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The Infrared Spectra of Some Silazanes and Disilazanes[1]

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The infrared spectra of four silazanes and two disilazanes are presented and discussed. No band appears in the 2.0 to 16.0 μ region which can be correlated unambiguously with the Si—N grouping. A possible exception, a band at 12 μ, is discussed in the text. The spectra of the disilazanes reveal two bands, 8.5 and 10.8 μ, which appear to be characteristic of the Si—N—Si grouping. Bands involving the N—H function were observed to be normal.

A considerable number of investigations have been directed towards the study of the infrared spectra of compounds which contain a silicon-carbon,[2] a silicon-hydrogen,[3] and a silicon-oxygen[4] linkage. However, there appear to be only two reported tabulations of the infrared bands of compounds containing a silicon-nitrogen linkage.[5]

This study is concerned with the investigation of the infrared spectra of compounds which contain this silazane linkage. In particular the spectra of triethylsilazane [$(C_2H_5)_3SiNH_2$], tripropylsilazane [$(C_3H_7)_3SiNH_2$] triphenylsilazane [$(C_6H_5)_3SiNH_2$], *N*,*N*-diethyltriethylsilazane [$(C_2H_5)_3SiN(C_2H_5)_2$], hexamethyldisilazane [$(CH_3)_5SiNHSi(CH_3)$], and hexaethyldisilazane [$(C_2H_5)_3SiNHSi(C_2H_5)_3$] are presented and discussed.

EXPERIMENTAL[6]

The final purifications of all liquid samples of the silazanes and disilazanes used in this study were accomplished by gas phase chromatography. Triphenylsilazane was recrystallized to a constant melting point.

Silazanes. Triethylsilazane, b.p. 135–137°, was prepared from triethylbromosilane in 76% yield using the procedure of Bailey, Sommer, and Whitmore (lit.,[7] b.p. 134–135°).

Tripropylsilazane. Tripropylsilane, b.p. 169–170°, was prepared in 53% yield using the method of Price (lit.,[8] b.p. 169–169.8°). The tripropylsilane was brominated and the product (not isolated) treated with liquid ammonia to yield tripropylsilazane, b.p. 75–76°/13 mm. (66%) using the method of Larsson.[9]

Triphenylsilazane, m.p. 59–60°, was prepared using the method of Kraus and Rosen.[10] The sample used in the infrared study was recrystallized to a constant melting point from petroleum ether (b.p. 30–60°) (lit.[10] m.p. 55–56°).

N,N-Diethyltriethylsilazane, b.p. 195–196° (lit.,[11] 85–86°/12 mm.) was prepared in 34% yield from triethylbromosilane and diethyl amine.

Disilazanes. Hexamethyldisilazane, b.p. 123–124°, was prepared *via* the method of Sauer[12] in 50% yield (lit.,[12] b.p. 124–126°). Gas phase analysis of this fraction indicated that it contained *ca.* 10% hexamethyldisiloxane which was separated by the gas phase isolation of the disilazane.

Hexaethyldisilazane. In a 50-ml. flask were placed 12.5 g. (0.09 mole) of triethylsilazane and a few crystals of ammonium sulfate. The mixture was heated at reflux overnight and was then distilled without further work-up. The main distillation fraction was collected at 135–137°/30 mm. Gas phase analysis of this fraction indicated that it was composed of approximately 30% hexaethyldisiloxane (lit.,[13] b.p. 128–129°/30 mm.) and 70% hexaethyldisilazane, the higher boiling component (lit.,[14] b.p. *ca.* 100°/1 mm.). A pure sample of the disilazane was isolated from this fraction using gas phase chromatography. The lower-boiling fractions of the distillation were chiefly composed of the disiloxane. Charring of the distillation residue indicated that considerable decomposition had occurred. The yield of the disilazane was 2.6 g. (25%).

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(1) This work was supported by a Frederick Gardner Cottrell grant from Research Corporation.

