Journal of Organometallic Chemistry, 251 (1983) 289–294
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND STRUCTURAL STUDY OF 1,3-DIOXA-6-AZA-2-SILACYCLOOCTANES

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(Received February 15th, 1983)

Summary

Several new dioxaazasilacyclooctane derivatives have been prepared and their conformations studied by determination of their dipole moments in solution or as neat liquids. The results indicate that the compounds are in conformational equilibrium, characterized by two extreme conformers, boat-boat (BB) and chair-chair (CC). In the BB conformer the existence of a Si ← N interaction is possible but this is much weaker than that observed in related silatranes. Our conclusions are in good agreement with structural data obtained by X-ray diffraction.

Introduction

Several research workers have studied the structure of dioxaazasilacyclooctanes ("pseudosilatranes" or "silocanes") with the general formula $R^1R^2Si(OCH_2CH_2)_2NR^3$. For example, the crystal structures of numerous derivatives have been determined by X-ray diffraction [1], and the conformations of molecules investigated by NMR spectroscopy [2,3] and by measurement and calculations of dipole moment [4,5]. We describe below the preparation of some new derivatives of this type, the determination of their dipole moments, and some calculations of bond moments. Using the latter we have tried to answer the question of whether or not there is a Si ← N dative bond in pseudosilatranes.

Results

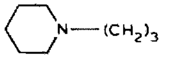
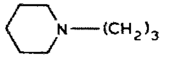
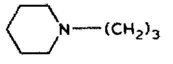
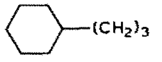
The compounds were prepared partly by an established method (eq. 1) [6], and partly by a new method (eq. 2).

$$R^3X + HN(CH_2CH_2OH)_2 \rightarrow R^3N(CH_2CH_2OH)_2 \xrightarrow{R^1R^2Si(OC_2H_5)_2} R^1R^2Si(OCH_2CH_2)_2NR^3 \qquad (1)$$

0022-328X/83/$03.00

TABLE 1

$R^1R^2Si(OCH_2CH_2)_2NR^3$

	R^1	R^2	R^3	Yield (%)	B.p. (°C/Pa)	$\delta(OCH_2)$ (ppm)
I	CH_3	CH_3		67	160–162/200	3.38
II	C_6H_5	CH_3		54	187–190/200	3.64
III	C_6H_5	C_6H_5		37	235–240/70	3.82
IV	C_6H_5	CH_3		48	175–178/270	3.74
V	CH_3	CH_3	H	52	95–98/4000 (93–94/4000 [6])	3.31
VI	C_6H_5	C_6H_5	H	40	160–168/600 [a]	3.90 (3.92 [2])
VII	C_6H_5	CH_3	H	44	150–152/670	3.67

[a] m.p. 123°C [7].

$$R^1R^2Si(OCH_2CH_2)_2NH + R^3X \xrightarrow{\text{acid acceptor}} R^1R^2Si(OCH_2CH_2)_2NR^3 \qquad (2)$$

where R^1, $R^2 = CH_3$, C_6H_5; $R^3 = C_5H_{10}N(CH_2)_3$, $C_6H_{11}(CH_2)_3$, H; X = Cl, Br

Some data for the prepared compounds, including some ^{1}H NMR parameters are shown in Table 1.

Of the numerous possible conformers for the dioxaazasilacyclooctane eight-membered ring, the two extreme conformers shown in Fig. 1 (boat-boat: BB and chair-chair: CC) were chosen for the calculations of dipole moments. Liepins and his co-workers [2] used these conformers as the basis for their NMR study of the conformations. For the calculations we used the experimental geometry for two derivatives determined by X-ray diffraction. The data for 2,2-diphenyl-1,3-dioxa-6-aza-2-silacyclooctane (VI) were used for the calculation in the case of the BB conformer [8]. In this compound the diethanolamine ring is in boat (BB) conformation, the Si and N atoms are close to each other (*d*(Si ← N) 2.301 Å), and the formation of a Si ← N dative bond is possible. The longest Si–N distance observed (*d*(Si ← N) 3.19 Å [1]) was that in 2,2-dimethyl-6-phenyl-1,3-dioxa-6-aza-silacyclooctane (IX), where the ring is in chair-chair conformation (CC), so transannular Si ← N bond cannot be formed.

