independent investigators[52,53] who employed the electron microscope was very good, leading to a maximum variation of ±70 Å., and a probable variation considerably smaller. The possibility of a small systematic error cannot be completely excluded,[54] and indeed is suggested by the light scattering measurements of Dandliker[55] and by some recent X-ray diffraction measurements[56] in which long wave length X-rays were employed. Both methods give a somewhat larger diameter, ranging from 2700–2800 Å. However, this is not enough to account for the difference between 3416 and 2980 Å. Furthermore, since the latex particles serve only as intermediate standards in the electron microscope work, a reproducible error in their size would not influence the electron microscope value[9] for the legnth of TMV.[57] Thus, the 14% difference in computed lengths cannot be discounted by invoking reasonable experimental errors, or hydration effects, or combinations of the two.

We next consider the probable magnitude of the error introduced by use of an hydrodynamic equation for molecular properties. It has been recognized that such applications are of limited accuracy, for example, in considering the rotational diffusion of a solution of polar molecules in a solvent consisting of molecules of comparable size.[58,59] Here, however, we are concerned with a huge macromolecule in a solvent of very small molecules. One therefore expects that the hydrodynamic assumption of a continuous fluid medium would require corrections not exceeding a few solvent molecule diameters. Such numbers would clearly be too small to explain the discrepancy of over 400 Å. in the lengths. It appears more likely that end effects, not treated in detail by Burgers,[46] could give rise to corrections of the right order of magnitude. The possible need for an appreciable correction for a rotational relaxation effect associated with the counterion atmosphere, similar to the translational effects in cataphoresis,[60] has been tentatively ruled out in view of the experiments which indicated that D was independent of the ionic strength. This leaves the problem of the discrepancy unresolved.

In the absence of detailed knowledge of the orienting mechanism, it is not possible at this time to calculate the percentages of dimer in the solutions, but the preparations may be arranged in order of increasing dimer, that is, I (no dimer), II, IV, III, from the results in Table I. This sequence does not correlate with the concentration of the stock solution, or the age of the preparation. Furthermore, separate measurements on I over a period of two years always yielded a single relaxation time. Since all solutions were run at the same concentration, the dimer concentration cannot be attributed to a simple monomer–dimer equilibrium situation; on the contrary, it must be attributed to uncontrolled variables in the process of preparation, or to an intrinsic but variable property of the biological system.

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[53] C. H. Gerould, *ibid.*, **21**, 183 (1950).

[54] See, for example, S. F. Kern and R. A. Kern, *J. Appl. Phys.*, **21**, 705 (1950).

[55] W. B. Dandliker, THIS JOURNAL, **72**, 5110 (1950).

[56] B. Henke and J. W. M. DuMond, *Phys. Rev.*, **89**, 1300 (1953); *Chem. Eng. News*, **32**, 2272 (1954).

[57] It was pointed out by R. C. Williams (private communication) that it is the latex particle diameter as determined in the electron microscope which is most relevant to the present discussion.

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Triarylboron Anions. II. Tri-β-methylnaphthylboron[1a]

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Tri-β-methylnaphthylboron reacts readily with sodium in tetrahydrofuran solution to form a green monosodium salt, NaTMeNB, which further reacts with sodium to form the dark brown disodium salt, Na_2TMeNB. The magnetic susceptibility of NaTMeNB has been measured in tetrahydrofuran, ether and two benzene–tetrahydrofuran mixtures by the Gouy method and compared with that of sodium trimesitylboron, NaTMB; their difference in behavior is discussed in terms of the steric requirements of the aryl groups as well as the relative electron affinities of the parent boron compounds. The electron affinity of TMeNB is higher than that of TMB by at least 3.5 kcal./mole, as shown by spectrophotometric studies of the electron transfer reaction NaTMB + TMeNB = NaTMeNB + TMB and its reverse reaction. The extent of the reaction NaTMB + NaTMeNB = Na_2TMeNB + TMB studied by susceptibility measurements also provides a rough measure of the relative electron affinities of TMB and $TMeNB^-$.

It has been demonstrated in previous papers[2,3] that sodium triphenylboron is diamagnetic in ether or tetrahydrofuran solution owing to the association of ion pairs into ion clusters by coulombic forces and that the replacement of phenyl groups in sodium triphenylboron by bulky mesityl groups causes the ion clusters to dissociate in tetrahydrofuran solution with the formation of a free radical. In non-polar solvents, such as benzene or cyclohexane, however, the coulombic interaction between ion pairs causes sodium trimesitylboron, NaTMB, to polymerize. Aside from the dielectric constant of the solvent, it appears that the steric factor is of great importance in the formation of monomeric sodium triarylboron. As a continua-

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[1] (a) Taken in part from the Ph.D. dissertation of T. J. Weismann, Duquesne University, 1956. Presented before the Division of Physical and Inorganic Chemistry at the 129th A.C.S. Meeting, Dallas, Texas, April, 1956. (b) Westinghouse Research Laboratories, Pittsburgh, Pa. (c) Gulf Research & Development Co., Pittsburgh, Pa.

