

ORGANOSILICON COMPOUNDS. LXXV.*

THE RELATIVE BASICITIES
OF SOME CYCLOSILAZANES AND CYCLOGERMAZANES

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The present work is a continuation of our studies on the basicity of compounds containing silicon–nitrogen¹ or germanium–nitrogen bonds². As model compounds we employed here the cyclic compounds of type $(R_2MNR')_n$ (where M = Si, Ge and R' = CH₃, H), in which a π -interaction of unshared nitrogen electron pair with vacant 3d or 4d orbitals can take place.

A relatively very low basicity of disilazanes has been already studied by several authors^{3–6}. However, the comparison of basic properties of their cyclic homologues (cyclotrisilazanes and cyclotetrasilazanes) could provide data on whether their basicity depends on the size of their ring, which is the case of analogical cyclosiloxanes⁷.

As the effect of a ($p \rightarrow d$) π interaction in the Ge–N–Ge bond on the properties of germazanes has not been so far studied, likely due to the difficult preparation and low stability of these compounds, we further attempted at preparing some cyclic germazanes with the aim to compare their properties with those of analogical silazanes.

EXPERIMENTAL

Compounds Used

Dimethyldichlorosilane and *diethyldichlorosilane* (commercial products, VCHZ Synthesia, Lučební závody, Kolín) were distilled before use; b.p. 70°C (lit.⁸ 70–1°C) and 129–130°C (lit.⁹ 129°C), resp.; n_D^{20} 1.4051 (lit.⁸ 1.4055) and 1.4319 (lit.⁹ 1.4309), resp.

Dimethyldichlorosilane was obtained by fractional distillation of the mixture of methylchloro-germanes prepared by direct synthesis from germanium (Lachema, Kaznějov; zone-melted, 10 μ m maximal grain size) and methyl chloride in the presence of a copper powder (Safina, Prostějov; Type I PPS 1: 96% Cu, 0.26% Co, 0.14% Sn, 0.1% Ni, 0.05% Pb, 0.04% Si, 0.03% Zn, traces of iron, oxygen; 10 μ m maximal particle size)^{10,11}. B.p. 118°C (lit.¹⁰ 119°C), n_D^{20} 1.4603 (lit.¹⁰ 1.4600).

Diethyldichlorosilane was prepared in part by the direct synthesis from germanium and ethyl chloride in a flow reactor (the copper powder as the catalyst)^{2,12}, in part by catalyzed redistribution reaction of germanium tetrachloride with tetraethylgermane¹³. B.p. 174°C (lit.¹² 173°C); n_D^{20} 1.4700 (lit.¹⁴ 1.4700).

Hexamethylcyclotrisilazane (I) and *octamethylcyclotetrasilazane* (II) were prepared by reaction of dimethyldichlorosilane with ammonia in benzene, which yields both the compounds¹⁵.

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TABLE I
Physical Properties of Some Cyclosilazanes and Cyclogermazanes

Compound	B.p., °C (Torr)		n_D^{20}		lit.	M. w.	Calculated/Found			Yield %
	found	lit.	found	lit.			%C	%H	%N	
Hexamethylcyclotrisilazane ^a (I)	110—112 (85)	188 ¹⁵ (756)	1.4403	1.4448 ¹⁵	—	219.5 233	32.83 32.79	9.61 9.61	19.14 18.74	26—48
Octamethylcyclo-tetrasilazane (II)	134—136 (35)	225 ¹⁵ (756)	^b	^b	^b	292.7 286	32.83 32.72	9.64 9.70	19.14 18.96	32—50
Nonamethylcyclo-trisilazane (III)	95—96 (10)	96—97 ¹⁶ (10)	^c	^c	^c	261.5 255	41.31 41.92	10.41 10.28	16.06 15.82	82
Hexaethylcyclo-trisilazane ^d (IV)	161—163 (12)	150 ¹⁵ (10)	1.4645	1.4670 ¹⁵	—	303.5 332	47.46 47.41	10.95 10.72	13.84 13.74	49
Octaethylcyclo-tetrasilazane ^e (V)	192 (8)	191 ¹⁵ (10)	1.4747	1.4769 ¹⁵	—	404.6 438	47.46 47.89	10.95 10.63	13.84 13.98	11
Nonamethylcyclo-trigermazane (VI)	81 (1)	80 ¹⁸	1.4998	—	—	395.0 415	27.34 —	6.89 —	10.64 10.8	57
N,N,N-Trimethylhexaethylcyclo-trigermazane (VII)	140—141 (2)	—	1.5008	—	—	479.1 466	37.58 —	8.21 —	8.77 8.6	34