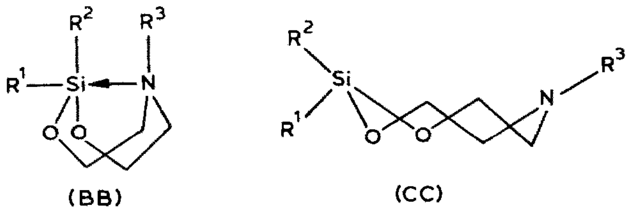


Fig. 1. Conformers of dioxaazasilacyclooctanes: boat-boat (BB) and chair-chair (CC).

TABLE 2

BOND MOMENTS AND GROUP MOMENTS (in Debye) $(\overset{+}{A} \rightarrow \overset{-}{B})$

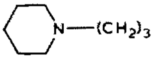
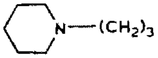
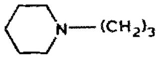
Si-O	1.51	Si-(CH_3)	0.2
C-O	0.77	Si-(C_6H_5)	0.445
C-N	0.48	(CH_3)-N	0.88
H-C	0.4	(C_2H_5)-N	0.58
H-N	1.3	(C_6H_5)-N	2.39
		N → Si	2.0

Calculations were carried out not only the compounds we prepared but also on some other derivatives for which the dipole moments were known. Three μ_{calc} values were calculated for every examined compound; for the BB conformation, with and without inclusion of a Si ← N bond, and for the CC conformation without a Si ← N bond. The bond and group moments required for the calculations were taken partly from the literature [9–11] and partly calculated from data for related compounds of known dipole moments and geometry. The values for the Si ← N dative bond were chosen on the basis of our calculations on silatranes $(\mathrm{R}\overline{\mathrm{Si}(\mathrm{OCH_2CH_2})_3\mathrm{N}})$. Calculations on six various silatrane molecules were carried out: R = CH_3, C_2H_5, CH_2=CH, α-C_6H_5, β-C_6H_5, γ-C_6H_5. The geometries of these compounds were known from X-ray structural determinations and their experimental dipole moments were also available. The m(Si ← N) bond moments range from 1.8 to 2.2 D, and cannot be correlated with the Si ← N distance and so we chose a m(Si ← N) value of 2.0 D for the calculation on the pseudosilatranes (see Table 2).

In case of compounds I–III the free rotation round the three CH_2 groups was taken into account by use of the Eyring formula. For these compounds the experimental dipole moment for *N*-methylpiperidine which we determined was used in the calculations. The results of the calculations are summarized in Table 3.

TABLE 3

DIPOLE MOMENTS FOR $R^1R^2Si(OCH_2CH_2)_2NR^3$ (in Debye)

	R^1	R^2	R^3	μ_{exp}	μ_{calc}		
					BB without Si ← N	BB with Si ← N	CC
I	CH_3	CH_3		2.78	2.746	4.548	2.175
II	C_6H_5	CH_3		2.75	2.963	4.785	2.345
III	C_6H_5	C_6H_5		3.58	2.843	4.702	2.158
V	CH_3	CH_3	H	2.83 [12]	2.991	4.772	2.464
VI	C_6H_5	C_6H_5	H	3.17 [4]	3.063	4.909	2.441
VIII	CH_3	CH_3	CH_3	2.52 [12]	2.662	4.511	2.058
IX	CH_3	CH_3	C_6H_5	1.44 [4]	3.926	5.542	3.552
X	C_6H_5	C_6H_5	CH_3	3.45 [4]	2.763	4.667	2.040
XI	C_6H_5	C_6H_5	C_2H_5	3.41 [5]	2.569	4.510	1.760
XII	C_6H_5	CH_3	CH_3	3.17 [4]	2.888	4.751	2.240

