the gas phase prior to condensation. The great similarity of the two curves makes it evident that the intensity of the 570-mμ absorption and the concentration of NF_2 (*i.e.*, degree of dissociation) exhibit the same temperature dependence as expected if NF_2NO is the species absorbing at 570 mμ.

The heat of dissociation of NF_2NO and gas phase equilibrium measurements

$$N_2F_4 \rightleftharpoons 2NF_2 + 2NO \rightleftharpoons 2NF_2NO$$

are currently under investigation in these Laboratories.

Acknowledgment.—The authors wish to express their appreciation to Mrs. Carolyn Haney for her valuable assistance in obtaining the F^{19} n.m.r. spectrum of NF_2NO. This work was carried out under Army Contract DA-01-021 ORD-11878 and Air Force Contract DA-01-021 ORD-784.

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A Phthalocyaninosiloxane[1]

BY RALPH D. JOYNER AND MALCOLM E. KENNEY

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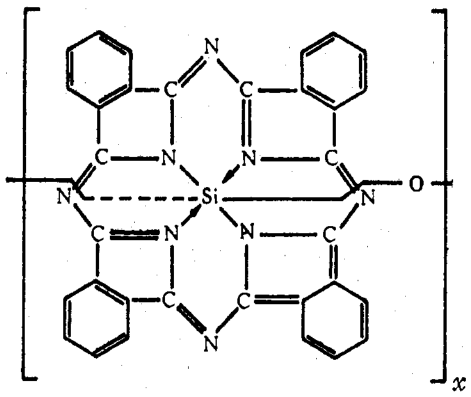
Recently it has been reported that oxy-linked polymers are formed by both phthalocyaninogermanium and phthalocyaninomanganese(IV) systems.[2,3] Work now has been carried out which shows that a related siloxane, $HO(PcSiO)_xH$, is formed by the dehydration of $PcSi(OH)_2$. The reaction by which it is formed, $x PcSi(OH)_2 \rightarrow HO(PcSiO)_xH + (x-1)H_2O$,[4] entails the cleavage of Si–O bonds in the presence of Si–N bonds.

The infrared spectra of $HO(PcSiO)_xH$ and of the material thought to be $HO(PcGeO)_xH$[5a] are very similar (720–1150 cm.$^{-1}$) except that a large broad band appears in the siloxane spectrum at 987 cm.$^{-1}$ and a similarly shaped band in the other spectrum at 872 cm.$^{-1}$. The 987-cm.$^{-1}$ band in the siloxane can be assigned to the Si–O stretching motion.

Because of the planar phthalocyanino ring encircling each silicon atom, the oxygen atoms must occupy *trans* positions. The minimum thickness typical of aromatic rings and the length characteristic of SiO bonds combine to suggest that the SiOSi bond angle approaches 180° and thus that the siloxane is nearly linear. This stereochemistry excludes small rings and the maximum of two OH groups per silicon atom rules out branched chains. Such a structural arrangement is consistent with the observed inertness of the siloxane.



Experimental

Thermal Dehydration of $PcSi(OH)_2$.—Measurements of the amounts of water vapor evolved during the thermal dehydration of $PcSi(OH)_2$ were used to obtain experimental evidence about the nature of the siloxane formed. The $PcSi(OH)_2$ was prepared from sublimed $PcSiCl_2$ by hy-

TABLE I

$PcSi(OH)_2$		H_2O				
Wt. (mg.)	mmoles (n_1)	*P* (mm.)	*V* (ml.)	*T* (°K.)	mmoles (n_2)	n_2/n_1
22.6	0.0393	14.6	49.3	300	0.0386	0.98
21.7	.0378	12.6	49.6	299	.0337	0.89
21.7	.0378	14.3	49.5	301	.0378	1.00
21.2	.0369	13.7	49.4	302	.3060	0.97
25.6	.0445	16.8	4.99	302	.0445	1.00

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(1) This paper is based on a thesis submitted by R. D. Joyner in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Research Corporation and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, and was presented at the 139th National American Chemical Society Meeting.

(2) R. D. Joyner and M. E. Kenney, *J. Am. Chem. Soc.*, **82**, 5790 (1960).

(3) J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 195 (1959).

(4) Pc = $C_{32}H_{16}N_8$.

(5) (a) Spectra available in the thesis of R. D. Joyner, University Microfilms No. 61-3317, p. 49; (b) spectrum shown in the thesis of J. E. Owen, University Microfilms No. 61-3309, p. 91.

drolysis with concentrated aqueous ammonia and pyridine as already described.[6]

The dehydration studies were carried out in an apparatus which consisted of a sample tube connected to both an outlet tube and a tube with a stopcock leading to a U-trap. The trap was in turn joined to a mercury manometer. At the beginning of each of the dehydration experiments the whole system including the sample was evacuated to 0.1 mm. Subsequent manipulations involved heating the sample, collecting the water in the U-trap (cooled with liquid nitrogen), and allowing the water collected to vaporize in a portion of the system which had a known volume and which was at room temperature.

