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1,4,6,9-Tetraazathianthrene: a Planar Thianthrene, $C_8H_4N_4S_2$

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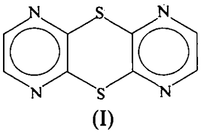
Abstract

The molecule of the title compound, 5,10-dithia-1,4,6,9-tetraaza-5,10-dihydroanthracene, lies around an inversion center and is nearly planar [the maximum deviation from planarity is 0.018 (1) Å for S5]. As a result of the planarity of the molecule, the C—S—C angle, 105.74 (7)°, is among the largest observed for thianthrenes, as are the C—C—S angles of the central ring which are 126.68 (11) and 127.57 (11)°.

Comment

Thianthrenes are a class of compounds related to anthracene with S atoms replacing the CH groups in the 9 and 10 positions. Among the more interesting features of the geometry of these compounds is the molecular dihedral angle, which is defined as the angle between the planes of the aromatic rings and is 128.28 (7)° for thianthrene (Larson, Simonsen, Martin, Smith & Puig-Torres, 1984). With the exception of the title compound (I) and bis(quinoxaline)-2,2′,3,3′-disulfide, BQD (Pignedoli, Peyronel & Antolini, 1977), which is also planar, all other reported azathianthrenes have dihedral angles ranging from 132.13 (6)° [observed for 1-azathianthrene (Larson *et al.*, 1984)] to 143.3° {found in 1,4-dithiino[2,3-*c*:5,6-*c*′]diquinolinium dichloride (Maslankiewicz, Wyszomirski & Glowiak, 1990)}.



(I)

The very large difference in the dihedral angle of BQD compared with other thianthrenes led us to examine the structure of BQD more carefully. The highly anisotropic thermal motion of the atoms of BQD with thermal ellipsoids elongated approximately perpendicular to the mean molecular plane (Fig. 1 in Pignedoli *et al.*, 1977) suggested that the structure might be disordered. A planar centrosymmetric distribution of electron density would result from a disordered and folded structure with half the molecules folded in one direction and half folded in the opposite direction. The resulting molecule would have atoms with elongated thermal ellipsoids like those observed for BQD. A situation similar to that described has been observed for *N*-methylphenothiazine in a 1:1 *N*-methylphenothiazine–7,7,8,8-tetracyanoquinodimethane complex (Kobayashi, 1973). Suitable crystals of BQD could not be obtained so the determination of the crystal structure of the related compound, 1,4,6,9-tetrazathianthrene, was undertaken.

The planarity of the title compound suggests that BQD is also planar. Pignedoli *et al.* (1977) stated that suitable crystals of BDQ were difficult to grow, as a result of which they were forced to study a very thin plate-like crystal (0.01 × 0.1 × 1.0 mm) and absorption errors (for which the data were not corrected) may have caused the thermal ellipsoids to be elongated. The geometry of the central ring in the title compound is similar to that found in BQD (Pignedoli *et al.*, 1977) but substantially different from that observed for thianthrene (Larson *et al.*, 1984). The angles around the bridgehead C atoms of thianthrene are all 120° to within three e.s.d.'s, which is indicative of a fairly strain-free ring system even though the S···S intramolecular distance, 3.1926 (8) Å, is considerably less than the sum of the van der Waals radius for S (3.4–3.6 Å; Bondi, 1964). Such close S···S contacts are usually observed in thianthrenes but are 3.5241 (5) Å for the title compound

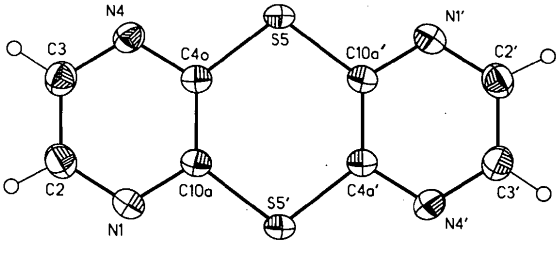


Fig. 1. Views of the title compound. The displacement ellipsoids are scaled to the 50% probability level. The molecule lies around an inversion center at 0,0,0. H atoms are scaled to an arbitrary size. A view perpendicular to the least-squares plane through the molecule, in which atoms labeled with a prime are related to the unprimed atoms by the operation $-x$, $-y$, $-z$, is shown above a side view of the title compound showing the planarity of the molecule.

