Preparation, crystal structure and thermal decomposition study of some trimethylsilyl esters of dicarbamic acids

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Abstract

Some new trimethylsilylated dicarbamic acid esters 1–9 and 10 were prepared. Their thermal decomposition was studied in n-alkanes as media. The reactions were monitored by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS), respectively. Some *N*-silylated cyclic ureas 11–15 were also prepared from the corresponding esters 2–6 by thermolysis. The crystal structures of 2, 5 and 8 are also discussed. The crystal and molecular structures of 2 and 5 have very similar characteristics. Both molecules are sited via their molecular centre of symmetry on crystallographic inversion centres. The carbamate groups are planar in all three cases as expected. An analysis of the data showed that the force due to Si–O conjugation which constrains the Si atom into the plane of the carbamate group is comparable to the crystal packing forces with a small out-of-plane movement being not unfavourable.

1. Introduction

Silyl carbamates are not only efficient silylating reagents but are also subject to various types of reactions [1]. Here we report a study of the thermally-induced decomposition of some silylated dicarbamic acid esters. The following compounds were prepared and studied:

R^1\
>N—C(=O)—OSiMe$_3$
X<
>N—C(=O)—OSiMe$_3$
R^2/
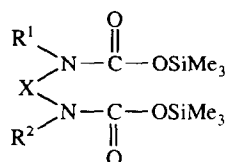
Compound	X	R^1	R^2
1	CH$_2$	SiMe$_3$	SiMe$_3$
2	(CH$_2$)$_2$	SiMe$_3$	SiMe$_3$
3	CH$_2$CHMe	SiMe$_3$	SiMe$_3$
4	(CH$_2$)$_3$	SiMe$_3$	SiMe$_3$
5	(CH$_2$)$_4$	SiMe$_3$	SiMe$_3$
6	(CH$_2$)$_3$	Me	SiMe$_3$
7	(CH$_2$)$_2$	H	H
8	(CH$_2$)$_3$	H	H
9	(CH$_2$)$_2$	Me	Me
10	Me$_2$N(CH$_2$)$_2$NMeCOOSiMe$_3$		

On the basis of our results, new methods have been developed to prepare *N*-silylated cyclic ureas without the use of phosgene.

R
|
N
X< >=O
N
|
SiMe$_3$

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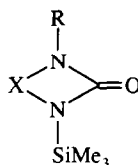
* Corresponding author.

Table 1
Yields, decomposition temperatures, physical and spectroscopic data for compounds 1–10

Compound	Yield (%)	GC retention index [a]	m.p. (°C)	Decomposition temp. (°C)	MS (70 eV, EI)		IR (in CCl$_4$)		^{1}H NMR (in TMS/CDCl$_3$)	
					M$^+$ ($m/z/\%$)	[M − 15]$^+$ (%)	ν(C=O) (cm^{-1})	ν(N–H) (cm^{-1})	δ(SiMe$_3$) (ppm)	δ(N–H) (ppm)
1	60	1689	–	180–190	422/1	0.3	1690	–	0.27–8	–
2	75	1856	123–124	190–200	436/0.3	21	1670	–	0.26; 0.29	–
3	70	1850	91–93	170–180	450/0	6	1675	–	0.20; 0.26	–
4	78	1937	83–85	190–200	450/3	7	1685	–	0.23; 0.29	–
5	83	2055	98–199	190–200	464/2	2	1680	–	0.22; 0.28	–
6	85	1859	oil	180–200	392/0.9	1	1670	–	0.17; 0.23	–
7	66	1677	132–134	200–220	292/0.3	0.2	1670 [e]	3450 [e]	0.28	~ 5.2
8	72	1766	96–98	200–220	306/1	0.9	1690	3450	0.28	~ 5.2
9	87	1644	113–115	230 [c]	320/0.2	0.5	1670	–	0.22	–
10	77	1243	liq. [b]	230 [d]	218/6	20	1675	–	0.28	–

[a] At 150°C oven temperatures. [b] B.p. 90°C/1 mb. [c] Conversion < 10%. [d] No conversion. [e] In CHCl$_3$.

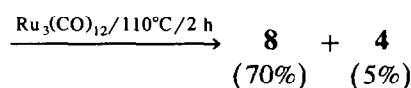| Compound	X	R
11	(CH$_2$)$_2$	SiMe$_3$
12	CH$_2$CHMe	SiMe$_3$
13	(CH$_2$)$_3$	SiMe$_3$
14	(CH$_2$)$_4$	SiMe$_3$
15	(CH$_2$)$_3$	Me

During the past decade some of these compounds have gained interest as model aglycons in urea nucleosides exhibiting potential cytidine deaminase inhibitor activity [2–4].

The crystal structures of 2, 5 and 8 were also determined by single-crystal X-ray diffraction.

