzed by a standard base similar to more conventional acid analyses.

A standard solution of 0.04644 *M* TNB in benzene was prepared. Ten-ml. aliquots of this solution were titrated with approximately 0.06–0.10 *N* solutions of sodium alkoxide in the corresponding alcohol. Phenolphthalein was used as the indicator. The results are summarized in Table III.

TABLE III

TITRATIONS OF TNB WITH SODIUM ALKOXIDES

Base	Normality	Volume of base used		Volume of base calcd.	End-point
Sodium methoxide	0.1050	4.46	4.49	4.42	Sharp
Sodium ethoxide	.1075	4.31	4.32	4.32	Sharp
Sodium isopropoxide	.0880	5.34	5.29	5.29	Sharp
Sodium *t*-butoxide	.0593	7.68		7.83	Indistinct[a]

[a] End-point taken as very faint pink which persisted.

Solubility of TNB.—The solubilities were determined by placing in a vessel excess solid TNB and 50 ml. of solvent. The mixture was stirred at constant temperature (under nitrogen) for twenty-four hours. The excess solid was permitted to settle and 5 ml. of the supernatant liquid was pipetted out. The solvent was removed under vacuum and the solid determined by weighing. The results indicated a solubility per 100 ml. of solvent at 25° of 1.7 g. in ether, 0.2 g. in alcohol, 6.4 g. in benzene, and 5.0 g. in carbon tetrachloride. At −80° the solubility was 1.4 g. per 100 ml. of ether.

Preparation of Addition Compounds. (a) By Condensation of Excess Amine.—A large excess of the amine was liquefied in a tube immersed in a Dry Ice-bath. Sodium was used to remove traces of moisture. The amine was then permitted to volatilize from the sodium and condense in a second tube containing 2–3 g. of TNB. The liquid amine and suspended solid were allowed to remain in contact for two hours at 20–30° below the boiling point of the amine. At the time the cooling bath was removed and the excess amine permitted to volatilize away as the temperature rose to 25°. In these operations the product was at all times protected from the atmosphere. The last traces of excess amine were removed by pumping the material with a high vacuum pump. Periodic weighings of the product showed asymptotic approach to 1:1 addition over a period of several hours. Composition of the products was verified by Kjeldahl analyses for nitrogen. Ammonia, methylamine and dimethylamine all yielded well-defined addition compounds whose properties have been previously described. Trimethylamine showed no signs of reaction; even at −80° a stream of nitrogen rapidly removed all of the amine from a mixture of the liquid amine and solid TNB.

(b) **Reaction with a Stream of the Gaseous Base.**—In a typical experiment, a stream of ammonia was passed over a sample of 0.9030 g. of TNB contained in a boat. Considerable heat was evolved as the ammonia reached the solid and there was a sharp drop in pressure as the gas was absorbed. The slow stream was continued for one hour. The product gained 0.0401 g. Calculated gain for 1:1 addition is 0.0392 g. The properties of the product obtained in this way were identical with those obtained in the first method. Trimethylamine was not absorbed in a similar experiment involving this base.

(c) **By Reaction of Measured Quantities of the Components in the High Vacuum Apparatus.**—The apparatus shown in Fig. 7, attached to the usual high vacuum line, was used. A weighed quantity of TNB was introduced into the small bulb and the tube sealed. The tube was evacuated through the manometer (with the mercury lowered) and the float valve. A quantity of amine was then measured out as a gas in the high vacuum line and then condensed in the tube with liquid nitrogen. Mercury was then raised into the manometer and the equilibrium pressures developed at room temperature and above were measured on the manometer.

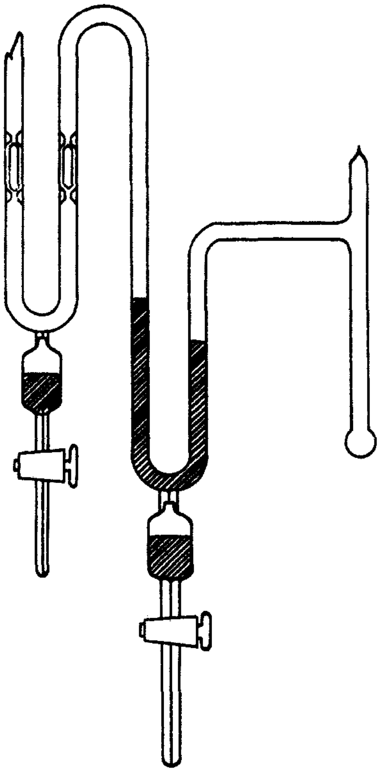


Fig. 7.—Apparatus for following the dissociation pressures of the addition compounds.

There was a remarkable difference in the time required for the equilibrium pressure to be reached. The ammonia derivative reached essentially stationary pressure values in five minutes; the monomethylamine derivative required approximately one hour; the dimethylamine compound required some five to twelve hours for the observed pressure to become sensibly constant. Over a period of some three months trimethylamine showed no signs of being absorbed.

(d) **By Reaction in Ether Solution.**—A solution of 2.04 g. of TNB in 250 ml. of anhydrous ether was mixed with 74.5 ml. of ether containing an equivalent quantity of ammonia. No precipitate was observed. A portion of the solution was cooled to approximately −80°, but no precipitate formed. Overnight a few crystals appeared. These were isolated and introduced into the high vacuum apparatus. They exhibited pressures corresponding to the stable form of ammonia-TNB[15] and analyzed for a 1:1 addition compound.