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and 3.522 (5) Å for BQD. The large differences in the S···S distances are related to the planarity of the latter two compounds. The S···S distances must increase as the molecule flattens in order for the C—S—C angles to remain near to the value of the normal valence angle for S, which, in such a ring system, should be near the values found for thianthrene [100.36 (8) and 99.75 (9)°]. This leads to very large deviations from 120° for the S—C—C and S—C—N angles. These observed changes, although much greater in magnitude, are consistent with those seen in other azathianthrenes (Larson, Simonsen, Lam, Martin, Lindsay & Smith, 1985).

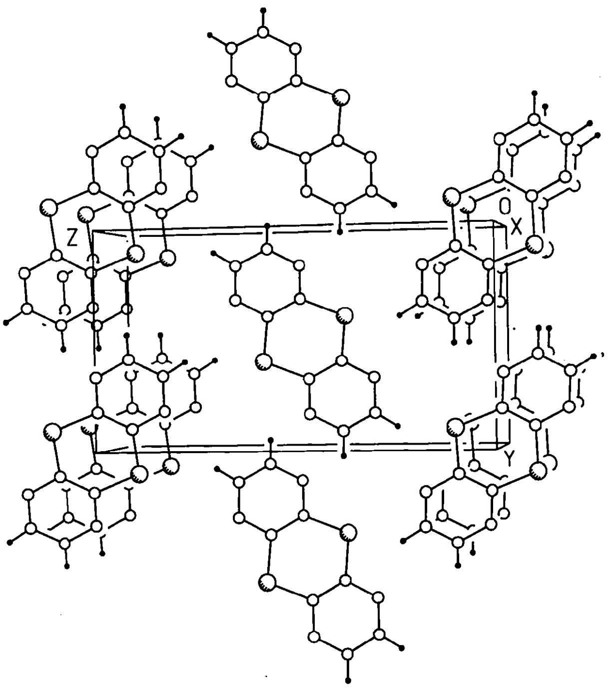

Fig. 2. Unit-cell packing diagram for the title compound viewed down the *a* axis.

Experimental

The title compound was synthesized by condensation of 2,3-dichloropyrazine with Na_2S (Lam, Musmar & Martin, 1984). Yellow needles were obtained by slow evaporation from $CHCl_3$.

Crystal data

$C_8H_4N_4S_2$
$M_r = 220.27$
Monoclinic
$P2_1/n$
$a = 3.894$ (1) Å
$b = 7.866$ (3) Å
$c = 14.297$ (7) Å
$\beta = 95.66$ (3)°
$V = 435.8$ (3) Å^3
$Z = 2$
$D_x = 1.68$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 45 reflections
$\theta = 10.8$–$15.9°$
$\mu = 0.544$ mm^{-1}
$T = 163$ (1) K
Needle
0.44 × 0.15 × 0.09 mm
Yellow

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: analytical from crystal shape
$T_{\min} = 0.920$, $T_{\max} = 0.953$
1274 measured reflections
1274 independent reflections

1076 observed reflections [$F > 4.0\sigma(F)$]
$\theta_{\max} = 30.0°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 11$
$l = -19 \rightarrow 20$
4 standard reflections monitored every 96 reflections intensity variation: none

Refinement

Refinement on F
$R = 0.0296$
$wR = 0.0408$
$S = 1.478$
1076 reflections
72 parameters
All H-atom parameters refined

Calculated weights $w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (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	U_{eq}
S5	0.17584 (10)	0.10237 (5)	−0.09398 (3)	0.02895 (13)
N1	−0.0191 (3)	0.1825 (2)	0.17509 (9)	0.0301 (4)
C2	0.1055 (4)	0.3410 (2)	0.18265 (12)	0.0334 (5)
C3	0.2503 (5)	0.4192 (2)	0.10946 (12)	0.0323 (5)
N4	0.2679 (3)	0.3406 (2)	0.02754 (9)	0.0287 (4)
C4a	0.1384 (3)	0.1846 (2)	0.01876 (10)	0.0228 (4)
C10a	−0.0038 (4)	0.1045 (2)	0.09357 (10)	0.0232 (4)

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

C4a—S5	1.756 (2)	N4—C3	1.332 (2)
C2—N1	1.338 (2)	C4a—N4	1.328 (2)
C10a—N1	1.324 (2)	C10a—C4a	1.402 (2)
C3—C2	1.381 (3)	S5^{i}—C10a	1.760 (2)
C2—N1—C10a	117.12 (14)	S5—C4a—N4	111.22 (11)
C3—C2—N1	121.7 (2)	N1—C10a—C4a	121.24 (14)
N4—C3—C2	121.3 (2)	S5^{i}—C10a—C4a	126.68 (11)
C4a—N4—C3	117.37 (14)	C4a—S5—C10a^{i}	105.74 (7)
C10a—C4a—S5	127.57 (11)	S5^{i}—C10a—N1	112.07 (11)
C10a—C4a—N4	121.21 (13)		

Symmetry code: (i) $-x, -y, -z$.