The results of a series of runs in which the sample was heated at 400° or above are given in Table I. The siloxane from the first run was not removed prior to the second run. In all but the last run the samples were heated at 460–470° for 2 to 4 hr. The sample in the final run was first heated at 330° for 2 hr. and then it was slowly heated to 400°. No observable amounts of gas were evolved below 400° but at 400° water was evolved rapidly for less than 15 min. and then the reaction ceased.

The amounts of water evolved during the formation of $HO(PcSiO)_xH$ indicate that the minimum value of x is greater than 10 ($n_2/n_1 = 0.90$), perhaps nearer 10^2 ($n_2/n_1 = 0.99$). The siloxane obtained was a blue air-stable powder. (It subsequently was shown to be soluble and stable for short periods in concentrated H_2SO_4.[7])

Elemental analysis of the siloxane did not differentiate between a short and a long chain polymer but did serve to indicate that gross decomposition had not occurred.

Anal. Calcd. for $C_{32}H_{16}N_8SiO$: C, 69.05; H, 2.90; N, 20.13. Found: C, 68.71; H, 3.07; N, 19.63. (*Anal.* Calcd. for $PcSi(OH)_2$: C, 66.88; H, 3.16; N, 19.50.)

Thermal Stability of the Polymer.—The polymer of the last run was heated further in the manometer system after evacuating the system and closing it off. The polymer withstood 520° *in vacuo* for 2.5 hr. with no detectable gas evolution and no discoloration of itself or the apparatus. Its infrared spectrum also was unchanged. At 550° for 1 hr. it produced 3.3 mm. of pressure in the apparatus along with a green sublimate on the walls of the sample tube. Another sample of the polymer when heated at 625° in the same setup gave evidence of more rapid decomposition by yielding 13.6 mm. of pressure in 15 min.

Infrared End Group Information.—It has been reported that the spectra of $PcSi(OH)_2$[5a] and $HO(PcSiO)_2H$[5b] have strong bands at 831 and 841 cm.$^{-1}$, respectively. These were assigned tentatively to the presence of the SiOH grouping. Spectra of KBr disks of the polymer showed only a very weak band at 840 cm.$^{-1}$. Spectra of a series of KBr disks with mixtures of siloxane and $PcSi(OH)_2$ containing the same total weight of phthalocyanine and KBr but with increasing amounts of $PcSi(OH)_2$ showed absorption near 831 cm.$^{-1}$ of increasing intensity (although the increase in intensity was not according to Beer's law). With high concentrations the maximum was at 831 cm.$^{-1}$, but at low concentrations it was shifted toward 840 cm.$^{-1}$. At 1.1 mole % there was a very small broad band including both 840 and 831 cm.$^{-1}$. If the 840-cm.$^{-1}$ band in the siloxane was due to OH end groups and its extinction coefficient was not much smaller than those of the 831 and 841-cm.$^{-1}$ bands in $PcSi(OH)_2$ and $HO(PcSiO)_2H$, the small intensity of this band was consistent with the small end group content indicated by the water evolution studies.

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[6] R. D. Joyner, R. G. Linck, J. Cekada, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **15**, 387 (1960); R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, **1**, 236 (1962).

[7] J. E. Owen and M. E. Kenney, *Inorg. Chem.*, **1**, 334 (1962).

CONTRIBUTION FROM THE WETHERILL MEMORIAL
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On the Properties of Trimethyl Silyl Azide[1]

BY JOHN W. CONNOLLY AND GRANT URRY

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West and Thayer[2] report the preparation of trimethyl silyl azide of 90% purity. We have prepared and completely characterized this compound using a modification of a synthetic technique described by Wiberg[3] for inorganic silicon azides. The modification used was similar to that employed by West and Thayer Unlike these workers, we have been able to obtain this substance in a virtually pure state.

The compound $(CH_3)_3SiN_3$ was prepared by the treatment of trimethyl chlorosilane with sodium azide in the presence of catalytic amounts of aluminum azide using tetrahydrofuran as a solvent. The crude product can be distilled at atmospheric pressure at approximately 85°. The crude product was purified by a brief treatment with anhydrous aluminum chloride to remove traces of tetrahydrofuran,[4] followed by repetitive fractional condensation, carried out in a standard vacuum apparatus, through a series of U-tube traps maintained at −30, −50, and −196°. The product was retained at −50°.

TABLE I

	Temp., °C				
	−30	−23	0	5	29
Obsd.	1.66	2.77	12.1	16.3	57.8
Calcd.	1.65	2.75	12.2	16.1	58.2

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[1] This research was supported in part by the Air Force Office of Scientific Research under Contract No. AF 49(638)927 and in part by a National Science Foundation Coöperative Fellowship.

[2] R. West and J. S. Thayer, *J. Am. Chem. Soc.*, **84**, 1763 (1962).

[3] E. Wiberg and H. Michaud, *Z. Naturforsch.*, **96**, 500 (1954).

[4] Extended periods of contact between trimethyl silyl azide and aluminum chloride result in a loss of trimethyl silyl azide through conversion to the chloride.