2. Results and discussion

2.1. Preparation of the silyl esters

Some years ago Zoeckler and Laine obtained 4 and 8 from the reaction between N,N'-bis(trimethylsilyl)-1,3-propanediamine and carbon dioxide under pressure in the presence of transition metal carbonyl catalysts. However, only 8 was isolated as a pure product [5].

$$CH_2(CH_2NHSiMe_3)_2 + CO_2$$

$$\xrightarrow{Ru_3(CO)_{12}/110°C/2\ h} \underset{(70\%)}{8} + \underset{(5\%)}{4}$$

We have obtained all these compounds in a one-pot reaction according to the method described in Ref. [1], e.g.:
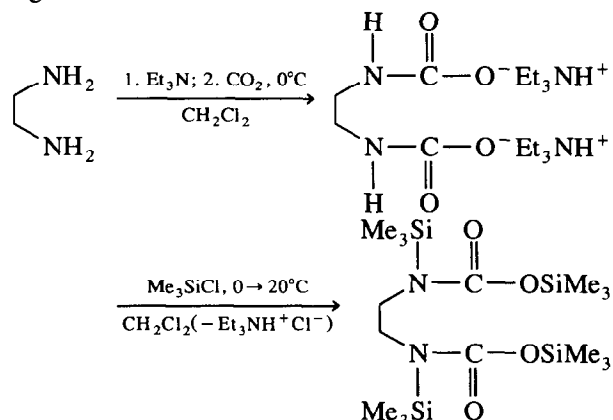

Esters containing the NH moiety (7, 8) were prepared in a similar way but an equivalent amount of

Table 2
Yields, physical and spectroscopic data for compounds 11–15

Compound	Yield (%)	GC retention index [a]	M.p. (°C)	MS (70 eV, EI)		IR (in CCl$_4$)	^{1}H NMR (in TMS/CDCl$_3$)
				M$^+$ ($m/z/\%$)	[M − 15]$^+$ (%)	ν(C=O) (cm^{-1})	δ(SiMe$_3$) (ppm)
11	87	1315	68–70 [b]	230/28	100	1670	0.25
12	90	1316	67–69	244/11	100	1670	0.24, 0.26
13	80	1358	76–78 [c]	244/28	100	1613 [d,g]	0.23
14	72	1375	oil	258/48	60	1650 [e,g]	0.21
15	65	1301	oil	186/18	100	1627 [f,g]	0.23

[a] At 80°C oven temperature. [b] Ref. [7], 67–68.5°C. [c] Ref. [10], 78–80°C. [d] Shoulders at 1640 and 1700 cm^{-1}. [e] Broad. [f] Split band pair with the second maximum at 1680 cm^{-1}. [g] One maximum when reacted with methanol at 1650 (13), 1675 (14) and 1645 (15) cm^{-1}, respectively.
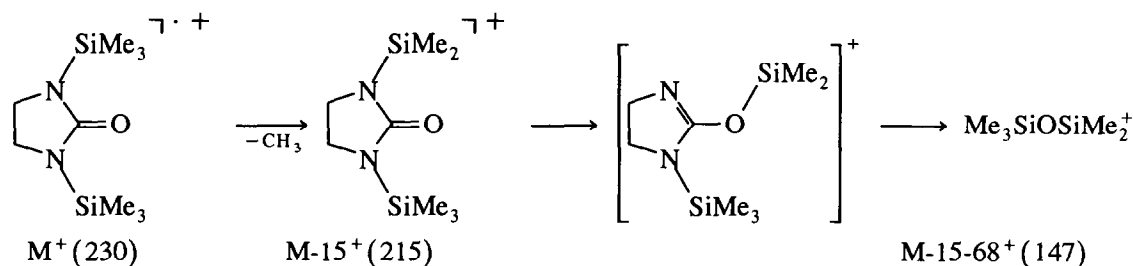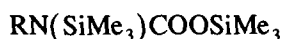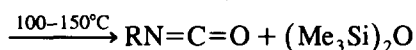
Scheme 1.

chlorosilane and only a slight excess of triethylamine were used. The yields, physical and spectroscopic data of the products are listed in Table 1.

2.2. Thermal decomposition

Mironov et al. first reported on the thermal decomposition of N,O-bis-silylcarbamates [6].

$$RN(SiMe_3)COOSiMe_3$$

$$(R = Me, {}^nBu, allyl)$$

$$\xrightarrow{100-150°C} RN{=}C{=}O + (Me_3Si)_2O$$

In order to study the thermal behaviour of 1–10, we heated them in an inert solvent (n-alkanes) at a controlled temperature. The decomposition was monitored by GC and GC–MS, respectively. It was necessary to maintain the temperatures listed in Table 1 to reach a total reactant conversion within 30–60 min.

Differences in the reactivity of compounds are marked at these temperature values. The N,O-silylated derivatives 1–6 usually decompose at lower temperatures and over a narrower range than ones containing the NH group (7, 8), whereas N-methyl-O-silyl derivatives (9, 10) are stable even at 220°C. On heating the NH compounds 7 and 8, some N,O,O'-trisilylated and, at a much lower concentration, N,N',O,O'-tetrasilylated derivatives (2, 4) always appeared in the reaction mixture with amounts which hardly changed until the consumption of the reactant was total. On the other hand, all the initial tetrasilylated compounds (1–5) always contained the trisilylated derivative in 3%–5% yield. At the decomposition temperature the concentrations of
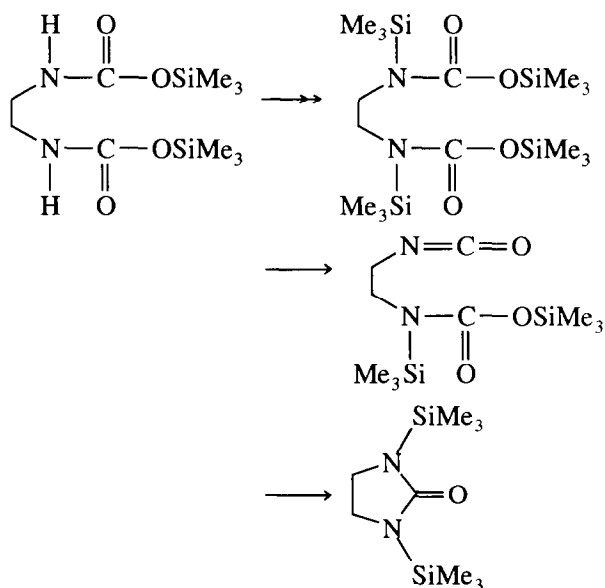
Table 3
Crystal data

