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Carbohydrate Research 302 (1997) 53–66

CARBOHYDRATE RESEARCH

The crystal and molecular structures of 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide and 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide

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Received 9 October 1996; accepted in revised form 10 April 1997

Abstract

Crystals of 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide (**1**) and 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide (**2**) are monoclinic, space group $P2_1$, with two independent thioxylosides molecules in the asymmetric unit. The unit cell dimensions are $a = 26.385$, $b = 5.934$, $c = 8.902$ Å, and $\beta = 109.90°$ for **1** and $a = 16.033$, $b = 16.676$, $c = 6.459$ Å, and $\beta = 91.26°$ for **2**. The present work provides structural information on the influence of substitution of intracyclic and glycosidic oxygen atoms by sulfur atoms, as well as on the influence of aromatic rings and of sulfoxide groups on the carbohydrate moiety. In both molecules, the xylopyranosides rings have the classical $^4C_1$ conformation. For **1**, the orientation of the phenyl substituent with respect to the xylopyranose is very similar in the two independent molecules: the Φ and Ψ torsion angles are respectively: (−99.5°, 153.8°) and (−102.1°, 154.2°). This is not the case for **2**, for which these values are strikingly different: (−79.4°, 172.1°) and (−130.2°, −178.4°). In each structure, the molecules are hydrogen bonded within a network of infinite chains. © 1997 Elsevier Science Ltd.

Keywords: Thioxylopyranosides; Synthesis; Crystal structure; Conformation; Glycosaminoglycans

1. Introduction

Following the structural characterization of β-D-xylopyranoside derivatives [1–3], we report in the present study the synthesis and the elucidation of the molecular and crystalline structures of 4-cyanophenyl

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PII S0008-6215(97)00113-4

1,5-dithio-β-D-xylopyranoside β-S-5 oxide (**1**) and 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside β-S-5 oxide (**2**) by X-ray diffraction. β-D-Xylopyranoside derivatives are inducers of the synthesis of glycosaminoglycans [4]. Some of them display antithrombotic activity, and they already have been evaluated in different animal models [4]. In order to relate the structural features of such molecules to their physical and biological properties, a description of their conformational preferences is required. Sugars and their derivatives containing sulfur in place of the ring oxygen give rise to a new type of carbohydrate by oxidation of the sulfur to the sulfoxide or sulfone levels. The crystal structure analyses of the title compounds have been undertaken to extend the structural data on thiocarbohydrates and to determine the influence of the sulfoxide groups on the molecular geometries and conformations of these β-D-thioxylopyranosides.

2. Experimental

General methods.—TLC was performed on precoated plates of Silica Gel $60F_{254}$ (E. Merck); components were detected by UV light and by spraying the plates with 10% H_2SO_4 and subsequent heating. Melting points were determined with an Electrothermal Apparatus. Specific rotations were recorded with a Perkin–Elmer 241 polarimeter. ^{1}H NMR spectra were recorded with Bruker AC-300 spectrometer, and chemical shifts refer to an internal standard of Me_4Si (δ 0.00). Elemental analyses were performed on a CHN 2400 Perkin–Elmer apparatus.

4-Cyanophenyl 1,5-dithio-β-D-xylopyranoside β-S-5 oxide (**1**).—To a suspension of 1.19 g (4.2 mmol) of **3** [22] in 40 mL of acetone was added, under inert atmosphere, at −78°, 1.04 g of 3-chloroperoxybenzoic acid (70%). The mixture was stirred at this temperature for 4 h, hydrolyzed with MeOH and concd under reduced pressure. The so-obtained white powder was chromatographed in solvent MeOH–$CHCl_3$; 1/9 (v/v). The product was then crystallized from MeOH (0.33 g; 27% yield); mp 240 °C; $[\alpha]_D^{23}$ −194.8° (*c* 0.15, Me_2SO); ^{1}H NMR (300 MHz, $Me_2SO + D_2O$): δ 7.78 (d, 2 H, Ar), 7.64 (d, 2 H, Ar), 4.73 (d, 1 H, $J_{1,2}$ 10.8 Hz, H-1), 3.96 (m, 1 H, H-4), 3.70 (t, 1 H, $J_{1,2}$ 10.8 Hz, H-2), 3.42 (t, 1 H, $J_{2,3}$ 10.8 Hz, H-3), 3.30 (dd, 1 H, $J_{5,5'}$ 14.1, $J_{4,5}$ 3.9 Hz, H-5), 2.87 (t, 1 H, $J_{4,5'}$ 14.1 Hz, H-5′). Anal. Calcd for $C_{12}H_{13}NO_4S_2$ (299.37): C, 48.15; H, 4.38; N, 4.68. Found: C, 48.15; H, 4.60; N, 4.73.

