

**(4*R*,5*R*)-2-(*N*-Methyl-benzylamino)-3-nitro-4-(1',2',3',4',5'-penta-*O*-acetyl-*D*-manno-pentitol-1-yl)-5-phenyl-5-phenylcarbamoyl-4,5-dihydrothiophene at 150 K**

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**Key indicators**

Single-crystal X-ray study  
*T* = 150 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
*R* factor = 0.041  
*wR* factor = 0.108  
Data-to-parameter ratio = 9.8

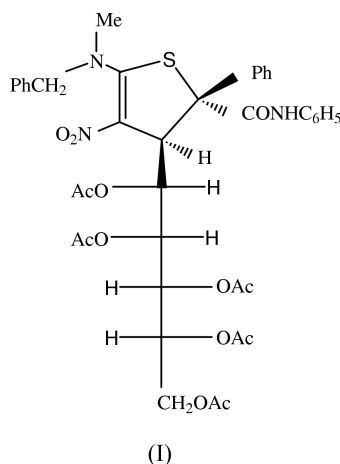
For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

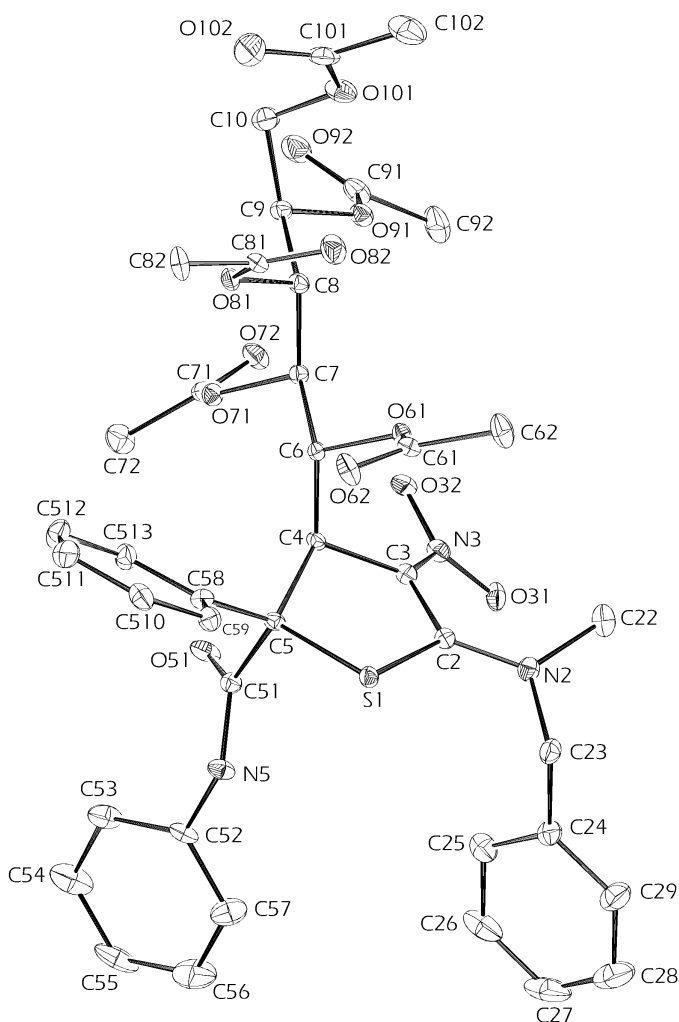
The crystal structure of the title compound,  $\text{C}_{40}\text{H}_{43}\text{N}_3\text{O}_{13}\text{S}$ , has been determined at room temperature and at 150 K. From the cycloaddition of thioisomünchnones with chiral nitroalkenes, two diastereomeric dihydrothiophenes were obtained, showing that regioselectivity and facial selectivity were involved in these cycloadditions reactions where only one of the two diastereomeric dihydrothiophenes could be isolated in the solid state. The chiralities of the two new centres at C4 and C5, determined with respect to that known at C6 are *R,R*. *N*-H...*O* hydrogen bonds join the molecules in chains running along the *c* axis.