Discussion

The calculations on the pseudosilatranes (Table 3) indicate that except for compound IX, the experimental values of the compounds we investigated lie between the calculated values for the two conformers ($\mu_{\text{calc}}(\text{BB} + \text{Si} \leftarrow \text{N}) > \mu_{\text{exp}} > \mu_{\text{calc}}(\text{CC})$). It can thus be assumed that the compounds are in conformational equilibrium in solution and in liquid state, and that this equilibrium can be characterized in terms of the two extreme conformers. The geometry of the BB conformer allows formation of the Si ← N bond but this interaction is much weaker than that in the related silatranes. This statement is in agreement with the X-ray diffraction data; the Si ← N distances are as follows: 2.301 Å (VI), 2.68 Å (X), 3.19 Å (IX) [1,8], silatranes: 2.02–2.21 Å [13]. Theoretically, the structure shown in Fig. 2 may also be possible for compounds I–III, in this structure the N atom of piperidine interact with the Si atom. This possibility is ruled out by the experimental and calculated dipole moments, since such interaction would lead to, considerably higher values of the dipole moments.

The crystal structure of compound IX (*d*(Si ← N) 3.19 Å) shows that there is not even a weak interaction in this case. The experimental dipole moment also reflects this, though the value (1.44 D) observed is puzzlingly low compared with our calculated value of 3.5 D.

Experimental

Preparation of I by method 1

To a solution of 7.5 g (0.0325 mol) of *N*-(3-piperidinopropyl)-diethanolamine in 20 cm^3 of anhydrous benzene mixed with 0.05 g of sodium a solution of 4.9 g (0.0325 mol) of dimethyldimethoxysilane in 10 cm^3 of benzene is added dropwise at 80–85°C. The mixture is heated and the ethanol produced is distilled off with the benzene through a 20 cm Vigreux column. The residual light yellow oil is purified by vacuum distillation. B.p.: 160–162°C/200 Pa, yield: 5.7 g (62%). Anal. Found: C, 58.37; H, 10.79; N, 9.28. $C_{14}H_{30}N_2O_2Si$ calcd.: C, 58.69; H, 10.55; N, 9.77%.

Compounds III and VII were prepared by the same method.

III: Anal. Found: C, 69.84; H, 8.58; N, 6.51. $C_{24}H_{34}N_2O_2Si$ calcd.: C, 70.19; H, 8.35; N, 6.82%.

VII: Anal. Found: C, 58.77; H, 8.02; N, 5.87. $C_{11}N_{17}NO_2Si$ calcd.: C, 59.15; H, 7.67; N, 6.27%.

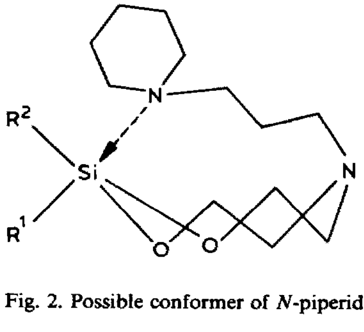


Fig. 2. Possible conformer of *N*-piperidinopropyl-dioxaazasilacyclooctanes.

TABLE 4

MEASURED AND OBSERVED DATA FOR DIPOLE MOMENTS OF COMPOUNDS $R^1R^2Si(OCH_2CH_2)NR^3$

Compound	Method	t (°C)	χ	n_D	d_4 (g/cm³)	ε	MR_D (obs) (cm³)	MR_D (calc) (cm³)	μ (D)
I	Onsager	50		1.46302	0.98302	6.201	80.28	81.83	2.78
II	Onsager	50		1.51018	1.02905	5.953	101.34	101.63	2.75
III	Hedestrand	25	0.0	1.49809	0.87338	2.2735			
			0.007123	1.49938	0.87965	2.4096			
			0.008052	1.49952	0.88011	2.4274			
							119.45	121.47	3.58
N-methyl-piperidine	Hedestrand	25	0.0	1.49815	0.87335	2.2727			
			0.01783	1.49650	0.87202	2.2870			
			0.02683	1.49586	0.87076	2.2933			
							31.89	31.68	0.79

