

# TRIMETHYL ORTHOBORATE - AMINE INCLUSION COMPOUNDS<sup>1</sup>

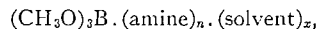
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## ABSTRACT

A new class of non-stoichiometric crystalline inclusion compounds has been discovered, having the general formula



where  $0.5 < n < 1.0$  and  $0 < x < 3$  depending on the method of preparation and on the nature of the amine and solvent. Such compounds have been prepared with ammonia and a variety of primary and secondary amines. Among the solvents which can be incorporated into the crystals are alcohols, ketones, ethers, esters, nitriles, nitroparaffins, and hydrocarbons. Such compounds are also formed by triphenyl orthoborate, with  $1.7 < n < 2.4$  and  $1.2 < x < 1.6$ .

The incorporated solvent has been shown to exert a definite vapor pressure. Furthermore, many of the compounds sublime at room temperature to form large transparent crystals which also contain incorporated solvent. The mechanism probably involves dissociation, followed by reassociation on the walls of the vessel. Preliminary X-ray diffraction measurements suggest that the trimethyl orthoborate - ammonia inclusion compounds have essentially the same crystal lattice as pure trimethyl orthoborate - ammonia.

## INTRODUCTION

In a discussion of various methods for preparing the compound  $(\text{CH}_3\text{O})_3\text{B}$ , Schechter (1) reported that treatment of the trimethyl orthoborate - methanol azeotrope with ammonia afforded crystals with incorporated methanol. The present work was undertaken to determine whether this phenomenon is a general one and, if so, to make a preliminary study of the properties of these inclusion compounds.

The literature on adducts of orthoboric acid esters and amines is scant. As recently as 1950, these esters were thought (2) to be insufficiently acidic (in the Lewis sense) to form such compounds.

In a series of papers on the reaction of trimethyl orthoborate with ammonia and amines, Goubeau *et al.* (3-5) described the preparation of  $(\text{CH}_3\text{O})_3\text{B} \cdot \text{NH}_3$  and its reactions with excess ammonia and with excess orthoborate. They also prepared and characterized the 1:1 addition compounds of trimethyl orthoborate with mono-, di-, and tri-methylamine (5). Urs and Gould (6) reported the formation of solid addition compounds on mixing trimethyl orthoborate with dimethyl-, diethyl-, di-*n*-propyl-, di-*n*-butyl-, di-*n*-amyl-, triethyl-, and tri-*n*-butyl-amine. The compounds formed with ethylenediamine, piperidine, methylamine, and *t*-butylamine were stable enough to be purified by sublimation *in vacuo*; melting points and analytical results were given for these 1:1 addition compounds. The addition reactions were strongly catalyzed by the lower aliphatic alcohols. No solids separated on mixing amines with triethyl-, tri-*n*-butyl-, and tri-*n*-amyl orthoborates, although considerable heat evolution was noted with the ethyl ester. Urs and Gould (6) found no evidence of interaction between trimethyl orthoborate and pyridine or quinoline, but a stable 1:1 adduct of tris(1,1,1-trifluoroethyl) orthoborate and pyridine has since been characterized by Gerrard *et al.* (7).

Horn and Gould (8) studied the interaction of trimethyl orthoborate with 19 aliphatic and 5 heterocyclic amines, by measuring partial vapor pressures of the borate over

<sup>1</sup>Contribution No. 68.

equimolar borate-amine mixtures. Departures from ideality, which were greatest for ethylenediamine, piperidine, and triethanolamine and least for trimethylamine, di-*i*-propylamine, and pyridine, afforded a measure of the degree of interaction. As found previously (6), methanol markedly increased the borate-amine interaction.

Addition compounds between triaryl orthoborates and amines have been prepared and characterized by Colclough, Gerrard, and Lappert (9, 10). Stable 1:1 adducts were obtained in most cases, but where steric hindrance was severe the adducts were found to be deficient in amine. Ammonia formed 3:1 and 2:1 adducts respectively with tris(2,4,6-trichlorophenyl) and triphenyl orthoborates.

## EXPERIMENTAL

### *Materials*

Trimethyl orthoborate - methanol azeotrope was prepared by fractionating orthoboric acid and methanol (1:4 mole ratio) at a 10:1 reflux ratio. Trimethyl orthoborate was separated by shaking the azeotrope with anhydrous lithium chloride (11) and purified by fractionation. The purity was checked by titrating a weighed sample with 0.1 *N* sodium hydroxide to the phenolphthalein end point in the presence of mannitol.

Triphenyl orthoborate was prepared by distilling orthoboric acid and phenol (1:5.3 mole ratio), the water formed being removed azeotropically with the excess phenol (9). The crude product was purified by vacuum distillation, the fraction boiling at 154-167° at 0.2 mm being used for subsequent experiments.

The ammonia was Dow refrigeration grade. The gaseous amines were supplied by the Matheson Company and the liquid amines and solvents were Eastman Kodak "White Label" quality.