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**Comment**

As a part of ongoing studies (Diáñez *et al.*, 1999) on compounds obtained by cycloaddition of thioisomünchnones with chiral nitroalkenes, a series of 1,3-thiazolium-4-olate systems have been prepared from thioureido derivatives. 1,3-Dipolar cycloadditions of thioisomünchnones with *trans*- $\beta$ -nitrostyrene give a mixture of two cycloadducts which convert into 4,5-dihydrothiophenes in moderate to good yields. Reactions are regioselective and proceed with a complete facial selectivity to form two diastereomeric dihydrothiophenes by attack of the mesoionic heterocycle on only one face of the nitroalkene. To clarify this type of reaction, the structure determination of (4*R*,5*R*)-2-(*N*-methyl-benzylamino)-3-nitro-4-(1',2',3',4',5'-penta-*O*-acetyl-*D*-manno-pentitol-1-yl)-5-phenyl-5-phenylcarbamoyl-4,5-dihydrothiophene, (I), was undertaken by X-ray diffraction. The absolute configuration of the molecule is established by the known configuration of the *D*-manno moiety of the starting material and the value of the resulting Flack (1983) parameter is in accordance with this configuration.





**Figure 1**

An ORTEP plot (Johnson, 1976) of (I) along the *c* axis, showing 30% probability displacement ellipsoids. For clarity, the H atoms have been omitted.

The structure of (I) was determined first at room temperature and later at 150 K, to reduce dynamical disorder. The displacement parameters at 150 K are almost half of those calculated at room temperature. It was in order to overcome these difficulties that the structure was studied at low temperature. Fig. 1 shows an ORTEP plot (Johnson, 1976) of the molecule viewed along the *c* axis, together with the atomic numbering scheme. The two bond lengths involving sulfur, namely S1–C2 and S1–C5, are unequal (see Table 1), the shorter one being involved in  $\pi$ -conjugation with the N2–C2=C3 system. The mean values for the bond lengths are C–C(phenyl) 1.385 (6), C–C(sugar chain) 1.525 (4), C–C(acetyl group) 1.490 (6), C=O(acetyl) 1.200 (4), O–C(acetyl) 1.443 and O–C(chain) 1.215 (4) Å. The sugar chain is not planar but the three phenyl groups are planar. The dihydrothiophene ring adopts a configuration intermediate between envelope and twist  ${}^4T_3$ . The Cremer & Pople (1975) puckering para-

eters are  $Q = 0.354$  (2) Å and  $\varphi = 135.0$  (4)°. The smallest asymmetry parameters (Nardelli, 1983) are  $\Delta C_2(C2) = 0.021$  (1) and  $\Delta C_s(C4) = 0.109$  (1). Atoms C58 and C6 are on the same side with respect to the best plane through the dihydrothiophene ring, at distances of 0.394 (3) and 1.715 (3) Å, respectively, and N3, N2 and C51 are on the opposite side, at distances of –0.548 (3), –0.100 (3) and –1.796 (3) Å, respectively. The chirality of the two chiral centres at C4 and C5 are *R,R* as determined with respect to that known at C6 from the reagent used in the synthesis. Selected torsion angles, C6–C4–C5–S1 –94 (2), H4–C4–C5–S1 147 (2), C3–C4–C5–S1 34 (2), C3–C4–C6–O61 –23 (3), C3–C4–C6–H6 –145 (3) and C3–C4–C6–C7 95 (3)° confirm this chirality. The crystal packing is stabilized by an extensive network of hydrogen bonds and the molecules are joined in chains running along the *c* axis by N–H...O hydrogen bonds whose geometry is given in Table 2; some intramolecular hydrogen bonds are also listed there.

## Experimental

Crystals of (I) were obtained by reaction between 3,5-diphenyl-2-(*N*-methylbenzylamine)-1,3-thiazolium-4-olate and (*E*)-3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-*C*-nitro-*D*-manno-hept-1-enitol in chloroethane at room temperature and recrystallization from ethoxyethane; only one of the two diastereoisomers could be isolated. Crystals of (I) were synthesized in the Organic Chemistry Department of Extremadura University by Avalos *et al.* (1996). The absolute configuration was assigned on the basis of the known chirality of the *D*-manno compound used in the synthesis. Since compound (I) crystallizes in a polar space group, polar-axis restraints were applied according to the method of Flack & Schwarzenbach (1988) and the absolute configuration was established, as described by Flack (1983).