The solution was permitted to stand at room temperature (protected from the atmosphere) for nearly two weeks. In this time, additional crystals of the same appearance as those already isolated were observed to precipitate, the amount increasing daily. Unless it is assumed that the crystallization is an exceedingly slow process, in contradiction to the observation of Krause and Nobbe,[7] one can only conclude that the crystalline material is the result of a slow change occurring in the dissolved soluble addition compound (presumably the metastable form is isomerizing to the stable form).

Acknowledgment.—This investigation was made possible by Grants No. 710 and 776 from the Penrose Fund of the American Philosophical

---

[15] The observed pressures, 5.5 mm. at 130°, 16.5 mm. at 150° and 57.0 mm. at 170°, differed slightly from the pressures measured for the addition compound prepared by direct synthesis. The cause of the discrepancy is under investigation.

Society. In addition, the financial assistance afforded by two graduate fellowships supported by the Ethyl Corporation is gratefully acknowledged.

Summary

1. Tri-α-naphthylboron has been prepared and found to possess somewhat different properties from the product previously described in the literature.

2. Addition compounds of tri-α-naphthylboron with ammonia, methylamine and dimethylamine were prepared. Trimethylamine did not combine with tri-α-naphthylboron.

3. The dissociation pressures of the addition compounds indicate a relative stability in the order, $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. This order is the theoretical limit predicted for a reference acid with an exceedingly high F-strain factor.

4. The addition compounds exist in two polymorphic modifications. It is suggested that these modifications result from restricted rotation of the α-naphthyl groups in the addition compounds.

5. The hypothesis is advanced that the discrepancies between the properties of the tri-α-naphthylboron prepared in the present investigation and the tri-α-naphthylboron previously described may be due to the existence of two rotation isomers of the compound.

LAFAYETTE, INDIANA RECEIVED NOVEMBER 28, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Hydrazine Hydrate on Nitro-Compounds and a New Route to Synthetic Oestrogens

BY HUANG-MINLON[1]

The reduction of nitrobenzaldehydes by alkaline treatment of the corresponding hydrazones is not successful.[2] The modified Wolff–Kishner reduction[3] has now been found to proceed normally, with the exception that nitro-groups are reduced simultaneously. *p*- or *m*-toluidine can be obtained by this method from *p*- or *m*-nitrobenzaldehyde, respectively, in good yield. The reduction of nitro compounds by hydrazine has been observed,[4] although a sealed tube or an autoclave was usually employed. The reduction by hydrazine of *p*- or *m*-nitrotoluene to the corresponding toluidines required reaction in a sealed tube at 130° for four hours.[5] In the present investigation, the reduction was found to proceed readily in refluxing diethylene glycol. *m*-Nitrotoluene can be reduced to *m*-toluidine in good yield in this way; alkali does not affect the course of the reduction. *p*-Toluidine is obtained from *p*-nitrotoluene in good yield only if alkali is absent; in the presence of alkali a dimeric product, 4,4′-diaminostilbene (I), is also formed. The action of alkali alone on *p*-nitrotoluene is known to yield a mixture of condensation products from which 4,4′-dinitrodibenzyl (II) and 4,4′-dinitrostilbene could be isolated (IV).[6] The initial products of the alkali treatment are believed to be nitroso dimeric compounds.[7] Consequently the formation of 4,4′-diaminostilbene from *p*-nitrotoluene undoubtedly proceeds through a nitro or nitroso dimeric product by reduction. The same diamino product in better yield can also be obtained from *p*-nitrobenzyl chloride by treatment with alkali and hydrazine hydrate.

4,4′-Dinitrostilbene (II) is readily reduced by hydrazine hydrate in the presence of alkali to 4,4′-diaminostilbene (I) (80% yield). If alkali is absent, the double bond is also saturated, and 4,4′-diaminodibenzyl (III) can be obtained in this way in 70% yield. Alkali also affects the reduction of 4,4′-dinitrodibenzyl (IV): Treatment with hydrazine alone yields 4,4′-diaminodibenzyl (III) in almost quantitative yield, whereas treatment with hydrazine and alkali yields 4,4′-diaminostilbene (I) in more than 90% yield. Since neither 4,4′-diaminostilbene (I) nor 4,4′-diaminodibenzyl (III) is affected by treatment with hydrazine, with or without alkali, the electron-attracting *p*-nitro group thus activates the methylene or methine group for the donation or acceptance of hydrogen.

Substitution of sulfonic acid groups in the 2,2′-positions does not alter the reaction (see chart, $R = SO_3H$).

p-Nitrophenylacetic acid can be converted to a dinitrodicarboxylic acid (m. p. 264–266°) by treatment with alkali in the presence of an oxidizing agent. This acid when treated with hydrazine gives 4,4′-diaminodibenzyl; reduction and decarboxylation both take place.

p-Nitropropylbenzene[8] on heating with hydrazine hydrate and alkali gives *meso* and racemic 4,4′-diamino-α,β-diethyldibenzyl (V) along with *p*-aminopropylbenzene. Both of these isomeric diamino compounds have been used by Carlisle and Crowfoot[9] for X-ray measurements but the methods of preparation have not been mentioned.

---

[1] On leave of absence from the National Research Institute of Chemistry, Academia Sinica.

[2] Lock and Stach, *Ber.*, **76**, 1252 (1943).

[3] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[4] Curtius, *J. prakt. Chem.*, **76**, 238, 281 (1907).

[5] Müller, *ibid.*, **111**, 278, 281 (1925).

[6] Fischer and Hepp, *Ber.*, **26**, 2231 (1893).

[7] Green, Davies and Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907).

[8] Baddeley and Kenner, *J. Chem. Soc.*, 303 (1935); *cf.* Kondo and Uyeo, *Ber.*, **70**, 1087 (1937).

[9] Carlisle and Crowfoot, *J. Chem. Soc.*, 6 (1941).