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Crystal Structure and Theoretical Investigation of the Configurations of 1,3-Dichloro-1,3-diazetidine-2,4-dione and 1,3-Bis(trimethylsilyl)-1,3-diazetidine-2,4-dione

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ABSTRACT

Crystal structures of 1,3-dichloro-1,3-diazetidine-2,4-dione (**1**) *and the hitherto unknown compound 1,3-bis(trimethylsilyl)-1,3-diazetidine-2,4-dione* (**2**) *have been determined by X-ray crystallography:* **1**: $(ClNCO)_2$, $M_r = 154.94$, $T = 295$ K, *orthorhombic*, Pbca, $a = 7.699(1)$, $b = 6.706(1)$, $c = 10.598(2)$ Å, $V = 547.2(2)$ Å^3, $Z = 4$, $d_x = 1.881$ g/cm^3, $\mu = 10.9$ cm^{-1}, $R = 3.14\%$, $R_w = 2.82\%$ *(660 observations, 38 parameters).* **2**: $[(CH_3)_3SiNCO]_2$, $M_r = 230.41$, $T = 100$ K, *monoclinic*, I2/a, $a = 20.257(2)$, $b = 6.416(1)$, $c = 21.260(3)$ Å, $\beta = 101.29(1)°$, $V = 2709.7(6)$ Å^3, $Z = 8$, $d_x = 1.130$ g/cm^3, $\mu = 2.4$ cm^{-1}, $R = 4.86\%$, $R_w = 4.39\%$ *(2375 observations, 151 parameters). In both compounds, the symmetry of the* $(XNCO)_2$ *framework* (X = *Cl, Si*) *was determined to be nearly* C_{2h} *with trans configuration of the exocyclic X atoms. Extreme values were observed for the angles between the ring plane and the exocyclic N–X bonds: 32.5(1)° in* **1** *and 2.5(2)° and 0.8(2)° in* **2**, *respectively. Quantum chemical procedures at various levels of theory (ab initio SCF and semi-empirical PM3) applied to* **1** *revealed the possible appearance of two isomers, a lower energy trans form and a higher energy cis form (approx. 2.4 kcal/mol above trans) differing mainly in the spatial arrangement of the chlorine atoms. The calculations excluded a planar heavy-atom configuration by missing a local energy minimum.*

INTRODUCTION

Up to now only two crystal structure determinations of 1,3-diazetidine-2,4-diones; i.e., the 1,3-dimethyl- [1] and the 1,3-diphenyl-derivative [2] have been reported. In both compounds, the four-membered rings are arranged around crystallographic symmetry centers and are therefore strictly planar, without a significant deviation of the oxygen atoms from that plane. The central $(CNCO)_2$ fragments show C_{2h} symmetry (trans configuration) with angles between the ring plane and the exocyclic N–C bonds of 21.9(1)° and 12.2(5)°, respectively. In contrast to these results a folded molecular structure of **1** possessing C_{2v} symmetry (cis configuration) has been deduced from IR and Raman measurements [3]. Since IR and Raman data do not provide conclusive structural evidence and as different skeletal configurations are possible, the crystal structures of **1** and **2** were determined by X-ray diffraction.

The configuration problem associated with 1,3-diazetidine-2,4-diones impelled us to undertake quantum chemical calculations as well. This article describes our results for the structures, the relative stabilities of the different configurational isomers, and the charge density distribution.

Dedicated to Prof. Dr. Edwin Henyge on the occasion of his sixtieth birthday.

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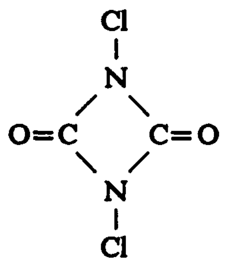

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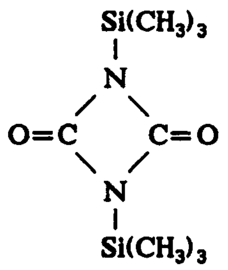

