S(3)—O(34)—C(34)—C(33)	96.2 (2)
S(3)—O(34)—C(34)—C(35)	−145.7 (2)
S(4)—C(36)—C(35)—O(35)	82.0 (2)
S(4)—C(36)—C(35)—C(34)	−159.6 (2)

The data collection was extended to include the measurement of the intensities of the Friedel opposites of all reflections in the unique octant with $2\theta < 50°$. Friedel pairs were not averaged during the data reduction so that the effects of anomalous dispersion could be used for the determination of the absolute configuration.

The displacement ellipsoids for one of the benzoyl groups indicate the presence of slight disorder or thermal motion, however, a disordered model could not be refined satisfactorily.

The absolute configuration was determined by using the *CRYSTALS* program system (Watkin, Carruthers & Betteridge, 1985) to refine the final atomic coordinates together with the enantiopole parameter (Flack, 1983). The refined value of the enantiopole parameter was 0.04 (5), thus confirming that the atomic coordinates represented the correct enantiomorph.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

References

Berman, H. M., Chu, S. S. C. & Jeffrey, G. A. (1967). *Science*, 157, 1576–1577.
Birch, G. G. (1963). *Adv. Carbohydr. Chem.* 18, 201–225.
Birch, G. G., Lee, C. K. & Richardson, A. C. (1974). *Carbohydr. Res.* 36, 97–109.
Brown, G. M., Rohrer, D. C., Berking, B., Beevers, C. A., Gould, R. O. & Simpson, R. (1972). *Acta Cryst.* B28, 3145–3158.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* 97, 1354–1358.
Elbein, A. D. (1974). *Adv. Carbohydr. Chem. Biochem.* 30, 227–256.
Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.
Jeffrey, G. A. & Nanni, R. (1985). *Carbohydr. Res.* 137, 21–30.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Labat-Robert, J. (1982). *Developments in Food Carbohydrates - 3*, edited by C. K. Lee & M. G. Lindley, pp. 81–106. London: Applied Science.
Lee, C. K. (1980). *Developments in Food Carbohydrates - 2*, edited by C. K. Lee, pp. 1–89. London: Applied Science.
Lee, C. K. (1987). *Adv. Carbohydr. Chem. Biochem.* 45, 199–351.
Lee, C. K. & Koh, L. L. (1994). *Carbohydr. Res.* 254, 281–287.
Lee, C. K., Koh, L. L., Xu, Y. & Linden, A. (1994). *Acta Cryst.* C50, 915–919.
Lee, C. K. & Linden, A. (1994). *J. Carbohydr. Chem.* In the press.
Linden, A. & Lee, C. K. (1995). *Acta Cryst.* C51, 747–751.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1990). *SHELXS86. Acta Cryst.* A46, 467–473.
Taga, T., Senma, M. & Osaki, K. (1972). *Acta Cryst.* B28, 3258–3263.
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS Users Guide.* Chemical Crystallography Laboratory, Univ. of Oxford, England.

A Dimeric Uracil Derivative

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Abstract

The structure of a dimeric uracil derivative, 5-ethoxy-methyl-1′-ethyl-1,5′-methylenedi-2,4(1H,3H)-pyrimidinedione, $C_{14}H_{18}N_4O_5$, was determined. The two uracil groups present in this molecule are almost identical. The torsion angles involving the bonds connecting the two uracil moieties, C6—N1—C13—C14 and C19—C14—C13—N1, are 77.5 (3) and 75.9 (3)°, respectively.

Comment

Since the discovery of the new anti-HIV-1 (human immunodeficiency virus type 1) lead compound HEPT, 1-[(2-hydoxyethoxy)methyl]-6-(phenylthio)thymine (Miyasaka *et al.*, 1989), extensive synthetic studies of HEPT analogues have been carried out (for a recent report see Tanaka *et al.*, 1992). The title compound, (I), was obtained as a by-product during the preparation of 5-ethoxymethyl-1-ethyluracil, which was then converted to the required regioisomeric analogue of HEPT by a procedure based on lithiation chemistry (Tanaka *et al.*, 1994).
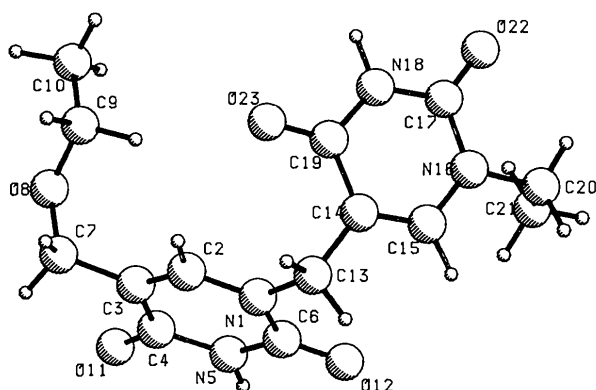