4-ethyl-2-oxo-2H-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside α- and β-S-5 oxide (**5** and **2**).—To a suspension of 8 g (23.6 mmol) of **4** [23] in 250 mL of acetone was added, under inert atmosphere, at −78°, 5.83 g of 3-chloroperoxybenzoic acid (70%). The mixture was stirred at this temperature for 4 h, then 0.58 g of 3-chloroperoxybenzoic acid (70%) was added, and 0.58 g of the peracid was again added 2 h later. The hydrolysis was then performed with MeOH. The mixture was concd under reduced pressure and the residue chromatographed in solvent acetone–CH_2Cl_2–water; 8:2:0.1 (v/v/v). Both isomers were crystallized from MeOH:

5 (2.51 g; 30% yield); mp 242 °C; $[\alpha]_D^{24}$ +75° (*c* 1.0, Me_2SO); ^{1}H NMR (300 MHz, $Me_2SO + D_2O$): δ 7.75 (d, 1 H, Ar), 7.30 (s, 1 H, Ar), 7.18 (d, 1 H, Ar), 6.20 (s, 1 H, CH=), 5.58 (d, 1 H, $J_{1,2}$ 9.2 Hz, H-1), 3.39 (m, 4 H, H-2, H-4, H-5, H-5′), 3.15 (t, 1 H, $J_{2,3}$ 11.1 Hz, H-3), 2.81 (dd, 2 H, *J* 7.2, J 14.5 Hz, CH_2), 1.23 (t, 3 H, CH_3). Anal. Calcd for $C_{16}H_{18}O_7S \cdot 0.44H_2O$ (362.29): C, 53.44; H, 5.25. Found: C, 53.51; H, 5.14.

2 (2.51 g; 30% yield); mp 268 °C; $[\alpha]_D^{24}$ −247° (*c* 1.0, Me_2SO); ^{1}H NMR (300 MHz, $Me_2SO + D_2O$): δ 7.78 (d, 1 H, Ar), 7.27 (s, 1 H, Ar), 7.11 (d, 1 H, Ar), 6.21 (s, 1 H, CH=), 5.25 (d, 1 H, $J_{1,2}$ 9.6 Hz, H-1), 4.00 (m, 2 H, H-2, H-4), 3.41 (t, 1 H, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 3.29 (dd, 1 H, $J_{4,5}$ 3.3 Hz, H-5), 2.86 (m, 3 H, CH_2, H-3), 3.39 (m, 4 H, H-2, H-4, H-5, H-5′), 3.20 (t, 1 H, $J_{2,3}$ 11.1 Hz, H-3), 2.79 (m, 3 H, CH_2, H-3), 1.18 (t, 3 H, CH_3). Anal. Calcd for $C_{16}H_{18}O_7S$ (354.38): C, 54.23; H, 5.12. Found: C, 53.94; H, 4.99.

Crystals of **1** and **2** were grown by slow evaporation from an ethanolic soln at room temperature. Single crystals of dimensions 0.08 × 0.31 × 0.15 mm and 0.25 × 0.41 × 0.19 mm were, respectively, used for **1** and **2**. Accurate unit-cell parameters were determined by a least-squares fit to the setting angles at high 2θ values. Lorentz and polarization corrections were applied. No absorption correction has been made, being given the crystal dimensions. The unit-cell parameters and crystallographic data of interest for **1** and **2** are given in Table 1.

For **1** and **2**, the intensities of 2200 and 2853 reflections, respectively, were measured inside the sphere limited by $2\theta < 125°$ at the Cu wavelength using the ω-2θ Philips PW1100 diffractometer. The average of three reference reflections monitored each hour showed no noticeable decreased during the data collection time. All the intensities were corrected from the background noise. From the 2200 (**1**) and

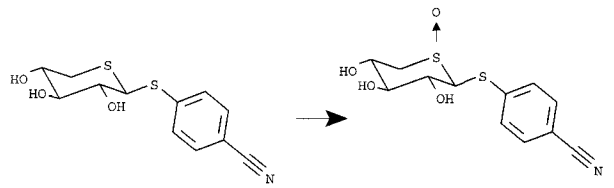
Table 1
Crystal data and structure determination data for 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide (**1**) and 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide (**2**)