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DISCUSSION

Bond lengths and angles for **1** and **2** are given in Figure 1 and packing plots in Figure 2. In the crystal, **1** and **2** show crystallographic C_i site symmetry with approximate C_{2h} symmetry of the $(XNCO)_2$ fragments (X = Cl, Si) in contrast to the cited structure proposal for **1** [3]. The ring geometries show a slight rhombic distortion with C–N–C angles larger (**1**) or smaller (**2**) than 90°. Whereas in **1** the oxygen atoms lie in the ring plane, there is a small but significant deviation (0.019(3) Å) of the oxygen atom O1 in **2**, probably due to packing effects. The angles between the C–N–C plane and the exocyclic N–X bond, α_{PNX}, are particularly different: 32.5(1)° in **1** and 2.5(2)° and 0.8(2)° in **2**, where the asymmetric unit contains two half molecules. These values are extremes referring to the known structural data of 1,3-diazetidine-2,4-diones.

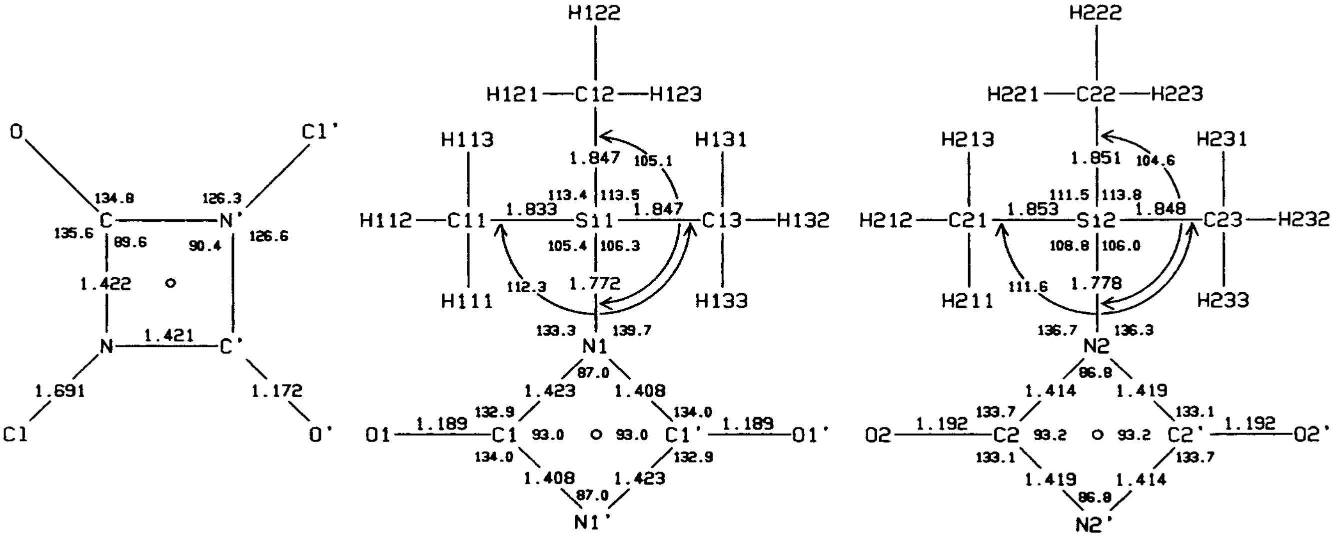
At the first approximation, **1** forms an orthorhombicly distorted cubic closed packing (see Figure 2). The short Cl· · ·O contacts (2.949(1) Å) with an N–Cl· · ·O angle of 173.49(6)° and an almost linear (174.6(1)°) C=O· · ·N geometry are remarkable. In **2**, the packing is dominated by an orientation of the C=O bond toward the Si(CH$_3$)$_3$ group with relatively short Si· · ·O distances of 3.365(2) Å and 3.494(2) Å and N–Si· · ·O bond angles of 174.6(1)° and 175.1(1)°.

In the difference electron density maps, representing the difference between the actual observed electron density and the superposition of spherically averaged free-atom densities allowed for anisotropic thermal vibration, for **1** and **2** the residual peaks lie 0.18 Å (average) outside the internuclear connecting lines, indicating the occurrence of bent C–N bonds in the diazetidine rings. According to the electron density distributions, the "true" C–N–C bond angles are about 118° in contrast to 90° (average) derived from the nuclear framework.

