located on a difference electron-density map and the remainder placed in calculated positions (Fayos & Martinez-Ripoll, 1980). A convenient weighting scheme of type $w = w_1 \times w_2$ with $w_1 = k/(a + b|F_o|)^2$ and $w_2 = 1/\{c + d[(\sin\theta)/\lambda] + e[(\sin\theta)/\lambda]^2\}$, was used in order to obtain flat dependence in $\langle w \times \Delta^2F\rangle$ *vs* $\langle F_o\rangle$ and *vs* $\langle(\sin\theta)/\lambda\rangle$ (Martinez-Ripoll & Cano, 1980). A final weighted anisotropic full-matrix refinement (fixed isotropic contribution for H atoms) gave the discrepancy indices: $R = 0{\cdot}069$ and $wR = 0{\cdot}077$. 136 parameters, $S = 1{\cdot}3$, maximum electron density in final difference map 0·20 e Å^{-3}, maximum Δ/σ 0·003. Scattering factors from *International Tables for X-ray Crystallography* (1974); geometrical calculations using *PARST* (Nardelli, 1983).

Discussion. Final positional parameters are reported in Table 1.* The molecular structure of the title compound including the atom-numbering scheme is illustrated in Fig. 1. Bond distances, bond angles and relevant torsion angles are shown in Table 2.

The six-membered ring C1, C2, C3, C4, C5, C6 is in a distorted chair conformation flattened at C3. Atoms C3 and C6 are displaced by −0·440 (3) and 0·889 (3) Å on opposite sides of the plane containing C2, C3, C4, C5. The ring flattening is also evidenced by the values of torsion angles C1—C2—C3—C4 (−40·9°) and C2—C3—C4—C5 (39·8°) compared with C2—C1—C6—C5 (−76·9°) and C5—C6—C1—C2 (71·8°). The five-membered ring has a twist conformation with the twofold axis of symmetry bisecting the bond between the two out-of-plane atoms (C5—C6) (see Table 2).

Table 3. *Geometry of the hydrogen bonds*

X—H···*Y*	*X*—H (Å)	*X*···*Y* (Å)	H···*Y* (Å)	*X*—H···*Y* (°)
O2—H2···O3^{i}	1·004 (2)	2·781 (3)	1·975 (3)	135·5 (1)
O4—H4···O2^{ii}	0·940 (2)	2·624 (3)	1·697 (2)	168·0 (2)

Symmetry-equivalent positions of the acceptor atoms: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Fig. 2 gives a representation of the hydrogen-bonding scheme around the $\bar{1}$ along the *a* axis; donor–acceptor distances are listed in Table 3. Each molecule is involved in four H bonds of the type O—H···O. The strongest interaction is O4—H4···O2 $(-x, y - 1/2, -z + 1/2)$ with O···O donor–acceptor distance of 2·624 (3) Å.

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Structures of Sila Analogues of Cyclic Nucleotides

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Abstract. (I) $C_{18}H_{29}N_5O_4Si$, 3′,5′-*O*-(di-*tert*-butylsilanediyl)adenosine, $M_r = 407{\cdot}6$, monoclinic, $P2_1$, $a = 9{\cdot}750\ (2)$, $b = 8{\cdot}373\ (2)$, $c = 13{\cdot}157\ (3)$ Å, $\beta = 104{\cdot}93\ (2)°$, $V = 1037{\cdot}8\ (3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 1{\cdot}188$ mm^{-1}, $F(000) = 436$, $T = 295$ K, $R = 0{\cdot}049$ for 1685 independent reflections $[I_o > 2\sigma(I_o)]$. The furanose ring is in the twist form, the six-membered silyl ring is in a flattened chair conformation and the glycosidic bond conformation is *anti*. (II)

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$C_{18}H_{29}N_5O_3Si.H_2O$, 3′,5′-*O*-(di-*tert*-butylsilanediyl)-2′-deoxyadenosine monohydrate, $M_r = 409{\cdot}6$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}434\,(1)$, $b = 9{\cdot}490\,(1)$, $c = 26{\cdot}897\,(4)$ Å, $V = 2152{\cdot}8\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 1{\cdot}146$ mm^{-1}, $F(000) = 880$, $T = 295$ K, $R = 0{\cdot}042$ for 1985 independent reflections $[I_o > 2\sigma(I_o)]$. The furanose ring is in the envelope form, the six-membered silyl ring is in a flattened chair conformation and the glycosidic bond conformation is *syn*.