	1	**2**
Molecular formula	$C_{12}H_{13}NO_4S_2$	$C_{16}H_{18}O_7S \cdot 2H_2O$
Molar mass	299.36	390.41
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Z	4	4
a (Å)	26.385(5)	16.033(5)
b (Å)	5.934(4)	16.676(4)
c (Å)	8.902(4)	6.459(4)
β (°)	109.90(5)	91.26(5)
Dc (kg·dm^{-3})	1.517	1.502
Crystal size (mm)	0.08×0.31×0.15	0.25×0.41×0.19
$F(000)$ (e^-)	624	824
μ (cm^{-1})	37.90	21.22
T (K)	292	291

2853 (**2**) measured reflections, 1812 and 2050 such as $I/\sigma(I) > 2\sigma$ were respectively considered as observed. Scattering factors were taken from the International Tables of Crystallography [24]. The structure was solved by direct methods [25,26] allowing the location of all C, O, S, and N atoms. The H atoms were located by successive difference Fourier maps and isotropic refinement. The last refinement cycles were performed using an anisotropic thermal temperature factor for the non-hydrogen atoms, whereas the hydrogen atoms were assigned an isotropic temperature factor. During the refinement, each reflection was given a weight $w = 1/\sigma(F_o)2$ derived from $\sigma(I)$. The final R-values were 0.055 and $Rw = 0.063$ for **1** and 0.055 and $Rw = 0.067$ for **2**. Final electron density maps showed no significant residual density.

3. Results and discussion

Synthesis.—The same method was used for the two xylosides **3** and **4** (see Schemes 1 and 2). The oxidation was performed with 3-chloroperoxybenzoic

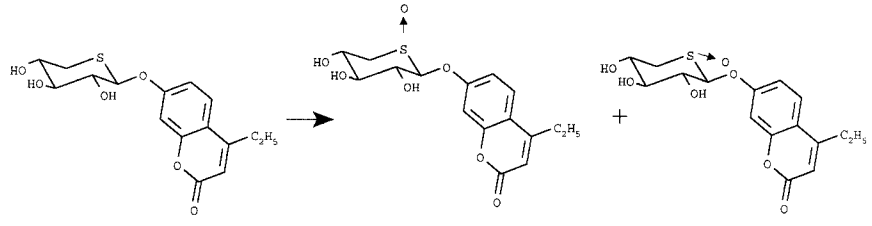


3 **1**

Scheme 1.

acid [5,6] rather than with sodium metaperiodate [7], which is less favorable. From compound **3**, the axial isomer **2** was only obtained in a poor yield (27%) due, in part, to crystallization problems. The xyloside **4**, in contrast, gave a mixture of sulfoxides **2** and **5** in a high yield (89%). This mixture was chromatographed to obtain, after crystallization, the pure isomers both in a 30% yield. On the basis of the ^{1}H NMR spectra, we can established the configuration of the S–O center in **1**, **2**, and **5**. A significant deshielding of the protons that are *syn*-axial to the axial sulfoxide group (Table 2) was noticed [5]. In addition, the chemical shift difference for the resonance of the protons H-5 and H-5′ is larger (0.15 ppm) when the sulfoxide oxygen is axial than when it is equatorial [5].

Structural studies.—A schematic representation of **1** and **2**, along with the labeling of the atoms, is given in Fig. 1. A representation of the pair of symmetry independent molecules **1**A and **1**B and **2**A and **2**B is respectively shown in Figs. 2 and 3. The structural analysis was performed with the aid of the PLATON program [8], which was also used to obtain the representations which depict the anisotropic temperature factors. The representations of the packing of the molecules in the unit cells have been obtained with the aid of PLUTON, the companion program of PLATON. The positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are



4 **2** **5**

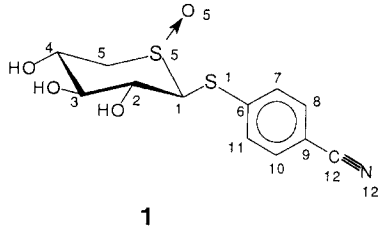
Scheme 2.

Table 2
^{1}H NMR chemical shifts (Me_2SO, 300 MHz) of compounds **1–5**

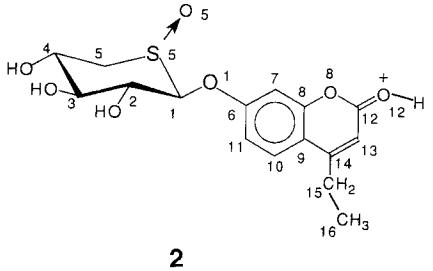
H	δ (ppm)				
	3	**1**	**4**	**2**	**5**
H-2	3.37	3.70	3.60	4.00	3.39
H-4	3.46	3.96	3.46	4.00	3.39

