

thermal vacuum dehydration of the new compound, $\text{PcSn}(\text{OH})_2$.⁸ It also has been found that $(\text{PcGeO})_x$ can be prepared by the usual vacuum dehydration technique. The nature of the Si, Ge, and Sn long-chain polymers has been determined by means of studies based on elemental analysis, infrared spectra, thermogravimetric analysis, and resistance to chemical attack. In general $(\text{PcSiO})_x$ is quite stable chemically, $(\text{PcGeO})_x$ less stable, and $(\text{PcSnO})_x$ relatively unstable; for example, $(\text{PcSiO})_x$ is unaffected by aqueous HF at 100°, aqueous 2 M NaOH at reflux, and H_2SO_4 at room temperature, while $(\text{PcGeO})_x$ withstands only the NaOH and $(\text{PcSnO})_x$ does not withstand even the NaOH.

A feature of all these systems is that the great planar phthalocyanino ring predetermines the over-all stereochemistry, forcing the tetravalent metals into octahedral coordination, the aluminum into square pyramidal coordination, and the chains into a truly linear arrangement. In the case of the polymers a further feature of these stereochemically locked systems is that the size of the planar phthalocyanino ring simplifies the interpretation of the X-ray powder patterns sufficiently so that definite structural information can be obtained.

X-Ray powder photographs of $(\text{PcSiO})_x$ reveal that the strongest reflection corresponds to an interplanar spacing of $3.32 \pm 0.02 \text{ \AA}$. The value of the spacing calculated from the second-order reflection is twice $1.659 \pm 0.003 \text{ \AA}$. The interplanar spacing of 3.32 \AA is attributed to the repeat distance of the polymer chain and if this is correct it follows directly that the adjacent phthalocyanino rings are stacked parallel in a "deck of cards" fashion. Because the oxygens are wedged between eight nitrogens it seems highly improbable that the SiOSi bond angle deviates from 180°. Therefore the value of 1.66 \AA must correspond to the octahedral Si-O bond length. For comparison it may be noted that ordinary tetrahedral Si-O bonds are in a range near 1.64 \AA .⁴

X-Ray powder photographs of $(\text{PcGeO})_x$ are very similar to those obtained for $(\text{PcSiO})_x$. Here the strongest reflection corresponds to a spacing of $3.50 \pm 0.02 \text{ \AA}$. The value calculated from the second-order reflection is twice $1.746 \pm 0.003 \text{ \AA}$. The 3.50 \AA spacing is assigned to the repeat distance of the polymer chain and it is concluded that the rings are again stacked parallel. This interpretation gives an octahedral Ge-O bond length of 1.75 \AA . The reported average tetrahedral Ge-O bond lengths in $(\text{GeO}_3)^{2-}$ are $1.84\text{--}1.86 \text{ \AA}$.⁴

The X-ray data for $(\text{PcSnO})_x$ are similar to those for $(\text{PcSiO})_x$ and $(\text{PcGeO})_x$ although the pattern is more diffuse. An intense line occurs corresponding to a spacing of $3.83 \pm 0.03 \text{ \AA}$. This is attributable to the repeat distance in the polymer chain. The value of this spacing based on the second-order reflection is twice $1.91 \pm 0.02 \text{ \AA}$. Again concluding that the

rings are parallel and the chain is linear the octahedral Sn-O bond length is $1.91 \pm 0.02 \text{ \AA}$. The Sn-O bond length is reported to be $1.93\text{--}1.98 \text{ \AA}$ in $\text{Sn}(\text{OH})_6^{2-}$.⁴ It is interesting to note that even at the separation of 3.83 \AA the rings are still parallel.

An experiment has verified the assignment of these intense *d*-spacings. A sample of $(\text{PcGeO})_x$ was heat-treated for 2.5 hr. at 500° under high vacuum. The infrared spectrum of the residue was identical with the spectrum of the starting material except that the absorption band resulting from the unsymmetrical stretching vibration of the Ge-O-Ge group shifted from 864 to 899 cm^{-1} . X-Ray powder photographs revealed that the sample became more crystalline. The strongest X-ray line corresponded to a spacing of $3.48 \pm 0.02 \text{ \AA}$ and the second-order reflection of this spacing to a value of twice $1.738 \pm 0.003 \text{ \AA}$. A simple picture that accounts for these phenomena is that an ordering of the polymer took place accompanied by a contraction of the Ge-O-Ge distance and an increase in the Ge-O bond strength. These data imply that the polymer units have special preferred orientation.