Introduction. Silyl derivatives of nucleosides are very interesting compounds in the field of synthetic chemistry of nucleic acids; especially their use for preparing protected monomers in nucleic acid synthesis.

We have found a very simple and effective method for preparing 3′,5′-*O*-silanediylnucleosides by using a bifunctional silyl reagent; treatment of nucleosides with highly reactive di-*tert*-butylsilyl diesters in *N*,*N*-dimethylformamide gave sila analogues of cyclic nucleotides which have a rigid *trans*(1,2)-fused six- to five-membered ring system (Furusawa, Ueno & Katsura, 1990). In these analogues, an Si atom occupies a position where a P atom usually lies in the cyclic nucleotides.

In the present work, we report the crystal structures of 3′,5′-*O*-(di-*tert*-butylsilanediyl)adenosine (I) and 3′,5′-*O*-(di-*tert*-butylsilanediyl)-2′-deoxyadenosine monohydrate (II).

Experimental. The compounds (I) and (II) were synthesized from corresponding nucleosides (Furusawa, Ueno & Katsura, 1990). Colorless prismatic crystals of (I) and (II) by slow evaporation of chloroform solutions. Crystals of (I) with dimensions $0{\cdot}33 \times 0{\cdot}20 \times 0{\cdot}11$ mm and of (II) with dimensions $0{\cdot}51 \times 0{\cdot}22 \times 0{\cdot}05$ mm used for X-ray measurement, Nicolet *P*3/*F* diffractometer with graphite-monochromated Cu $K\alpha$ radiation, lattice parameters from least-squares refinement of 2θ values of 24 reflections [$8 < \theta < 18°$ for (I), and $8 < \theta < 19°$ for (II)], θ–2θ scan, scan speed 4° min^{-1}, scan width $(1{\cdot}2 + 0{\cdot}45\tan\theta)°$, background 10 s at each end of scan, $2\theta_{\max} = 151°$, *hkl* range 0–12, 0–9, −16–15 (I) and 0–9, 0–12, 0–34 (II), three standard reflections measured every 200 reflections showed no significant decay, 1847 independent reflections measured of which 1685 with $I_o > 2\sigma(I_o)$ for (I), 2211 independent reflections measured of which 1985 with $I_o > 2\sigma(I_o)$ for (II), no correction for absorption. Structures were solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least-squares analysis on *F* with *SHELX*76 (Sheldrick, 1976), H atoms of N(C6), O(C2′) and water molecules were located in difference Fourier maps and included in refinement, others were located at calculated positions and not refined. Final $R = 0{\cdot}049$, $wR = 0{\cdot}058$ with $w^{-1} = \sigma^2(F_o) + 0{\cdot}0065(F_o)^2$, $S = 1{\cdot}24$, $(\Delta/\sigma)_{\max} = 0{\cdot}29$ for non-H atoms, $(\Delta\rho)_{\max} = 0{\cdot}29$ e Å^{-3} for (I), $R = 0{\cdot}042$, $wR = 0{\cdot}051$ with $w^{-1} = \sigma^2(F_o) + 0{\cdot}0031(F_o)^2$, $S = 1{\cdot}30$, $(\Delta/\sigma)_{\max} = 0{\cdot}47$ for non-H atoms, $(\Delta\rho)_{\max} = 0{\cdot}25$ e Å^{-3} for (II).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (I)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
N(1)	0·8914 (4)	0·2365 (7)	0·3881 (3)	3·23 (11)
C(2)	0·8213 (6)	0·1953 (7)	0·2902 (3)	3·61 (12)
N(3)	0·7640 (5)	0·2885 (6)	0·2077 (3)	3·17 (11)
C(4)	0·7864 (4)	0·4418 (7)	0·2329 (3)	2·71 (11)
C(5)	0·8528 (4)	0·5048 (7)	0·3309 (3)	2·75 (11)
C(6)	0·9075 (4)	0·3948 (7)	0·4125 (3)	2·84 (11)
N(7)	0·8556 (4)	0·6702 (6)	0·3279 (3)	2·81 (10)
C(8)	0·7921 (5)	0·7050 (7)	0·2288 (3)	3·01 (11)
N(9)	0·7476 (4)	0·5724 (6)	0·1683 (2)	2·68 (10)
N(C6)	0·9753 (4)	0·4353 (7)	0·5114 (3)	3·36 (10)
C(1′)	0·7045 (4)	0·5677 (7)	0·0539 (3)	3·05 (11)
C(2′)	0·5940 (4)	0·6889 (7)	−0·0036 (3)	3·07 (11)
C(3′)	0·6818 (4)	0·7929 (7)	−0·0593 (3)	2·68 (10)
C(4′)	0·7900 (4)	0·6742 (7)	−0·0777 (3)	3·04 (11)
C(5′)	0·9139 (5)	0·7544 (8)	−0·1047 (4)	4·13 (12)
O(2′)	0·4855 (3)	0·6034 (6)	−0·0737 (2)	3·27 (10)
O(3′)	0·6046 (3)	0·8647 (6)	−0·1533 (2)	2·95 (9)
O(4′)	0·8302 (3)	0·5868 (6)	0·0184 (2)	3·82 (10)
O(5′)	0·8613 (3)	0·8618 (6)	−0·1892 (3)	3·62 (10)
Si	0·69968 (11)	0·93249	−0·23292 (7)	2·74 (4)
C(*tB*1)	0·7118 (5)	1·1556 (7)	−0·2185 (4)	3·65 (12)
C(*tB*2)	0·7639 (8)	1·1906 (9)	−0·0981 (5)	5·75 (14)
C(*tB*3)	0·5663 (6)	1·2389 (9)	−0·2559 (5)	5·12 (13)
C(*tB*4)	0·8178 (8)	1·2300 (10)	−0·2696 (6)	8·22 (14)
C(*tB*5)	0·6213 (6)	0·8475 (8)	−0·3680 (3)	4·17 (12)
C(*tB*6)	0·6879 (6)	0·9297 (13)	−0·4483 (4)	7·50 (13)
C(*tB*7)	0·4622 (5)	0·8756 (10)	−0·4020 (4)	5·56 (13)
C(*tB*8)	0·6497 (10)	0·6726 (10)	−0·3648 (6)	8·48 (14)

