

Fig. 3. Specific interaction between the carboxyl group and the carbamoyl group. The asparagine side chains are not shown for clarity.

molecules corresponds to that which is sterically least favoured on the basis of population distribution studies (Bhat, Sasisekharan & Vijayan, 1979). The peptide link is essentially planar [ $\omega = -179.2(2)^\circ$  (molecule A) and  $-177.0(2)^\circ$  (molecule B)] and the N—C $\alpha$  bond has a partial double-bond character as in other peptide units.

The crystal structure is stabilized by extensive hydrogen bonding (Table 2, Fig. 2). The hydrogen bonds involving the ureido O atoms O(4) and O(8) are strong [O(1)···O(4) = 2.56 Å and O(8)···O(5) = 2.55 Å] as found in the crystal structure of *N*-carbamoyl-L-aspartic acid (Jagannatha Rao, Krishna Murthy, Appaji Rao & Vijayan, 1982). Normally

O···O hydrogen-bond distances in organic crystals are of the order of 2.72 Å (Kuleshova & Zorkii, 1981). Atoms O(3) and O(7) of the asparagine side chain accept two hydrogen bonds each. According to Kuleshova & Zorkii (1981), only 31 such cases (with a common acceptor for two hydrogen bonds) were observed among 2220 hydrogen bonds in organic homomolecular crystals examined by them. The terminal O and N atoms of the carbamoyl group are connected to the carboxyl group of a neighbouring molecule through a pair of nearly parallel hydrogen bonds in a head-to-tail fashion (Fig. 3).

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## Structure of 1-Methylsilatranone, $\text{CH}_3\text{Si}(\text{OCOCH}_2)(\text{OCH}_2\text{CH}_2)_2\text{N}$

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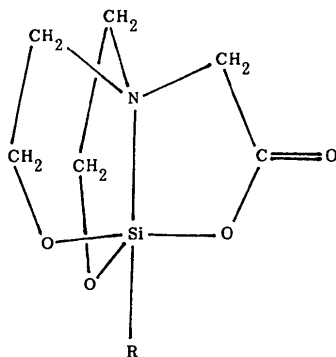
**Abstract.** 1-Methyl-2,8,9-trioxa-5-aza-1-silatricyclo-[3.3.3.0<sup>1,5</sup>]undecan-3-one,  $\text{C}_7\text{H}_{13}\text{NO}_4\text{Si}$ ,  $M_r = 203.27$ , monoclinic,  $P2_1/c$ ,  $a = 8.348(1)$ ,  $b = 10.931(1)$ ,  $c = 9.890(1)$  Å,  $\beta = 91.95(1)^\circ$ ,  $V = 902.0(3)$  Å<sup>3</sup>,  $Z$

$= 4$ ,  $D_x = 1.50$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 2.21$  mm<sup>-1</sup>,  $F(000) = 432$ ,  $T = 295(1)$  K, final  $R = 0.040$  for 1679 unique observed reflections. The structure of the title compound is compared with those of the analogous silatranes and silatranones bearing various substituents [*p*-F—C<sub>6</sub>H<sub>4</sub>—, *m*-CF<sub>3</sub>—C<sub>6</sub>H<sub>4</sub>—,

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$C_6H_5-$ ,  $Cl-CH_2-$ ,  $Cl-(CH_2)_3-$ , etc.] on the Si atom with the conclusion that the Si←N dative bonds are shortened (*i.e.* strengthened) by the C=O group entering into the silatrane skeleton. This observation is in good agreement with the CNDO/2 calculations performed on these related compounds. The observed Si←N distances for the title compound and the analogous 1-methylsilatrane [2.134 (1) vs 2.175 (4) Å] are accompanied by inversely proportional Wiberg [*Tetrahedron* (1968), **24**, 1083–1096] bond indices (0.403 vs 0.368).

**Introduction.** Crystal-structure determinations of silatranones (2,8,9-trioxa-5-aza-1-silatricyclo[3.3.3.0<sup>1,5</sup>]-undecan-3-ones) depicted by the general formula



where  $R = p-F-C_6H_4-$ ,  $m-CF_3-C_6H_4-$  (Párkányi, Hencsei & Popowski, 1980),  $\gamma-Cl-(CH_2)_3-$  (Dai, Zhang & Wu, 1983),  $Cl-CH_2-$  (Dai, Zhang, Wu & Wu, 1983) and  $C_6H_5-$  (Párkányi, Hencsei, Csonka & Kovács, 1987) have been reported so far. These structures enabled us to analyse the substituent effect upon the length (*i.e.* strength) of the dative Si←N bond. The shortest bond length was observed with the  $R = Cl-CH_2-$  substituent [2.085 (3) Å] while the others are clustered around the mean value of 2.126 (4) Å. Consequently, it was of primary importance to see how the Si←N bond distance developed in the presence of the simplest organic (alkyl) substituent:  $-CH_3$ . Since the crystal and molecular structures of the analogous 1-alkyl(aryl)silatrane have also been determined and scrutinized (Hencsei & Párkányi, 1985, and references therein), the effect of the C=O group entering into the silatrane skeleton upon the dative Si←N bond could also be estimated by the use of CNDO/2 calculations.