given in Tables 3 and 4. Bond lengths and angles are reported in Tables 5 and 6. The standard deviations for the non-hydrogen-atom bond distances and angles are given in the tables. For bond distances and angles involving hydrogen atoms the respective standard deviations amount to 0.02 Å and 2°. The mean C–H distance for both independent molecules of **1** is 1.00 Å (**1**A: range 1.00–1.01 Å; **1**B: range 0.99–1.01 Å), whereas in **2** it is 1.02 Å (**2**A: range 0.98–1.06 Å; **2**B: range 1.00–1.03 Å). For **1**, the mean O–H distances of the two molecules are 1.00 (**1**A: range 0.91–1.08 Å) and 0.94 Å (**1**B: range 0.98–1.01 Å), whereas in **2** these are 0.99 (**2**A: range 0.98–1.00 Å) and 1.00 Å (**2**B: range 0.99–1.00 Å). The mean C–C distance in the phenyl groups is 1.39 (**1**A) and 1.38 Å (**1**B) for **1** and 1.38 (**2**A) and 1.39 Å (**2**B) for **2**.

The crystal structural investigations of carbohydrate thio-analogs reported in the literature deal mainly with monosubstituted derivatives (either in the ring or in the glycosidic position [9–11]). To our knowledge, only two X-ray investigations have been reported for molecules substituted in both positions



1



2

Fig. 1. Schematic representation of 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide (**1**) and 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide (**2**) together with the labeling of some atoms.

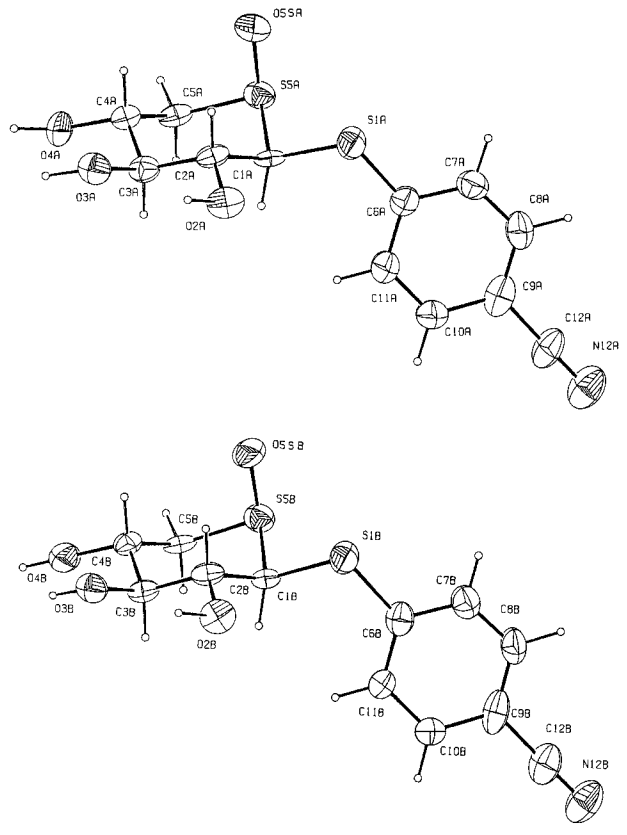


Fig. 2. ORTEP plot of 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide. Thermal ellipsoids at 50% probability.

[12,3]. The present work therefore extends the structural data available on this family of compounds and can be used to analyze the structural influence of the oxygen-sulfur atoms substitutions in both positions. It can also be used to determine the influence of the sulfoxide groups on the molecular geometry and conformation of such derivatives.

The geometrical characteristics of the xylopyranose rings of the two independent molecules of **1** are in agreement with the one reported for carbohydrate structures in which both intracyclic and glycosidic oxygen atoms have been substituted by a sulfur atom [12,3]. The two xylopyranose residues have the expected $^4C_1$ conformation. The internal C–C–C pyranose ring angles exhibit a significant opening: molecule A: range 110.2–112.8°, mean 112.2°; molecule B: range 110.5–112.5°, mean 111.8°. The endocyclic C–C–S angles have an average of 112.3° for molecule A and 112.1° for molecule B. The exocyclic C–C–O bond angles show a wide variation: from 107.0° to 111.1°, with an average of 109.8° for molecule A; from 106.7° to 110.8°, with an average of 109.4° for molecule B. The endocyclic

C-1–S-5–C-5 angle, of 98.7 and 97.0° for molecule A and B, respectively, is more acute than for a cyclic oxygen, this value being in agreement with the ones already reported for 1,5-dithiopyranosides [12,3]. The torsion angles around the pyranose rings and the glycosidic linkages are given in Table 7. As observed by Girling and Jeffrey [12], the angles about the C–S ring bonds are among the smallest torsion angles in the ring, whereas in the pyranose sugars, the corresponding C–O torsion angles are the largest.