The *y* coordinate of Si was fixed to define the origin.

Final atomic coordinates for non-H atoms are given in Tables 1 and 2.* Bond lengths and bond angles are given in Tables 3 and 4 respectively. Figs. 1 and 2 are *ORTEP* drawings (Johnson, 1965) of compounds (I) and (II) showing crystallographic atom numbering. Molecular packing arrangements of (I) and (II) in the crystal are shown in Figs. 3 and 4 respectively.

Discussion. The bond lengths and bond angles in the adenine and furanose rings of (I) and (II) are in good agreement with the values found in cyclic AMP (Varughese, Lu & Kartha, 1982). The ring C—O bond distances, C(1′)—O(4′) and C(4′)—O(4′), are equal within experimental error for both molecules, as is found to be the case for the 3′,5′-cyclic nucleo-

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen bonding have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52727 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (II)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
N(1)	0·5655 (4)	0·7570 (3)	0·05783 (10)	3·33 (11)
C(2)	0·5282 (4)	0·7499 (4)	0·10563 (13)	3·44 (12)
N(3)	0·6211 (3)	0·7301 (3)	0·14542 (9)	3·10 (10)
C(4)	0·7749 (4)	0·7174 (3)	0·13102 (11)	2·68 (11)
C(5)	0·8305 (4)	0·7224 (4)	0·08292 (11)	2·90 (12)
C(6)	0·7208 (4)	0·7446 (4)	0·04440 (11)	2·91 (11)
N(7)	0·9946 (3)	0·7069 (4)	0·08200 (10)	3·59 (11)
C(8)	1·0315 (4)	0·6910 (5)	0·12876 (12)	3·50 (12)
N(9)	0·9042 (3)	0·6980 (3)	0·16069 (8)	3·00 (10)
N(C6)	0·7564 (4)	0·7542 (4)	−0·00315 (11)	4·01 (11)
C(1′)	0·9176 (4)	0·6913 (4)	0·21434 (11)	3·21 (11)
C(2′)	0·8345 (5)	0·8118 (4)	0·24298 (12)	3·66 (13)
C(3′)	0·7104 (4)	0·7316 (3)	0·27368 (11)	2·83 (11)
C(4′)	0·7886 (5)	0·5906 (4)	0·27960 (12)	3·17 (12)
C(5′)	0·6757 (6)	0·4794 (4)	0·29890 (13)	4·11 (14)
O(3′)	0·6744 (3)	0·7942 (3)	0·32048 (8)	3·63 (9)
O(4′)	0·8486 (4)	0·5610 (3)	0·23081 (8)	3·70 (10)
O(5′)	0·6186 (4)	0·5283 (3)	0·34511 (9)	4·24 (11)
Si	0·59092 (12)	0·69150 (11)	0·36374 (3)	3·05 (3)
C(*tB*1)	0·3696 (5)	0·7217 (4)	0·36630 (14)	3·88 (13)
C(*tB*2)	0·3242 (7)	0·8634 (5)	0·3873 (2)	7·32 (17)
C(*tB*3)	0·2913 (7)	0·6052 (6)	0·3954 (2)	8·25 (18)
C(*tB*4)	0·3080 (6)	0·7181 (8)	0·3139 (2)	8·81 (18)
C(*tB*5)	0·7037 (6)	0·7219 (6)	0·42289 (14)	5·43 (15)
C(*tB*6)	0·8691 (7)	0·6705 (10)	0·4156 (2)	12·36 (19)
C(*tB*7)	0·6332 (9)	0·6379 (7)	0·4661 (2)	8·24 (18)
C(*tB*8)	0·7040 (10)	0·8793 (7)	0·4376 (2)	9·90 (19)
O(*W*)	0·3477 (4)	0·5931 (3)	0·19587 (12)	4·79 (12)

Table 3. *Interatomic bond distances* (Å)

	(I)	(II)		(I)	(II)
N(1)—C(2)	1·339 (7)	1·325 (5)	C(3′)—C(4′)	1·514 (6)	1·500 (5)
N(1)—C(6)	1·363 (6)	1·364 (4)	C(3′)—O(3′)	1·407 (6)	1·425 (4)
C(2)—N(3)	1·336 (7)	1·340 (5)	C(4′)—C(5′)	1·502 (7)	1·514 (5)
N(3)—C(4)	1·330 (7)	1·359 (4)	C(4′)—O(4′)	1·426 (6)	1·434 (4)
C(4)—C(5)	1·389 (7)	1·377 (5)	C(5′)—O(5′)	1·419 (6)	1·411 (5)
C(4)—N(9)	1·377 (6)	1·364 (4)	O(3′)—Si	1·667 (4)	1·673 (3)
C(5)—C(6)	1·410 (6)	1·404 (5)	O(5′)—Si	1·642 (4)	1·645 (3)
C(5)—N(7)	1·386 (6)	1·392 (4)	Si—C(*tB*1)	1·878 (6)	1·890 (4)
C(6)—N(C6)	1·342 (6)	1·314 (5)	Si—C(*tB*5)	1·884 (6)	1·876 (5)
N(7)—C(8)	1·323 (6)	1·304 (5)	C(*tB*1)—C(*tB*2)	1·562 (9)	1·507 (7)
C(8)—N(9)	1·370 (6)	1·377 (5)	C(*tB*1)—C(*tB*3)	1·543 (8)	1·507 (7)
N(9)—C(1′)	1·456 (6)	1·449 (4)	C(*tB*1)—C(*tB*4)	1·505 (10)	1·504 (7)
C(1′)—C(2′)	1·531 (7)	1·547 (5)	C(*tB*5)—C(*tB*6)	1·538 (9)	1·491 (8)
C(1′)—O(4′)	1·428 (6)	1·437 (4)	C(*tB*5)—C(*tB*7)	1·518 (8)	1·530 (8)
C(2′)—C(3′)	1·533 (7)	1·535 (5)	C(*tB*5)—C(*tB*8)	1·489 (11)	1·546 (8)
C(2′)—O(2′)	1·406 (6)	—			

Table 4. *Bond angles* (°)