A search in the Cambridge Structural Database (CSD) [4] for C–N(–Cl)–C fragments yielded 12 fragments in 6 crystal structure determinations [5] with angles α_{PNX} in the range from 0.2° to 67.5°. In order to gain aplanarity determining parameters, different searches in the CSD for C^a–N(–X)–C^a fragments (C^a = annular C atom; X = C, Cl, Si) were carried out for 3-, 4-, 5-, and 6-membered ring compounds. Because of the small number of known samples, the search for fragments with X = Si was not limited to ring compounds only. Table 1 shows a comparison of the geometries of the C^a–N(–X)–C^a fragments with X = C (type **A**, **D**, **E**), X = Cl (type **B**, **F**), and X = Si (type **C**, **G**), in which the C^a atoms are both hybridized either sp^3 (type **A**, **B**, **C**) or sp^2 (type **D**, **E**, **F**, **G**). For X = Si, the compounds were classified only according to the hybridization at the C^a atoms. The term hybridization does not mean that we have actually studied the electronic structure, but instead the different coordination number (2 or 3) at the C^a atoms should be distinguished.

As one can see from Table 1, the obvious dif-

FIGURE 1 Schematic presentation of the bond lengths and bond angles in the crystal structures of **1** (*left*) and **2** (*center* and *right*). The standard deviations are 0.002 Å and 0.1° for **1** and 0.003 Å and 0.2° for **2**.



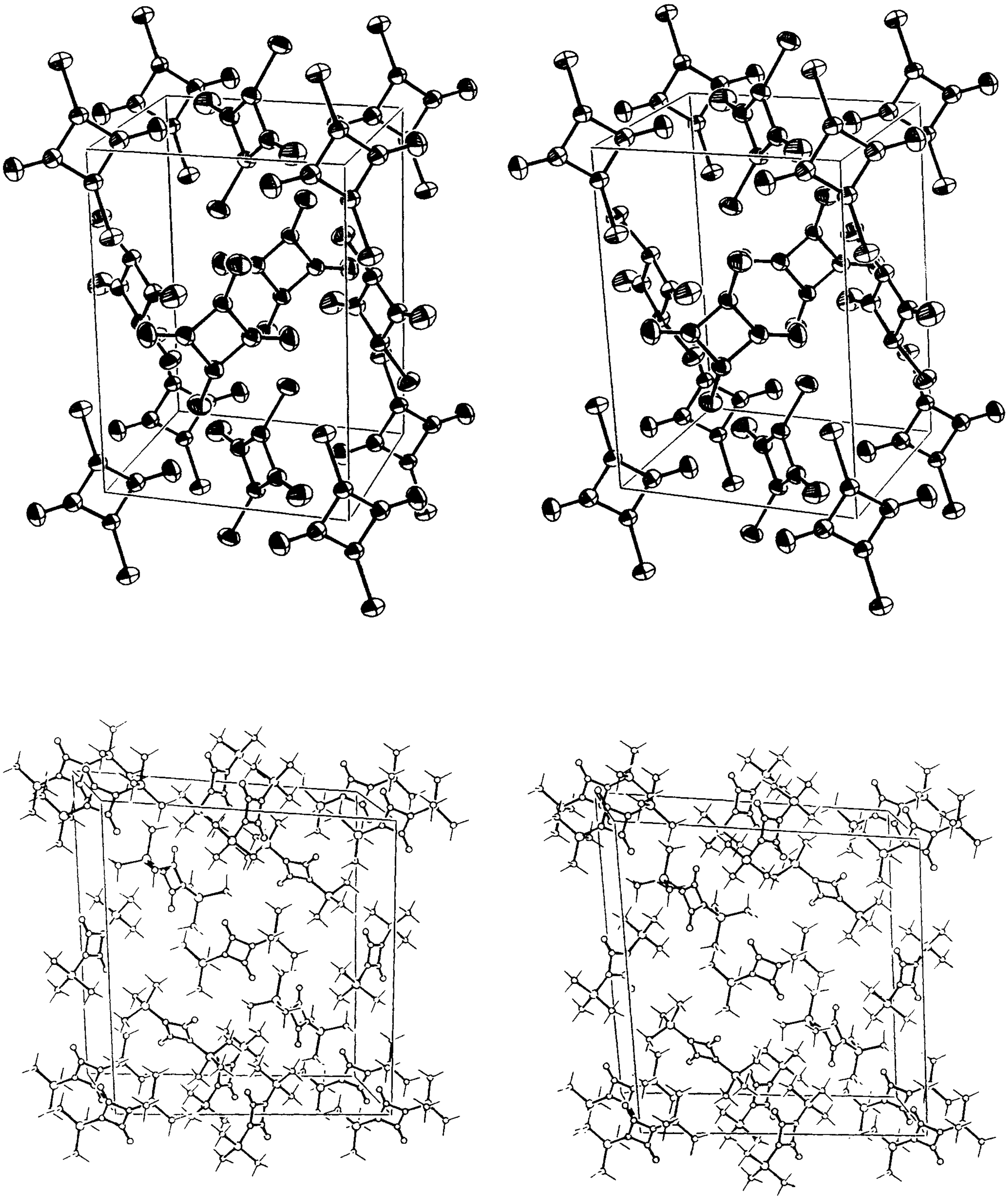
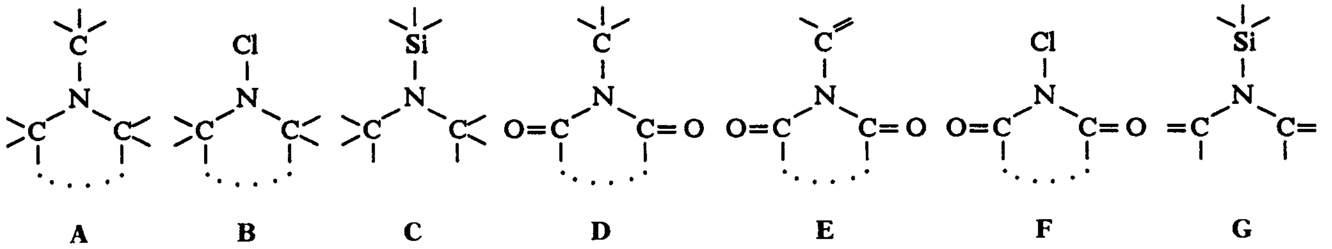