Compounds	2	5	8
Formulae	$C_{16}H_{40}N_2O_4Si_4$	$C_{18}H_{44}N_2O_4Si_4$	$C_{11}H_{26}N_2O_4Si_2$
MW	436.86	464.91	306.52
$a(\text{Å})$	6.506(2)	6.743(2)	10.109(9)
$b(\text{Å})$	10.854(3)	7.892(4)	14.686(12)
$c(\text{Å})$	18.935(5)	27.872(3)	6.207(5)
$\alpha(°)$	90	90	99.00(9)
$\beta(°)$	98.04(2)	94.22(2)	97.10(9)
$\gamma(°)$	90	90	93.42(7)
$V(\text{Å}^3)$	1323.9(6)	1479.2(9)	900.2(13)
Space group	$P2_1/n$	$P2_1/n$	$P1$
Z	2	2	2
$D_{calc}(\text{g cm}^{-3})$	1.096	1.044	1.131
N_{tot}	4872	3255	2032
N_{indep}	2731	2991	2032
$N_{obs}(I > 2\sigma(I))$	1328	2290	1756
R_{int}	0.0287	0.0630	0.0608
R_1 (all data)	0.0673	0.1560	0.0842
wR_2 (all data)	0.1393	0.2140	0.2242
$R_1(I > 2\sigma(I))$	0.0543	0.0491	0.0756
$wR_2(I > 2\sigma(I))$	0.1306	0.1114	0.2099
Data/restraints/param.	2731/0/120	2986/0/130	2032/0/176
Goodness of fit on F^2	1.122	1.045	1.065
$2\Theta_{max}(°)$	52.00	150.00	52.00
$\lambda(\text{Å})$	0.7071	1.5418	0.7071
μ (mm^{-1})	2.252	2.040	1.890
Largest diff. peak (e Å^{-3})	0.204	0.239	0.180
Largest diff. hole (e Å^{-3})	-0.227	-0.286	-0.226
Extinction coeff.	0.0020(5)	0.0009(2)	0.09(2)

tetrasilylated compounds rapidly decreased whereas those of the trisilylated compounds hardly changed. Of course, upon prolonged heating, the latter also vanished. From these results, it is possible to conclude that N,O-silylated derivatives, whether present as reactants or formed by autosilylation, are involved in the process.

The decomposition products were analyzed by GC–MS methods and identified as the corresponding cyclic urea (Table 2 and Scheme 1) in addition to the hexamethyl disiloxane and carbon dioxide; however, **7** and **8** yielded a somewhat complex mixture containing mainly di- and mono-silylated ureas. Heating **9** led to the formation of the N,N'-dimethyl- and N-methyl-N'-trimethyl-silyl urea, respectively, in a low percentage. Only oligomers and polymers were obtained from **1** beside volatile products. On the other hand, upon heating **5** considerable amounts of $Me_3SiO_2CN(Si-Me_3)(CH_2)_4N=C=O$ formed as an intermediate as shown by its mass spectrum; M^+ ($m/z/\%$): 302/2, $M - CH_3^+$; 287/26, $(CH_3)_2SiOSi(CH_3)_3^+$; 147/100. The GC–IR measurements also showed the presence of the isocyanate group [ν_{as}(NCO) = 2270 cm^{-1}].

To supply further proof of the reaction between the isocyanate and siloxycarbonyl moieties, phenyl isocyanate and N,N-dimethylcarbamic acid trimethylsilyl ester were heated together above 180°C in n-tetradecane in a separate experiment which led to the formation of the corresponding urea derivative, as expected.

On the basis of these results, the main route involved in the thermal decomposition of silylated dicarbamic acid esters involves the following steps, e.g. for **8**:

2.3. Preparation of N-silylated ureas

Several routes have been described in the literature for the silylation of cyclic ureas to yield the corresponding N,N'-bis(trimethylsilyl) derivative [2,3,7–9]; how-

Atom	x	y	z	U_{eq} [a]
Si1	2567(1)	2427(1)	4970(1)	53(1)
Si2	911(1)	3400(1)	7049(1)	57(1)
O1	1398(3)	3420(2)	6203(1)	65(1)
O2	2644(4)	5349(2)	6169(1)	84(1)
N1	2871(3)	3980(2)	5259(1)	55(1)
C1	4113(5)	1386(3)	5614(2)	82(1)
C2	3547(5)	2333(3)	4101(2)	76(1)
C3	−185(5)	1972(3)	4832(2)	77(1)
C4	−409(7)	1915(4)	7094(2)	99(1)
C5	−739(6)	4697(4)	7223(2)	100(1)
C6	3364(6)	3410(4)	7644(2)	110(1)
C7	2343(4)	4347(3)	5897(1)	62(1)
C8	3852(4)	4945(2)	4872(1)	58(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ever, only an early report exists on the direct formation of the N-silylated ring starting from the diamine [10].
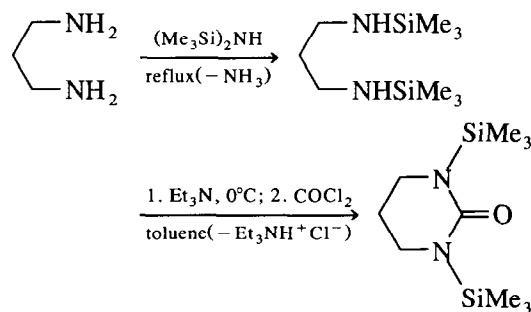
Our method proved to be efficient in preparing N-silylated cyclic urea (**11–15**) from the corresponding diamine via the silylated dicarbamic acid ester (**2–6**). The principle may be generalized for the respective synthesis of cyclic ureas and other derivatives.