### *Preparation of Inclusion Compounds*

#### *(i) Trimethyl Orthoborate plus Gaseous Amines*

Trimethyl orthoborate (5 ml) and the solvent to be incorporated (10 ml) were mixed in a 50-ml Erlenmeyer flask and saturated with the amine under slight excess pressure. Cooling the mixture in an ice bath helped to initiate crystallization and was useful in controlling the subsequent temperature rise. The crystals were separated by filtration on a sintered-glass funnel, in a dry box, washed with the same solvent if sufficiently volatile, otherwise with methanol, acetone, or *n*-pentane. After drying by suction, samples of the solid were transferred to tared weighing bottles for analysis. A small quantity was crushed on a porous plate and placed in a melting point tube which was sealed immediately after removal from the dry box.

#### *(ii) Trimethyl Orthoborate plus Liquid Amine*

Trimethyl orthoborate, solvent, and amine (5 ml of each) were added in turn to a 50-ml Erlenmeyer flask cooled in an ice bath. The resultant crystals were filtered in the dry box as described above.

#### *(iii) Trimethyl Orthoborate plus Liquid Ammonia*

A few inclusion compounds were formed using liquid ammonia, in an attempt to obtain an exactly 1:1 ratio of B:N. A mixture of trimethyl orthoborate, solvent, and ammonia in the mole ratio 1:8:5 was found to provide a sufficient excess of ammonia and enough solvent to prevent the trimethyl orthoborate from freezing. One part of trimethyl orthoborate and four parts of solvent were cooled to -28° C (boiling CF<sub>2</sub>Cl<sub>2</sub>) and a mixture of five parts of liquid ammonia and four parts of solvent added cautiously with stirring. A soda lime trap was attached to the flask and the contents were allowed to warm to room temperature. Filtration was carried out in a dry box, as usual.

#### *(iv) Triphenyl Orthoborate*

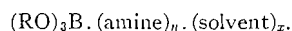
Triphenyl orthoborate-ammonia compounds were made by dissolving the ester in the solvent to be incorporated (using a slight excess of solvent over that required to effect solution) and saturating the solution with ammonia.

### *Analysis of Inclusion Compounds*

Weighed samples of the inclusion compounds were dissolved in water and titrated against 0.1 *N* hydrochloric acid to the methyl red end point. Mannitol was added and the solution then titrated against 0.1 *N* sodium hydroxide to the phenolphthalein end point. The first titration gives the amount of amine, the second gives the amount of boric acid liberated on hydrolysis.

The methanolysis procedure of Thomas (12) was used to determine the boron content of the triphenyl orthoborate inclusion compounds. Later experiments, however, showed that direct titration gives the correct answer despite the presence of free phenol.

All inclusion compounds were assumed to correspond to the formula



The values of *n* and *x* could be calculated from the above analytical results.

## RESULTS

*Trimethyl Orthoborate - Ammonia Compounds*

Analytical and other data for inclusion compounds involving trimethyl orthoborate, ammonia, and a series of alcohols are given in Table I. The solvents used to wash the

TABLE I  
 $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{NH}_3)_n \cdot (\text{alcohol})_x$   
 (Prepared by saturating an alcoholic solution of trimethyl orthoborate with ammonia gas)

Alcohol	% N	% B	<i>n</i>	<i>x</i>	Washed with	Appearance	Crystal growth
Methyl	8.95	5.98	1.16	1.79	MeOH	Wet	xxx
	8.04	5.73	1.09	2.09	*	Wet	xxx
Ethyl	4.55	4.23	0.83	2.99	MeOH	Wet	xxx
<i>n</i> -Propyl	6.92	5.15	1.04	1.47	MeOH	Wet	
<i>i</i> -Propyl	7.57	6.33	0.92	0.85	MeOH	Wet	xxx
<i>n</i> -Butyl	5.94	8.52	0.54	0.19	MeOH	Wet	
<i>i</i> -Butyl	7.76	6.53	0.92	0.62	<i>n</i> -Pentane		xx
<i>s</i> -Butyl	7.86	7.60	0.80	0.34	Col. 1	Slightly wet	xxx
<i>t</i> -Butyl	5.44	6.72	0.63	0.63	Col. 1		
<i>n</i> -Amyl	4.04	5.05	0.62	1.13	Col. 1	Wet	xx
<i>i</i> -Amyl	6.84	6.66	0.79	0.51	Col. 1	Wet	xxx
<i>t</i> -Amyl	7.57	7.58	0.77	0.29	Col. 1	Dry	xxx
<i>n</i> -Hexyl	4.50	6.50	0.54	0.52	Acetone	Wet	x
<i>n</i> -Heptyl	3.65	8.03	0.35	0.22	—	Wet	
<i>n</i> -Octyl	4.94	5.60	0.68	0.60	—	Wet	
<i>n</i> -Decyl	7.14	7.69	0.72	0.16	Acetone	Dry	xxx
<i>n</i> -Dodecyl	5.96	9.16	0.50	0.03	Acetone	Wet	xx

