Br—N(1)^{i}	3.346 (2)	Br—N(1)^{iii}	3.359 (2)
Br—N(1)^{ii}	3.279 (2)	Br—N(2)^{iii}	3.560 (3)

Symmetry codes: (i) $-x, y-\frac{1}{2}, 1-z$; (ii) $x, y, 1+z$; (iii) $1-x, y-\frac{1}{2}, 1-z$.

Data collection and cell refinement: Enraf-Nonius CAD-4 software. Data reduction program used to solve and refine structure, software used to prepare material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The *ORTEP* diagram was prepared using *ORTEP*II (Johnson, 1976).

The θ-scan width was $(0.8+0.35\tan\theta)^{\circ}$ with a θ-scan rate of $5.79^{\circ}\ \mathrm{min}^{-1}$ and background counts for 5 s on each side of every scan.

The absolute configuration was determined unequivocally by refinement of the chirality value η to a value of +1.02(2) (Rogers, 1981). Least-squares refinement (with η fixed at 1.00) and subsequent analysis of the reflections for which the Bijvoet differences were most significant readily demonstrated that this is the correct model. Of the top 144 pairs of Bijvoet reflections, none was in disagreement with the model. The absorption correction (ψ scans) using nine strong low-angle (χ values close to 90°) reflections, on the full dataset using the *NRCVAX* programs, lowered the *R* factor from 0.060 to 0.021. All H atoms were refined isotropically and gave reasonable *U* values and dimensions.

GF thanks NSERC Canada and DP thanks SERC for Grants in Aid of Research.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55474 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1027]

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Acta Cryst. (1992). C**48**, 2275–2277

Structure of 3,6-Bis(dimethylamino)-2,5-diisopropylthieno[3,2-*b*]thiophene

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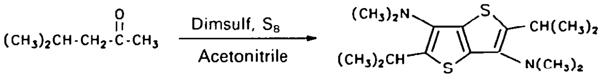
Abstract

The bicyclic thieno[3,2-*b*]thiophene skeleton of the title compound has an inversion centre and is exactly planar. The two C—S bond lengths differ by a small but significant amount (0.032 Å) and are somewhat longer than the standard C—S value. All other bond distances and bond angles are in the expected ranges.

Comment

Substituted acetophenones react with the 1:1 addition compound of dimethylamine and sulfur dioxide (dimsulf) to yield dark red betaines (Matschiner, Maschmeier & Hansen, 1992). We have determined the structure of 2-(*N*,*N*-dimethyliminio)-2-phenyldithioacetate (Heinemann, Hartung, Hansen, Maschmeier & Matschiner, 1992) formed by this reaction. In contrast to the previous results, under the same reaction conditions isobutyl methyl ketone (1) gave the white 3,6-bis(dimethylamino)-2,5-diisopropylthieno[3,2-*b*]thiophene (2) rather than a betaine.



(1) (2)

Fig. 1. shows the molecular structure of (2). As the molecule has an inversion centre in the middle of the C1—C1′ bond and the thiophene ring is planar to within experimental error, the whole thienothiophene skeleton is also planar. In addition, the attached atoms N1 and C6 deviate only very slightly [0.024 (1) and 0.027 (2) Å respectively] from the ring plane. Both C—S bonds [C1—S1 = 1.728 (2), C5—S1 = 1.750 (2) Å] are somewhat longer than the standard value [1.712 (13) Å] derived from the structures of 60 thiophene derivatives (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). All other dimensions of the ring system agree well with those expected and are in complete agreement with corre-

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sponding values in 2,5-di-*tert*-butyl-3,6-dineopentylthieno[3,2-*b*]thiophene (McKenzie, 1975) and in the parent unsubstituted thieno[3,2-*b*]thiophene (Cox, Gillot & Jeffrey, 1949), taking into account the lower precision of those structure analyses.