FIGURE 2 Stereographic projection of the molecule package in the crystal structures of **1** (*above*) and **2** (*below*). The thermal ellipsoids of **1** are drawn at the 90% probability level, the atoms of **2** as spheres of an arbitrary radius.

TABLE 1 Comparison of the Geometrics of Cyclic Molecules[a] and Comparison of the Molecular Geometrics of the 1,3-Diazetidine-2,4-diones[b] (All compounds considered were classified according to the hybridization of the C^a atoms in the following fragment.)



X	Type	N_r	α_{PNX}	N–X	N–C^a	X–N–C^a	C^a–N–C^a	N_{obs}	Ref.
C	A	3	60.3(21)	1.467(17)	1.468(14)	115.2(17)	61.2(8)	12	
C	A	4	45.4(67)	1.449(20)	1.478(1)	119.2(25)	91.5(28)	2	
C	A	5	48.3(48)	1.467(21)	1.477(18)	114.1(21)	104.6(31)	44	
C	A	6	48.4(60)	1.464(27)	1.468(12)	112.3(26)	109.9(34)	190	
Cl	B	3	66.0(18)	1.765(26)	1.517(19)	110.5(15)	59.6(16)	4	[5a]
Cl	B	5	58.3(6)	1.774(5)	1.494(9)	110.4(1)	96.5(12)	2	[5b,c]
Si	C	—	10.0(73)	1.691(28)	1.475(20)	122.8(12)	112.6(20)	7	
C	D	4	3.7(1)	1.453(2)	1.403(5)	132.7(13)	94.4(1)	4	
C	D	5	3.7(27)	1.459(12)	1.382(10)	123.8(5)	112.2(11)	79	
C	D	6	4.0(29)	1.478(15)	1.385(9)	117.5(6)	124.7(11)	74	
C	E	5	3.2(27)	1.435(10)	1.394(9)	124.1(7)	111.6(14)	66	
C	E	6	3.4(52)	1.463(19)	1.397(8)	118.0(1)	123.8(7)	4	
Cl	F	5	8.6(17)	1.688(16)	1.394(24)	122.0(13)	115.2(15)	1	[5d]
Cl	F	6	3.3(41)	1.690(1)	1.393(6)	115.9(8)	127.9(6)	3	[5e]
Si	G	—	9.3(71)	1.769(25)	1.433(13)	121.7(9)	115.1(26)	11	
CH_3	D	4	21.9(1)	1.448(1)	1.405(1)	131.6(1)	88.6(1)	1	[1]
C_6H_5	E	4	12.2(6)	1.402(8)	1.429(9)	133.5(6)	90.5(5)	1	[2]
Cl	F	4	32.5(1)	1.691(1)	1.421(2)	126.4(1)	90.4(1)	1	this work (**1**)
$Si(CH_3)_3$	G	4	1.6(9)	1.775(3)	1.416(5)	136.5(26)	86.9(1)	2	this work (**2**)