\*Prepared using liquid ammonia.

crystals are listed in column 6 ("col. 1" means that the crystals were washed with the same alcohol). The appearance of the crystals is noted in column 7. These compounds were generally quite wet and sticky, so that it was not possible to measure melting points. Thus the compound containing ethanol became practically liquid on storage. Many of the compounds showed a marked tendency to sublime at room temperature. After a few weeks' storage in weighing bottles, large transparent crystals were deposited on the upper surfaces of the bottles. In some cases, such crystals were found buried in the original powder at the bottom of the bottles. The tendency for crystal growth by sublimation is indicated in column 8 (*x* = slight, *xx* = moderate, *xxx* = pronounced). The compounds with *t*-amyl and *n*-decyl alcohols formed large, dry crystals, which were removed with tweezers and analyzed (see Table IX).

In Table II are listed the results obtained for inclusion compounds containing trimethyl orthoborate, ammonia, and a series of saturated and unsaturated hydrocarbons. All these compounds were fine, dry powders. For all the alkanes except neopentane and cyclohexane, *x* is equal to zero within the experimental error. In contrast, significant values of *x* were found for all the unsaturated hydrocarbons except isoprene. Benzene and cyclohexane gave almost identical *x* values. Melting points (sealed tube) for some of these compounds are recorded in the last column.

Results for compounds containing trimethyl orthoborate, ammonia, and a variety of organic solvents are given in Table III. Some of these compounds were prepared using liquid ammonia and are designated "liq." in column 6. Crystals of the compound containing 1,1-dimethoxyethane, which had sublimed on storage, were removed and analyzed (Table IX). The compound containing  $\text{CF}_2\text{Cl}_2$  (b.p.  $-28^\circ\text{C}$ ) was prepared as follows.

TABLE II  
 $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{NH}_3)_n \cdot (\text{hydrocarbon})_x$   
 (Prepared by saturating a hydrocarbon solution of trimethyl orthoborate with ammonia gas)

Hydrocarbon	% N	% B	<i>n</i>	<i>x</i>	Washed with	Crystal growth	M.p. (°C)
Alkanes							
<i>n</i> -Butane	10.38	9.26	0.87	-0.03	Col. 1		
<i>n</i> -Pentane	10.51	8.79	0.92	0.05	Col. 1		
2-Me-butane	10.37	9.48	0.85	-0.06	Col. 1	xxx	
Neopentane	9.46	8.31	0.87	0.16	Col. 1	x	
<i>n</i> -Hexane	11.17	9.35	0.92	-0.05	Col. 1		67.5-69
2-Me-pentane	11.11	9.08	0.95	-0.01	Col. 1		
3-Me-pentane	11.09	9.25	0.93	-0.03	Col. 1		60-63
2,3-DiMe-butane	11.28	9.00	0.97	0.00	Col. 1		
2,2-DiMe-butane	11.30	8.90	0.98	0.01	Col. 1		68-77
<i>n</i> -Heptane	10.05	8.72	0.89	0.04	Col. 1	xxx	
Cyclohexane	7.98	7.34	0.84	0.35	Col. 1	x	
Alkenes							
2-Pentene	9.33	8.62	0.84	0.11	—		
Isoprene	10.67	9.22	0.89	-0.02	—		
2-Me-1-pentene	9.51	8.55	0.86	0.10	—		
1-Heptene	8.27	7.82	0.82	0.21	—		
3-Et-2-pentene	9.97	8.29	0.93	0.11	Col. 1	x	
Aromatic hydrocarbons							
Benzene	7.89	7.65	0.81	0.31	Col. 1		

TABLE III  
 $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{NH}_3)_n \cdot (\text{solvent})_x$   
 (Prepared with gaseous or liquid ammonia)

Solvent	% N	% B	<i>n</i>	<i>x</i>	Method	Washed with	Crystal growth	M.p. (°C)
$\text{CH}_2\text{Cl}_2$	5.92	6.65	0.69	0.55	Gas	Col. 1		
	7.53	8.20	0.71	0.19	Liq.	—		62-64
$\text{CHCl}_3$	7.94	7.79	0.79	0.18	Liq.	—		
$\text{CCl}_4$	5.36	5.65	0.73	0.49	Gas	Col. 1	x	
	5.15	5.80	0.69	0.46	Liq.	—		67-71
$\text{CF}_2\text{Cl}_2$					Gas	—	Loses $\text{CF}_2\text{Cl}_2$	
$\text{Et}_2\text{O}$	8.32	7.99	0.81	0.24	Liq.	—		
<i>n</i> -Pr <sub>2</sub> O	7.15	6.46	0.86	0.48	Gas	Col. 1	xxx	
1,1-( $\text{CH}_3\text{O}$ ) <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	6.19	6.13	0.78	0.66	Gas	Col. 1	xxx	
MeCOEt	6.07	8.91	0.53	0.12	Liq.	—		
MeCOOEt	8.82	8.30	0.82	0.14	Gas	Col. 1		
MeNO <sub>2</sub>	8.13	6.87	0.91	0.62	Gas	Col. 1	x	
HCONH <sub>2</sub>	7.64	8.33	0.71	0.31	Gas	Acetone	x	
MeCN	8.72	7.80	0.86	0.49	Gas	—	x	
EtCN	7.55	7.48	0.78	0.50	Gas	—	xx	