The geometrical characteristics of the xylopyranose rings of the two independent molecules of **2** are in agreement with the one reported for carbohydrates structures in which the intracyclic oxygen atom has been substituted by a sulfur atom [12–15]. The two xylopyranose residues have the expected $^4C_1$ conformation. The internal C–C–C pyranose ring angles exhibit a significant opening: molecule A: range 110.5–113.9°, mean 111.9°; molecule B: range 111.6–113.0°, mean 112.3°. The endocyclic C–C–S angles have an average of 110.7° for molecule A and 112.7° for molecule B. The exocyclic C–C–O bond angles show a wide variation: from 104.4° to 110.8°, with an average of 108.4° for molecule A; from 106.0° to 109.4°, with an average of 108.0° for molecule B. The endocyclic C-1–S-5–C-5 angle, of

Table 3
Atomic positional parameters and equivalent thermal parameters for 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide (**1**)

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)
S-1A	0.0566(1)	0.8268(6)	0.6308(3)	0.0353
S-5A	0.1391(1)	1.0395(5)	0.8954(3)	0.0420
O-2A	0.1500(3)	0.5570(1)	0.5851(7)	0.0389
O-3A	0.2568(3)	0.665(1)	0.7246(7)	0.0384
O-4A	0.2955(2)	0.884(1)	1.0195(8)	0.0427
O-5SA	0.1439(5)	1.2290(5)	0.7864(1)	0.0487
N-12A	−0.1303(4)	0.149(2)	0.840(1)	0.0562
C-1A	0.1239(4)	0.787(2)	0.772(1)	0.0248
C-2A	0.1655(4)	0.745(2)	0.688(1)	0.0285
C-3A	0.2217(4)	0.711(2)	0.810(1)	0.0319
C-4A	0.2421(4)	0.918(2)	0.918(1)	0.0298
C-5A	0.2070(4)	0.976(2)	1.016(1)	0.0308
C-6A	0.0148(4)	0.674(2)	0.710(1)	0.0356
C-7A	−0.0384(4)	0.742(2)	0.671(1)	0.0399
C-8A	−0.0757(4)	0.615(2)	0.707(1)	0.0445
C-9A	−0.0604(4)	0.410(2)	0.784(1)	0.0397
C-10A	−0.0075(4)	0.334(2)	0.826(1)	0.0448
C-11A	0.0297(4)	0.465(2)	0.788(1)	0.0448
C-12A	−0.0994(4)	0.260(2)	0.814(1)	0.0450
S-1B	0.4431(1)	0.3177(6)	0.5176(3)	0.0435
S-5B	0.3603(1)	0.1055(5)	0.6158(3)	0.0372
O-2B	0.3498(3)	0.595(1)	0.2869(7)	0.0421
O-3B	0.2432(4)	0.4879(4)	0.210(1)	0.0376
O-4B	0.2042(3)	0.270(1)	0.4275(9)	0.0446
O-5SB	0.3555(6)	−0.0750(7)	0.4975(3)	0.0547
N-12B	0.6309(4)	1.005(2)	1.099(1)	0.0605
C-1B	0.3752(4)	0.366(2)	0.523(1)	0.0435
C-2B	0.3343(4)	0.405(2)	0.358(1)	0.0295
C-3B	0.2783(4)	0.443(2)	0.368(1)	0.0305
C-4B	0.2577(4)	0.237(2)	0.434(1)	0.0290
C-5B	0.2929(4)	0.179(2)	0.602(1)	0.0267
C-6B	0.4857(4)	0.480(2)	0.681(1)	0.0387
C-7B	0.5383(4)	0.411(2)	0.748(1)	0.0423
C-8B	0.5758(4)	0.535(2)	0.857(1)	0.0435
C-9B	0.5606(5)	0.743(5)	0.903(1)	0.0386
C-10B	0.5080(4)	0.818(2)	0.840(1)	0.0436
C-11B	0.4701(4)	0.687(2)	0.727(1)	0.0418
C-12B	0.6000(4)	0.895(2)	1.011(1)	0.0295

Table 4
Atomic positional parameters and equivalent thermal parameters for 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylo-pyranoside S-5 oxide (**2**)