[a] The upper part of the table shows a comparison of the geometries of cyclic molecules, containing at least one C^a–N(–X)–C^a fragment with X = Cl, C, or Si, with the exception of 1,3-diazetidine-2,4-diones. Referring to the Cambridge Crystallographic Database [4], only crystal structure data marked as error free and with *R*-factors below 7.5% were taken into consideration. Caused by the small number of known structures, the search for fragments with X = Si was not restricted to ring compounds only.

[b] The lower part of the table shows a comparison of the molecular geometries of the 1,3-diazetidine-2,4-diones. The angle α_{PNX} between the N–X bond and the C^a–N–C^a plane, the N–X and averaged N–C^a distances, the averaged X–N–C^a and C^a–N–C^a bond angles, as well as the number of independent fragments observed N_{obs} are given for the different fragment types and ring sizes N_r. The values given for $N_{obs} > 1$ are the mean values with the standard deviations of the samples in parentheses.

ferences in aplanarity (α_{PNX}) are mainly dependent on the hybridization of both C^a atoms. Shorter N–C^a distances, larger X–N–C^a angles, and a nearly planar structure are typical for fragments with sp^2-hybridized C^a atoms. However, such differences are not observed in fragments with X = Si. The aplanarity of fragments with sp^3-hybridized C^a atoms decreases in the order Cl > C > Si, but no dependence on ring size is observed with the exception of three membered ring systems, which show a significantly higher aplanarity. It is remarkable that the N–X distances in fragments with sp^3-hybridized C^a atoms are longer for X = Cl and about the same for X = C, but smaller for X = Si than those in fragments with sp^2-hybridized C^a atoms.

Concerning the 1,3-diazetidine-2,4-diones, the aplanarity decreases in the order Cl > C > Si as well. In comparison to all other systems with sp^2-hybridized C^a atoms, a significantly larger aplanarity is shown by the 1,3-diazetidine-2,4-diones with the exception of **2**. The N–X distances are in agreement with those values observed in the other systems with sp^2-hybridized C^a atoms. The structural parameters of the 1,3-diazetidine-2,4-diones therefore reveal a special electronic situation in these compounds.

Molecular structures of the two isomers of **1** have been determined at the SCF/3-21G* level of theory using the program GAUSSIAN 82 [6] as well as at the semi-empirical PM3 level [7]. The respective calculated geometry data are listed in Table 2 together with experimental results. The structure of **1** exhibits significantly pyramidalized N atoms for both the cis and trans configurations. Despite

TABLE 2 Calculated Molecular Structures of *cis*- and *trans*-$(ClNCO)_2$ (**1**) and of $[(CH_3)_3SiNCO]_2$, (**2**) (Distances in Å, angles in degrees)[a,b]

