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STRUCTURE AND TAUTOMERISM OF CYCLIC SILYLAMIDES

I. DISILOXANE DERIVATIVES OF ACETAMIDE AND BENZAMIDES

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Summary

The reactions of 1,3-dichlorotetramethyldisiloxane (DCTDS) with acetamide and a series of ring-substituted benzamides give disiladioxazines. The acetamide derivative exists in a tautomeric equilibrium with *N*-acetyltetramethylcyclosilazoxane, whose structure represents a novel type of four-membered ring. The equilibrium concentration of the latter compound is increased by lowering the temperature and increasing the polarity of the solvent. The disiladioxazines produced from benzamides and DCTDS do not undergo tautomerization. Their structures were studied by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy; the spectra do not change over a wide range of temperature.

Introduction

The dynamic isomerism observed for many silylamides has mainly been studied for linear compounds. A number of mono-silylsubstituted amides were found to exist in tautomeric equilibria between the *N*-silylamido and *O*-silylimidato forms [1,2]. Among the disilylamides a related phenomenon is the fast and reversible intramolecular migration of silyl groups between nitrogen and oxygen in their *N*-silyl-*O*-silylimidato form, which occurs in all but one of the known compounds of this class [3].

On the other hand, the cyclic silyl derivatives of acid amides have received little attention. Linking two silicon atoms by an atom or chain should have two interconnected effects, both leading to an increase of free energy of internal silyl migration relative to the energy requirements for the analogous process in linear molecules: (1) the lack of freedom of rotation around the N–Si (O–Si) bonds, which are incorporated into the ring structure; (2) the possible need to break bonds between silicon and the linking entity. Thus a cyclic disilylamide molecule, as represented by formula I, would be expected to be more rigid than its linear counterpart.

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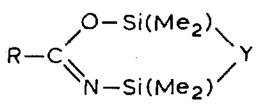
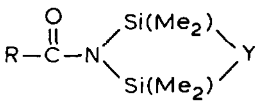
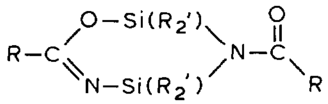


(Ia)



(Ib)



(II)

However, Klebe found a series of disilaoxadiazines (II) to have very labile structures with fast ring rearrangements involving N—O-silyl migration taking place at fairly low temperatures [4]. It should be noted that these compounds contain within a single molecule both canonical forms of a disilylamide, the *N*,*N*-disilylamido and the *N*,*O*-disilylimidato functions.

We have found that putting in I $Y = O$ and $R = CH_3$, which is achieved by reacting acetamide with 1,3-dichlorotetramethyldisiloxane, results in the formation of a tautomeric mixture of the expected pentamethyldisiladioxazine (Ia) with the isomer of structure Ib, *N*-acetyltetramethyldisilazoxane. Full publication of the results communicated earlier [5] was postponed in the hope of finding more examples of *N*,*O*-silyl tautomerism in other compounds of similar structure. The main objective of further work was to examine the structural effects of changing the nature of the acyl group (varying R) and the linking unit (Y) in cyclic silylamides of general formula I.

Results and discussion

The tautomeric equilibria Ia $\rightleftarrows$ Ib ($R = CH_3$, $Y = O$) were quantitatively studied by ^1H NMR spectroscopy at variable temperatures in a series of solvents. The equilibrium constants $K = [Ia]/[Ib]$ derived from the intensities of sets of signals assigned to each tautomer are shown in Table 1. The assignment is made easy by the fact that the relative intensities of acetyl to methylsilyl protons for each tautomer (1/2/2 for Ia and 1/4 for Ib) are independent of temperature or solvent.

The ^{13}C NMR spectra in chlorobenzene contain two signals attributable to acetyl carbons at δ 18.98 and 20.86 ppm whose relative intensity changes from 82/44 at 35 to 29/62 at 100°C. By making use of the observed trend in K with changing temperature (Table 1) the signal at higher field can be assigned to Ib. In the methylsilyl region three singlets are observed, which on the same ground can be assigned to Ib: (δ, ppm) −3.70/35°C, (−3.83/100°C) and to Ia: −4.36/35°C, (−4.61/100°C) and −4.48/35°C, (−4.75/100°C); the relative intensity of these three signals changes, respectively, from 398/146/150 at 35°C to 195/161/188 at 100°C.

