Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.323 (3)	N3—C3	1.468 (3)
N1—C6	1.332 (3)	N3—C4	1.381 (3)
C2—N2	1.319 (3)	C4—O4	1.210 (3)
C2—N3	1.376 (3)	C4—C5	1.469 (3)
N2—C21	1.447 (3)	C5—N5	1.316 (3)
C21—C22	1.497 (3)	C5—C6	1.444 (3)
C22—O21	1.207 (3)	N5—O5	1.296 (2)
C22—O22	1.292 (3)	C6—N6	1.311 (3)
C2—N2—C21—C22	−81.3 (3)	C6—C5—N5—O5	0.0 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O2	0.82	1.97	2.779 (3)	169
O1—H1*B*···O21^{i}	0.82	1.99	2.784 (3)	163
N2—H2···O1^{ii}	0.86	2.09	2.862 (3)	149
O2—H2*A*···O4^{iii}	0.82	2.39	2.901 (3)	121
O2—H2*A*···N5^{iii}	0.82	2.46	3.228 (3)	158
O2—H2*B*···O1^{iv}	0.82	2.10	2.908 (3)	170
N6—H6*A*···O2	0.86	2.07	2.914 (3)	169
N6—H6*B*···O5	0.86	2.02	2.645 (3)	129
N6—H6*B*···O4^{iii}	0.86	2.50	2.900 (3)	109
O22—H22···O5^{v}	1.10	1.44	2.491 (3)	155
O22—H22···N5^{v}	1.10	2.08	2.902 (3)	129

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$; (iii) $\frac{3}{2} - x, -y, z - \frac{1}{2}$; (iv) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, z$.

H atoms were placed in calculated positions, except for H22, which was located in a $\Delta\rho$ map, 1.10 Å from O22, and held in that position. They were treated as riding atoms in the refinement (C—H 0.93–0.98, N—H 0.86, and O—H 0.82 and 1.10 Å).

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* and *PLUTON* (Spek, 1995*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1473). Services for accessing these data are described at the back of the journal.

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trans- and *cis*-S—C—C—S Conformations in 5-(2,2′-Dithien-5-yl)-2′-deoxyuridine

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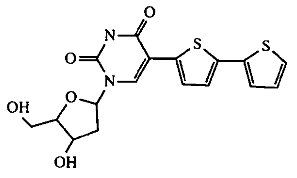
Abstract

The title compound, $C_{17}H_{16}N_2O_5S_2$, adopts a *transoid–cisoid* disordered crystal structure of the terminal thienyl group at room temperature, with occupancies of 0.55 and 0.45. The structure was solved by direct methods and refined by least-squares calculations to a final *R* of 0.048. Molecular cohesion is stabilized by hydrogen bonding involving the two hydroxyl groups of the sugar moiety and the uridine ring.

Comment

As part of our attempts to identify antiherpes agents by rational drug-design approaches, the structures of a series of deoxyuridine analogues have been characterized (Creuven *et al.*, 1996; Olivier *et al.*, 1994, and references therein). In this contribution, we present the crystal structure of 5-(2,2′-dithien-5-yl)-2′-deoxyuridine, (I), a compound that shows moderate activity against herpes simplex virus type 1 (Luyten *et al.*, 1995).



(I)

The molecular structure with the atom-numbering scheme is given in Fig. 1. The observed geometry corresponds to standard values (Allen *et al.*, 1987) and is similar to that of previously reported structures for analogues of 5-substituted 2′-deoxyuridines (Olivier *et al.*, 1994; Creuven *et al.*, 1996).