A mixture of approximately equal volumes of trimethyl orthoborate and liquid  $\text{CF}_2\text{Cl}_2$  (they are not completely miscible) was held at  $-28^\circ\text{C}$  in a boiling- $\text{CF}_2\text{Cl}_2$  bath and saturated with ammonia gas. Extensive precipitation was observed in both gas and liquid phases. The mixture was warmed to room temperature, whereupon all the uncombined  $\text{CF}_2\text{Cl}_2$  and ammonia evaporated. The weight of the residual solid was measured as a function of time; the sample lost weight continuously over a period of 24 hours. The same results were obtained in a subsequent experiment in which  $(\text{CH}_3\text{O})_3\text{B} \cdot \text{NH}_3$  (1.785 g) was treated with excess liquid  $\text{CF}_2\text{Cl}_2$  at its boiling point. After warming to room temperature and allowing the excess  $\text{CF}_2\text{Cl}_2$  to boil off, the solid was reweighed and found to

have occluded 0.172 g of  $\text{CF}_2\text{Cl}_2$  ( $x = 0.096$ ). This sample also lost weight slowly at room temperature.

*Trimethyl Orthoborate - Methylamine Compounds*

Results for compounds of trimethyl orthoborate, monomethylamine, and alcohols are shown in Table IV. Under the conditions used, no crystals could be obtained in the

TABLE IV  
( $\text{CH}_3\text{O}$ )<sub>3</sub>B. ( $\text{CH}_3\text{NH}_2$ )<sub>n</sub>. (alcohol)<sub>x</sub>  
(Prepared by saturating an alcoholic solution of trimethyl orthoborate with methylamine gas)

Alcohol	% N	% B	<i>n</i>	<i>x</i>	Washed with	Appearance	Crystal growth	M.p. (°C)
Methyl	8.29	6.58	0.97	0.95	—		xx	
Ethyl	Could not be formed	Could not be formed						
<i>n</i> -Propyl	6.93	5.89	0.91	0.86	—	Dry	x	78-82
<i>i</i> -Propyl	Could not be formed	Could not be formed						
<i>n</i> -Butyl	7.24	6.24	0.90	0.56	—	Wet	xx	74
<i>i</i> -Butyl	7.22	5.95	0.94	0.66	—	Wet	x	73-74
<i>s</i> -Butyl	6.24	5.76	0.84	0.66	Col. 1	Wet	xx	
<i>t</i> -Butyl	Unstable							
<i>n</i> -Amyl	6.93	5.78	0.93	0.62	Col. 1	Dry	x	
<i>i</i> -Amyl	5.85	5.45	0.83	0.67	Col. 1	Mod. dry	x	
<i>t</i> -Amyl	Unstable							
<i>n</i> -Hexyl	Unstable							
<i>n</i> -Decyl	Unstable							
<i>n</i> -Dodecyl	Unstable							

presence of ethanol, *n*-propanol, *n*- and iso-butanol; with isoamyl alcohol, *n*-decanol, and *n*-dodecanol, the crystals were not stable enough to permit filtration. The remaining alcohols in Table IV formed stable compounds having substantial values of *x*, comparable (excepting methanol) to those found for the corresponding ammonia adducts (Table I). Values of *n* showed far less variation than those in Table I. In the case of methanol and *n*-hexanol, the crystals formed by sublimation during storage were hand-picked and analyzed (Table IX).

The results shown in Table V, for compounds involving trimethyl orthoborate, monomethylamine, and hydrocarbons, are remarkably similar to those for the corresponding

TABLE V  
( $\text{CH}_3\text{O}$ )<sub>3</sub>B. ( $\text{CH}_3\text{NH}_2$ )<sub>n</sub>. (hydrocarbon)<sub>x</sub>  
(Prepared by saturating a hydrocarbon solution of trimethyl orthoborate with methylamine gas. Crystals washed with the same hydrocarbon)

Hydrocarbon	% N	% B	<i>n</i>	<i>x</i>	Crystal growth	M.p. (°C)
<i>n</i> -Pentane	8.90	8.54	0.81	-0.03		73.5-76
Neopentane	7.36	7.88	0.72	0.15	x	
2-Me-butane	8.07	7.41	0.84	0.39	xxx	
<i>n</i> -Heptane	8.51	8.56	0.77	-0.01		
Cyclohexane	8.84	8.39	0.81	0.00		73.5-74
Benzene	7.90	6.88	0.89	0.33		71.5-72
$\text{CH}_2\text{Cl}_2$	7.75	8.26	0.73	0.05		
$\text{CCl}_4$	8.06	7.65	0.81	0.08		64-66

compounds made with ammonia (Table II). The values of *x* are almost identical except for 2-methylbutane, which is occluded with methylamine but not with ammonia, and

for cyclohexane, for which the reverse is true. With methylamine, the values of  $n$  are slightly lower than with ammonia. Results for  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  are also included in Table V. These solvents give very low  $x$  values, in contrast to their behavior with ammonia (cf. Table III).