Atom	*x/a*	*y/b*	*z/c*	*U*(iso)
S-5A	0.1938(2)	0.1757(2)	1.3866(4)	0.0586
O-1A	0.2335(4)	0.0282(6)	1.4666(2)	0.0472
O-2A	0.1605(3)	−0.0385(5)	1.1284(2)	0.0663
O-3A	0.0367(4)	0.0495(6)	0.9206(2)	0.0848
O-4A	0.0559(4)	0.2144(6)	0.8746(2)	0.0612
O-5SA	0.1215(5)	0.1703(5)	1.507(1)	0.0586
O-8A	0.5191(3)	0.1151(3)	1.4914(9)	0.0387
O-12A	0.6492(3)	0.1585(4)	1.496(1)	0.0467
C-1A	0.2142(5)	0.0767(5)	1.291(1)	0.0395
C-2A	0.1358(6)	0.0411(6)	1.192(2)	0.0549
C-3A	0.1078(6)	0.0885(6)	1.006(2)	0.0567
C-4A	0.0849(5)	0.1748(5)	1.054(1)	0.0454
C-5A	0.1602(6)	0.2196(5)	1.147(2)	0.0529
C-6A	0.3137(5)	0.0338(5)	1.552(1)	0.0379
C-7A	0.3800(5)	0.0749(5)	1.471(2)	0.0387
C-8A	0.4555(4)	0.0725(4)	1.578(1)	0.0285
C-9A	0.4667(5)	0.0317(4)	1.763(1)	0.0296
C-10A	0.3978(5)	−0.0089(5)	1.835(1)	0.0421
C-11A	0.3224(5)	−0.0080(5)	1.738(1)	0.0435
C-12A	0.5972(5)	0.1192(5)	1.583(1)	0.0360
C-13A	0.6109(4)	0.0768(5)	1.772(1)	0.0352
C-14A	0.5493(5)	0.0355(5)	1.862(1)	0.0322
C-15A	0.5616(5)	−0.0084(6)	2.062(1)	0.0435
C-16A	0.6491(6)	−0.0055(6)	2.153(2)	0.0435
S-5B	0.1635(2)	−0.1843(2)	1.5954(4)	0.0564
O-1B	0.2343(3)	−0.2035(3)	1.9495(9)	0.0419
O-2B	0.2016(4)	−0.3667(4)	1.9848(9)	0.0473
O-3B	0.0862(4)	−0.4359(4)	1.711(1)	0.0545
O-4B	0.0942(4)	−0.3836(4)	1.3000(9)	0.0537
O-5SB	0.0798(6)	−0.1649(7)	1.676(2)	0.1169
O-8B	0.5208(3)	−0.2829(4)	1.9858(9)	0.0328
O-12B	0.6515(3)	−0.3230(4)	1.995(1)	0.0477
O-31	0.0197(5)	0.8636(5)	0.055(2)	0.0936
O-32	0.1360(7)	0.4421(5)	0.030(2)	0.1226
O-33	0.0628(1)	0.4309(8)	0.438(2)	0.1377
O-34	0.8226(9)	0.8420(9)	0.296(3)	0.2189
C-1B	0.2151(5)	−0.2511(5)	1.778(1)	0.0372
C-2B	0.1594(5)	−0.3202(6)	1.832(1)	0.0348
C-3B	0.1411(5)	−0.3731(6)	1.646(1)	0.0411
C-4B	0.0999(5)	−0.3281(6)	1.467(1)	0.0452
C-5B	0.1496(5)	−0.2572(6)	1.403(1)	0.0461
C-6B	0.3132(5)	−0.2028(5)	2.037(1)	0.0361
C-7B	0.3802(5)	−0.2554(5)	1.955(1)	0.0435
C-8B	0.4552(5)	−0.2398(5)	2.068(1)	0.0328
C-9B	0.4675(5)	−0.1952(5)	2.247(1)	0.0326
C-10B	0.3967(5)	−0.1531(5)	2.313(1)	0.0386
C-11B	0.3231(5)	−0.1546(5)	2.209(1)	0.0346
C-12B	0.5982(5)	−0.2834(5)	2.077(1)	0.0386
C-13B	0.6094(4)	−0.2393(5)	2.263(1)	0.0374
C-14B	0.5481(5)	−0.1968(5)	2.347(1)	0.0357
C-15B	0.5601(6)	−0.1517(6)	2.546(1)	0.0463
C-16B	0.6441(7)	−0.1564(7)	2.649(2)	0.0634

97.6 and 94.8° for molecule A and B, respectively, is more acute than for a cyclic oxygen, this value being in agreement with the ones already reported for 5-thiopyranosides [12–15]. The torsion angles around the pyranose rings and the glycosidic linkages are given in Table 8. The angles about the C–S ring bonds follow the trends observed for **1** when compared to the corresponding C–O torsion angles in pyranose sugars.