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The Structure of (Methylphenylamino)-methylphenylborane

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The existence of double bond character for the boron-nitrogen linkage of aminoboranes has long been advocated by Wiberg.² Recently, unsymmetrically substituted aminoboranes have become available and, based primarily on physicochemical constants, a suggestion has been made that such compounds may exhibit *cis-trans* isomerism.³ Two recent short communications on the proton magnetic resonance spectra of two selected aminoboranes, substituted unsymmetrically at either the boron⁴ or the nitrogen⁵ atom,

(1) (a) Technische Hochschule, Stuttgart; (b) Duke University; (c) University of Florida; (d) U. S. Army Research Office.

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substantiate the concept of restricted rotation about the B-N linkage. A detailed spectroscopic investigation of one sample compound, unsymmetrically substituted at both the nitrogen and the boron atoms, seemed of interest. At room temperature, (methylphenylamino)-methylphenylborane, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{N}-\text{B}(\text{CH}_3)(\text{C}_6\text{H}_5)$, appears to exist in both a liquid and a solid phase.³ It was thought that this might indicate the presence of *cis* and *trans* isomers and therefore this compound was selected for the present investigation.

Infrared and Raman Data

The Raman and infrared spectra of the liquid (methylphenylamino)-methylphenylborane recorded at room temperature are presented in Table I. Assignments have been made on the basis of previous work⁶ and will be presented in more detail elsewhere.

TABLE I
RAMAN AND INFRARED SPECTRUM OF
(METHYLPHENYLAMINO)-METHYLPHENYLBORANE^a

Raman spectrum		Infrared spectrum	
215 w			
245 m-w			
410 m-w		670 w	ν_{BC}
495 w		695 s	γ_{ring}
540 w		740 m	γ_{CH}
560 w		770 m-w	γ_{CH}
625 m		860 m	γ_{CH}
680 m	ν_{BC}	905 w	$\delta_{\text{B-CH}_3}, \gamma_{\text{CH}}$
772 w	γ_{CH}	990 w	
870 w	γ_{CH}	1000 m-w	ν_{ring}
920 w	$\delta_{\text{B-CH}_3}$	1030 w	
1005 s	ν_{ring}	1048 m-w	$\delta_{\text{N-CH}_3}$
1032 m-w	δ_{CH}	1068 m-w	δ_{CH}
1130 m-w	ν_{NC}	1120 m	ν_{NC}
1160 m-w	δ_{CH}	1155 w	δ_{CH}
1210 m-w	$\nu_{\text{B-phenyl}}$	1180 w	δ_{CH}
1250 w	$\nu_{\text{N-phenyl}}$	1215 m	$\nu_{\text{B-phenyl}}$
1270 w	δ_{CH}	1235 m-w	$\nu_{\text{N-phenyl}}$
1290 w	$\delta_{\text{B-CH}_3}$	1265 m	δ_{CH}
1315 w	$\delta_{\text{B-CH}_3}$	1302 s	$\delta_{\text{B-CH}_3}$
1390 m	ν_{BN}	1385 s	ν_{BN}
1440 m	$\nu_{\text{ring}}, \delta_{\text{N-CH}_3}$	1440 s	$\nu_{\text{ring}}, \delta_{\text{N-CH}_3}$
1480 w		1495 s	ν_{ring}
1500 m	ν_{ring}	1600 m	ν_{ring}
1600 s	ν_{ring}	2800 s	ν_{CH_3}
2900 m	ν_{CH_3}	2960 s	ν_{CH_3}
3058 s	ν_{CH}	3020 m	ν_{CH}

^a Frequencies in cm.^{-1} ; w, weak; m, medium; s, strong.

The assignments of the valence vibrations of the grouping $(\text{C}_{\text{alkyl}}, \text{C}_{\text{aryl}})\text{N}-\text{B}(\text{C}_{\text{alkyl}}, \text{C}_{\text{aryl}})$ of the investigated compound can be made with reasonable certainty; some of them should differ in the case of *cis-trans* isomerism. However, none of the absorptions evidenced any splitting or doubling as would be expected for an equilibrium between two rotational isomers. A Raman spectrum taken at 125° did not identify a second species, since the spectrum was iden-

tical with the one recorded at room temperature. Also, a spectrum of the solid compound revealed only slight changes which should be expected with transition from the liquid to the solid state. However, the Raman spectrum of the solid was considerably less intense.