[2] T. L. Chu, THIS JOURNAL, **75**, 1730 (1953).

[3] T. L. Chu and T. J. Weismann, *ibid.*, **78**, 23 (1956).

tion of these studies, this paper reports the behavior of mono- and disodium salts of tri-β-methylnaphthylboron.

TMeNB reacts readily with sodium in tetrahydrofuran solution to form a green monosodium salt, NaTMeNB, which further reacts with sodium to form the dark brown disodium salt, Na_2TMeNB. With 40% sodium amalgam, however, the formation of Na_2TMeNB is incomplete, indicating that the second sodium is held relatively loosely.

The magnetic susceptibility of NaTMeNB was measured in several solvents at 25 ± 1° by the procedures described previously.[2] The susceptibility results together with the dielectric constants of the solvents are summarized in Table I.

TABLE I

MOLAR SUSCEPTIBILITIES OF NaTMeNB IN SEVERAL SOLVENTS OF VARYING DIELECTRIC CONSTANTS

Solvent	Concn. of NaTMeNB, M	Dielectric const. of solvent at 25°	$\chi_M \times 10^6$ at 25 ± 1°
Tetrahydrofuran	0.0404	7.39	1241 ± 30
	.0599		1252 ± 30
	.0787		1240 ± 30
	.1092		1235 ± 20
THF–C_6H_6 (4:1 by wt.)	.0767	6.16	1084 ± 20
THF–C_6H_6 (1:1 by wt.)	.0672	4.35	740 ± 30
Ether	.0345	4.35	810 ± 50
Benzene	Diamagnetic		

It is seen from the susceptibility data that, similar to NaTMB, NaTMeNB is also monomeric in tetrahydrofuran solution on the basis of usual assumptions, having one unpaired electron. The monomeric nature of NaTMeNB in tetrahydrofuran may be ascribed to the large steric requirements of the three β-methylnaphthyl groups. The addition of benzene to a tetrahydrofuran solution of NaTMeNB lowers the dielectric constant of the medium and the molar susceptibility of NaTMeNB decreases due to the association of ion pairs. The extent of association runs parallel with the dielectric constant of the medium. In the 1:1 by weight tetrahydrofuran–benzene mixture, NaTMeNB associates to a considerable extent, whereas NaTMB remains monomeric.[3] The sodium triarylborons are presumably tetrahedral; however, the exact arrangement of the aryl groups about the central boron atom is unknown. The difference in the degree of association of NaTMB and that of NaTMeNB is probably due to the greater steric requirements of the three mesityl groups in NaTMB.

Ether has the same dielectric constant as the 1:1 tetrahydrofuran–benzene mixture; the molar susceptibility of NaTMeNB in ether is of the same order of magnitude as that in a 1:1 tetrahydrofuran–benzene mixture if the difference in concentration of the two solutions is taken into consideration. Contrary to the behavior of NaTMB, which is initially monomeric in ether solution and gradually polymerizes,[3] NaTMeNB is stable in ether solution, as is indicated by the reproducibility of its magnetic susceptibility.

NaTMeNB is diamagnetic in benzene solution due to polymerization. The evaporation of a tetrahydrofuran solution of NaTMeNB and prolonged pumping of the residue also cause the salt to polymerize; its molecular weight was determined by the freezing point depression method described previously.[3] A freezing point depression of 0.036 ± 0.004° was obtained from 0.2961 g. of the solid in 19.28 g. of benzene yielding an apparent molecular weight 4.8 ± 0.6 times the formula weight of NaTMeNB.