^a d_4^{20} 0.918 (ref.¹⁵ 0.9196). ^b M.p. 96.5°C (ref.¹⁵ 97°C). ^c M.p. 33°C (ref.¹⁶ 33—34°C). ^d d_4^{20} 0.922 (ref.¹⁵ 0.9287). ^e d_4^{20} 0.951 (ref.¹⁵ 0.9521).

Hexaethylcyclotrisilazane (IV) and *octaethylcyclotetrasilazane* (V) were prepared from diethyl-dichlorosilane and ammonia in benzene in the usual way¹⁵.

Nonamethylcyclotrisilazane (III) was obtained by reaction of dimethyldichlorosilane with methylamine (Fluka AG, Buchs SG) in diethyl ether, giving dimethylbis(methylamino)silane, in turn transformed into nonamethylcyclotrisilazane by heating to 155°C for 6 hours in the presence of ammonium sulphate¹⁶.

Nonamethylcyclotrigermazane (VI) was prepared by the reaction of dimethyldichlorogermene with methylamine in diethyl ether¹⁷. To a 250 ml three-necked flask cooled to -75°C were placed 40 ml (25 g, 0.8 mol) of methylamine in 100 ml of ether, and then 20 g (0.12 mol) of dimethyldichlorogermene were dropwise added with stirring. The reaction mixture was allowed to stir until its temperature reached room temperature. Then the liquid phase was separated from the precipitated methylamine hydrochloride and the ether removed by distillation. The fractionation of the residue afforded nonamethylcyclotrigermazane, b.p. 81°C/1 Torr.

N,N,N-Trimethylhexaethylcyclotrigermazane (VII) was obtained by the reaction of diethyl-dichlorogermene with an excess of methylamine in anhydrous ether in similar fashion. The rectification yielded the expected product, b.p. 141–142°C/2 Torr, the structure of which was confirmed by molecular weight determination and the IR and NMR analysis.

The purity and structure of all the compounds prepared was checked by elemental analysis, glc, and the IR and NMR spectroscopy. Their physical constants are presented in Table I.

Measurements

The *NMR spectra* were taken on a modified Tesla BS 477 (60 MHz) spectrometer provided with proton stabilization.

The *molecular weights* of the compounds studied were determined osmotically on a Knauer osmometer (Knauer, West Germany) at 37°C in cyclohexane. The instrument was calibrated with *n*-eicosan (m.w. 282.6).

The *infrared spectra* of prepared compounds were measured with a Zeiss UR 20 double-beam spectrophotometer (Zeiss, Jena) over 850–400 cm⁻¹ (KBr prism), 1650–650 cm⁻¹ (NaCl prism) and 1600–4000 cm⁻¹ (LiF prism) regions. The frequency scale of the instrument was

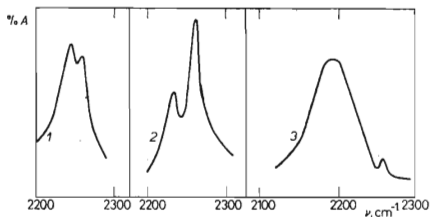


FIG. 1

The Form of Absorption Bands of the Associated and Nonassociated Deuteriochloroform C—D Stretching Vibrations for Systems Containing [(CH₃)₂MNR₂]₃ as the Proton Acceptor