	(I)	(II)
C(2)—N(1)—C(6)	118·4 (4)	118·7 (3)
N(1)—C(2)—N(3)	129·4 (5)	130·0 (3)
C(2)—N(3)—C(4)	110·7 (4)	110·1 (3)
N(3)—C(4)—C(5)	127·3 (4)	126·1 (3)
N(3)—C(4)—N(9)	127·7 (4)	127·5 (3)
C(5)—C(4)—N(9)	105·1 (4)	106·4 (3)
C(4)—C(5)—C(6)	116·9 (4)	118·3 (3)
C(4)—C(5)—N(7)	111·1 (4)	110·6 (3)
C(6)—C(5)—N(7)	132·0 (4)	131·1 (3)
N(1)—C(6)—C(5)	117·3 (4)	116·7 (3)
N(1)—C(6)—N(C6)	118·1 (4)	118·1 (3)
C(5)—C(6)—N(C6)	124·6 (4)	125·2 (3)
C(5)—N(7)—C(8)	104·0 (4)	103·4 (3)
N(7)—C(8)—N(9)	113·1 (4)	114·2 (3)
C(4)—N(9)—C(8)	106·8 (4)	105·4 (3)
C(4)—N(9)—C(1′)	125·3 (4)	130·7 (3)
C(8)—N(9)—C(1′)	125·9 (4)	123·9 (3)
N(9)—C(1′)—C(2′)	118·2 (4)	115·3 (3)
N(9)—C(1′)—O(4′)	107·0 (4)	108·3 (3)
C(2′)—C(1′)—O(4′)	108·6 (4)	107·4 (3)
C(1′)—C(2′)—C(3′)	101·8 (4)	102·1 (3)
C(1′)—C(2′)—O(2′)	107·6 (4)	—
C(3′)—C(2′)—O(2′)	113·2 (4)	—
C(2′)—C(3′)—C(4′)	101·6 (4)	101·5 (3)
C(2′)—C(3′)—O(3′)	115·2 (4)	114·5 (3)
C(4′)—C(3′)—O(3′)	112·1 (4)	111·8 (3)
C(3′)—C(4′)—C(5′)	112·4 (4)	112·5 (3)
C(3′)—C(4′)—O(4′)	103·8 (4)	103·5 (3)
C(5′)—C(4′)—O(4′)	112·6 (4)	113·5 (3)
C(4′)—C(5′)—O(5′)	108·5 (4)	106·7 (3)
C(3′)—O(3′)—Si	116·1 (3)	117·5 (2)
C(1′)—O(4′)—C(4′)	106·5 (4)	104·9 (3)
C(5′)—O(5′)—Si	128·6 (3)	128·8 (2)
O(3′)—Si—O(5′)	107·2 (2)	106·1 (1)
O(3′)—Si—C(*tB*1)	107·8 (2)	110·7 (2)
O(5′)—Si—C(*tB*1)	107·1 (2)	107·1 (2)
O(3′)—Si—C(*tB*5)	107·9 (2)	106·7 (2)
O(5′)—Si—C(*tB*5)	108·3 (2)	109·4 (2)
C(*tB*1)—Si—C(*tB*5)	118·1 (3)	116·5 (2)
Si—C(*tB*1)—C(*tB*2)	106·5 (4)	113·6 (3)
Si—C(*tB*1)—C(*tB*3)	112·9 (4)	109·9 (3)
C(*tB*2)—C(*tB*1)—C(*tB*3)	105·7 (5)	110·4 (4)
Si—C(*tB*1)—C(*tB*4)	113·5 (5)	107·7 (3)
C(*tB*2)—C(*tB*1)—C(*tB*4)	107·1 (5)	106·5 (4)
C(*tB*3)—C(*tB*1)—C(*tB*4)	110·6 (5)	108·6 (4)
Si—C(*tB*5)—C(*tB*6)	109·8 (4)	108·2 (4)
Si—C(*tB*5)—C(*tB*7)	110·8 (4)	111·5 (4)
C(*tB*6)—C(*tB*5)—C(*tB*7)	108·0 (5)	107·0 (5)
Si—C(*tB*5)—C(*tB*8)	108·5 (5)	111·5 (4)
C(*tB*6)—C(*tB*5)—C(*tB*8)	110·6 (6)	110·4 (5)
C(*tB*7)—C(*tB*5)—C(*tB*8)	109·2 (6)	108·0 (4)

tides (Chwang & Sundaralingham, 1974). The Si—C distances have usual values (Yamazaki, Hamada, Yamagata, Fujiwara & Tomita, 1982). As for the Si—O bond distances, Si—O(3′) is longer than Si—O(5′) for both molecules, as is found in compounds having a cyclic disiloxane skeleton (Verdegaal, de Kok, Westerink, van Boom & Romers, 1981; Yamazaki, Hamada, Yamagata, Fujiwara & Tomita, 1982; Robins, Wilson, Sawyer & James, 1983).