Data reduction was carried out as described by Riley & Davis (1976). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1991). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *FUER* (Larson, 1982); *MPLN* (Cordes, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1′-C-Branched Uracil Nucleoside

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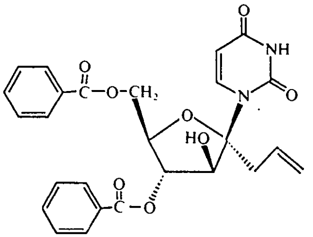
Abstract

The structure of the 1′-C-branched uracil nucleoside, 1-(1′-allyl-3′,5′-di-*O*-benzoyl-β-D-arabinofuranosyl)-2,4(1*H*,3*H*)-pyrimidinedione, $C_{26}H_{24}N_2O_8$, has been determined. The uracil nucleobase has the β orientation in this molecule.

Comment

Isolation of the nucleoside antibiotic 9-(β-D-psicofuranosyl)adenine, psicofuranine (Yüntsen, Ohkuma, Ishii & Yonehara, 1956), stimulated the synthesis of nucleosides having a carbon substituent at the anomeric position. Synthetic methods so far available for this class of compounds involve inital preparation of sugar components which are then condensed with nucleobases, forming a mixture of both α- and β-anomers in most cases [for a recent example see Faiver-Buet, Grouiller & Descotes (1992)]. Quite recently, a new stereospecific method for the synthesis of a variety of 1′-C-branched uracil nucleosides from a 1′,2′-unsaturated derivative has been reported (Haraguchi, Itoh, Tanaka, Yamaguchi & Miyasaka, 1994). The title compound (I) was obtained from 1-[1′-allyl-2′-bromo-3′,5′-bis-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-β-D-arabinofuranosyl]-uracil, which was synthesized by the Haraguchi *et al.* (1994) method, through hydrolysis of the O^2,2′-anhydro intermediate.



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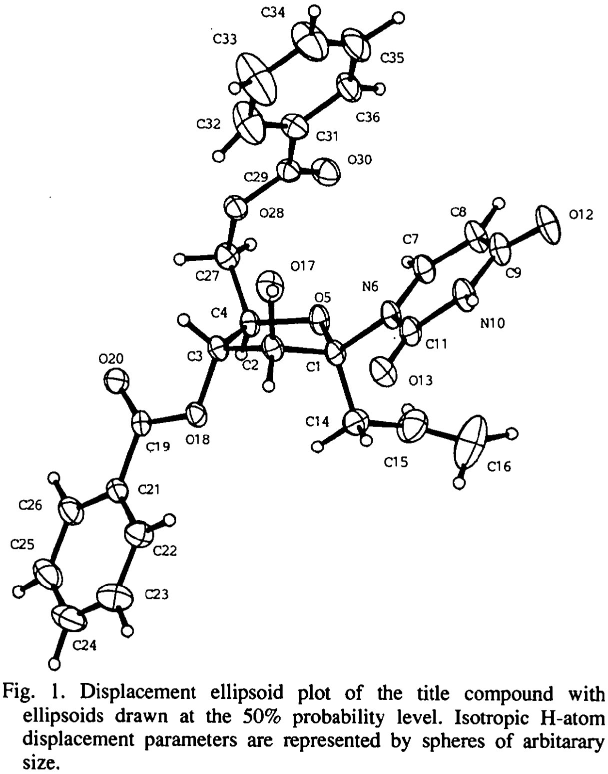

Fig. 1. Displacement ellipsoid plot of the title compound with ellipsoids drawn at the 50% probability level. Isotropic H-atom displacement parameters are represented by spheres of arbitarary size.

Experimental

Crystal data

$C_{26}H_{24}N_2O_8$
$M_r = 492.48$

Cu *Kα* radiation
λ = 1.5418 Å