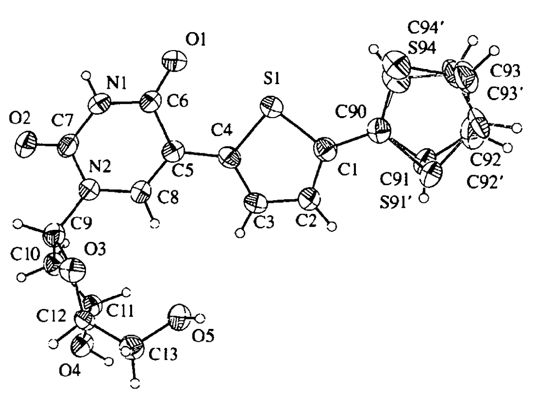


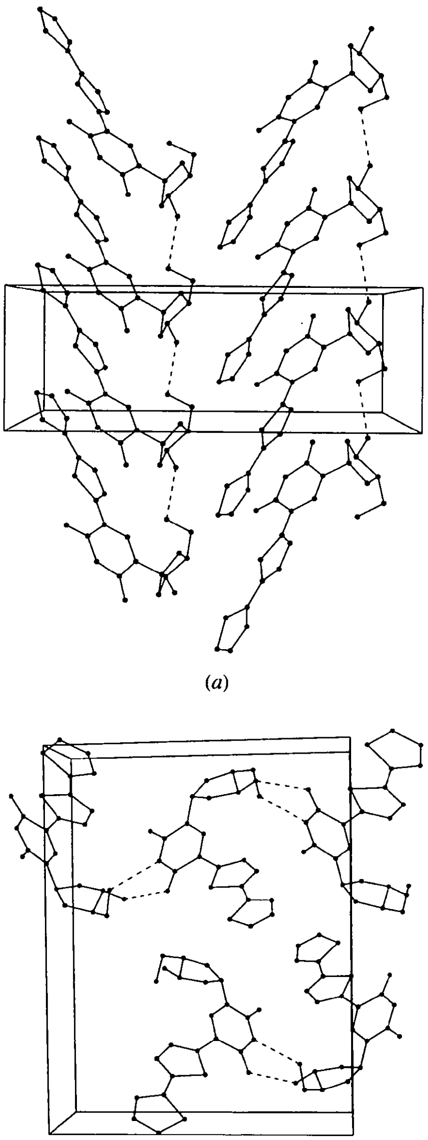
Fig. 1. Molecular structure and conformation (note the disorderd terminal thienyl ring) of the title compound. Displacement ellipsoids, representing non-H atoms, are drawn at the 50% probability level. The atom-numbering scheme used in the paper is shown.

Two alternative conformations of the terminal thienyl ring (numbered C90–C93, S94 and C90, S91′, C92′–C94′) were refined in such a way that, in the final model, the title compound adopts a *transoid–cisoid* disordered terminal thienyl group with occupancies of 0.55 and 0.45. While the majority of structures reported for polythiophenes (di-, ter-, quater-, hexathienyls) are planar with a *transoid* conformation (Visser, Heeres, Wolters & Vos, 1968; Pelletier & Brisse, 1994; Herrema, Wildeman, van Bolhuis & Hadziioannou, 1994; Hotta & Waragai, 1991; Bien, Kapon, Gronowitz & Hornfeldt, 1989; Aleman *et al.*, 1993), several cases of *cisoid–transoid* disordered structures have also been reported [*e.g.* tetrabutylhexathione (0.60:0.40) by Liao, Benz, LeGoff & Kanatzidis (1994); dithienyl (0.85:0.15) by Chaloner, Gunatunga & Hitchcock (1994); bithiophene-5-carbaldehyde (0.80:0.20) by Armes, Chaloner, Hitchcock & Simmons (1994)].

The planar thienyl rings (r.m.s. deviation from the best plane through the atoms is 0.003, 0.018 and 0.016 Å for rings *A*, *B* and *C*, respectively, with a maximum deviation of 0.003 for C2, 0.031 for C90 and 0.022 Å for S91′; *A* = thienyl ring S1, C1–C4; *B* = C90–C93, S94; *C* = C90, S91′, C92′–C94′) adopt a quasiplanar conformation, the torsion angle around the thienyl inter-ring C1—C90 bond being close to 0 or 180° (Table 1). This planar entity is slightly tilted *versus* the planar (r.m.s. deviation from the best plane through the atoms of the ring = 0.003 Å with a maximum deviation of 0.055 Å for C7) uracil ring as the S1—C4—C5—C6 torsion angle is 25.3 (4)°. The consequence for the internal geometry is that electronic delocalization is marked between the dithienyl rings [C1—C90 = 1.441 (4) Å] but not between the uracyl and thienyl rings [C4—C5 = 1.468 (4) Å; overall C_{sp^2}—C_{sp^2} single bond = 1.460 (15) Å (Allen *et al.*, 1987)].

The uracyl ring is perpendicular to the deoxyribose group [C7—N2—C9—C10 = 86.2 (3)°]. However, the orientation of the sugar moiety *versus* the uracil ring is highly variable when compared with similar structures (C7—N2—C9—C10 ranging from 80 to 140°; Creuven *et al.*, 1996).

The S1 atom is located in the vicinity of the carbonyl group of the uracil ring, resulting from an intramolecular interaction between the S and O atoms [S1···O1 2.949 (3) Å, shorter than the sum of the contact radii of S (1.80 Å) and O (1.52 Å) (Bondi, 1964)]. A similar intramolecular interaction has already been observed in analogues (Creuven *et al.*, 1996). Interestingly, the *cis*


(*a*)

(*b*)

Fig. 2. Crystal-packing diagram (dotted lines indicate hydrogen-bond interactions; only the main component of the disordered dithienyl group is presented; H atoms are omitted). (*a*) View perpendicular to *ac*, (*b*) view perpendicular to *ab*.

coplanar conformation of the dithienyl moiety places the two S atoms of those rings in close proximity as the S1···S94 distance [3.313 (5) Å] is indicative of an intramolecular contact.