(I)
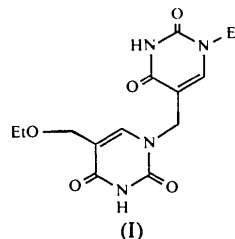
Fig. 1. The molecular structure of the title compound with the atom-numbering scheme.

	x	y	z	Ueq
C4	0.5830 (2)	0.8300 (1)	0.4882 (2)	0.046 (1)
N5	0.4244 (2)	0.8048 (1)	0.3857 (2)	0.046 (1)
C6	0.3092 (2)	0.8286 (1)	0.4390 (2)	0.043 (1)
C7	0.8014 (3)	0.9241 (2)	0.7940 (3)	0.061 (1)
O8	0.8101 (2)	0.8206 (1)	0.8643 (2)	0.076 (1)
C9	0.7393 (2)	0.7975 (2)	1.0033 (3)	0.074 (1)
C10	0.7432 (5)	0.6827 (3)	1.0597 (5)	0.105 (2)
O11	0.6707 (2)	0.8016 (1)	0.4208 (2)	0.070 (1)
O12	0.1703 (1)	0.8002 (1)	0.3406 (2)	0.059 (1)
C13	0.2472 (2)	0.9132 (2)	0.6864 (3)	0.047 (1)
C14	0.1324 (2)	0.7970 (1)	0.7275 (2)	0.042 (1)
C15	−0.0218 (2)	0.7267 (2)	0.6169 (3)	0.047 (1)
N16	−0.1263 (2)	0.6159 (1)	0.6448 (2)	0.044 (1)
C17	−0.0775 (2)	0.5714 (1)	0.7910 (2)	0.046 (1)
N18	0.0793 (2)	0.6453 (1)	0.9064 (2)	0.046 (1)
C19	0.1923 (2)	0.7564 (1)	0.8846 (2)	0.044 (1)
C20	−0.2896 (2)	0.5379 (2)	0.5097 (3)	0.059 (1)
C21	−0.2779 (5)	0.4529 (3)	0.3710 (4)	0.086 (1)
O22	−0.1677 (1)	0.4716 (1)	0.8175 (2)	0.058 (1)
O23	0.3328 (1)	0.8110 (1)	0.9953 (1)	0.053 (1)

Experimental

Crystal data

$C_{14}H_{18}N_4O_5$	Cu $K\alpha$ radiation
$M_r = 322.32$	$\lambda = 1.5418$ Å
Triclinic	Cell parameters from 20
$P\bar{1}$	reflections
$a = 9.326$ (2) Å	$\theta = 28.0–30.0°$
$b = 11.991$ (3) Å	$\mu = 0.865$ mm^{-1}
$c = 7.964$ (1) Å	$T = 297$ K
$\alpha = 94.58$ (2)°	Prism
$\beta = 105.39$ (2)°	0.30 × 0.30 × 0.50 mm
$\gamma = 113.84$ (3)°	Clear
$V = 767.5$ (3) Å^3	
$Z = 2$	
$D_x = 1.395$ Mg m^{-3}	

Data collection

Rigaku AFC-5 diffractometer	$R_{int} = 0.013$
$\omega/2\theta$ scans	$\theta_{max} = 60°$
Absorption correction:	$h = -10 \rightarrow 10$
none	$k = -13 \rightarrow 13$
2531 measured reflections	$l = 0 \rightarrow 8$
2288 independent reflections	3 standard reflections
2099 observed reflections	monitored every 150
[$F > 3\sigma(F)$]	reflections
	intensity decay: <3%