**Experimental.** The title compound was synthesized by the method published by Popowski, Michalik & Kelling (1975). Transparent prismatic crystal  $ca$  0.25 × 0.30 × 0.40 mm was mounted on a CAD-4 diffractometer equipped with a graphite monochromator using  $Cu K\alpha$  radiation. Lattice parameters were obtained by least-squares fit for 25 centred reflections in the range

$35 \leq \theta \leq 40^\circ$ . One quarter ( $0 \leq h \leq 10$ ,  $0 \leq k \leq 13$ ,  $-12 \leq l \leq 12$ ) of the independent reflections was measured in the range  $0.017 \leq (\sin\theta)/\lambda \leq 0.626 \text{ \AA}^{-1}$  with  $\omega/2\theta$  scan. Of 1951 observations 1777 were unique. The structure determination and refinement were based on 1679 reflections with  $I \geq 3.0\sigma(I)$ . 98 unobserved reflections. Three standard reflections (642, 472, 008) were measured every hour, but no intensity variation was detected. The structure was solved by direct methods (*MULTAN82*, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) using  $222 E \geq 1.52$ . Full-matrix least squares minimized the  $\sum w(\Delta F)^2$  function for 118 parameters. At the end of the isotropic refinement an empirical absorption correction was also carried out with the program *DIFABS* (Walker & Stuart, 1983); the relative transmission coefficients ranged from 0.769 to 1.339 (mean value 0.994). Positions of H atoms were generated from assumed geometries but not refined. They were only included in the final structure-factor calculations with a mean isotropic temperature factor [ $B_{iso}(H) = B_{iso}(C) + 1 \text{ \AA}^2$ ]. Final  $R = 0.040$ ,  $wR = 0.077$ ,  $R_{tot} = 0.043$ ,  $S = 1.86$ ,  $w = 4F_o^2/\sigma^2(F_o^2)$ ,  $(\Delta/\sigma)_{max} = 0.26$ . The highest peak in the final  $\Delta\rho$  map was 0.33 (6)  $e \text{ \AA}^{-3}$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Programs applied: Enraf-Nonius *SDP-Plus* (Frenz, 1983), *PLUTO* (Motherwell & Clegg, 1978) and local programs adapted to a PDP 11/34 minicomputer.

**Discussion.** The atomic coordinates of non-H atoms are in Table 1.\* The bond lengths and angles for non-H atoms are listed in Table 2. The molecular geometry of the title compound depicted in Fig. 1 resembles those of the analogous silatranones and silatranes (Hencsei & Párkányi, 1985). The Si←N bond length [2.134 (1) Å] falls in the range 2.106 (3) – 2.149 (5) Å formed – except for the 1-chloromethyl derivative (Dai, Zhang, Wu & Wu, 1983) – by the other silatranones. However, it is considerably shorter (by *ca* 10%) than 2.175 (4) Å measured in the related 1-methylsilatrane (Párkányi, Bihátsi & Hencsei, 1978). This is in accordance with the observations that the Si←N dative bonds in the related chloromethyl, chloropropyl and phenyl derivatives are also shorter than the corresponding distances in the analogous silatranes (Párkányi *et al.*, 1987). This shortening can be attributed to the electron-withdrawing effect of the carbonyl moiety of silatranones. Changes in the bonding of these compounds with respect to the corresponding silatranes have been estimated by CNDO/2 calculations carried

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44569 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for non-H atoms, with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> <sup>*</sup>
Si(1)	0.24191 (4)	0.10640 (3)	0.12716 (4)	2.22 (1)
O(2)	0.4109 (1)	0.1327 (1)	0.2279 (1)	2.56 (3)
C(3)	0.4882 (1)	0.0475 (1)	0.3005 (1)	2.55 (5)
C(4)	0.4163 (1)	-0.0788 (1)	0.2857 (1)	2.87 (5)
N(5)	0.2522 (1)	-0.0650 (1)	0.2304 (1)	2.29 (4)
C(6)	0.2078 (2)	-0.1550 (1)	0.1237 (1)	3.10 (5)
C(7)	0.2839 (2)	-0.1084 (1)	-0.0031 (2)	3.56 (7)
O(8)	0.2673 (1)	0.0206 (1)	-0.0087 (1)	3.39 (4)
O(9)	0.0672 (1)	0.1194 (1)	0.2006 (1)	3.09 (4)
C(10)	-0.0003 (2)	0.0245 (1)	0.2780 (2)	3.25 (6)
C(11)	0.1334 (2)	-0.0538 (1)	0.3374 (1)	3.14 (6)
O(12)	0.6066 (1)	0.0693 (1)	0.3686 (1)	3.90 (5)
C(13)	0.2415 (2)	0.2580 (1)	0.0416 (2)	3.56 (6)

\*  $B_{eq} = \frac{1}{3}$  trace (B.G) where G is the direct metric tensor.