Some details of the IR spectra of pure Ia and Ib were reported previously [5] and shown to be consistent with the proposed structures. When the synthesis is carried out at low temperature (−20°C) and the spectrum of the neat, crude product is taken at −40°C it contains the following peaks expected for Ib (cm^{-1}): 1670 (C=O), 1195(C–N), 955(Si–N–Si), 995(Si–O–Si). After heating the sample to 30°C another set of absorptions is observed, indicating the predominance of Ia in the analyzed mixture: 1730 and 1230 (C=N), 1000(Si–N), 1040–1070 (Si–O–Si) with a shoulder at 1100 (Si–O–C). Cooling the liquid again to −40°C did not lead to reproduction of the previous spectrum. The IR spectra in solution (carbon disulfide) taken at varying temperatures, were too complicated by overlapping of peaks, to allow straightforward interpretation [6].

TABLE 1

^{1}H NMR CHEMICAL SHIFTS AND EQUILIBRIUM CONSTANTS FOR THE TAUTOMERIC MIXTURE Ia $\rightleftarrows$ Ib ($R = CH_3$, $Y = O$)

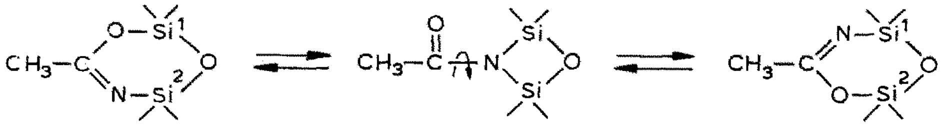
Solvent	δ (ppm)[a]		K = Ia/Ib	T (°C)
	set Ia	set Ib		
Benzonitrile	2.00 (3H)	2.10 (3H)	0.45	−10
	0.26 (6H)	0.43 (12H)	0.68	0
	0.25 (6H)		1.87	30
			4.75	60
			9.25	90
Pyridine	2.07 (3H)	2.10 (3H)	0.26	−30
	0.30 (6H)	0.45 (12H)	0.69	−10
	0.27 (6H)		0.91	0
			1.50	20
Carbon tetrachloride	2.01 (3H)	2.04 (3H)	0.8	−10
	0.11 (6H)	0.27 (12H)	0.915	0
	0.09 (6H)		1.2	20

[a] T 26°C; chemical shifts vary within 0.01 to 0.04 ppm with varying temperature.

It is seen from Table 1 that in all the solvents used the equilibrium is being shifted towards the *N*,*O*-silyl form by increase in temperature. This may simply result from the inherent instability of Ib due to its strained four-membered ring structure, but it can also be taken as a manifestation of the high energy of the silicon–oxygen bond. In fact, many silylamides have been shown to decompose thermally to give the appropriate nitriles and siloxanes [4,7,8] (also vide infra).

The enthalpies of tautomerisation derived from the straight line plot of log K vs T^{-1} are: ΔH (kcal mole^{-1}) 6.5 (C_6H_5CN), 6.2 (C_5H_5N) and 2.2 (CCl_4). The entropies of the reaction at 30°C are: ΔS(cal mole^{-1} deg.$^{-1}$) 21.3, 23.0 and 7.0, respectively. The polarity of the solvent favours the four-membered Ib tautomer by stabilizing its highly polar resonance structure containing the $=\overset{+}{N}=C-\overline{O}$ form. Thus, in the least polar solvent, carbon tetrachloride, the smallest amount of energy is required to pass from Ib to Ia and the smallest gain in entropy is observed in the process.