1 M = Si, R = H; 2 M = Si, R = CH₃; 3 M = Ge, R = CH₃.

calibrated in the usual way¹⁹. The individual wavenumbers were determined with the accuracy of $\pm 2 \text{ cm}^{-1}$. The spectra of liquid compounds were measured in a KBr cell of 0.002 cm thick and in carbon disulphide and carbon tetrachloride solutions (conc. 5%) using a KBr cell of 0.01 cm thickness. The spectra of solids were measured in nujol oil, using a demountable cell. The spectra of hydrogen bonds were measured in binary mixture containing 2.5M deuteriochloroform or 0.03M pyrrole in a cyclosilazane and a cyclogermazane, resp. In the case of nonamethylcyclotrisilazane, which was insoluble in the above compounds, we used its saturated solution in carbon tetrachloride as the proton acceptor. The acidity of the hydrogen of the N—H bonds of cyclosilazanes was determined with the aid of tetrahydrofuran (0.02M cyclosilazane in tetrahydrofuran).

RESULTS

Table II summarizes the obtained values of C—D frequency shifts for deuteriochloroform, upon hydrogen formation with cyclosilazanes and cyclogermazanes. For the sake of comparison in the Table are included also (C—D) for some linear silazanes. In the case of cyclosilazane containing N—H bonds, pyrrole could not be employed for determining their basicity, due to their absorption $\nu(\text{N—H})$ in the 3400 cm^{-1} region. As these compounds should be relatively weak bases, we measured also their relative acidity employing tetrahydrofuran as the proton acceptor (Table III). The form of the absorption bands of the associated and nonassociated deuteriochloroform stretching vibrations, $\Delta\nu(\text{C—D})$, for mixtures of the proton donor with hexamethylcyclotrisilazane, nonamethylcyclotrisilazane, and with nonamethylcyclotrigermazane are shown summarily in Fig. 1. The obtained frequency shifts for deuteriochloroform upon hydrogen bonding with hexamethylcyclotrisilazane and with nonamethylcyclotrisilazane are smaller than those

TABLE II

The Values of Deuteriochloroform C—D Frequency Shifts, $\Delta\nu(\text{C—D})$, upon Hydrogen Bond Formation with Some Dimethylaminosilanes and with Nonamethylcyclotrigermazane

Compound	I	IV	V	III	$[(\text{CH}_3)_3\text{Si}]_2\text{NH}$	$[(\text{CH}_3)_3\text{Si}]_2\text{NCH}_3$	VI
$\Delta\nu_{\text{C—D}}, \text{cm}^{-1}$	15	14	15	25	15 ^b	26 ^b	66

^a The absorption band of free deuteriochloroform C—D stretching vibration at 2255 cm^{-1} .

^b Taken from ref.⁶.

TABLE III

The Values of $\Delta\nu(\text{cm}^{-1})$ for 0.02M Solutions of Cyclosilazanes in Tetrahydrofuran

Proton donor	I	II	IV
$\Delta\nu \text{ N—H}$	68 ^a	64 ^a	71

^a Slightly different values were reported in the literature⁵.

reported³, likely as a result of the different way of frequency shift calculation employed in the present work.

DISCUSSION

The relative basicity of the nitrogen atom in cyclosilazanes is by far lower than in the case of mono(dimethylamino)silane. (The $\Delta\nu(\text{C}-\text{D})$ for triethyl(dimethylamino)silane was reported¹ to be 40 cm^{-1}). This can be attributed to the fact that here the two silicon atoms are attached to the nitrogen atom, which increases the possibility of the ($p \rightarrow d$) π interaction of an unshared electron pair of the nitrogen. Consequently, such a nitrogen atom is less capable of interacting with the proton of deuteriochloroform than in the case of aminosilanes. Nonamethylcyclotrisilazane and heptamethyldisilazane display higher basicity than does a silazane possessing the N—H bond, in accordance with the $+\text{I}$ effect of methyl group.