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with their *e.s.d.*'s in parentheses

Si(1)—O(2)	1.723 (1)	C(4)—N(5)	1.466 (2)
Si(1)—N(5)	2.184 (1)	N(5)—C(6)	1.480 (2)
Si(1)—O(8)	1.658 (1)	N(5)—C(11)	1.479 (2)
Si(1)—O(9)	1.658 (1)	C(6)—C(7)	1.514 (3)
Si(1)—C(13)	1.861 (2)	C(7)—O(8)	1.418 (2)
O(2)—C(3)	1.330 (2)	O(9)—C(10)	1.417 (2)
C(3)—C(4)	1.511 (2)	C(10)—C(11)	1.510 (3)
C(3)—O(12)	1.201 (2)		
O(2)—Si(1)—N(5)	81.4 (1)	C(4)—C(3)—O(12)	123.5 (3)
O(2)—Si(1)—O(8)	116.0 (1)	C(3)—C(4)—N(5)	107.8 (2)
O(2)—Si(1)—O(9)	116.6 (1)	Si(1)—N(5)—C(4)	106.9 (2)
O(2)—Si(1)—C(13)	95.9 (1)	Si(1)—N(5)—C(6)	103.7 (2)
N(5)—Si(1)—O(8)	83.5 (1)	Si(1)—N(5)—C(11)	104.6 (2)
N(5)—Si(1)—O(9)	83.5 (1)	C(4)—N(5)—C(6)	113.9 (2)
N(5)—Si(1)—C(13)	177.4 (1)	C(4)—N(5)—C(11)	112.4 (2)
O(8)—Si(1)—O(9)	122.8 (1)	C(6)—N(5)—C(11)	114.0 (2)
O(8)—Si(1)—C(13)	97.7 (1)	N(5)—C(6)—C(7)	105.3 (2)
O(9)—Si(1)—C(13)	97.8 (1)	C(6)—C(7)—O(8)	108.9 (3)
Si(1)—O(2)—C(3)	124.6 (2)	Si(1)—O(8)—C(7)	123.1 (2)
O(2)—C(3)—C(4)	113.9 (2)	Si(1)—O(9)—C(10)	123.1 (2)
O(2)—C(3)—O(12)	122.6 (3)	O(9)—C(10)—C(11)	108.8 (3)
		N(5)—C(11)—C(10)	105.8 (2)

out for the title compound and 1-methylsilatrane as summarized in Table 3. As an effect of the C=O group entering into the silatrane skeleton the partial charges on Si, N, O and carbonyl C atoms change characteristically. The Wiberg (1968) index for the Si←N bond is increased considerably from 0.368 to 0.403. A somewhat smaller increase of the Wiberg (1968) bond index was obtained for the Si—O bonds in the carbonyl-free five-membered rings, which is accompanied by a drastic decrease (from 1.178 to 1.059) for the Si—O bond conjugated with the C=O moiety. Since the structure of 1-methylsilatrane dione [CH<sub>3</sub>Si(OCOCH<sub>2</sub>)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N] is also known from the literature (Kemme, Bleidelis, Lapsina, Fleisher, Zelčans & Lukevics, 1985), the CNDO/2 calculations were also extended to its bonding. The Wiberg (1968) index for its Si←N bond is practically the same as for the title compound in accordance with the similar Si←N bond distance of 2.146 (7) Å, if the 3σ criteria are taken into account. The higher *e.s.d.*'s for this structure do not

Table 3. Bond lengths, net atomic charges and Wiberg (1968) bond indices in 1-methylsilatrane derivatives CH<sub>3</sub>Si(OCOCH<sub>2</sub>)<sub>n</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3-n</sub>N

	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2*
Bond lengths ( $\text{\AA}$ )			
Si←N	2.175 (4)	2.134 (1)	2.146 (7)
Si—O(C=O)	—	1.723 (1)	1.701 (6)†
Si—O(CH <sub>2</sub> )	1.670 (4)†	1.658 (1)†	1.656 (6)
O—C(=O)	—	1.330 (2)	1.33 (1)†
O—C	1.425 (7)†	1.418 (2)†	1.40 (1)
Si—C	1.870 (6)	1.861 (2)	1.84 (1)
Net atomic charges			
Si	0.4828	0.4897	0.5060
O(C=O)	—	-0.3219	-0.3180†
O	-0.3013†	-0.2995†	-0.2932
C(=O)	—	0.4087	0.4140†
N	-0.0903	-0.0857	-0.0842
Wiberg (1968) bond indices			
Si←N	0.368	0.403	0.404
Si—O(C=O)	—	1.059	1.107†
Si—O(CH <sub>2</sub> )	1.178†	1.203†	1.195
Si—C	1.112	1.110	1.129

\* *n* = 0: Párkányi *et al* (1978), *n* = 1: present work, *n* = 2: Kemme *et al.* (1985).