Another question concerns the mechanism of the ring rearrangements involved in the tautomerization. It has been suggested that the fast and reversible silyl migration between nitrogen and oxygen in linear *N*,*O*-disilimidates proceeds through an unstable *N*,*N*-disilylamide intermediate [3,9]. The lifetime of that intermediate was evidently too short to make it detectable by NMR. By analogy, in the present case Ib can be considered as an intermediate between two equivalent Ia forms, in which the silicon atoms have exchanged their positions in the *N*,*O*-disilylimidate six-membered ring.



This intermediate is so stable as to allow separation of the pure compound by distilling the crude product from synthesis at low temperature. As the temperature of the solution is raised the overall silyl exchange process becomes faster, which is reflected by the diminishing population of Ib in the equilibrium mixture as determined by NMR spectroscopy. At still higher temperatures, e.g. above 100°C in benzonitrile, the NMR signals assigned to Ib have almost disappeared and the situation becomes similar to that observed for linear *N*,*O*-disilylimidates. Further increase in the temperature was not possible for technical reasons, but it could be expected to lead to coalescence of the methylsilyl signals in the spectrum of Ia. Indeed, at 145°C in benzonitrile the singlets at 0.28 and 0.25 ppm tend to come closer together and assume a shape symptomatic of approaching coalescence.

It follows, by analogy, from these results that the suggested mechanism of *N*,*O*-silyl exchange in linear *N*,*O*-disilylimidates is probably correct. Furthermore, the stability of the intermediate Ib lends support to the earlier suggestion that the "migration step" and not the rotation of the acyl group in the intermediate is rate determining [3]. The coalescence temperature in the present case is expected to be high, which correlates with a high free energy for the dynamic process observed by NMR, almost certainly outside the range of the normally found energy barriers for rotation around C–N bonds in silylamides.

A unimolecular reaction Ia → Ib would necessitate a transannular attack of nitrogen on the siloxane silicon. This sort of mechanism was suggested by Klebe for the "slow exchange" in disilaoxadiazines [1]. An alternative mechanism for the latter compounds involving attack on silicon by the exocyclic carbonyl oxygen in II and formation of an eight-membered ring intermediate was proposed after X-ray diffraction studies revealed no evidence for transannular interactions between nitrogen and silicon in the ground state of 2,4-bis(dimethylsila)-3-benzoyl-6-phenyl-1,3,5-oxadiazine [10]. In the present case such a mechanism is ruled out because of the absence of a exocyclic carbonyl group in Ia. It should be noted, however, that the situation of silicon in Ia between two oxygen atoms, instead of oxygen and the less electronegative nitrogen in disilaoxadiazines, would make it more susceptible to nucleophilic action, possibly lowering the energy barrier for transannular attack, which on purely conformational grounds is likely to require a high energy.

On the other hand, the relative stability of Ib can be accounted in terms of the rigidity of the four-membered, probably planar, ring *. The most likely mechanism of reaction Ib → Ia requires nucleophilic attack by carbonyl on silicon, which, relative to that in linear disilylamides, will be hindered by the restricted mobility of the silyl group.

In order to determine the effects of changing R in the acyl group on the tautomeric equilibrium Ia ⇄ Ib a series of substituted benzamides were reacted with 1,3-dichlorotetramethyldisiloxane and the products of the reaction were analysed and examined spectroscopically. In each case, however, a single crystalline, moisture sensitive compound was formed in good yield (Table 2). Elemental analyses and molecular peaks in the mass spectra agreed with the values calculated for the cyclization products Ia or Ib ($R = XC_6H_4$, $Y = O$).

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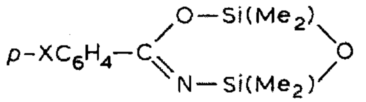
* By analogy to the cyclodisilazane ring structure, which has been shown by X-ray diffraction to be planar [11,12].

TABLE 2

DISILADIOXAZINES



X	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))				Molecular weight [a]
			C	H	N	Si	
H	65	50–51	51.1	6.7	5.4	22.4	251
			(52.5)	(6.8)	(5.6)	(22.3)	
CH_3O	68	54–55	50.7	6.2	5.1	19.9	281
			(51.2)	(6.8)	(4.9)	(20.0)	
Cl	63	58–60	46.0	5.7	4.9	19.6	285
			(46.2)	(5.6)	(4.9)	(19.6)	
NO_2	61	137–138	44.2	5.4	9.0	18.9	295
			(44.6)	(5.4)	(9.4)	(19.0)	

[a] M-calcd. and found as molecular ion peak in mass spectrum.