Preparation of II by method 2

To a solution of 11.61 g (0.052 mol) of 2-methyl-2-phenyl-1,3-dioxa-6-aza-2-silacyclooctane in 25 cm³ of benzene containing 10.92 g (0.052 mol) of isopropyl(diethyl)amine as acid acceptor, a solution of 8.4 g (0.052 mol) of 3-chloropropylpiperidine in 15 cm³ of benzene is added dropwise with gentle heating. The mixture is refluxed for 3 h, the precipitated hydrochloride is filtered off, and the filtrate is evaporated. The residual yellow oil is purified by fractional distillation. B.p.: 187–190°C/200 Pa, yield: 9.78 g (54%). Anal. Found: C, 65.18; H, 9.40; N, 7.69. $C_{19}H_{32}N_2O_2Si$ calcd.: C, 65.46; H, 9.25; N, 8.03%.

Compound IV was prepared similarly. Anal. Found: C, 68.57; H, 9.90; N, 3.70. $C_{20}H_{33}NO_2Si$ calcd.: C, 69.11; H, 9.57; N, 4.03%.

The ^1H NMR spectra were recorded on a JEOL-60 instrument with TMS as internal standard.

The instrument used for dipole moments measurements was a WTW DM Ol Dipolmeter. The dipole moments of I and II were determined as neat liquids by the Onsager method, and those of III and of *N*-methylpiperidine in a benzene solution by the Hedestrand method. The sum of the atom and electron polarization was assumed to be given by $P_{a+e} = 1.10\ MR_D$ (where MR_D is the molar refraction). The experimental data are summarised in Table 4.

References

1 A. Kemme, J. Bleidelis, I. Urtane, G. Zelchan and E. Lukevics, J. Organomet. Chem., 202 (1980) 115.

2 E. Liepins, J. Popelis, I. Birgele, I. Urtane, G. Zelchan and E. Lukevics, J. Organomet. Chem., 201 (1980) 113.

3 V.A. Pestunovich, B.Z. Shterenberg, S.N. Tandura, V.P. Baryshok, E.I. Brodskaya, N.G. Komalenkova and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 264 (1982) 632.

4 I.P. Urtane, G.I. Zelchan, E.E. Liepiņs, I.S. Yankovska and E. Lukevics, Khimija i prakticheskoye primenenie kremnij i fosfororganicheskikh soedinenij, Leningrad, 1979, p24.

5 I.S. Birgele, Dissertation, Riga, 1981.

6 M.G. Voronkov and Yu. P. Romadan, Khim. Geterots. Soed., (1966) 879.

7 T.E. Graham and J.M.C. Tompson, unpublished results, cited in: V. Bažant, V. Chvalovsky and J. Rathousky, Organosilicon Compounds, Prague, 1965, vol.2.

8 J.J. Daly and F. Sanz, J. Chem. Soc. Dalton Trans., (1974) 2051.

9 V.I. Minkin, O.A. Osipov and Yu.A. Zhdanov, Dipole moments in organic Chemistry, Plenum Press, New York, 1970.

10 J. Nagy, S. Ferenczi-Gresz and S.G. Durgarjan, Acta Chim. Acad. Sci. Hung., 60 (1969) 357.

11 J. Nagy, S. Ferenczi-Gresz, K. Becker-Pálossy and A. Borbély-Kuszmann, Acta Chim. Acad. Sci. Hung., 61 (1969) 149.

12 I.B. Mazheika, L.I. Libert, E. Lukevics and M.G. Voronkov, Khim. Geterots. Soed., (1968) 561.

13 M.G. Voronkov and V.M. Dyakov, Silatrani. Izd. Nauka, Novosibirsk, 1978.