† Mean values.

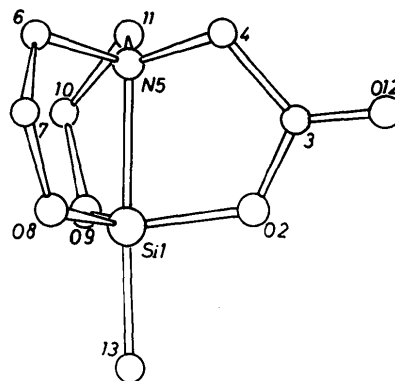


Fig. 1. Perspective view of the molecular structure with atomic labelling. Numbers denote C atoms unless indicated otherwise. The H atoms are deliberately omitted.

permit any deeper comparison. It is worth noting, however, that the second carbonyl group does not considerably alter the bonding of 1-methylsilatrane dione in contrast with its primary effect on the title compound relative to 1-methylsilatrane.

Other features of the title compound are similar to those of the 'parent' silatrane molecule. While the distance of Si from the plane of the equatorial O atoms ( $\Delta$ Si) is increased relative to the expected value [0.209 (1) *vs* 0.178 Å] inferred from a correlation found between  $\Delta$ Si and Si←N values (Hencsei & Párkányi, 1985), the distance of N from the plane of its adjoining three C atoms ( $\Delta$ N) and the mean  $\alpha$ (NSiO) angle are not affected by the presence of the C=O group (Table 4). The out-of-plane positions of the  $\alpha$ -C atoms (relative to N) from the best plane of the

Table 4. *Calculated (Hencsei & Párkányi, 1985) molecular parameters (Si–N),  $\Delta$ Si,  $\Delta$ N and  $\alpha$ (NSiO) for the title compound compared with the corresponding experimental data*

	Calculated	Observed
Si–N	2.172 Å	2.134 (1) Å
$\Delta$ Si	0.178	0.209 (1)
$\Delta$ N	0.380	0.384 (1)
$\alpha$ (NSiO)	83.8°	82.8 (1)°

Si,O,C,N moiety are similar in dimensions and direction [ $\Delta$ C(4): 0.380 (2),  $\Delta$ C(6): 0.557 (2),  $\Delta$ C(11): 0.494 (2) Å].

It can be concluded that in contrast with the silatranes (Hencsei & Párkányi, 1985) where Si–N bond lengths can be correlated with the character of the R substituents, in silatranones the effect of the C=O group on their bonding weakens the direct influence of the R substituents. This is substantiated by the structure determination of the title compound with R = CH<sub>3</sub>, the Si–N distance of which falls in the middle of the range observed for the known silatranone structures.

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## Structure of *tert*-Butylhydrazine Hydrochloride

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**Abstract.** C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>·HCl,  $M_r = 124.613$ , orthorhombic, *Pbca*,  $a = 9.878$  (4),  $b = 10.638$  (1),  $c = 13.751$  (2) Å,  $V = 1444.98$  (6) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.125$  (9),  $D_x = 1.145$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54180$  Å,  $\mu(\text{Cu}) = 39.342$  cm<sup>-1</sup>,  $F(000) = 544$ ,  $T = 293$  K,  $R = 0.048$  for 956 observed reflections. The structure consists of symmetry-related [(CH<sub>3</sub>)<sub>3</sub>C(NH)(NH<sub>2</sub>)] and HCl moieties arranged in a chain structure on the *yz* plane. (CH<sub>3</sub>)<sub>3</sub>C and (NH)(NH<sub>2</sub>) are coordinated by a C–N bond. The coordination around the C bonding to C atoms of (CH<sub>3</sub>)<sub>3</sub> is a slightly distorted tetrahedron. Hydrogen bonds contribute significant stabilizing force in holding the molecule in a stable crystalline state.

**Introduction.** The title compound is of chemical importance as it is used to determine some organic compounds (e.g. aldehydes) in certain organic reactions. Its crystal and molecular structures are therefore described here.

**Experimental.** Prismatic colourless crystals were obtained by slow evaporation of an aqueous solution of [(CH<sub>3</sub>)<sub>3</sub>C(NH)(NH<sub>2</sub>)]·HCl at room temperature for a week. Experimental data and structure refinement procedures are listed in Table 1. The H atoms were located on difference Fourier maps and a riding model was used in the refinement of H positions.

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