IR spectroscopy does not allow differentiation between Ia and Ib. The spectra contain strong absorption bands at approx. (cm^{-1}): 1645 (C=N) * or (C=O), 1090(Si–O–Si) but also (C–O–Si), 970(C–O–Si) or (Si–N–Si) and a weak band at 1010 cm^{-1} (Si–N). The spectra in CS_2 did not change in the range −80 to 30°C.

The ^1H NMR spectra of the compounds consist of two singlets of equal intensity in the methylsilyl region. They do not undergo any changes in chemical shifts and intensities in the range of −50 to 100°C. If the magnetical nonequivalence of the signals were due to hindered rotation in Ib they would be expected to coalesce within that range of temperatures. (Cf. the coalescence temperatures for bis(trimethylsilyl)formamide −46°C [3] and for two series of mono-silylsubstituted amides −18 to 31°C [2] and −3 to 71°C [14].) Thus, the observed lack of coalescence can be taken as evidence that the benzamide derivatives exist in the form Ia. This conclusion is supported by the effect of changing the solvent. As it is seen from Table 3 for $X = NO_2$ the silylmethyl proton signals undergo shifts in reverse directions, which can be taken to indicate that both silyl groups are in entirely different environments in the molecule.

Two well-separated and temperature insensitive singlets of equal intensity appear also in the ^{29}Si NMR spectra (Table 3). It is hard to make a precise assignment of the signals. The closest analogy can be sought in the recent assignments [15] made for some silylamides on the basis of comparisons with chemical shifts in model compounds which contained isolated C=N–Si and C–O–Si units. The former were found to have chemical shifts upfield relative to the latter. This allows tentative assignment of the ^{29}Si resonances for two of the cyclic benzamide derivatives as shown in Table 3. It should be noted, however, that ^{29}Si chemical shifts reported for hexamethylcyclotrisiloxane, δ − 9.2 ppm [16] and hexamethylcyclotrisilazane, δ −4.7 ppm [17] would suggest a reverse assignment.

^{13}C NMR spectra were taken for two compounds ($X = NO_2$ and Cl) and

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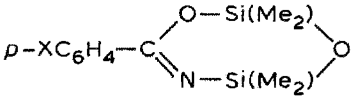
* Incidentally this band coincides exactly with the C=N absorption in 1,3-oxazine derivatives [13].

TABLE 3

^{1}H- and ^{29}Si-NMR CHEMICAL SHIFTS (δ in ppm, solutions in methylene chloride) FOR

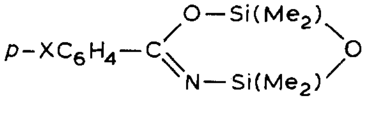


X	^{1}H NMR			^{29}Si NMR	
	N–Si(Me$_2$)–O	O–Si(Me$_2$)O	C_6H_4	N–Si(Me$_2$)O	O–Si(Me$_2$)O
H	0.31 (s,6H)	0.27 (s,6H)	8.15–797 (m,5H)	−4.81 (s,1Si)	0.98 (s,1Si)
Cl	0.51 (s,6H)	0.44 (s,6H)	7.56 (d,1H); 7.42 (d,1H) 8.13 (d,1H); 8.24 (d,1H)		
NO_2	0.31 (s,6H) 0.29 (s,6H) [a] 0.22 (s,6H) [b]	0.21 (s,6H) 0.14 (s,6H) [a] 0.18 (s,6H) [b]	8.21 (s,4H)	−5.95 (s,1Si)	0.54 (s,1Si)
OCH_3	0.52 (s,6H)	0.45 (s,6H)	7.09 (d,1H); 7.22 (d,1H) 8.14 (d,1H); 8.24 (d,1H)		

[a] 10% solution in benzene. [b] 10% solution in carbon tetrachloride.