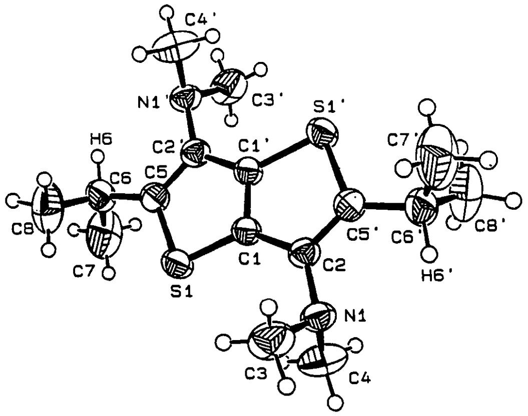

Fig. 1. Molecular structure and atomic numbering of (2). The thermal ellipsoids are drawn at the 50% level and the H atoms are shown as spheres of arbitrary radius.

Experimental

Crystal data

$C_{16}H_{26}N_2S_2$
$M_r = 310.53$
Triclinic
$P\bar{1}$
$a = 5.796$ (1) Å
$b = 8.714$ (1) Å
$c = 9.152$ (1) Å
$\alpha = 92.290$ (9)°
$\beta = 97.17$ (1)°
$\gamma = 103.47$ (1)°
$V = 444.8$ Å^3
$Z = 1$
$D_x = 1.159$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 100 reflections
$\theta = 10$–17.5°
$\mu = 0.28$ mm^{-1}
$T = 293$ K
Needle
0.53 × 0.23 × 0.19 mm
White
Crystal source: recrystallized from ethanol

Data collection

Stoe Stadi-4 diffractometer
ω-θ scans
Absorption correction: none
5200 measured reflections
2526 independent reflections
2393 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.018$

$\theta_{\rm max} = 30.0$°
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity variations: 5.9, 7.2, 10.3%

Refinement

Refinement on F
Final $R = 0.047$
$wR = 0.037$
$S = 6.84$
2393 reflections
143 parameters
$w = 2.56/[\sigma^2(F_o)]$

$(\Delta/\sigma)_{\rm max} = 0.064$
$\Delta\rho_{\rm max} = 0.256$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.233$ e Å^{-3}
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

Data collection: *DIF4* (Stoe & Cie, 1991*a*) using the learnt-profile method (Clegg, 1981). Data reduction: *REDU4* (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELX76*. Program used to draw the structural diagram: *ORTEPII* (Johnson, 1976). Software used to perform geometrical calculations: *EDIT* (Jaskólski, 1982).

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

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

	x	y	z	$U_{\rm eq}$
S1	0.48012 (8)	0.25944 (5)	0.48788 (4)	0.052 (2)
N1	0.8498 (2)	0.4958 (2)	0.7876 (1)	0.048 (4)
C1	0.5567 (3)	0.4576 (2)	0.5477 (2)	0.041 (4)
C2	0.7079 (3)	0.5511 (2)	0.6720 (2)	0.042 (4)
C3	0.7096 (4)	0.3733 (3)	0.8649 (3)	0.076 (6)
C4	1.0531 (4)	0.4496 (4)	0.7363 (3)	0.081 (7)
C5	0.2953 (3)	0.2938 (2)	0.3325 (2)	0.048 (4)
C6	0.1644 (4)	0.1597 (2)	0.2218 (2)	0.059 (5)
C7	0.3370 (6)	0.0962 (4)	0.1388 (4)	0.103 (7)
C8	0.0018 (6)	0.0302 (4)	0.2915 (3)	0.094 (6)

Table 2. *Geometric parameters* (Å, °)

S1—C1	1.728 (2)	C1—C2	1.439 (2)
S1—C5	1.750 (2)	C2—C5′	1.358 (2)
N1—C2	1.427 (2)	C5—C6	1.506 (2)
N1—C3	1.449 (3)	C6—C7	1.516 (4)
N1—C4	1.454 (3)	C6—C8	1.510 (4)
C1—C1′	1.369 (2)		
C1—S1—C5	91.8 (1)	N1—C2—C5′	121.8 (1)
C2—N1—C3	112.8 (1)	C1—C2—C5′	111.4 (1)
C2—N1—C4	112.0 (1)	S1—C5—C2′	112.0 (1)
C3—N1—C4	112.4 (2)	S1—C5—C6	120.6 (1)
S1—C1—C1′	110.6 (1)	C6—C5—C2′	127.4 (1)
S1—C1—C2	135.2 (1)	C5—C6—C7	111.3 (2)
C1′—C1—C2	114.3 (1)	C5—C6—C8	112.1 (2)
N1—C2—C1	126.8 (1)	C7—C6—C8	111.8 (2)

The structure was solved by direct methods and refined by full-matrix least squares. All H atoms were localized in a difference Fourier map and refined isotropically.