### Crystal data

$C_{40}H_{43}N_3O_{13}S$	$D_x = 1.352 \text{ Mg m}^{-3}$
$M_r = 805.83$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 15.575$ (3) Å	$\theta = 6\text{--}10^\circ$
$b = 10.434$ (8) Å	$\mu = 0.15 \text{ mm}^{-1}$
$c = 12.217$ (3) Å	$T = 150$ (2) K
$\beta = 94.65$ (1)°	Prism, yellow
$V = 1978.8$ (16) Å <sup>3</sup>	0.40 × 0.28 × 0.24 mm
$Z = 2$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	$h = 0 \rightarrow 20$
$\omega$ –2 $\theta$ scans	$k = 0 \rightarrow 13$
5019 measured reflections	$l = -16 \rightarrow 16$
5019 independent reflections	3 standard reflections
4290 reflections with $I > 2\sigma(I)$	frequency: 120 min
$\theta_{\text{max}} = 28.0^\circ$	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\text{max}} = 0.029$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
5019 reflections	$\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$
514 parameters	Absolute structure: Flack (1983)
H-atom parameters not refined	Flack parameter = 0.00 (8)

**Table 1**

Selected geometric parameters (Å, °).

S1—C2	1.766 (2)	N2—C22	1.468 (4)
S1—C5	1.838 (3)	N2—C23	1.470 (4)
O31—N3	1.243 (3)	N3—C3	1.402 (3)
O32—N3	1.249 (3)	N5—C51	1.351 (3)
O51—C51	1.215 (4)	N5—C52	1.430 (4)
O61—C61	1.362 (3)	C2—C3	1.384 (4)
N2—C2	1.340 (3)		
C2—S1—C5	92.53 (12)	C3—C2—S1	110.9 (2)
C2—N2—C22	122.2 (2)	C2—C3—N3	123.7 (2)
C2—N2—C23	121.3 (2)	N3—C3—C4	119.1 (2)
C22—N2—C23	116.4 (2)	C4—C5—S1	105.05 (18)
O31—N3—O32	121.6 (2)	N2—C23—C24	113.8 (3)
O31—N3—C3	120.6 (2)	O51—C51—N5	123.5 (3)
O32—N3—C3	117.7 (2)	N5—C51—C5	116.3 (2)
C51—N5—C52	122.5 (2)	C53—C52—N5	121.2 (3)
N2—C2—C3	131.1 (2)	C57—C52—N5	118.6 (3)
N2—C2—S1	117.8 (2)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C7—H7...O32	1.00	2.29	3.076 (3)	134
C9—H9...O72	1.00	2.60	3.172 (4)	116
C22—H22 <i>A</i> ...O31	0.98	2.19	2.676 (4)	109
C53—H53...O51	0.95	2.59	2.916 (4)	100
N5—H5...O92 <sup>i</sup>	0.88	2.13	2.966 (4)	160
C23—H23 <i>B</i> ...O31 <sup>ii</sup>	0.99	2.54	3.265 (5)	130
C22—H22 <i>B</i> ...O31 <sup>ii</sup>	0.98	2.50	3.171 (5)	126
C511—H511...O62 <sup>iii</sup>	0.95	2.97	3.350 (4)	105
C512—H512...O62 <sup>iii</sup>	0.95	2.63	3.176 (4)	117

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

All H atoms were placed at idealized positions using a riding model and not refined. The isotropic displacement parameters of each methyl H atom was fixed at 1.5 times the equivalent isotropic displacement parameters of the attached C atom; for other H atoms

the factor was 1.2.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *SET4* (de Boer & Duissenberg, 1984) and *CELDIM* (in *CAD4*; Retting, 1989); data reduction: *XRAY76* (Stewart *et al.*, 1976); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

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