TABLE 4

^{13}C NMR CHEMICAL SHIFTS (δ in ppm, 10% solutions in methylene chloride) FOR



X	$Si(CH_3)_2$		C_6H_4	O–C=N
NO_2	−1.3	−0.6	121.9; 128.7; 133.7; 140.2	155
Cl	−1.3	0.5	131.5; 132.9; 135.1; 138.7	154

contained the signals expected for all the carbon atoms contained in the molecule (Table 4). The spectra have weak peaks at δ 154–155 ppm. These are outside the range of the normally found carbonyl resonances above δ 160 ppm and can be assigned to the C=N grouping thus giving further support to structure Ia.

In summary, no tautomeric equilibria of the type Ia $\rightleftarrows$ Ib are observed for the cyclic derivatives of benzamides and disiloxane. Relative to the analogous acetamide derivatives, the π-character of the C–N bond is possibly diminished by introduction of the phenyl substituent, which leads to destabilization of the amido Ib form; this is the commonly suggested reason for the preference of the imidate form in most linear silylamides. Further research is needed to define the structural conditions which would assure high internal mobility resulting in *N*,*O*-silyl tautomerism in cyclic silylamides, and appropriate experiments are in progress.

Experimental

All operations were carried out under nitrogen using carefully dried glassware and dry reagents. 1,3-Dichloro-1,1,3,3-tetramethyldisiloxane was prepared from dichloro-dimethylsilane by a known procedure [18].

1,1,3,3-Tetramethyl-4-acetylcyclodisilazoxane (Ib) and 1,1,3,3,5-pentamethyl-1,3-disila-2-4-dioxazine (Ia)

To an ice-cooled, stirred mixture of 0.1 mol of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane and 0.1 mol of acetamide in 150 cc of acetonitrile was slowly added 32 cc of triethylamine. Stirring was continued for 2 h without external cooling. The precipitated triethylamine hydrochloride was filtered off and the filtrate was concentrated and distilled in vacuo; b.p. 28–29°C/6 mmHg; yield 50% (Ib); (Found: C, 37.51; H, 7.67; N, 7.21; Si, 29.53. $C_6H_{15}NO_2Si_2$ calcd.: C, 38.09; H, 7.94; N, 7.41; Si, 29.63%, Mol.wt.,calcd. and molecular ion peak: 189). Continued fractional distillation gave a fraction of b.p. 34–35°C/6 mmHg containing mainly Ia, which can be prepared in better yield by starting with the same proportions of reagents and carrying out the reaction in benzene (150 cc) at room temperature; b.p. 64°C/40 mmHg; yield 71% (Found: C, 37.90; H, 7.81; N, 7.28; Si, 29.60. Calcd: elemental composition and mol.wt.as over). IR and NMR data are given in the main text and in [5]. Both compounds are readily decomposed by atmospheric moisture.

1,1,3,3-Tetramethyl-5-phenyl-1,3-disila-2,4-dioxazine and derivatives substituted in the benzene ring were prepared in a similar way from 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, substituted benzamide, and triethylamine in benzene with stirring continued for 2 h at 60°C. After filtering off of the amine hydrochloride the filtrate was concentrated in vacuo and the solid residue was purified by sublimation (Tables 2, 3 and 4). Attempts to distil the compounds at normal or slightly reduced pressure resulted in decomposition with formation of appropriate nitriles and polysiloxanes, which were identified by GLC.

The ^{1}H and ^{13}C-NMR spectra were recorded on a Jeol-60 and a Bruker 90 spectrometers equipped with variable temperature probe. The ^{29}Si NMR spectra were recorded in the conventional FT-mode with proton noise decoupling at 19.87 MHz using the Jeol PS-100/PTF-180 spectrometer.

Mass spectra were taken on a mass spectrometer LKB 9000 coupled to a gas chromatograph. The samples were introduced by direct inlet in the form of solutions in methylene chloride. IR spectra were obtained on a Pye Unicam SP 1200 and a Beckman spectrometer.

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