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.005F^2]$
$R = 0.042$	$(\Delta/\sigma)_{max} = 0.18$
$wR = 0.043$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$S = 1.81$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
2099 reflections	Atomic scattering factors
280 parameters	from *International Tables*
All H-atom parameters	*for X-ray Crystallography*
refined	(1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	Ueq
N1	0.3659 (2)	0.8898 (1)	0.6150 (2)	0.039 (1)
C2	0.5234 (2)	0.9201 (1)	0.7236 (2)	0.041 (1)
C3	0.6320 (2)	0.8925 (1)	0.6708 (2)	0.043 (1)

Table 2. *Selected geometric parameters (Å, °)*

N1—C2	1.372 (2)	C9—C10	1.492 (6)
N1—C6	1.383 (2)	C13—C14	1.500 (3)
N1—C13	1.478 (3)	C14—C15	1.336 (2)
C2—C3	1.336 (4)	C14—C19	1.436 (3)
C3—C4	1.443 (3)	C15—N16	1.370 (2)
C3—C7	1.496 (3)	N16—C17	1.365 (3)
C4—O11	1.226 (3)	N16—C20	1.473 (2)
C4—N5	1.380 (3)	C17—O22	1.227 (2)
N5—C6	1.373 (3)	C17—N18	1.370 (2)
C6—O12	1.212 (2)	N18—C19	1.383 (2)
C7—O8	1.424 (4)	C19—O23	1.235 (2)
O8—C9	1.423 (3)	C20—C21	1.499 (5)
C2—N1—C6	121.2 (2)	N1—C13—C14	110.9 (2)
C2—N1—C13	120.8 (1)	C15—C14—C19	119.0 (1)
C6—N1—C13	117.8 (1)	C15—C14—C13	121.6 (2)
C3—C2—N1	123.7 (1)	C19—C14—C13	119.3 (1)
C2—C3—C4	118.5 (2)	C14—C15—N16	123.1 (2)
C2—C3—C7	122.4 (2)	C17—N16—C15	121.1 (1)
C4—C3—C7	119.2 (2)	C17—N16—C20	118.6 (1)
O11—C4—N5	119.8 (2)	C15—N16—C20	120.2 (2)
O11—C4—C3	125.5 (2)	O22—C17—N16	122.3 (1)
N5—C4—C3	114.7 (2)	O22—C17—N18	122.1 (2)
C6—N5—C4	127.7 (1)	N16—C17—N18	115.6 (1)
O12—C6—N5	123.3 (2)	C17—N18—C19	126.3 (2)
O12—C6—N1	122.5 (2)	O23—C19—N18	119.6 (2)
N5—C6—N1	114.1 (1)	O23—C19—C14	125.5 (1)
O8—C7—C3	112.4 (1)	N18—C19—C14	114.9 (1)
C9—O8—C7	112.8 (2)	N16—C20—C21	111.3 (2)
O8—C9—C10	109.0 (3)		

Initial structure analysis was performed, with a continuous process connected to the data collection, using the fully automatic *FASE* procedure (Yamaguchi, 1993). The structure was solved by direct methods, which is included in *FASE*. Further refinement was by a full-matrix least-squares method.

Data collection: *AFD* (Rigaku Corporation, 1985*a*). Cell refinement: *AFD*. Data reduction: *FASE*. Program(s) used to solve structure: *SAPI85* (Yao *et al.*, 1985). Program(s) used to refine structure: *RCRYSTAN* (Rigaku Corporation, 1985*b*). Molecular graphics: *ACV* (Stardent Computer Inc., 1990). Software used to prepare material for publication: *XPACK* (Yamaguchi, 1987).

References

Miyasaka, T., Tanaka, H., Baba, M., Hayakawa, H., Walker, R. T., Balzarini, J. & De Clercq, E. (1989). *J. Med. Chem.* **32**, 2507–2509.

Rigaku Corporation (1985a). *AFD. Diffractometer Control Program System*. Rigaku Corporation, Tokyo, Japan.

Rigaku Corporation (1985b). *RCRYSTAN. X-ray Analysis Program System*. Rigaku Corporation, Tokyo, Japan.

Stardent Computer Inc. (1990). *ACV. Application Chemistry Viewer*. Stardent Computer Inc., Mewton, Massachusettes, USA.

Tanaka, H., Baba, M., Takahashi, E., Matsumoto, K., Kitaka, A., Walker, R. T., De Clercq, E. & Miyasaka, T. (1994). *Nucleosides and Nucleotides*, **13**, 155–162.