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(6) All melting and boiling points are uncorrected. Distillations were made using a modified Podbielniak column as described by Cason and Rapoport (J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice Hall, Inc., New York, 1950, p. 237). All distillations were conducted at atmospheric pressure unless otherwise noted. The gas chromatography work was carried out using an Aerograph gas chromatography unit equipped with a 5′ Silicone column. The conditions employed in a given run depended upon the compound to be detected or isolated. In general, the temperature of the unit was 10° to 20° below the boiling point of the compound with a helium flow between 40 and 60 ml./min.

(7) D. L. Bailey, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 435 (1948).

(8) F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).

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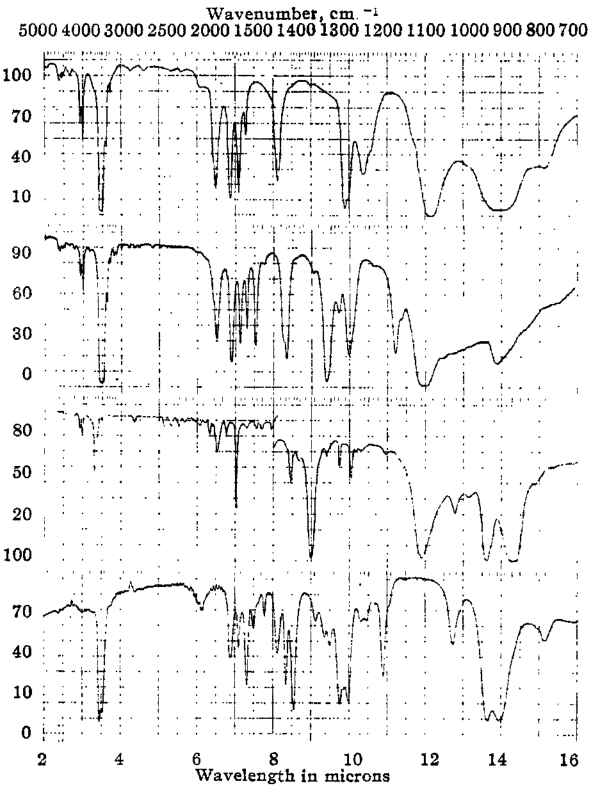

Fig. 1. The infrared spectra of triethylsilazane, tripropylsilazane, triphenylsilazane and *N,N*-diethyltriethylsilazane

Infrared spectra. Spectra were obtained using a Beckman IR-5 recording spectrophotometer. Samples were purified immediately prior to the spectral work. Spectra of the 2.0 to 8.0 μ region were obtained using carbon tetrachloride as solvent, and of the 8.0 to 16.0 μ region, using carbon disulfide. Approximately 10% concentrations and a 0.10-mm. cell were used. Exceptions to the above were tripropylsilazane, run only in carbon tetrachloride, and *N,N*-diethyltriethylsilazane and hexaethyldisilazane, run as thin films.

DISCUSSION

Discussion of spectra. Vibrations of the N—H. All the silazanes and disilazanes which were studied showed characteristic N—H vibrations in their spectra. As may be seen in Fig. 1, the silazanes exhibit N—H stretching vibrations (two bands) at 2.92 and 2.99 μ. The disilazanes (Fig. 2) show a one-band stretching vibration which appears at slightly lower wave lengths (3.05 μ) than those observed in the silazanes. George, Sommer, and Whitmore[5b] report bands at 2.82 μ and 2.95 μ for di-*t*-butoxydiaminosilane and a band at 2.93 μ for hexa-*t*-butoxycyclotrisilazane. All of these bands are at slightly higher wave lengths than those observed in this study. However, the N—H stretching of the aminosilanes appears to be normal and may be found at 2.82 to 3.05 μ.