The large number of assigned frequencies and their small variations on transition from solid (25°) to liquid (25°) to liquid (125°) leads one to assume the presence of a single structural species. However, considering the relatively large number of recorded absorptions (which might cause band overlap) and the weak Raman spectrum of the solid, it is probable that less than 15% of a rotational isomer cannot be detected.

Nuclear Magnetic Resonance Data

The B¹¹ resonance of (methylphenylamino)-methylphenylborane was recorded as a singlet at -26.2 p.p.m. relative to trimethyl borate. This substantiates previous evidence⁸ obtained by conventional molecular weight determination which excluded dimerization to any appreciable degree.⁷

At -25° the proton magnetic resonance spectrum of the compound is clearly the superposition of those of two isomers. For the methyl group attached to nitrogen there are two single peaks at 6.80 and 6.90 τ and for the methyl groups attached to boron, two single peaks with values of 9.214 and 9.571 τ . At room temperature, the peaks of the two rotamers are in the process of merging: the N-methyl peak is broadened to a single band, and the B-methyl peaks are nearly joined together but can still be recognized as distinct. At 75°, the N-methyl peak is a sharp singlet at 6.90 and the B-methyl is a singlet at 9.474 τ .

The ratio of the two forms has been measured as a function of temperature. This could be done from -25 to +15° for the N-methyl peaks and -25 to +40° for the B-methyl peaks. The results are illustrated in Fig. 1, with the slope at room temperature corresponding to an enthalpy difference of 1.7 ± 0.5 kcal./mole.

Conclusion

The observation of only one species in the Raman and infrared spectra of (methylphenylamino)-methylphenylborane suggests the presence of only one rotational species with respect to the B-N linkage. Examination of molecular models illustrates that the *trans* configuration is favored, although even this form is probably not planar, and that both phenyl groups should be skewed out of plane. (This is consistent with the results reported for dimethylstilbene.⁸) If this is the situation it is then possible to explain the observation of two n.m.r. signals for both the boron and the nitrogen-attached methyl groups by the indicated structures (a) and (b). Preference of one species (namely, b) should be expected (and is in agreement

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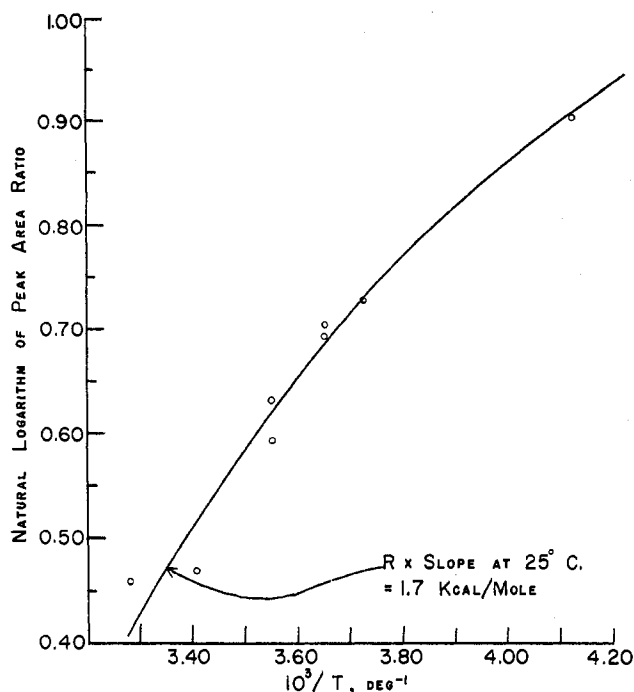
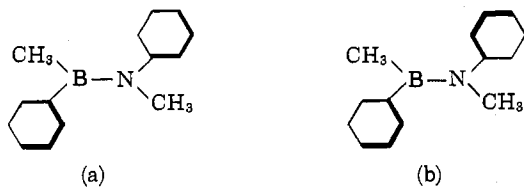


Fig. 1.—Temperature dependence of the equilibrium ratio of isomers of (methylphenylamino)-methylphenylborane.

with the experimental results) if steric effects produce not only nonplanar arrangement of the phenyl groups but also cause a minor tilting about the B–N linkage. This tilting then can lead to different magnetic environments for the corresponding methyl groups in the two forms.