If we compare the $\Delta\nu(\text{C}-\text{D})$ values for the couples $[(\text{CH}_3)_2\text{SiNH}]_3 - [(\text{CH}_3)_3\text{Si}]_2\text{NH}$ and $[(\text{CH}_3)_2\text{SiNCH}_3]_3 - [(\text{CH}_3)_3\text{Si}]_2\text{NCH}_3$, we find that they are practically identical. In both the cases the nitrogen atom has the same neighbouring atoms, *i.e.* Si—N(H)—Si and Si—N(CH₃)—Si, resp. This finding seems to indicate that in the case where a nitrogen atom is adjacent to the same atoms or groups it is of little importance whether we deal with a linear or a cyclic silazane. Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane display almost the same relative basicities (or acidities) for the three- and four-membered ring; the obtained frequency shifts are practically identical with those reported⁶ for linear disilazanes. This can obviously be accounted for by the smaller Si—N—Si bond angle, which is not significantly deformed, as different from the Si—O—Si bond in cyclosiloxanes⁷.

Of the cyclogermazanes studied we succeeded in determining the value of $\Delta\nu(\text{C}-\text{D})$ for nonamethylcyclotrigermazane. In this case the frequency shift is only slightly smaller than with triethyl(dimethylamino)germane (40 cm^{-1} (ref.¹)) which can be taken as indirect evidence of a lesser extent of ($p \rightarrow d$) π bonding in the germanium–nitrogen bond, compared to the silicon–nitrogen one. On the other hand, the above result speaks for the ($p \rightarrow d$) π nature of the former bond, since otherwise the frequency shift should have been by far greater due to the $+\text{I}$ effect of the two electropositive germanium atoms bonded to the nitrogen of the cyclotrigermazane.

The following sequence of the relative basicity of oxygen atoms can be derived from the data reported in the literature^{20,21}: Ge—O—Ge > Ge—O—C > C—O—C > Si—O—C > Si—O—Si. The data obtained in the present work show the following order of the basicity of nitrogen atoms in dependence on the type of compounds: C—N—C > Ge—N—Ge \sim Ge—N—C > Si—N—C > Si—N—Si. On the basis of these results it can be concluded that a 'more significant ($p \rightarrow d$) π bonding takes place in the germanium–nitrogen bond than in the germanium–oxygen one.

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ASYMMETRIC REACTIONS. XXXIX.*

CIRCULAR DICHROISM OF SOME ALKYLPHENYLACETIC ACIDS

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The results of chemical correlation¹⁻⁴ and ORD measurements⁵ indicate that all (-)- α -alkylphenylacetic acids are configurationally related and have the absolute *S* configuration.** The *N*-methylthioamide derivatives of the positively rotating acids of this series all show a positive Cotton effect⁵. In order to confirm the absolute configuration of these acids we determined their circular dichroism (CD) (Table I). *S*-(+)-Hydratropic acid (*Ia*) exhibits, e.g. in ethanol, a band with fine structure at about 260 nm with a very small positive Cotton effect ($\Delta\epsilon_{\text{max}} = 0.04$), a strongly positive CD-band at 223 nm (+4.4), and another negative at 205 nm (-1.0). The band at longest wavelength showing characteristic fine structure was clearly the ¹*L*_b-band of the benzene chromophore. The other two bands must be the aromatic ¹*L*_a-band and the carboxylic *n*- π^* -band. According to Legrand and Viennet⁶ we attribute the most intense CD-band at 223 nm to carboxylic absorption and that at 205 nm to the benzene ring. This correlation

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** After the manuscript had been completed, a similar CD study by Barth G., Voelter W., Mosher H. S., Bunnenberg E., Djerassi C. on α -substituted phenylacetic acids appeared in J. Am. Chem. Soc. 92, 875 (1970).