Compound **11** was also prepared by the silylation of 2-imidazolidinone. The melting points, MS, IR and ^{1}H NMR spectra of the two products obtained by the different routes employed were the same.

Thermolysis of **2** and **3** gave **11** and **12** in high purity, respectively. However, compounds **4–6** resulted in a mixture containing the corresponding **13–15** in 65%–80% yield (Table 2).

2.4. X-Ray diffraction study

The crystal structures of compounds **2**, **5** and **8** were determined by single-crystal X-ray diffraction methods. The crystal data for these compounds are listed in Table 3 while the fractional coordinates for non-hydrogen atoms are listed in Tables 4, 6 and 8, respectively. The relevant bond lengths, bond angles and interesting torsion angles are listed in Tables 5, 7 and 9. The molecules structures of **2**, **5** and **8** are shown in Figs. 1, 2 and 3, respectively.

An attempt has also been made to prepare the 1,3-propylene analogue **4** of **2** and **5**, but the crystals were unsuitable for single-crystal X-ray diffraction studies.

The crystal structures of **2** and **5** appear to be fairly similar, although they are not isostructural in a crystallographic sense since the unit cell parameters are somewhat different. The driving force for the packing in both cases appears to be the hydrophobic interaction between the SiMe$_3$ groups of neighbouring molecules. While

Table 5
Bond lengths (Å), angles (°) and torsion angles (°) for **2**

Si1–C3	1.841(3)
Si1–C2	1.848(3)
Si1–C1	1.853(3)
Si2–O1	1.674(2)
Si2–C6	1.820(4)
Si2–C4	1.835(4)
O1–C7	1.352(3)
O2–C7	1.208(3)
N1–C7	1.361(3)
N1–C8	1.475(3)
C8–C8#1 [a]	1.509(5)
N1–Si1–C3	111.29(13)
N1–Si1–C2	106.87(12)
C3–Si1–C2	108.0(2)
N1–Si1–C1	110.45(14)
C3–Si1–C1	110.9(2)
C2–Si1–C1	109.2(2)
O1–Si2–C6	109.0(2)
O1–Si2–C5	110.92(14)
C6–Si2–C5	111.7(2)
O1–Si2–C4	102.00(13)
C6–Si2–C4	110.6(2)
C5–Si2–C4	112.2(2)
C7–O1–Si2	125.3(2)
C7–N1–C8	114.5(2)
C7–N1–Si1	121.4(2)
C8–N1–Si1	124.0(2)
O2–C7–O1	122.9(2)
O2–C7–N1	126.6(2)
O1–C7–N1	110.5(2)
N1–C8–C8#1	111.9(3)
C6–Si2–O1–C7	−64.0(3)
C5–Si2–O1–C7	59.4(3)
C4–Si2–O1–C7	179.0(3)
C3–Si1–N1–C7	64.2(3)
C2–Si1–N1–C7	−178.1(2)
C1–Si1–N1–C7	−59.5(3)
C3–Si1–N1–C8	−121.0(2)
C2–Si1–N1–C8	−3.3(2)
C1–Si1–N1–C8	115.4(2)
Si2–O1–C7–O2	−12.2(4)
Si2–O1–C7–N1	167.9(2)
C8–N1–C7–O2	−1.9(4)
Si1–N1–C7–O2	173.4(3)
C8–N1–C7–O1	178.1(2)
Si1–N1–C7–O1	−6.7(3)
C7–N1–C8–C8#1	83.1(3)
Si1–N1–C8–C8#1	−92.1(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 −x+1, −y+1, −z+1.

Table 6
Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **5**

Atom	x	y	z	U_{eq} [a]
Si1	1743(2)	−1798(2)	5874(1)	73(1)
Si2	−718(2)	−5731(2)	6777(1)	73(1)
O1	352(5)	−4555(4)	6365(1)	77(1)
O2	908(5)	−6680(4)	5857(1)	90(1)
N1	1703(5)	−3933(4)	5678(1)	60(1)
C1	3441(8)	−1583(8)	6422(2)	118(2)
C2	2747(9)	−536(7)	5394(2)	130(2)
C3	−810(7)	−1043(7)	5963(2)	102(2)
C4	−1269(9)	−4152(8)	7234(2)	114(2)
C5	−3028(7)	−6680(7)	6508(2)	99(2)
C6	1050(8)	−7300(8)	7033(2)	119(2)
C7	989(7)	−5189(7)	5952(2)	68(1)
C8	2431(6)	−4473(6)	5221(1)	65(1)
C9	4641(5)	−4801(6)	5244(1)	63(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

this feature is still present in the crystal structure of **8**, another important factor comes into play: neighbouring molecules are connected by a pair of hydrogen bonds in a manner somewhat resembling the architecture of β-sheets (Fig. 4). The two hydrogen bonds are associated with the atoms N2–H2 · · · O1$1 and N1–H1 · · · O4$2, respectively. Table 10 summarizes the most important characteristics of these H-bonds. A further interesting characteristic of this group of compounds is that **2** and **5** crystallize with half of a molecule in the crystallographic asymmetric unit. These molecules sit with their molecular centres of symmetry on the crystallographic inversion centres. It is not possible for compound **8** to achieve such an arrangement.