		*SCF/3-21G**	*PM3*	*Exp.*
trans-$(ClNCO)_2$ (C_{2h})	Cl–N	1.672	1.705	1.691(2)
	N–C	1.409	1.476	1.421(2)
	C–O	1.157	1.194	1.172(2)
	N–C–N	89.0	88.4	89.6(1)
	Cl–N–X[c]	149.6	143.4	147.5(1)
cis-$(ClNCO)_2$ (C_{2v})	Cl–N	1.666	1.705	
	N–C	1.410	1.477	
	C–O	1.158	1.194	
	N–C–N	88.5	87.9	
	Cl–N–X	149.9	144.0	
	N–X–N	162.2	166.8	
	O–C–X	170.8	175.5	
trans-$[(CH_3)_3SiNCO]_2$	Si–N		1.782	1.775(3)
	N–C		1.459	1.416(5)
	C–O		1.205	1.190(3)
	N–C–N		89.2	93.1(2)
	Si–N–X		11.3	1.6(9)

[a] The molecular structures of *cis*- and *trans*-$(ClNCO)_2$ (**1**) were calculated at the ab initio SCF/3-21G* and at the semi-empirical PM3 level; the structure of $[(CH_3)_3SiNCO]_2$ (**2**) was calculated only at the semi-empirical PM3 level.

[b] The minima on the energy hypersurface are proven by the calculated complete sets of harmonic vibrational frequencies. The experimentally determined structural parameters result from the crystal structure analysis of **1** and **2** (this work).

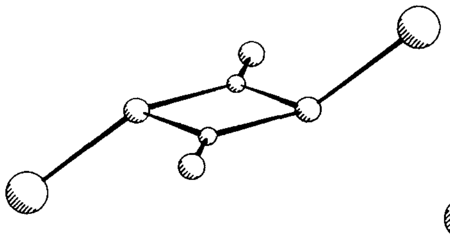
[c] X is defined as midpoint between the ring C atoms.

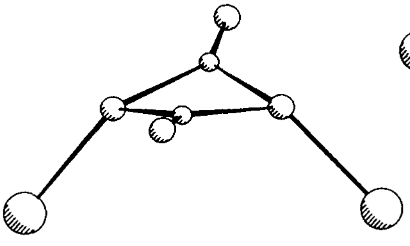
low occupation numbers of *d*-functions (Cl: 0.045, N: 0.066, C: 0.161, O: 0.043), compound **1** turned out to be planar (D_{2h}-symmetry) when *d*-functions at nitrogen are removed. In contrast PM3 yielded pyramidality at nitrogen although *d*-functions are not considered in this approach. The search for a cis-structure (C_{2v}) of **1** yielded a local energy minimum in the ab initio as well as in the semi-empirical approach for the cis–cisoid–cis-**1** but not for the cis–transoid–cis-**1** configuration. Both local energy minima (cis and trans) have been confirmed by the calculated complete set of harmonic vibrational frequencies. Ab initio and semi-empirical calculations agree with respect to the energy difference between the cis–cisoid–cis-**1** and the lower energy trans-**1** form (2.3 and 2.5 kcal/mol, respectively). The planar arrangement (D_{2h}) of **1** corresponds to a stationary point with two imaginary frequencies; the respective vibrational modes are cis and trans distortions leading to the calculated local minima.

For **2** no local minimum could be found for a cis configuration using the semi-empirical method. The trans configuration is a local minimum as is indicated by real vibrational frequencies; the out-of-plane angle α_{PNX} turned out to be 11.3°. The atomic charges in Table 3 indicate the same pattern of charge distribution in both molecules **1** and **2**, with significantly positive charges at Cl/Si and C and excess negative charges at N and O.

SUMMARY

In the solid state **1** and **2** show approximate C_{2h} symmetry of the $(XNCO)_2$ fragments (X = Cl, Si). As we could see from the IR spectrum of a highly purified sample, some of the reported infrared bands for **1** [3] are due to impurities. In **1** and **2** the largest and smallest deviations from planarity of $(XNCO)_2$ fragments in 1,3-dichloro-1,3-diazetidine-2,4-diones ever determined in crystal structures were observed. Due to the low cis-trans energy gap calcu-


trans-**1**


cis–transoid–cis-**1**

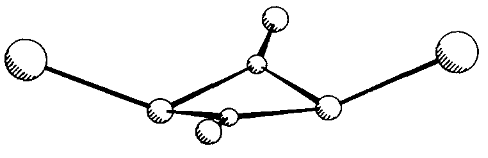

cis–cisoid–cis-**1**

TABLE 3 Atomic Charges for **1** and **2** (Negative sign means electron excess.)