*Trimethyl Orthoborate - Higher Amine - Methanol Compounds*

In Table VI are given the results for compounds involving trimethyl orthoborate and higher amines, methanol being the incorporated solvent in each case. The first five

TABLE VI  
 $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{amine})_n \cdot (\text{MeOH})_x$   
 (Prepared by treating a methanolic solution of trimethyl orthoborate with gaseous or liquid amine)

Amine	% N	% B	$n$	$x$	Appearance	Crystal growth	M.p. (°C)
Ammonia	8.95	5.98	1.16	1.79	Wet	xxx	
Monomethyl	8.29	6.58	0.97	0.95	Mod. wet	xx	
Dimethyl	Unstable at room temperature						
Trimethyl	Unstable at room temperature						
Monoethyl	7.50	5.52	1.05	1.40	Mod. dry	xxx	56-60
Diethyl	6.53	4.98	1.01	1.23	Wet	xxx	45-50
Triethyl	No crystals formed						
<i>n</i> -Butyl	5.99	4.66	0.99	1.74	Wet		
Tri- <i>n</i> -butyl	No crystals formed						
<i>t</i> -Butyl	Unstable at room temperature						
<i>n</i> -Amyl	6.21	4.86	0.99	1.02	Wet	xx	Decomp.
<i>n</i> -Heptyl	No crystals formed						
Piperidine	5.93	4.76	0.96	1.29	Mod. dry	xx	65-69

amines were added as gases. The data for ammonia and methylamine (from Tables I and IV) are listed for the sake of completeness. All the compounds analyzed contained substantial amounts of included methanol ( $0.95 < x < 1.79$ ) and exhibited B:N ratios close to unity ( $0.96 < n < 1.16$ ). The trimethyl orthoborate - diethylamine - methanol compound showed a pronounced tendency to sublime, producing spectacular clusters of large crystals on the walls of the weighing bottle in which it was stored. A photograph of the crystals is shown in Fig. 1; the black strip on the outside of the weighing bottle is 1 cm in length. These crystals were hand-picked and analyzed (Table IX).

In order to determine the effect of solvent concentration on the value of  $x$ , a number of preparations of the methyl borate - piperidine - methanol compound were made, by adding 5 ml of piperidine to 5 ml of methyl borate dissolved in 1-10 ml of methanol. The results, given in Table VIII, will be discussed later.

*Sublimed Crystals*

The  $n$  and  $x$  values for large sublimed crystals, which were hand-picked and analyzed, are compared in Table IX with the corresponding values for the fine crystals from which they were grown.

*Triphenyl Orthoborate - Ammonia Compounds*

Results for compounds involving triphenyl orthoborate, ammonia, and solvent are summarized in Table VII. The amounts of pentane, benzene, and methylene chloride incorporated are much larger than with the trimethyl orthoborate - amine compounds. Furthermore,  $n$  is nearer 2 than 1, in accord with the work of Colclough, Gerrard, and Lappert (10), who found  $n = 2$  for the pure compound triphenyl orthoborate - ammonia.