Tanaka, H., Takashima, H., Ubasawa, M., Sekiya, K., Nitta, I., Baba, M., Shigeta, S., Walker, R. T., De Clercq, E. & Miyasaka, T. (1992). *J. Med. Chem.* **35**, 4713–4719.

Yamaguchi, K. (1987). *XPACK. Programs for X-ray Parameters Report*. Showa Univ., Tokyo, Japan.

Yamaguchi, K. (1993). *Chem. Pharm. Bull.* **41**, 424–429.

Yao, J.-X., Zheng, C.-D., Qian, J.-Z., Han, F.-S., Gu, Y.-X. & Fan, H.-F. (1985). *SAPI85. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

the deviation from a planar N-atom coordination geometry could be related to the electronegative bonding partners N in hydrazines and O in hydroxylamines, and lone-pair repulsion effects, as supported by theoretical calculations (Mitzel, Hofmann, Waterstradt, Schleyer & Schmidbaur, 1994).

All trisilylamines studied until now show a completely flat geometry at the N atoms. $(H_3Si)_3N$ (Hedberg, 1955; Beagley & Conrad, 1970), $(Me_2HSi)_3N$ (Ebsworth, Murray, Rankin & Robertson, 1981) and $(Me_3Si)_3N$ (Anderson, Rankin & Robertson, 1990) were studied by electron diffraction in the gas phase, and the solid-state structures of a few compounds were elucidated by single-crystal X-ray diffraction: $(H_3Si)_3N$ (Barrow & Ebsworth, 1984), $(Cl_3Si)_3N$ and $(Cl_3Si)N(SiCl_2)_2N(SiCl_3)$ (Wannagat, Flindt, Brauer, Büger & Dörrenbach, 1989), $(PhH_2Si)_3N$ (Mitzel, Schier & Schmidbaur, 1992) and some amines with mixed ligands (Mitzel, Schier, Beruda & Schmidbaur, 1992).

Tris(p-tolylsilyl)amine

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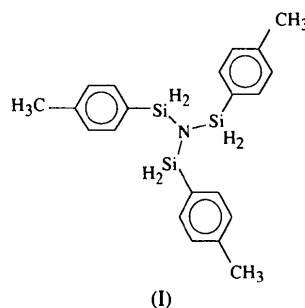
Abstract

The title compound, $C_{21}H_{27}NSi_3$, shows a virtually planar coordination geometry of the N atom. Unlike in $(PhH_2Si)_3N$, the three p-tolylsilyl substituents are not related by crystallographic symmetry.

Comment

The planar configuration of the N atom is the most striking structural feature of most of the silylated nitrogen compounds (Lucevics, Pudova & Strukokovich, 1989). Only a few exceptions of this general rule are known: aminosilanes with NH_2 substituents at bulky organosilyl groups (Ruhlandt-Senge, Bartlett, Olmstead & Power, 1993), two silylhydrazine compounds (Dressler, Niecke, Pohl, Saak, Schoeller & Schaefer, 1986; Schrenk & Mattes, 1988), and silylated hydroxylamines (Mitzel, Angermaier & Schmidbaur, 1994). In the latter two cases,

(I)

The present investigation of tris(p-tolylsilyl)amine, (I), is part of a more extensive study of the factors contributing to nitrogen planarization in Si–N systems.

A perspective view showing the atomic numbering scheme is given in Fig. 1. Selected bond lengths and angles are listed in Table 2.
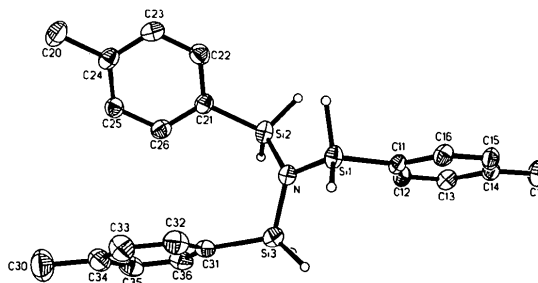

Fig. 1. Plot of tris(p-tolylsilyl)amine. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Tris(p-tolysilyl)amine (I) was prepared by a known method (Mitzel, Riede, Schier, Paul & Schmidbaur, 1993) and crystallized by slowly cooling the melt diluted with a minimum amount of hexane to 253 K.