As far as the intramolecular geometry is concerned, all three compounds can be described in terms of two major sections. Firstly, the planar carbamate groups with their attached atoms. It should be mentioned that in **2** (Fig. 1), Si2 (the ester-like Si atom) is 0.263(3) Å out of the plane of the carbamate moiety (atoms N1, C2, O1, O2, Si1, C7, C8 with r.m.s. 0.04 Å). In the case of **5** (Fig. 2), the corresponding Si atom is in the carbamate plane, while in the case of compound **8** (Fig. 3) Si1 is in the plane, but Si2 is well out of it [0.320(5) Å]. It looks as if the force arising from Si–O conjugation which constrains the Si atom into the plane of the carbamate group is comparable to the crystal packing forces with a small out-of-plane movement of being not unfavourable.

In terms of torsion angles, in compound **2** the 'intraplanar' torsion angles not involving Si1 are planar to within 2°, while those involving Si1 are planar to within 7° (Table 5). In contrast, the Si2–O1–C7–N1 torsion angle [167.9(2)°] is 12° out of the general plane of the carbamate moiety. In compound **5**, all 'coplanar' torsion angles, whether they involve Si1 and Si2 or not, are within 3.5° of total planarity. Only ester-like SiMe$_3$

groups exist in compound **8** and they behave somewhat ambiguously. Thus Si1 along with C9 remains in the plane of the carbamate group to within 5°, but in this case both the Si and C atoms exhibit considerable deviations from totally planar torsion angles. On the

Table 7
Bond lengths (Å) angles (°) and torsion angles (°) for **5**

Si1–N1	1.771(4)
Si1–C2	1.836(5)
Si1–C1	1.850(6)
Si1–C3	1.856(5)
Si2–O1	1.678(3)
Si2–C6	1.828(5)
Si2–C5	1.838(5)
Si2–C4	1.840(5)
O1–C7	1.354(5)
O2–C7	1.207(5)
N1–C7	1.360(5)
N1–C8	1.463(4)
C8–C9	1.509(5)
C9–C9#1 [a]	1.510(7)
N1–Si1–C2	106.9(2)
N1–Si1–C1	109.6(2)
C2–Si1–C1	108.3(3)
N1–Si1–C3	110.7(2)
C2–Si1–C3	108.7(3)
C1–Si1–C3	112.5(3)
O1–Si2–C6	109.9(2)
O1–Si2–C5	110.0(2)
C6–Si2–C5	113.1(3)
O1–Si2–C4	102.6(2)
C6–Si2–C4	110.3(3)
C5–Si2–C4	110.5(3)
C7–O1–Si2	123.8(3)
C7–N1–C8	115.6(4)
C7–N1–Si1	121.3(3)
C8–N1–Si1	123.1(3)
O2–C7–O1	122.3(4)
O2–C7–N1	126.8(4)
O1–C7–N1	110.8(4)
N1–C8–C9	114.0(3)
C8–C9–C9#1	112.2(4)
C6–Si2–O1–C7	63.7(4)
C5–Si2–O1–C7	−61.4(4)
C4–Si2–O1–C7	−178.9(4)
C2–Si1–N1–C7	−178.5(4)
C1–Si1–N1–C7	64.4(4)
C3–Si1–N1–C7	−60.3(4)
C2–Si1–N1–C8	1.8(4)
C1–Si1–N1–C8	−115.3(3)
C3–Si1–N1–C8	120.0(3)
Si2–O1–C7–O2	−3.2(7)
Si2–O1–C7–N1	177.0(3)
C8–N1–C7–O2	0.4(7)
Si1–N1–C7–O2	−179.3(4)
C8–N1–C7–O1	−179.9(3)
Si1–N1–C7–O1	0.5(5)
C7–N1–C8–C9	−94.5(5)
Si1–N1–C8–C9	85.1(4)
N1–C8–C9–C9#1	−174.8(5)

[a] Symmetry transformations used to generate equivalent atoms: #1
− x + 1, − y − 1, − z + 1.