PLATE I

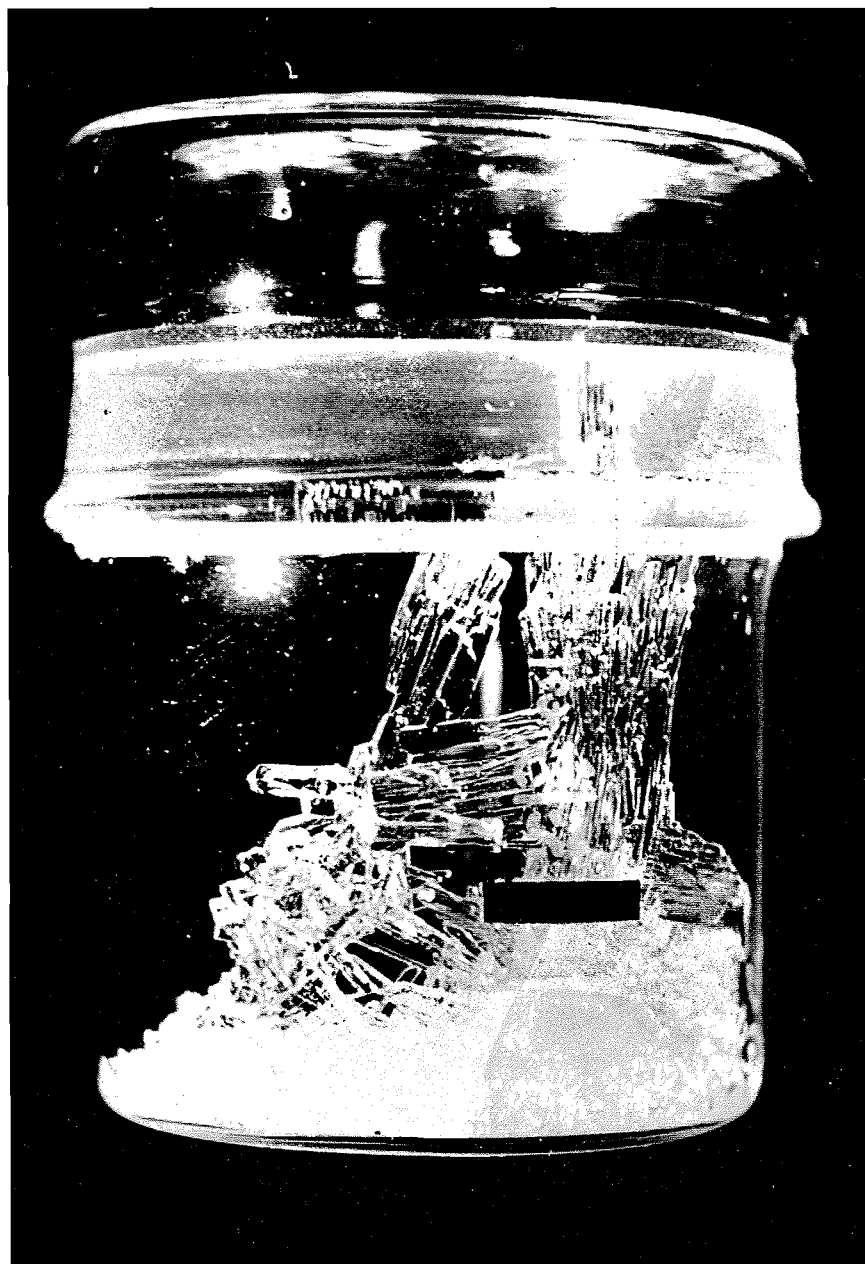


FIG. 1. Sublimed crystals of the trimethyl orthoborate - dimethylamine - methanol compound. The black strip is 1 cm long.





TABLE VII  
 $(C_6H_5O)_3B \cdot (NH_3)_n \cdot (solvent)_x$   
 (Prepared by saturating a solution of triphenyl orthoborate with ammonia gas.  
 Crystals washed with same solvent)

Solvent	% N	% B	$n$	$x$	M.p. (°C)
<i>n</i> -Pentane	5.69	2.58	1.70	1.39	84-88
Benzene	7.43	2.37	2.42	1.60	
CH <sub>2</sub> Cl <sub>2</sub>	5.90	2.54	1.80	1.24	

## DISCUSSION

In the absence of any detailed physicochemical or crystallographic information on the pure inclusion-free borate-amine compounds, there is little hope of being able to give a satisfactory interpretation of the mass of results obtained in this work. It may be worthwhile, however, to assemble the facts which theory must eventually explain.

The most striking feature of the compounds is that they are non-stoichiometric with respect to the B:N ratio. Thus with trimethyl orthoborate - ammonia - heptanol,  $n$  is as low as 0.35, while with the first member of the same series, trimethyl orthoborate - ammonia - methanol,  $n = 1.16$ . Triphenyl orthoborate - ammonia inclusion compounds also exhibit wide variations in  $n$ .

Considering now the values of  $x$ , it must be borne in mind that this parameter is sensitive to the method of preparation and time of drying with suction on the filter. In a number of instances,  $x$  and  $n$  have been determined as a function of time of drying. In all cases, long drying causes a decrease in  $x$ , but  $n$  remains constant. Care was therefore taken to prepare the compounds under similar conditions; indeed, duplicate preparations have shown  $x$  and  $n$  to be fairly reproducible.

The series trimethyl orthoborate - ammonia - alcohol (Table I) merits detailed examination, because it is the largest group and exhibits the widest range of  $x$  and  $n$  values. The results indicate a rough correlation between  $x$  and  $n$ , as shown in Fig. 2. Excluded from this graph are the data for ethanol, which exhibits an abnormally high affinity for trimethyl orthoborate - ammonia, the results for the methanol compound prepared using liquid ammonia, and those for the resublimed compounds. It should be emphasized that in all cases a constant volume of solvent was used. If the value of  $x$  is a function of the mole fraction of the solvent in the mixture during precipitation, more meaningful values of  $x$  might have obtained if in all preparations a constant initial mole fraction of solvent had been used.