Molecular cohesion (Fig. 2) is ensured by intermolecular hydrogen-bond interactions involving the two hydroxy groups and an N atom of the deoxyuridine moiety. In particular, molecules are connected in the *ac* plane [Fig. 2(*a*)] by a network of hydrogen bonds between O5 and O4, the two hydroxyl groups of the deoxyribose moiety: O4···O1^{i} = 2.716 (3) Å, O4—H4···O1^{i} = 178°; O5···O4^{ii} = 2.720 (3) Å, O5—H5···O4^{ii} = 180°; symmetry codes: (i) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$; (ii) x, y, $z+1$. A second network of hydrogen bonds links the molecules in the *ab* plane [Fig. 2(*b*)] *via* the O5 hydroxyl group and N1 atom of the uracil ring: N1···O5^{iii} = 2.891 (3) Å, N1—H1···O5^{iii} = 178°; symmetry code: (iii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$. The O2 atom does not form hydrogen bonds. This has an indirect consequence on the internal geometry of the molecule: the O1—C6 bond length [1.234 (4) Å] is significantly longer than the O2—C7 bond [1.213 (4) Å]. The N—C(O) group however is not affected as N1—C6 = 1.374 (4) Å and N1—C7 = 1.375 (4) Å. Crystal packing is also characterized by a stacked arrangement of the coplanar uracyl–dithienyl moiety of the molecules leading to short intermolecular ring interactions with centroid (Cg) distances of 3.5–4.0 Å [Cg(I)—Cg(II) = 3.76 Å; α = 3.2, β = 23.9, γ = 22.2° (Spek, 1990); *A* = thienyl ring, S1, C1–C4; *B* = thienyl ring, C90–C93, S94].

Experimental

The compound was synthesized according to Luyten *et al.* (1995).

Crystal data

$C_{17}H_{16}N_2O_5S_2$
$M_r = 392.42$
Orthorhombic
$P2_12_12_1$
$a = 14.580\,(2)$ Å
$b = 18.5345\,(10)$ Å
$c = 6.44770\,(10)$ Å
$V = 1742.4\,(3)$ Å^3
$Z = 4$
$D_x = 1.496$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 40$–$45°$
$\mu = 3.063$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.15 × 0.07 × 0.07 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3268 measured reflections
2864 independent reflections
2695 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0134$
$\theta_{\rm max} = 71.71°$
$h = 0 \rightarrow 17$
$k = -22 \rightarrow 19$
$l = 0 \rightarrow 7$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0461$
$wR(F^2) = 0.1160$
$S = 1.065$
2864 reflections
268 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.093$
$\Delta\rho_{\rm max} = 0.466$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.314$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0034 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.01 (2)