The difference in electron affinities of TMeNB and TMB in tetrahydrofuran solution can be demonstrated by the electron transfer reaction between NaTMB and TMeNB

$$\text{NaTMB} + \text{TMeNB} = \text{NaTMeNB} + \text{TMB}$$

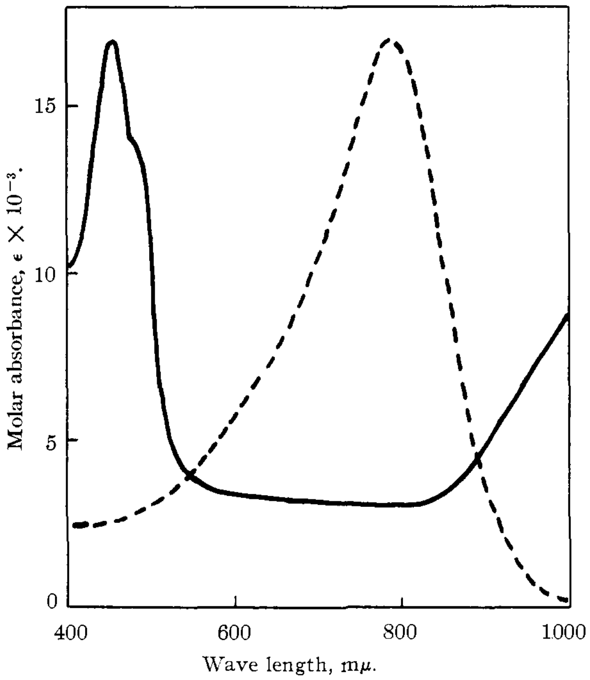

Fig. 1.—Absorption spectra of NaTMeNB (solid curve) and NaTMB (dashed curve) in tetrahydrofuran.

Since these triarylborons do not absorb light in the visible region and NaTMB and NaTMeNB exhibit characteristic absorption bands in dilute solutions at 7900 and 4520 Å., respectively (Fig. 1), spectrophotometry offers a convenient means for studying the extent of the reaction. When a 10^{-4} M solution of NaTMB was mixed with an equivalent amount of TMeNB, the characteristic absorption band of NaTMB disappeared completely with simultaneous appearance of an absorption band whose intensity corresponds approximately to that of a 10^{-4} M NaTMeNB solution. On the other hand, the addition of TMB to a NaTMeNB solution causes no measurable change in the absorption spectrum of the latter. These experiments indicate that the reaction between equivalent quantities of NaTMB and TMeNB is over 95% complete within experimental error and sets an upper limit, −3.5 kcal., for the free energy change of this reaction at 25°. The nature of the reactants and products would lead one to expect that the entropy change for the reaction is very small, hence the free energy change is approximately equal to the change in heat content. TMB and TMeNB melt and sublime at about the same temperatures, indicating that their sublimation energies do not differ appreciably. Furthermore, the solvation energies of TMB^- and $TMeNB^-$ by tetrahydrofuran molecules are both small and of the same order of magnitude. It therefore appears not unreasonable to conclude that the electron affinity of TMeNB is higher than that of TMB by at least 3.5 kcal. per mole.

NaTMB and NaTMeNB are individually monomeric in tetrahydrofuran solution. However, the molar susceptibility of their mixture is lower than that corresponding to one unpaired electron due to the reaction

$$\mathrm{NaTMB} + \mathrm{NaTMeNB} = \mathrm{Na_2TMeNB} + \mathrm{TMB}$$

Since the reaction products are diamagnetic, the extent of this reaction was studied by magnetic susceptibility measurements. In a typical run, a 5-ml. solution containing 0.1658 mmole of NaTMB, 0.2136 mmole of NaTMeNB and 0.0435 mmole of TMB exhibited a molar susceptibility of $1113 \pm 20 \times 10^{-6}$ c.g.s. units at 20°. The molar susceptibility would have been 1265×10^{-6} c.g.s. units were there no reaction between NaTMB and NaTMeNB. The equilibrium constant calculated on this basis was 0.056 ± 0.010. The reverse reaction was also studied, a 5-ml. solution containing 0.1002 mmole of Na_2TMeNB, 0.1628 mmole of TMB and 0.0674 mmole of NaTMeNB showed a molar susceptibility of $1158 \pm 20 \times 10^{-6}$ c.g.s. units at 20° and the reciprocal of the equilibrium constant of the reverse reaction was calculated to be 0.061 ± 0.010. The equilibrium constants determined from both sides of the reaction are in good agreement, the free energy change of the reaction is of the order of 1.70 kcal., which may be considered as a rough measure of the relative electron affinities of TMB and $TMeNB^-$.

Na_2TMeNB has an even number of electrons and is diamagnetic, because the orbital degeneracy in the π orbitals of TMeNB is not permitted. The susceptibility measurements indicate that Na_2TMeNB reacts reversibly with TMeNB in tetrahydrofuran solution to form NaTMeNB.