	*SCF/3-21G**		*PM3*		
	trans-**1**	cis-**1**[a]	trans-**1**	cis-**1**[a]	trans-**2**
Cl/Si	0.242	0.254	0.128	0.133	0.581
N	−0.927	−0.926	−0.226	−0.229	−0.302
C	1.247	1.236	0.328	0.328	0.344
O	−0.562	−0.564	−0.231	−0.233	−0.328

[a] cis-1 = cis–cisoid–cis-**1**.

lated for **1**, the cis configuration might be present in the vapor phase and detectable by means of microwave spectroscopy or electron diffraction measurements.

EXPERIMENTAL

Preparation of 1,3-Dichloro-1,3-diazetidine-2,4-dione (**1**)

According to the literature [8, 9], the preparation of **1** was obtained by dimerization of ClNCO at −40°C and 1 atm. The crude product was sublimated at 50°C.

Preparation of 1,3-Bis(trimethylsilyl)-1,3-diazetidine-2,4-dione (**2**)

Similar to the silylation of $(ClNCO)_3$ [10], **1** was silylated by reaction with trimethylsilylcyanide: To 10 g of trimethylsilylcyanide, cooled to 10°C, 5 g of **1** was added in small portions (0.2 g). The temperature of the reaction mixture must be kept below 30°C. The clear yellow solution was cooled to 0°C and trimethylsilylcyanide and ClCN were removed under reduced pressure. Compound **2** was sublimated at 40–50°C and 0.1 torr. Yield: 3.6 g (48.5%) colorless crystals; mp 71°C. If the reaction is carried out in inert solvents (e.g., CH_2Cl_2, CCl_4) the yield is reduced to 2–5%. IR-spectrum (KBr): 3622 vw, 2969 w, 2906 vw, 2463 vw, 2150 vw, 2100 vw, 1741 vs, 1508 vw, 1418 m, 1322 vs, 1253 s, 987 s, 848 vs, 817 s, 761 m, 705 w, 675 s.

Chemical Properties of **2**

Compound **2** is a hydrophobic and slightly moisture sensitive substance. If **2** is added to water at 75°C a colorless solution is obtained, from which **2** is recrystallized when cooling below 70°C. By heating in boiling water (>10 minutes) ring opening and cleavage of the trimethylsilyl groups result in quantitative formation of urea and CO_2. This behavior agrees with the hydrolysis of

TABLE 4 Experimental Crystal Data, Data Collection, and Refinement Data for **1** and **2**

	1	**2**
Formula	$(ClNCO)_2$	$[(CH_3)_3SiNCO]_2$
Molecular weight	154.94	230.41
Crystal size [mm]	0.22 × 0.35 × 0.42	0.25 × 0.35 × 0.40
Temperature of measurements [K]	295	100
Diffractometer used	Modified STOE with NONIUS low-temp. equipment	
Radiation	Graphite-monochromatized MoKα λ = 0.71069 Å	
Space group	*Pbca*	*I2/a*
Cell dimensions: *a* [Å]	7.699(1)	20.257(2)
b [Å]	6.706(1)	6.416(1)
c [Å]	10.598(2)	21.260(3)
β [°]		101.29(1)
V [Å³]	547.2(2)	2709.7(6)
Reflections used for cell refinement	48	100
Z (number of formula units per cell)	4	8
Calculated density d_x [g/cm³]	1.881	1.130
Linear absorption coefficient μ [cm^{-1}]	10.9	2.4
Collection range	$h, k, \pm l$; $2\Theta \le 70°$	$\pm h, k, l$; $2\Theta \le 60°$
Scan type and range	ω-Scan; 1.2°	ω-Scan; 1.2°
Unique data measured	1204	3888
Observed data with $I > 3\sigma(I)$	666	2375
Solution and refinement method	Direct methods; full-matrix least squares	
Absorption correction	Empirical with DIFABS [13c]	
Extinction correction: no. of excluded refl.	6	0
Weighting scheme	$w = 1/\sigma^2(\lvert F_0 \rvert)$	$w = 1/\sigma^2(\lvert F_0 \rvert)$
No. of observations; no. of variables	660; 38	2375; 151
$R = \Sigma \lVert F_0 \rvert - \lvert F_c \rVert / \Sigma \lvert F_0 \rvert$	0.0314	0.0486
$R_w = [\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_0 \rvert^2]^{1/2}$	0.0282	0.0439
Max. height in final diff. Fourier map [eÅ^{-3}]	0.278	0.268