This assumption could also provide an explanation for the behavior of the N-methyl resonances, where the merged peak at 75° is observed at 6.90 p.p.m. Normally, merged peaks have a chemical shift which is the concentration-weighted average of separate isomer peaks, as was observed for the B-methyl resonance.

Experimental

(Methylphenylamino)-methylphenylborane was distilled into Raman cuvettes under high vacuum; greased joint connections were avoided. A slight fluorescence of the compound was observed in the blue region but it was possible to record useful spectra. The ratio of line intensities to the background was comparable to those of other Raman spectra of aromatic substituted aminoboranes reported previously.^{3d} The Raman spectra were recorded with a Cary Raman spectrophotometer Model 81 of a liquid sample at room temperature and at 125° and of a solidified sample which had crystallized after prolonged standing in the Raman cuvette at room temperature. The spectrum of the crystalline material was less intense due to a generally increased amount of scattered light in the spectra of solid materials. However, all lines of medium or strong intensity which were observed in the spectra of the liquid species were also found in the spectrum of the crystalline material at identical frequencies.

Infrared spectra were obtained of mulls in Kel-F and Nujol and of a carbon tetrachloride solution with a Perkin-Elmer Model 21 double beam spectrophotometer using sodium chloride optics.

Nuclear magnetic resonance data were obtained on a Varian Model V-4300-B spectrometer at 40 and 12.8 Mc. and a Varian 4013-B at 60 Mc. The final p.m.r. spectra were obtained on a Varian V-4300-2 high-resolution spectrometer at 60 Mc., using the Varian variable-temperature probe. Side bands were applied by an audio oscillator, monitored continuously by an electronic counter, and peak separations were taken as an average of measurements on replicate spectra. The sample was dissolved to a concentration of approximately 35% in carbon tetrachloride, and tetramethylsilane was used as an internal standard. In addition, spectra were recorded of the neat liquid.

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Structure of $\text{Se}_2\text{Fe}_3(\text{CO})_9$ and Evidence for a New Type of Seven-Coordinated Metal^{1a}

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We wish to report the structural determination of $\text{Se}_2\text{Fe}_3(\text{CO})_9$ by X-ray diffraction which not only provides definite stereochemical information concerning the iron carbonyl chalcogenides, $\text{X}_2\text{Fe}_3(\text{CO})_9$ (where X = S, Se, and Te),² and related derivatives, but also confirms the existence of a new type of seven-coordinated metal. These relatively stable trinuclear metal complexes were first prepared and characterized by Hieber and Gruber² as diamagnetic, hydrophobic solids which display similar infrared absorption bands characteristic of only terminal carbonyl groups.

The dark violet crystals of $\text{Se}_2\text{Fe}_3(\text{CO})_9$ are triclinic with reduced cell parameters: $a = 6.83 \text{ \AA}$., $b = 9.22 \text{ \AA}$., $c = 13.12 \text{ \AA}$., $\alpha = 93^\circ 50'$, $\beta = 94^\circ 20'$, $\gamma = 110^\circ 40'$. There are two molecules per unit cell in the general positions of the space group $\bar{P}1$. The molecular parameters have been obtained from a least-squares refinement³ and error analysis⁴ based on 2003 independent reflections. Weights for the least-squares process were based on the precision of the visually-judged photographic data obtained with Mo $K\alpha$ radiation. The discrepancy index after refinement with individual isotropic temperature factors is $R_1 = 13.5\%$.

The molecular configuration (Fig. 1) consists of an $\text{Se}_2\text{Fe}_2(\text{CO})_6$ fragment of idealized C_{2v} -2mm symmetry bonded to an $\text{Fe}(\text{CO})_3$ group via two bent Fe–Se bonds and two bent Fe–Fe bonds. The idealized configuration

(1) (a) Presented in part at the National Meeting of the American Crystallographic Association, Cambridge, Mass., March 28–30, 1963. (b) National Science Foundation Predoctoral Fellow.

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