Table 1. *Selected geometric parameters (Å, °)*

S1—C4	1.723 (3)	C5—C8	1.340 (4)
S1—C1	1.735 (3)	C5—C6	1.464 (4)
C1—C2	1.364 (4)	C6—O1	1.234 (3)
C1—C90	1.441 (4)	C6—N1	1.374 (4)
C2—C3	1.397 (4)	N1—C7	1.375 (4)
C3—C4	1.361 (4)	C7—O2	1.213 (4)
C4—C5	1.468 (4)	C7—N2	1.381 (4)
C90—C94′	1.357 (14)	N2—C8	1.370 (4)
C90—C91	1.398 (12)	N2—C9	1.485 (4)
C90—S94	1.673 (4)	C9—O3	1.414 (4)
C90—S91′	1.703 (3)	C9—C10	1.520 (4)
C91—C92	1.40 (2)	C10—C11	1.518 (4)
C92—C93	1.37 (2)	C11—O4	1.421 (3)
C93—S94	1.72 (2)	C11—C12	1.517 (4)
S91′—C92′	1.72 (2)	C12—O3	1.452 (3)
C92′—C93′	1.363 (14)	C12—C13	1.512 (4)
C93′—C94′	1.42 (2)	C13—O5	1.428 (4)
C4—S1—C1	92.2 (1)	C6—C5—C4	121.0 (3)
C2—C1—C90	128.3 (3)	O1—C6—N1	120.8 (3)
C2—C1—S1	110.1 (2)	O1—C6—C5	124.6 (3)
C90—C1—S1	121.6 (2)	N1—C6—C5	114.7 (3)
C1—C2—C3	113.5 (3)	C6—N1—C7	127.5 (2)
C4—C3—C2	113.9 (3)	O2—C7—N1	123.2 (3)
C3—C4—C5	124.9 (3)	O2—C7—N2	122.6 (3)
C3—C4—S1	110.4 (2)	N1—C7—N2	114.2 (3)
C5—C4—S1	124.6 (2)	C8—N2—C7	121.3 (2)
C94′—C90—C1	128.2 (8)	C8—N2—C9	122.0 (2)
C91—C90—C1	125.5 (7)	C7—N2—C9	116.6 (3)
C91—C90—S94	109.4 (6)	C5—C8—N2	123.7 (3)
C1—C90—S94	124.9 (3)	O3—C9—N2	107.8 (3)
C94′—C90—S91′	111.6 (8)	O3—C9—C10	107.1 (2)
C1—C90—S91′	120.2 (2)	N2—C9—C10	113.6 (2)
C90—C91—C92	112.9 (14)	C11—C10—C9	102.8 (2)
C93—C92—C91	114 (2)	O4—C11—C12	112.3 (2)
C92—C93—S94	109 (2)	O4—C11—C10	111.4 (2)
C90—S94—C93	94.7 (9)	C12—C11—C10	101.9 (2)
C90—S91′—C92′	92.2 (7)	O3—C12—C13	109.7 (2)
C93′—C92′—S91′	110.6 (16)	O3—C12—C11	104.4 (2)
C92′—C93′—C94′	112.9 (17)	C13—C12—C11	117.1 (2)
C90—C94′—C93′	112.6 (14)	O5—C13—C12	110.2 (2)
C8—C5—C6	117.6 (3)	C9—O3—C12	109.9 (2)
C8—C5—C4	121.3 (3)		
S1—C1—C90—S91′	174.4 (2)	C7—N2—C9—O3	−155.2 (2)
S1—C1—C90—S94	−4.0 (5)	C7—N2—C9—C10	86.2 (3)
S1—C1—C90—C94′	−8.8 (1.2)	C9—C10—C11—O4	154.9 (2)
S1—C1—C90—C91	−179.2 (8)	C10—C11—C12—C13	−156.7 (2)
S1—C4—C5—C6	25.3 (4)	C11—C12—C13—O5	49.4 (3)

The cell parameters were refined from a list of 25 well centred reflections. Data were collected at room temperature on a CAD-4 diffractometer using Cu radiation. Data reduction included correction for background, decay, Lorentz and polarization factors, but not for absorption effects (an attempt to correct for absorption based on ψ scans was unsuccessful). The structure was solved by direct methods, resulting in reliable positions for all non-H atoms of the main disordered component. The initial model was refined by least-squares techniques. A disordered component was observed for the terminal thienyl group. Occupancy of both parts refined to 0.55 and 0.45 and was fixed at these values for further refinement. Non-H atoms were refined with anisotropic displacement parameters. H atoms potentially involved in hydrogen bonds (*i.e.* on atoms O4 and O5) were located by Fourier difference while the others were calculated. The positions of all the H atoms except H4 and H5 were refined using the riding model method. *PLATON*94 (Spek, 1990) was used for geometric analysis of the structure. Most machine calculations were conducted on an IBM *RS*6000.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *NONIUS* (Baudoux & Evrard, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PLATON*94 (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1017). Services for accessing these data are described at the back of the journal.

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2-Oxazolidinone

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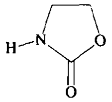
Abstract

Redetermination of the crystal structure of the title compound, $C_3H_5NO_2$, leads to a precise geometry for this molecule that is compared with the conformation of several aryl-substituted oxazolidinones. Molecular cohesion is stabilized by hydrogen bonds between the amine and carbonyl groups. The coplanar approach of the NH group can be rationalized in terms of the *ab initio* calculated molecular electrostatic potential generated by the C=O group.

Comment

As a part of our interest in the structural study of aryl oxazolidinones (Moureau *et al.*, 1992, 1994, 1995; Wouters *et al.*, 1993, 1994; Wouters, Evrard & Durant, 1994; Wouters, Perpete, Norberg, Evrard & Durant, 1994) we redetermined the structure of 2-oxazolidinone (R_1 = 0.039), (I), previously reported in the literature (R_1 = 0.132; Turley, 1972).



(I)

The molecular structure with the atom-numbering scheme is illustrated as an *ORTEP*II (Johnson, 1976) plot in Fig. 1. Bond distances and angles are close to those previously reported for the title compound but are determined with more precision. The N—C1 and N—C3 bonds [1.441 (2) and 1.326 (2) Å, respectively] are slightly shorter than corresponding bonds in γ-lactams [C*—NH—C=O: C_{sp^3}—N(3) = 1.457 and C_{sp^2}—N(3) = 1.331 Å according to Allen *et al.* (1987)]. The C3—O2 bond length [1.219 (2) Å] is slightly longer than a C=O double bond (C=O: 1.196 Å in esters

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