1,3-bis(trifluorosulfenyl)-1,3-diazetidine-2,4-dione [11, 12]. The reaction is catalyzed by addition of acids (HCl) or bases (NaOH). In 10% NH_3 solution ring opening and cleavage of the trimethylsilyl groups result in quantitative formation of biuret. Addition of **2** to liquid ammonia at −50°C results in a colorless solution, from which NH_4NCO is obtained after removing all volatile components under reduced pressure at 0°C. At room temperature, **2** is soluble in CCl_4, CH_2Cl_2, ether, or 1,4-dioxane without decomposition. In tetrahydrofuran and acetonitrile, **2** is immediately decomposed to form trimethylsilylisocyanate. This decomposition could also be obtained by heating **2** in 1,4-dioxane.

TABLE 5. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Coefficients (× 10^4 in Å^2) for **1** and **2**[a]

Atom	x/a	y/b	z/c	U_{iso}
Cl1	1116(1)	785(1)	2253(0)	443(3)
N1	173(2)	-128(2)	933(1)	310(7)
C1	1040(2)	-883(2)	-151(1)	336(8)
O1	2248(2)	-1908(2)	-334(1)	542(8)
O1	9588(1)	-480(3)	853(1)	344(12)
C1	9814(1)	-234(4)	383(1)	240(14)
N1	10384(1)	872(3)	260(1)	233(12)
Si1	11018(0)	2379(1)	748(0)	235(4)
C11	11626(2)	2989(6)	240(2)	474(21)
H111	12011	3950	523	801(72)
H112	11406	3801	-196	801(72)
H113	11846	1544	121	801(72)
C12	11364(2)	679(5)	1435(1)	365(17)
H121	11740	1508	1773	693(65)
H122	11587	-696	1270	693(65)
H123	10956	227	1664	693(65)
C13	10596(2)	4732(5)	977(2)	454(20)
H131	10935	5718	1303	756(72)
H132	10183	4259	1199	756(72)
H133	10401	5582	542	756(72)
O2	7842(1)	105(3)	3206(1)	374(12)
C2	7655(1)	1421(4)	2817(1)	243(14)
N2	7871(1)	2086(3)	2256(1)	230(12)
Si2	8487(0)	1303(1)	1811(0)	237(4)
C21	9305(1)	2493(6)	2178(2)	395(18)
H211	9695	1950	1937	637(64)
H212	9399	1911	2664	637(64)
H213	9303	4176	2185	637(64)
C22	8171(2)	2318(5)	993(1)	397(18)
H221	8517	1953	681	690(67)
H222	8126	3989	1029	690(67)
H223	7684	1658	798	690(67)
C23	8521(2)	-1573(5)	1858(2)	414(19)
H231	8905	-2052	1601	766(70)
H232	8051	-2322	1651	766(70)
H233	8668	-2016	2356	766(70)

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[a] The equivalent isotropic temperature factor U_{iso} is defined as one-third the trace of the orthogonalized U_{ij} tensor and has the form $T = \exp(-8\pi^2 U_{iso} \sin^2 \Theta/\lambda^2)$.

Crystal Structure Analyses

X-ray intensities were collected on a modified STOE 4-circle diffractometer with NONIUS low temperature equipment. Single crystals of **1** were sealed in a glass capillary, single crystals of **2** were immersed in oil and cooled quickly. The data collection and refinement data are summarized in Table 4. The nonhydrogen atoms were refined with anisotropic temperature factors, the methyl groups as rigid groups with common isotropic temperature factors of the hydrogen atoms, and C–H bond lengths fixed to 1.08 Å. Atomic coordinates are given in Table 5, computer programs used in lit. [13].

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