The molecular structures of (I) and (II) are very similar to each other, except for the glycosidic bond conformation (Figs. 1 and 2). The glycosyl torsional angle χ[C(8)—N(9)—C(1′)—O(4′)] (Sundaralingam, 1969) is 71·8 (8)° in (I), corresponding to the *anti* conformation and 248·2 (6)° in (II), corresponding to the *syn* conformation.

The 3′,5′-cyclization restricts the conformation of the furanose ring; the ribose ring of (I) is in the twist form, $_4T^3$ [C(4′)-*exo*,C(3′)-*endo*], and the deoxyribose ring of (II) is in the envelope form, $_4E$ [C(4′)-*exo*], which is adjacent to $_4T^3$ in the pseudorotation pathway. The pseudorotation (Altona & Sundaralingam, 1972) phase angle P and the maximum amplitude of puckering τ_m for the furanose ring of (I) are 43·4 and 41·7°, and those of (II) are 52·2 and 45·2°, respectively.

The existence of an inter-relationship between the glycosyl torsional angle χ and the sugar pucker have been pointed out for nucleosides and nucleotides (Arnot & Hukins, 1969; Sarma, Lee, Evans, Yathindra & Sundaralingam, 1974; Kitamura, Wakahara, Mizuno, Baba & Tomita, 1981). In the case of 3′,5′-cyclic nucleotides, both *syn* and *anti* conformations are found in cyclic AMP crystal structures (Watenpaugh, Dow, Jensen & Furberg, 1968) although energy calculations show a conformational preference for *anti* over *syn* (Yathindra & Sundaralingam, 1974). It should be noted that *syn* conformations are accompanied by higher values of the pseudorotation phase angle P, both in cyclic AMP and in our case.

The six-membered rings are in the chair conformation and are remarkably flattened at the silicon end, probably because the Si—O bonds are longer than the other bonds in the ring.

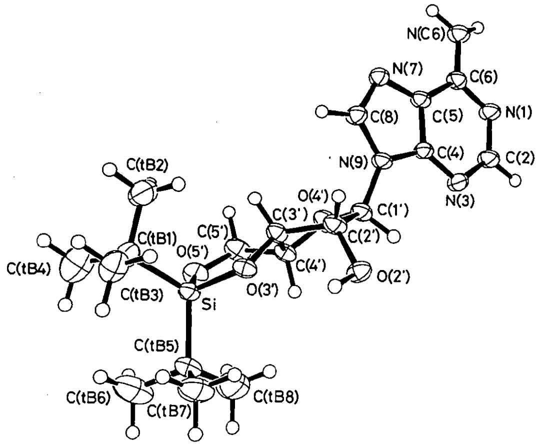

Fig. 1. *ORTEP* drawing of (I), with the atomic numbering.

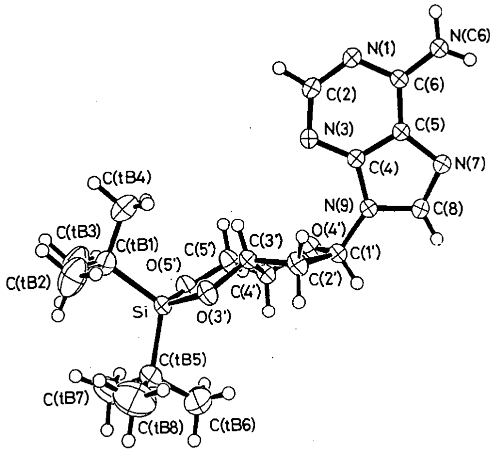

Fig. 2. *ORTEP* drawing of (II), with the atomic numbering.

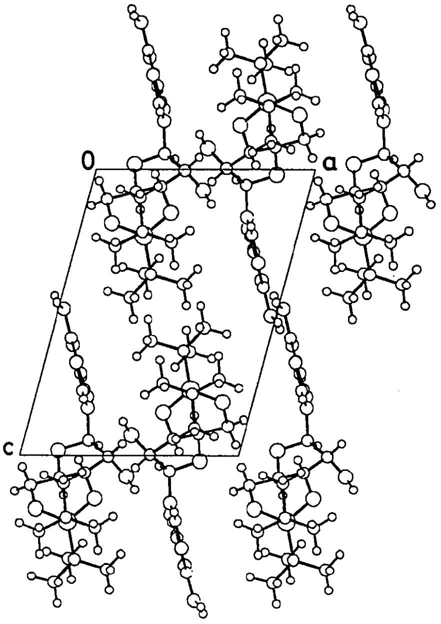

Fig. 3. The molecular packing of (I) viewed down **b**.