In order to determine the dependence of  $x$  on the mole fraction of solvent in the mixture at the start of the reaction, a series of preparations of the compound  $(CH_3O)_3B \cdot (\text{piperidine})_n \cdot (\text{methanol})_x$  was made, using varying amounts of methanol. This system was selected because liquid amines form adducts more rapidly than gaseous amines and because moderately dry crystals with high  $x$  values could be obtained. The variation of  $x$  with the amount of methanol used followed no regular pattern in this case (Table VIII). However, the results are of unusual interest in that they show very clearly the relation between  $x$  and  $n$  (see Fig. 3) and confirm the correlation inferred from Fig. 2.

If the incorporated solvent molecules occupy holes in the trimethyl orthoborate - amine crystal lattice, one would expect  $x$  to be high for small molecules and zero for large ones. This general behavior is found in the series trimethyl orthoborate - ammonia - alcohol. In Fig. 4, the value of  $x$  is plotted against the number of carbon atoms in the

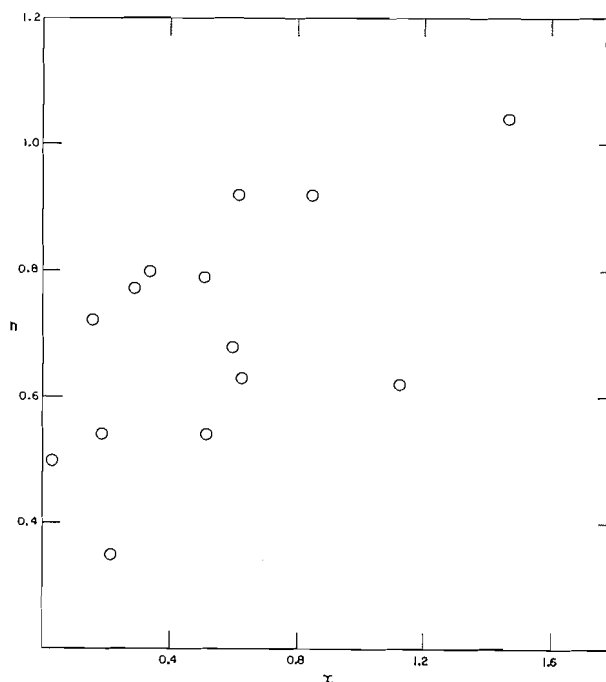


FIG. 2. Plot of  $n$  versus  $x$  for the series of compounds  $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{NH}_3)_n \cdot (\text{alcohol})_x$ .

TABLE VIII

$(\text{CH}_3\text{O})_3\text{B} \cdot (\text{piperidine})_n \cdot (\text{MeOH})_x$   
(Prepared by adding 5 ml of piperidine to 5 ml of trimethyl orthoborate dissolved in methanol)

MeOH (ml)	% N	% B	$n$	$x$
1	6.33	5.34	0.92	0.65
1	6.53	6.17	0.82	0.05
2	6.42	5.55	0.89	0.47
3	6.39	5.40	0.92	0.57
4	6.32	5.38	0.91	0.62
5	6.31	5.19	0.94	0.77
7	6.54	5.76	0.88	0.29
7	6.34	5.16	0.95	0.78
10	6.45	5.54	0.90	0.47

alcohol, for primary straight-chain alcohols. Since it has been shown that  $x$  does not exhibit a systematic variation with the mole fraction of alcohol in the mixture (see above), the results in Fig. 4 may be cited as partial evidence for this "molecular sieve" effect.

The marked tendency of the trimethyl orthoborate - amine inclusion compounds to sublime is most probably due to dissociation, migration of the volatile components through the vapor space, and reassociation on the cooler parts of the vessel. The same behavior has been found with pure trimethyl orthoborate - ammonia. It is interesting to note (Table IX) that the sublimed crystals have substantially higher values of  $n$  and  $x$  than

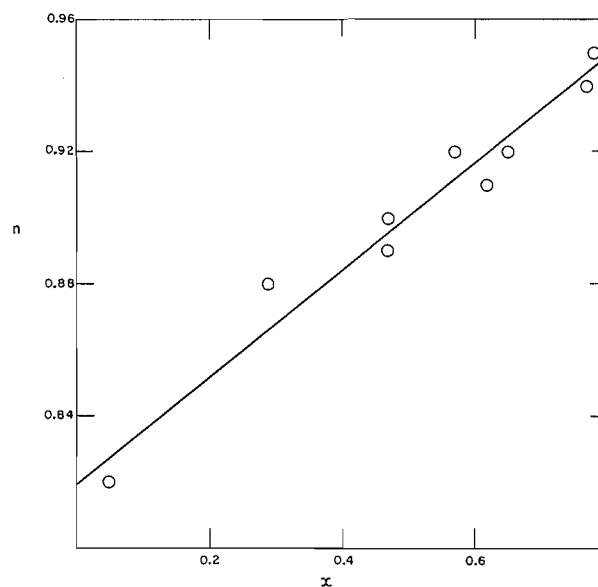
FIG. 3. Plot of  $n$  versus  $x$  for the series of compounds  $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{piperidine})_n \cdot (\text{CH}_3\text{OH})_x$ .