The authors wish to thank the Fonds der Chemischen Industrie for support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55381 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1010]

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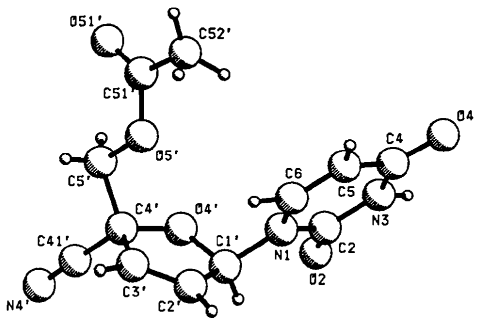

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule.

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Structure of a 4′-*C*-Branched 2′,3′-Didehydro-2′,3′-dideoxyuridine

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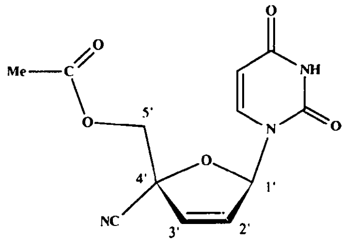
Abstract

The structure of a 4′-*C*-branched 2′,3′-unsaturated uracil nucleoside, 4′-cyano-2′,3′-didehydro-2′,3′-dideoxyuridine 5′-acetate, has been determined. The *N*-glycoside torsion angle χ has a value of −82.7(3)° in the *anti* range. The C4′—C5′ side-chain conformation is +*sc* with γ = 47.2(4)°. The sugar ring is essentially planar. The conformational parameters are in accordance with the IUPAC-IUB Joint Commission on Biochemical Nomenclature [*Pure Appl. Chem.* (1983), **55**, 1273-1280] guidelines.

Comment

Despite the recent finding that 4′-cyanothymidine acts as a potent inhibitor of the replication of human immunodeficiency virus (O-Yang, Wu, Fraser-Smith & Walker, 1992), only two methods for introducing carbon substituents to the 4′-position of nucleosides have been available. These are 4′-hydroxymethylation of nucleoside 5′-aldehydes (Youssefyeh, Tegg, Verheyden, Jones & Moffatt, 1977) and a Claisen-type rearrangement of nucleoside 4′,5′-enamines (Secrist & Winter, 1978). A new approach to produce a series of 4′-*C*-branched 2′,3′-unsaturated uracil nucleosides has been disclosed quite recently (Haraguchi, Tanaka, Itoh, Saito & Miyasaka, 1992), wherein carbon nucleophiles generated from organosilicon reagents of various types can be transferred to a 3′,4′-unsaturated derivative through an allylic rearrangement. The use of trimethylsilyl cyanide in this reaction gave an epimeric mixture of two 4′-cyano derivatives from which the title compound (1) was isolated as the major product after deprotection followed by acetylation. This molecule shows an *anti* conformation with respect to the sugar ring: χ(C2—N1—C1′—O4′) = −82.73(3)°. The sugar ring is essentially planar. The maximum displacement from the least-squares plane is 0.023 Å (O4′). The C4′—C5′ side-chain conformation is +*sc* with the torsion angle γ(C3′—C4′—C5′—O5′) = 47.2(4)°. Two weak C—H—O intermolecular hydrogen bonds are observed: O2—C1′(1 −*x*, 1/2 + *y*, 2 − *z*) 3.174(4) Å and O4—C1′(*x*, *y*, 1 + *z*) 3.148 Å.



(1)

Experimental

Crystal data

$C_{12}H_{11}N_3O_5$
M_r = 277.24
Monoclinic
$P2_1$
a = 14.870 (1) Å
b = 5.411 (1) Å
c = 8.150 (1) Å
β = 95.71 (2)°
V = 652.5 (1) Å^3
Z = 2
D_x = 1.411 Mg m^{-3}

Cu $K\alpha_1$ radiation
λ = 1.5405 Å
Cell parameters from 20 reflections
θ = 29.0-30.5°
μ = 0.913 mm^{-1}
T = 297 K
Plate
0.55 × 0.50 × 0.08 mm
Clear

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