Table 8
Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **8**

Atom	x	y	z	U_{eq} [a]
Si1	4812(1)	7774(1)	1592(2)	76(1)
Si2	471(1)	1668(1)	−6396(2)	72(1)
O1	5047(3)	6368(3)	−2132(6)	91(1)
O2	3630(3)	7142(3)	−155(6)	79(1)
O3	1404(3)	2426(2)	−7478(6)	72(1)
O4	−81(3)	3534(3)	−7858(7)	84(1)
N2	2071(3)	3796(2)	−8308(6)	64(1)
N1	2825(3)	6151(3)	−3139(7)	76(1)
C1	2924(5)	5445(4)	−4961(10)	85(2)
C2	1810(5)	5451(4)	−6799(9)	76(1)
C3	1957(4)	4746(3)	−8762(8)	71(1)
C4	3907(4)	6528(4)	−1860(9)	71(1)
C5	1049(4)	3283(3)	−7886(8)	63(1)
C6	−1070(6)	1302(5)	−8218(12)	102(2)
C7	1590(7)	696(4)	−6211(13)	103(2)
C8	154(6)	2200(5)	−3652(10)	101(2)
C9	3841(7)	8422(6)	3556(11)	113(2)
C10	5715(8)	8581(5)	126(13)	112(2)
C11	5951(6)	7016(5)	2971(11)	99(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

other hand, the Si2–O3–C5–N2 torsion angle [167.1(3)°] is again almost 13°, out of planarity. At the same time, the 'in-plane' torsion angles are planar to within 1°.

As far as the bond lengths are concerned, it is noticable that the (O–Si–C bond lengths [1.831(7) Å is the average of six sets of data] in **2** and **5** are consistently shorter by about 0.017 Å (ca. three times the esd of the corresponding bond lengths) than the (N–Si–C bond lengths [1.848(7) Å is the average of six sets of data]. In **8**, the standard deviation of the average of the six (O–)Si–C bond lengths is very large [1.851(27) Å] although the estimated standard deviation of the individual bond lengths is around 0.007 Å.

A consistent feature in all three compounds is also that the O–Si–C bond angle formed by the carbon atom which is part of the antiperiplanar C–O–Si–C torsion angle is always around 102° as opposed to the other C–Si–C angles which are always around 110°. A similar argument applies to a lesser extent to the N–Si–C bond angles, although here it leads to an increased repulsion between the terminal bonds of the synperiplanar O–Si–N–C torsion angle. This can be recompensated for by a widening of the Si–N–C(sp^3) bond angles (123–124°). The C–O–Si bond angle always exhibits sp^2 character with values above 120° demonstrating the delocalization of the oxygen lone pairs.

The second major section of the structures is the central linkage region, i.e. alkylene chains with nitrogen atoms at their termini. The non-hydrogen atoms of this region in **2** and **5** form an open-chain conformation, whose plane is more or less perpendicular to that of the carbamate group [84.9(2)°, 85.6(3)°]. In **8**, the chain also

has other torsion angles. In the C4–N1–C1–C2–C3–N2–C5 chain, the torsion angles are *anti*, *anti*, + *gauche*, + *gauche*. This is probably needed for the proper alignment of the hydrogen–bond donor and acceptor groups.

3. Experimental details

All the operations described below were undertaken under moisture-free conditions.

3.1. Preparation of the N,N',O,O'-tetrakis (trimethylsilyl)-ethylene-1,2-dicarbamic acid ester (2)

Into a 1 l three-necked flask equipped with a stirrer, dropping funnel and condenser was added 19.6 g (0.33 mol) of ethylenediamine and 250 ml (1.80 mol) of triethylamine in 300 ml of absolute dichloromethane. On cooling with ice, dry carbon dioxide was introduced to the vigorously stirred solution for 2 h. Then 200 ml (1.58 mol) of trimethylchlorosilane was added dropwise while allowing the mixture to warm up to ambient temperature with stirring being continued for a further 2 h. The ammonium chloride precipitated was filtered off and the solvent evaporated under reduced pressure. Then 300 ml of hot n-hexane was added to the residue and any ammonium chloride still present was filtered off once more. After concentration of the solution, colourless crystals were isolated from the mother liquor; yield, 75% (110 g).

The other compounds were prepared in a similar manner (Table 1) starting from the diamine, except for 1 when the corresponding dihydrochloride salt (Fluka) was used. Compound 10 was purified by vacuum distillation.

3.2. Silylation of the 2-imidazolidinone

Into a 500 ml three-necked flask equipped with a dropping funnel and condenser was placed 10.1 g (105 mmol) of 2-imidazolidinone · 0.5H$_2$O and 50 ml (360 mmol) of triethylamine in 200 ml of dichloromethane. Then 45 ml (350 mmol) of trimethylchlorosilane was added dropwise while stirring for 2 h. Work-up of mixture was similar to that described above. The white crystalline product was identified as 11.

3.3. Thermolysis studies

Thick-walled screw-capped vials containing 1–10 in n-dodecane and n-tetradecane as reaction medium, respectively, were equipped with a Mininert valve or a Teflon-coated silicone rubber septum and heated in a thermostated metal block. Occasionally 1 μl of the sample was transferred to the GC column to be analyzed. Since samples containing either C$_{12}$ or C$_{14}$ hydrocarbon covered different parts of the chromatograms, both had to be measured each time.

3.4. Preparation of the N-silylated ureas

For preparative purposes, thermolysis was first attempted in clean paraffin and silicone oil but the method in the absence of solvent proved to be more convenient.