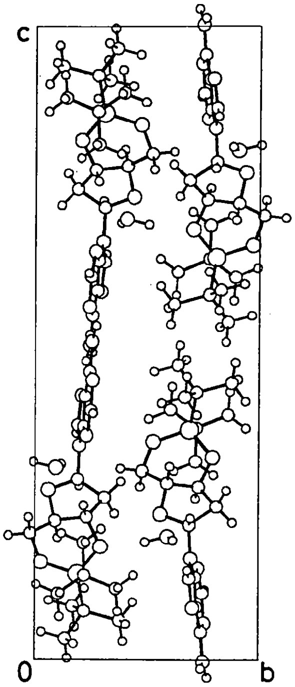

Fig. 4. The molecular packing of (II) viewed down **a**.

The molecular packing in the crystals of (I) and (II) is also very similar (Figs. 3 and 4). Three intermolecular H bonds connect the (I) molecules, whereas four H bonds link the (II) molecules; the

N(C6) amino group is H bonded to N(1) and N(7) of the adjacent molecules in both (I) and (II), to form ribbons along 2_1 axes. These ribbons are connected by H bonds O(2′)—N(3) in (I), and O(*W*)—N(3) and O(*W*)—O(3′) in (II).

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Structure of Tetramethylammonium Hydrogen Phthalate

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Abstract. *N*,*N*,*N*,-Trimethylmethanaminium 1,2-benzenedicarboxylate, $C_4H_{12}N^+.C_8H_5O_4^-$, M_r = 239·3, monoclinic, $P2_1/c$, a = 12·960 (4), b = 8·591 (2), c = 11·384 (2) Å, β = 94·55 (3)°, V = 1263·5 Å^3, Z = 4, D_x = 1·258 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·09 mm^{-1}, $F(000)$ = 512, room temperature (295 K), wR = 0·040 for 1195 observed reflections. The phthalate anions form infinite chains along [001] *via* a strong intermolecular hydrogen bond [O···O distance 2·555 (4) Å]. There are (100) layers of anions and cations. The tetramethylammonium ion has the usual tetrahedral configuration.

Introduction. As part of a study of acid salts of phthalic acid, new examples of compounds with intramolecular hydrogen bonds were sought. IR spectroscopic investigations of the title compound (Barry, Finkelstein & Ross, 1982; Barry, Finkelstein, Ross, Mateescu, Valeriu & Svensson, 1988) suggested the presence of an asymmetric hydrogen bond. In order to confirm this result and to distinguish between an intermolecular and an intramolecular bond, this X-ray structure analysis was undertaken.

Experimental. The material was synthesized from a stoichiometric solution of tetramethylammonium hydroxide and phthalic acid in methanol (Barry, Finkelstein & Ross, 1982). The crystals were commonly twinned, as seen in (*h*0*l*) and (*h*1*l*) Weissenberg photographs. No twinning was visible in the (*hk*0) plane. An (*h*0*l*) precession photograph clearly showed that the twin plane was (100). From these X-ray photographs, the space group was unambiguously determined as $P2_1/c$. The structure was determined on an untwinned splinter. Its quality was checked with optical polarizing microscopy and Weissenberg photographs. Since this substance is moisture sensitive, it was necessary to place the crystal (0·1 × 0·3 × 0·5 mm) in a sealed capillary. Lattice parameters were refined using 20 reflections in the range $34 < 2\theta < 44°$. The intensities of 4083 reflections were collected on a Siemens–Stoe AED-2 diffractometer in the $\theta/2\theta$ mode, no absorption correction was applied due to the small absorption coefficient. The maximum ($\sin\theta/\lambda$) was 0·704 Å^{-1}; range of h, k, l was −18/18, 0/12, 0/16. Standard reflections $43\bar{2}$, $2\bar{1}3$ and $3\bar{1}\bar{4}$, monitored every hour, showed no significant variation. 2750 reflections were