The N—H deformation bands of the aminosilanes also are similar to those of the normal organic amines. With the silazanes, a strong band is found at 6.50 to 6.53 μ. A band is reported at 6.45 μ for the di-*t*-butoxydiaminosilane[5b] which may also be correlated with the N—H deformation bands observed in this study. In the spectra of the disilazanes using the normal concentrations no band is observed in this region. When the concentration of hexamethyldisilazane was increased, a very weak band, difficult to differentiate from the background, was observed at 6.6 μ. This situation is analogous to the normal organic secondary amines, where this band is reported to be very weak.[15] In the case of the hexa-*t*-butoxycyclotrisilazane, however, a strong band is reported at 6.45 μ,[5b] which would correspond to the N—H deformation frequency. Thus, the N—H deformation of the aminosilanes can be assigned to the 6.4–6.6 μ region.

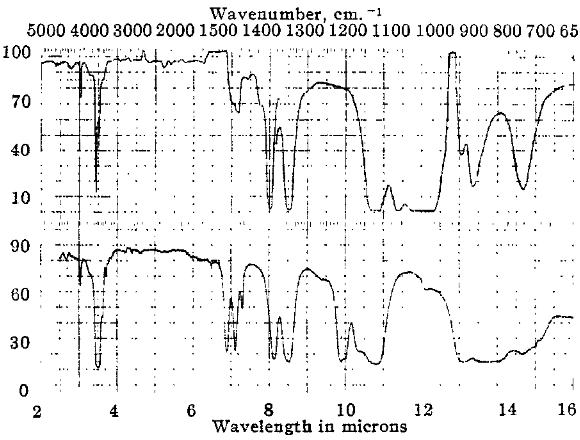

Fig. 2. The infrared spectra of hexamethyldisilazane and hexaethyldisilazane

Vibrations of the Si—N *bond.* In the spectra of the disilazanes[16] (see Fig. 2) two bands, 8.5 and 10.7 μ, are observed which appear to be characteristic of the Si—N—Si grouping. Neither of these bands appears in any of the silazanes studied. Hexa-*t*-butoxycyclotrisilazane also has been reported to exhibit bands at 8.55 and 10.53 μ.[5b] It is interesting to note that the spectrum of tetrapyrrylsilane contains a band at 8.25 μ but does not contain a band at 10.7 μ.[17] Pyrrole shows no absorption at either wave length. Di-*t*-butoxydiaminosilane, which also contains a N—Si—N grouping, apparently shows no absorption at either wave length.[5b]

The spectra of the silazanes (see Fig. 1) exhibit no characteristic band which can be correlated, at this time, with the Si—N stretching vibration. Triethylsilazane, tripropylsilazane, and triphenylsilazane all exhibit strong absorption in the 12 μ region, which could be due to the Si—N grouping. However, *N,N*-diethyltriethylsilazane fails to exhibit any absorption in this region. The added mass of the ethyl groups would be expected to shift the stretching frequency of the Si—N to lower wave lengths; and, indeed, there is splitting observed in the 13.7 μ region.[18]

The assignment of this region to the Si—N stretching vibration, however, is complicated by two factors: (1) di-*t*-butoxydiaminosilane shows two bands in this region, 11.15 μ and 12.80 μ,[5b] and (2) primary amino compounds exhibit absorption in this region because of external deformation of the NH_2 grouping.[15] In the dibutoxy case the 11.15 μ band may be due to the *t*-butoxy function[19] which would leave

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[15] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1958, p. 256.

[16] The spectrum of hexamethyldisilazane has been published by Cerate, Lauer, and Beachell (Ref. 5a). Their spectrum shows a band at 9.4 μ (Si—O) which, in this study, disappears with removal of the disiloxane by gas chromatographic separation.

[17] R. Fessenden and D. F. Crowe, *J. Org. Chem.*, **25**, 598 (1960).

[18] The weaker band observed at 12.75 μ would not be expected to be the shifted band due to its lack of intensity. Infrared bands involving silicon are normally about five times more intense than their carbon analogs (Ref. 4a).

[19] Ref. 15, p. 121.

the 12.8 μ band to the Si—N function. The second complication is considerably more serious. Since primary amines exhibit absorption in this region and as the *N*,*N*-diethyltriethylsilane failed to show any characteristic absorption, no assignment of this region to the Si—N function can be made. The spectrum of a *N*,*N*-dideuterosilazane would shed considerable light upon this problem.