Experimental

Tri-β-methylnaphthylboron (TMeNB).—TMeNB was prepared by the reaction of boron trifluoride with excess β-methylnaphthylmagnesium bromide in the manner described for trimesitylboron.[4] The product was distilled under vacuum and the fraction boiling at 245–250° (10^{-3} mm.) recrystallized successively from ethanol to yield light yellow crystals of melting point 198°.[5] However, the vacuum sublimation of these crystals yielded a product exhibiting two distinct melting points: one at 108–110°, followed by solidification on further heating and remelting at 198°. This material, on reheating, showed only one melting point at 198°. Several preparations were carried out and this phenomenon found reproducible. Recrystallization of the sublimed product from ethanol gave only the higher melting product. The solubility of the sublimed product in ether at 25° is 25.25 g./l., while that of the higher melting product is 18.50 g./l. These physical properties seem to indicate that TMeNB can exist in two isomeric forms in which the three β-methylnaphthyl groups are arranged either symmetrically or unsymmetrically about the central boron atom; these isomeric forms are similar to those proposed by Brown and Sujishi[6] for tri-α-naphthylboron. The lower melting form isomerizes readily in solution. Further isomerization studies are now being carried out in this Laboratory.

Spectrophotometric Measurements.—Spectrophotometric measurements were made on a Beckman Model DU spectrophotometer using 1.0 cm. Pyrex cells, calibrated in the usual manner, for all the measurements.

The preparation of a NaTMB solution for quantitative absorption measurements was made in the following manner. An aliquot of a stock solution of TMB in benzene was placed in a dumper on the vacuum line and the solvent evaporated. Excess 40% sodium amalgam was introduced and a measured amount of predried tetrahydrofuran distilled in. After sufficient shaking of the reaction mixture, the NaTMB solution was transferred into the absorption cell and the dumper thoroughly rinsed by repeatedly distilling solvent back from the absorption cell. The absorption cell was sealed off while under vacuum and the absorption spectrum determined immediately after the preparation. The NaTMeNB solution was prepared using 2% sodium amalgam which, on reaction with TMeNB, yielded NaTMeNB almost quantitatively without forming measurable amounts of NaTMeNB.

In studying the extent of the reaction between NaTMB and TMeNB, an aliquot portion of a stock solution of TMeNB was introduced into the absorption cell and the solvent evaporated. The NaTMB solution, prepared in the vacuum dumper, was transferred quantitatively to the absorption cell. After sealing off the absorption cell, the absorbance of the solution was measured at 7900 and 4520 A., characteristic absorptions of NaTMB and NaTMeNB.

Magnetic Susceptibility Measurements.—The magnetic measurements were carried out in the manner described previously.[3] In studying the extent of the reaction between Na_2TMeNB and TMB, a weighed amount of TMB was placed in the calibrated sample tube and an equivalent amount of TMeNB in a dumper on the vacuum line. Sodium amalgam (40%) was introduced into the dumper and a measured amount of tetrahydrofuran distilled in. The solution in the dumper, after prolonged shaking, was transferred quantitatively into the sample tube and the latter sealed off. After the magnetic measurements, the solution was hydrolyzed and the liberated alkali titrated with standard hydrochloric acid. Since the formation of Na_2TMeNB by the reduction of TMeNB with 40% sodium amalgam is incomplete, the original concentrations of NaTMeNB and Na_2TMeNB were calculated from the weight of TMeNB used and the amount of alkali liberated. The concentrations of all species at equilibrium were computed from the original concentrations, the measured susceptibility and the susceptibility calculated on the basis of complete reaction of Na_2TMeNB.

The reaction between NaTMB and NaTMeNB was studied as follows. Tetrahydrofuran solutions of NaTMB and NaTMeNB were prepared in separate dumpers connected by a Y joint to a calibrated sample tube. When the molar ratio of sodium reacted to triarylboron originally present was slightly below unity, the two solutions were mixed and the magnetic measurements carried out. The solution was then hydrolyzed and analyzed for total sodium content. Because of the higher electron affinity of TMeNB over TMB, it was assumed that all of the former was completely converted into the monosodium salt, the original concentration of NaTMB being the difference between the total sodium ion concentration and the concentration of NaTMeNB. The equilibrium concentrations of all species were calculated as described above.

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(4) V. H. Dodson, Ph.D. Thesis, Purdue University, 1952.

(5) The product was analyzed for boron by the method of D. E. Fowler and C. A. Kraus [THIS JOURNAL, **62**, 1143 (1940)] as well as for carbon and hydrogen. Calcd. for $C_{33}H_{27}B$: C, 91.23; H, 2.27; B, 2.49. Found C, 91.10; H, 6.16; B. 2.49. The high degree of purity of the product was also indicated by the fact that 0.2929 mmole of the product, after treatment with sodium in tetrahydrofuran solution, yielded 0.5858 mmole of sodium hydroxide on hydrolysis.

(6) H. C. Brown and S. Sujishi, THIS JOURNAL, **70**, 2793 (1948).