The glycosidic linkage represents a molecular segment where two electronegative atoms bearing lone pairs of electrons are linked to the anomeric C atom. The electronic structure of this arrangement affects the geometry and conformation of the molecule, the resulting consequences being termed the anomeric and exo-anomeric effect [16]. If their influence on molecular geometry is well described for the C–O–C–O–C sequence, this is not the case when oxygen atom(s) are substituted by sulfur atom(s). This work illustrates the geometry of the C–S(O)–C–S–C and C–S(O)–C–O–C sequences.

The bond-length distribution in the C-5–S-5(O)–C-1–S-1 sequence observed in **1** does not follow the predicted and observed bond trends in methyl pyranosides [17]. The mean value of the C-1–S-1 bond distances is 1.831 Å, being of the same order of magnitude as the standard value of 1.817 Å for a single C–S bond. For both molecules, the C-1–S-1 bonds are larger (**1**A: 1.831 Å; **1**B: 1.831 Å) than the S-1–C-6 distances (**1**A: 1.751 Å; **1**B: 1.787 Å). For both molecules, the C-5–S-5 bond is shorter (**1**A: 1.787 Å; **1**B: 1.794) than the S-5–C-1 distance (**1**A: 1.808 Å; **1**B: 1.857 Å). Comparable differences in C–S bond lengths have been reported for 1,5-dithio-β-D-pyranosides [12,3] and for 5-thio-β-D-pyranosides [15].

The mean value of the C-1–O-1 bond distances of **2** (1.407 Å) is larger than the standard value of 1.385 Å taken by β-glycosides [18], but shorter than the standard value of 1.430 Å for a single C–O bond. The bond-length distribution in the C-5–S-5(O)–C-1–O-1 sequence observed in **2** does not follow the

Table 5
Bond lengths (Å) and angles (°) of **1**A and **1**B

Atom 1	Atom 2		Distance (Å)	
			1A	**1**B
C-1	C-2		1.524(13)	1.516(12)
C-2	C-3		1.524(14)	1.527(16)
C-3	C-4		1.539(15)	1.534(16)
C-4	C-5		1.512(15)	1.507(12)
C-1	S-1		1.808(10)	1.831(11)
S-1	C-6		1.750(11)	1.787(10)
C-1	S-5		1.820(11)	1.857(12)
C-2	O-2		1.413(12)	1.420(13)
C-3	O-3		1.411(13)	1.421(12)
C-4	O-4		1.406(12)	1.407(14)
C-5	S-5		1.788(11)	1.794(14)
S-5	O-5		1.518(7)	1.478(12)
Atom 1	Atom 2	Atom 3	Angle (°)	
			1A	**1**B
C-1	S-1	C-6	104.8(5)	104.1(6)
S-1	C-1	C-2	111.6(6)	112.3(7)
S-1	C-1	S-5	105.9(6)	103.8(6)
C-2	C-1	S-5	111.2(8)	111.7(8)
C-1	C-2	C-3	110.8(7)	110.5(8)
C-1	C-2	O-2	110.2(9)	109.6(9)
C-3	C-2	O-2	110.8(9)	109.9(9)
C-2	C-3	C-4	112.8(9)	112.4(9)
C-2	C-3	O-3	107.4(7)	106.7(8)
C-4	C-3	O-3	109.7(9)	109.4(8)
C-3	C-4	C-5	112.9(9)	112.5(9)
C-3	C-4	O-4	110.4(9)	110.8(9)
C-5	C-4	O-4	109.8(7)	110.1(8)
C-4	C-5	S-5	113.0(6)	112.6(7)
C-1	S-5	C-5	98.7(6)	97.0(7)