A 50 ml three-necked flask equipped with a thermometer and gas inlet was attached to a distillation apparatus. The silyl ester (2–6) was weighed in and the flask heated at 210–220°C with passage of a slow
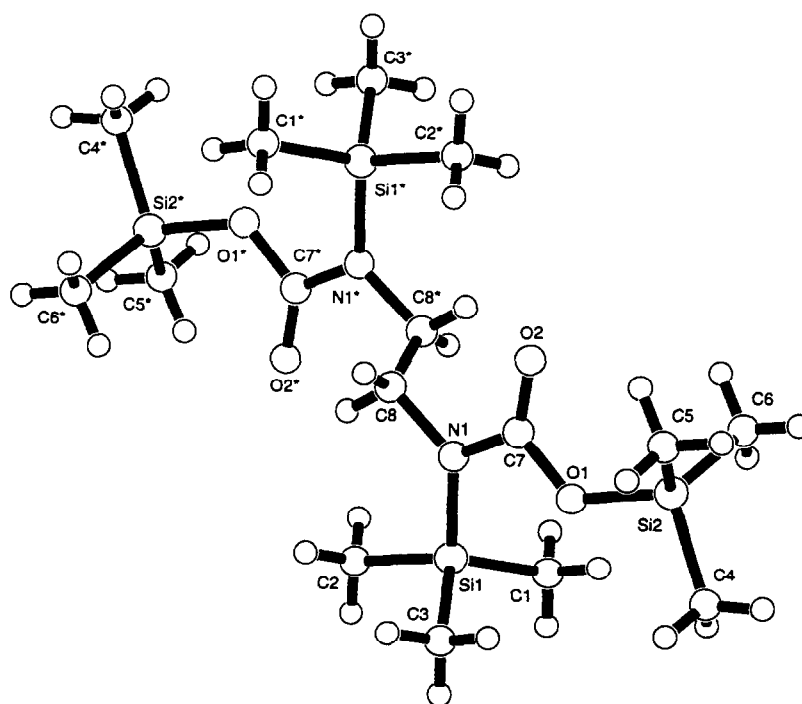

Fig. 1. The molecular structure of 2.

Table 9
Bond lenghts (Å), angles (°) and torsion angles (°) for **8**

|	
Si1–O2	1.643(4)
Si1–C9	1.844(6)
Si1–C10	1.866(7)
Si1–C11	1.873(7)
Si2–O3	1.686(4)
Si2–C6	1.808(7)
Si2–C8	1.834(6)
Si2–C7	1.882(7)
O1–C4	1.216(5)
O2–C4	1.347(6)
O3–C5	1.382(6)
O4–C5	1.222(5)
N2–C5	1.318(5)
N2–C3	1.475(6)
N1–C4	1.308(6)
N1–C1	1.427(7)
C1–C2	1.503(8)
C2–C3	1.499(7)
O2–Si1–C9	102.0(3)
O2–Si1–C10	109.3(3)
C9–Si1–C10	110.4(4)
O2–Si1–C11	110.4(3)
C9–Si1–C11	111.4(3)
C10–Si1–C11	112.8(3)
O3–Si2–C6	109.8(3)
O3–Si2–C8	109.6(3)
C6–Si2–C8	111.6(3)
O3–Si2–C7	102.4(2)
C6–Si2–C7	112.2(4)
C8–Si2–C7	110.9(3)
C4–O2–Si1	122.1(3)
C5–O3–Si2	125.8(2)
C5–N2–C3	122.6(3)
C4–N1–C1	119.8(3)
N1–C1–C2	111.1(4)
C3–C2–C1	111.1(4)
N2–C3–C2	114.9(4)
O1–C4–N1	125.7(4)
O1–C4–O2	122.2(5)
N1–C4–O2	112.1(3)
O4–C5–N2	124.2(4)
O4–C5–O3	123.7(4)
N2–C5–O3	112.1(3)
C9–Si1–O2–C4	– 177.8(5)
C10–Si1–O2–C4	65.3(5)
C11–Si1–O2–C4	– 59.3(4)
C6–Si2–O3–C5	62.8(5)
C8–Si2–O3–C5	– 60.1(5)
C7–Si2–O3–C5	– 177.8(4)
C4–N1–C1–C2	– 150.4(5)
N1–C1–C2–C3	176.8(4)
C5–N2–C3–C2	72.3(6)
C1–C2–C3–N2	54.5(6)
C1–N1–C4–O1	4.1(9)
C1–N1–C4–O2	– 176.5(5)
Si1–O2–C4–O1	4.3(7)
Si1–O2–C4–N1	– 175.1(4)
C3–N2–C5–O4	1.0(7)
C3–N2–C5–O3	– 179.0(4)
Si2–O3–C5–O4	– 12.9(7)
Si2–O3–C5–N2	167.1(3)
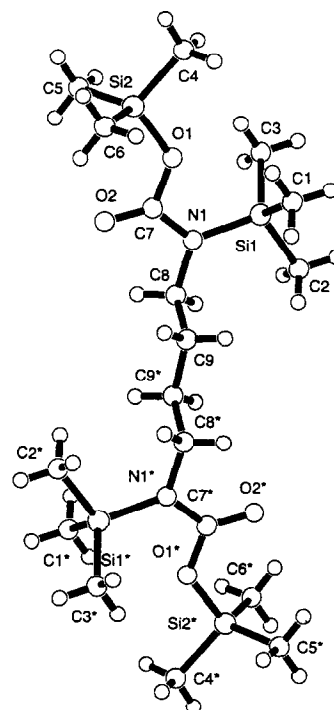
Fig. 2. The molecular structure of **5**.

stream of dry nitrogen. Carbon dioxide bubbles evolved at a constant rate and some hexamethyldisiloxane exited the still. After bubbling had ceased, traces of the siloxane were distilled out. Yields, physical and spectroscopic data of products are summarized in Table 2.
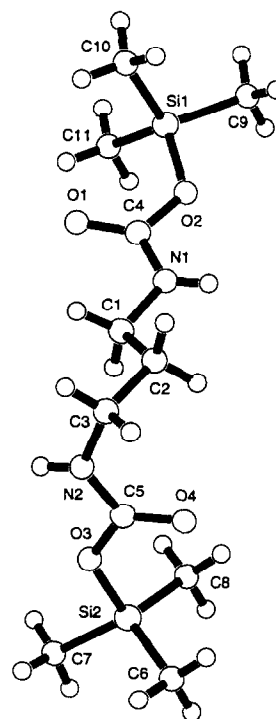

Fig. 3. The molecular structure of **8**.