TABLE IX

Amine	Incorporated solvent	Original crystals		Large sublimed crystals	
		$n$	$x$	$n$	$x$
Ammonia	<i>t</i> -Amyl alcohol	0.77	0.29	1.03	0.89
	<i>n</i> -Decanol	0.72	0.16	0.93	0.24
	1,1- $(\text{CH}_3\text{O})_2\text{C}_2\text{H}_4$	0.78	0.66	0.90	0.71
Monomethyl	Methanol	0.83	0.67	0.78	0.60
	<i>n</i> -Hexanol	0.97	0.95	0.97	0.95
Diethyl	Methanol	1.01	1.23	0.98	1.02

the original crystals, when ammonia is the amine, whereas with methylamine and diethylamine  $n$  and  $x$  are unchanged or lower than in the original crystals.

From the behavior of the  $\text{CF}_2\text{Cl}_2$  inclusion compound it is clear that  $\text{CF}_2\text{Cl}_2$  is incorporated into the crystal lattice of trimethyl orthoborate - ammonia in such a way that it is in equilibrium with a definite partial pressure of  $\text{CF}_2\text{Cl}_2$ , as if it were adsorbed on charcoal, for example. The same undoubtedly holds true for the other incorporated solvents. The problem of measuring this equilibrium partial pressure is complicated, however, by the fact that trimethyl orthoborate and the amine also exert appreciable equilibrium partial pressures. If a compound could be prepared from an involatile orthoborate ester and an involatile amine, this solid could be treated as the sorbent and the solvent to be incorporated as the sorbate, sorption isotherms could be measured, and the thermodynamic functions for the system calculated in the usual way.

The melting points of the inclusion compounds are thought to be dissociation temperatures rather than true melting points; therefore little significance is attached to the fact that those for the trimethyl orthoborate - ammonia compounds lie close to that ( $72^\circ\text{C}$ ) reported by Goubeau and Link (5) for the pure compound trimethyl orthoborate - ammonia. In contrast, the melting point of the methylene chloride inclusion compound

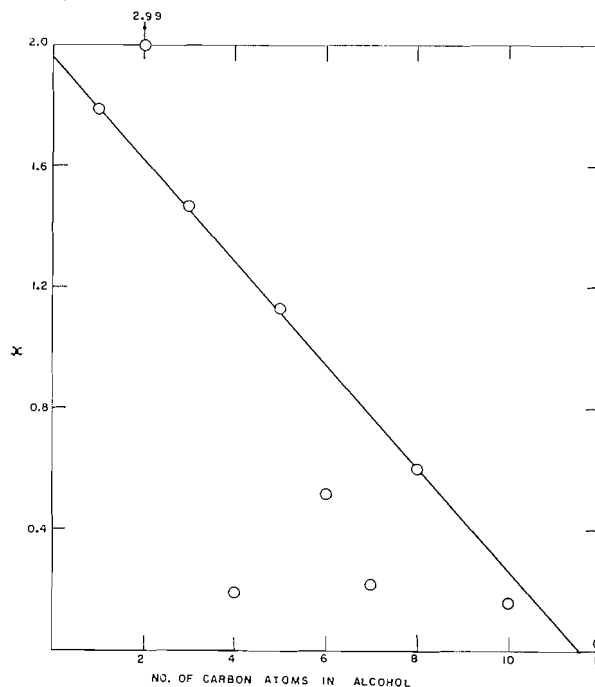


FIG. 4. Dependence of  $x$  on the number of carbon atoms in the alcohol, for the series of compounds  $(\text{CH}_3\text{O})_3\text{B} \cdot (\text{NH}_3)_n \cdot (\text{alcohol})_x$ .

of triphenyl orthoborate - ammonia (84–88°) is much lower than the value (125°) reported for the pure adduct (10).

The finding that alkanes are not occluded by trimethyl orthoborate - ammonia and trimethyl orthoborate - methylamine forms the basis for a proposed method (13) for making these compounds, free from incorporated solvent, avoiding the disadvantages of the vapor phase method (1). It is interesting to note that, although the alkanes are not incorporated, the crystal growth of the pure amine compounds prepared from alkane solutions depends on the nature of the alkane. Thus (Table II), crystals of trimethyl orthoborate - ammonia prepared in 2-methylbutane or *n*-heptane show a pronounced tendency for crystal growth, whereas those prepared in other alkanes do not. In all these cases  $x = 0$  within experimental error. The same general behavior is exhibited with trimethyl orthoborate - methylamine compounds prepared from alkane solutions (Table V).

Preliminary X-ray diffraction measurements on some trimethyl orthoborate - ammonia inclusion compounds have indicated that the crystal lattice is essentially the same as that of pure trimethyl orthoborate - ammonia, confirming the idea that the included solvent molecules occupy holes in the crystal lattice.

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