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Photochemical Reactions of Azo Compounds. I. Spectroscopic Studies of the Conjugate Acids of *cis*- and *trans*-Azobenzene

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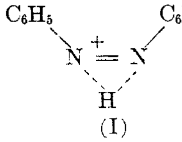
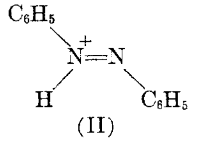
As part of the investigation of the photocatalyzed cyclization of azobenzene in acidic solution, the behavior of the conjugate acids of *cis*- and *trans*-azobenzene in the presence and absence of light has been studied spectroscopically. The basicities of the isomers and of benzo[c]cinnoline have also been examined.

It has been reported recently that azobenzene is oxidatively cyclized to benzo[c]cinnoline when exposed to light in strongly acidic solutions.[1] The properties of the conjugate acids of *cis*- and *trans*-azobenzene are of special interest in this reaction because no difference could be detected between their rates of cyclization. As irradiation of azobenzene in neutral solutions is known to result in *cis* ⇌ *trans* equilibration[2] it seemed that the photocatalyzed cyclization is most probably preceded by rapid *cis* ⇌ *trans* isomerization of the cations. A plausible alternative assumption, however, is that *cis*- and *trans*-azobenzene could form conformationally identical cations immediately upon protonation, such being consistent with Jaffé's[3] contention that even the conjugate acid derived from *trans*-azobenzene should be assigned the *cis*-structure (I) in preference to the commonly accepted classical structure (II).



(I)



(II)

The properties of *cis*- and *trans*-azobenzene in strongly acidic solutions, alternatively in the absence and presence of light, have now been studied by means of absorption spectroscopy. The results show conclusively that the former of the above alternatives is correct. Spectroscopic determinations of the ionization constants of the azobenzene isomers and benzo[c]cinnoline have also been made and satisfactorily correlated.

In Fig. 1 are recorded the absorption spectra of *cis*- and *trans*-azobenzene and benzo[c]cinnoline measured in 22*N* sulfuric acid containing 10% (v.:v.) ethanol. At this acidity all three compounds exist as the first conjugate acids.

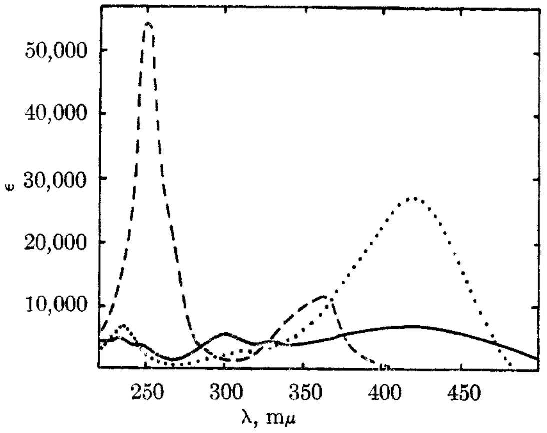


Fig. 1. Absorption spectra of conjugate acids in 22*N* 10% (v.:v.) ethanolic sulfuric acid: *cis*-azobenzene(——); *trans*-azobenzene (· · · ·); benzo[c]cinnoline (– – – –)

Apart from the periods required for spectral measurements the solutions were protected from light. Under these conditions the conjugate acids of *trans*-azobenzene and benzo[c]cinnoline were stable, but the absorption of the *cis* cation changed over the course of several days to that of the *trans*. The half-time for the *cis*→*trans* conversion was 10.5 ± 0.5 hr. A small amount of extrapolation at certain wave lengths was therefore necessary in constructing an accurate curve for the *cis* ion. When concentrated sulfuric acid alone was tried as solvent, isomerization occurred too rapidly to permit reliable measurements. In this respect it is interesting that some authors,[2,4] although not employing solutions of sufficient acidity for examination of the conjugate acid, found that the rate of *cis*→*trans* isomerization of the free base increases with acidic strength of solution.

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