Table 10
Hydrogen bond data for **8**

	N2-H2-O1$1 [a]	N1-H1-O4$2
N···O (Å)	2.921 (0.005)	2.963 (0.005)
H···O (Å)	2.120 (0.004)	2.118 (0.004)
N-H···O (°)	154.59 (0.15)	167.64 (0.16)

[a] $1 indicates that O1$1 belongs to a molecule that can be generated from the unsigned one by the following symmetry operation: $1 - x$, $1 - y$, $-z - 1$.

3.5. Instrumental

Mass spectra were recorded with a Kratos MS 25 spectrometer. IR spectra were obtained with a Zeiss Specord grid instrument. ^{1}H NMR spectra were measured on a Bruker AC-80 spectrometer. The GC measurements were made with a Chrompack CP 9000 gas chromatograph on a WCOT fused silica column (CP-Sil 5CB, 10 m × 0.25 mm i.d.× 0.12 μm), FID, He carrier gas. The GC–MS system consisted of a Varian GC (col. DB-5, 30 m × 0.25 mm × 0.25 μm) and a Finnigan MAT Magnum, 70 eV EI. The GC–IR measurements

were recorded on a Bruker IFS 55 IR spectrometer coupled with a Chrompack CP 9001 chromatograph.

3.6. X-Ray diffraction study

X-Ray diffraction data for **2** and **5** were collected using a Rigaku RAXIS-II imaging plate area detector using graphite-monochromated Mo K α radiation, while those for **5** were collected on a Rigaku AFC6S single-crystal diffractometer using graphite-monochromated Cu K α radiation at 293 K. Crystallographic data are summarized in Table 3. Data processing was carried out using the program system supplied with both of the diffractometers. Structure solution with direct methods and refinement with full-matrix least-squares on F^2 were carried out with the teXsan [11] package of the Molecular Structure Co. and SHELXL-93 [12]. Hydrogen atoms were generated and constrained to a distance relative to their corresponding parent atom. This distance was dependent on the chemical nature of the H-atom in question. The anisotropic thermal motion parameters for non-H atoms and isotropic thermal motion parameters for hydrogens were refined.
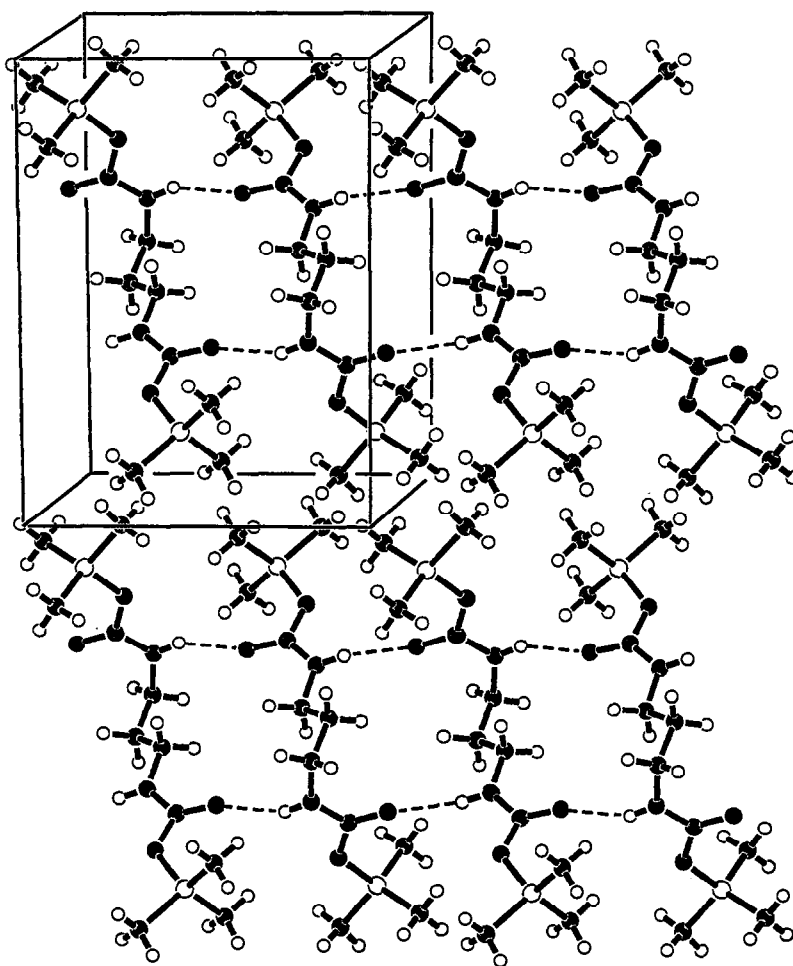

Fig. 4. The packing diagram for **8** showing the hydrogen bonds.

4. Supplementary material

Hydrogen atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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