Table 6
Bond lengths (Å) and angles (°) of **2**A and **2**B

Atom 1	Atom 2		Distance (Å)	
			2A	**2**B
C-1	C-2		1.519(13)	1.504(12)
C-2	C-3		1.499(17)	1.514(11)
C-3	C-4		1.519(12)	1.517(11)
C-4	C-5		1.531(13)	1.489(13)
C-1	O-1		1.422(9)	1.392(9)
O-1	C-6		1.391(10)	1.374(9)
C-1	S-5		1.795(9)	1.809(8)
C-2	O-2		1.447(13)	1.416(10)
C-3	O-3		1.414(12)	1.437(11)
C-4	O-4		1.404(9)	1.423(10)
C-5	S-5		1.785(12)	1.749(9)
S-5	O-5S		1.413(8)	1.486(11)
Atom 1	Atom 2	Atom 3	Angle (°)	
			1A	**1**B
C-1	O-1	C-6	117.5(4)	121.2(6)
O-1	C-1	C-2	106.1(6)	112.0(6)
O-1	C-1	S-5	106.7(6)	104.9(5)
C-2	C-1	S-5	110.4(6)	111.0(5)
C-1	C-2	C-3	111.2(8)	111.6(7)
C-1	C-2	O-2	104.4(7)	107.7(7)
C-3	C-2	O-2	109.6(7)	108.4(6)
C-2	C-3	C-4	113.9(7)	113.0(6)
C-2	C-3	O-3	107.1(8)	107.6(7)
C-4	C-3	O-3	108.6(7)	108.9(7)
C-3	C-4	C-5	110.5(7)	112.2(7)
C-3	C-4	O-4	110.8(7)	106.0(5)
C-5	C-4	O-4	109.8(6)	109.4(7)
C-4	C-5	S-5	111.1(6)	114.5(7)
C-1	S-5	C-5	97.6(4)	94.9(4)

Table 7
Torsion angles (°) of **1**A and **1**B

Atom 1	Atom 2	Atom 3	Atom 4	Angle (°)	
				1A	**1**B
O-5	S-5	C-1	S-1	−68.3(7)	−68.1(8)
O-5	S-5	C-1	C-2	54.2(9)	53.1(10)
S-5	C-1	S-1	C-6	−99.5(6)	−102.1(5)
C-1	S-1	C-6	C-7	153.3(8)	154.2(8)
S-5	C-1	C-2	C-3	61.2(11)	63.5(11)
C-1	C-2	C-3	C-4	−61.2(12)	−62.6(11)
C-2	C-3	C-4	C-5	61.2(11)	61.8(11)
C-3	C-4	C-5	S-5	−60.1(11)	−62.0(11)
C-4	C-5	S-5	C-1	53.4(9)	54.4(9)
C-5	S-5	C-1	C-2	−54.1(8)	−56.4(8)
C-5	S-5	C-1	S-1	−176.8(5)	−177.5(4)
S-1	C-1	C-2	O-2	−56.9(10)	−59.1(10)
O-2	C-2	C-3	O-3	55.1(11)	56.4(10)
O-3	C-3	C-4	O-4	−55.8(10)	−56.1(10)

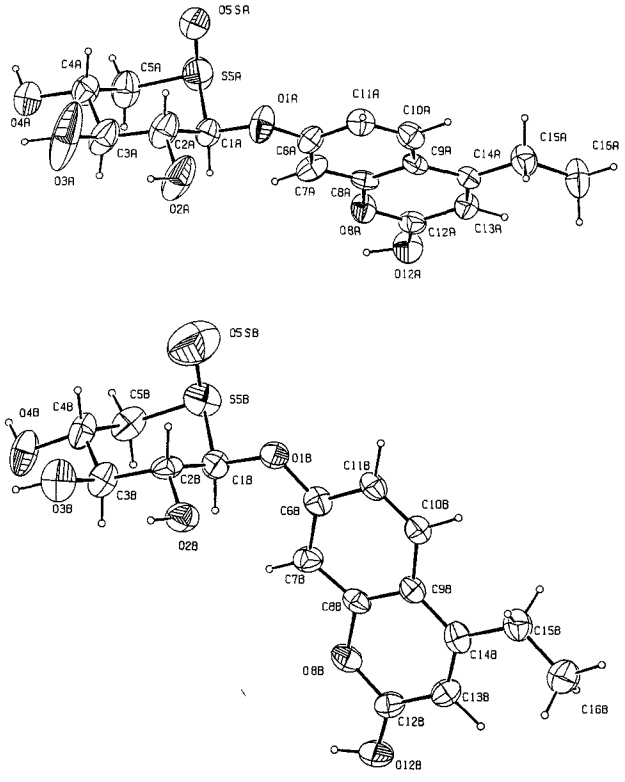


Fig. 3. ORTEP plot of 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide. Thermal ellipsoids at 50% probability.

predicted and observed bond trends in methyl pyranosides [17]. As reported by Miler-Srenger et al. [15], the C-5–S-5 bond is significantly shorter [**2B**: 1.749(9) Å] than the S-5–C-1 distance [**2B**: 1.809(8)]. For molecule **2A**, however, the C-5–S-5 and S-5–C-1 distances of 1.785(12) and 1.795(9) Å, respectively, are not significantly different from each other.

The present results also illustrate how the geometry at the anomeric center is influenced by an aromatic ring. Such structural data are available for the C–O–C–O–C and C–S–C–O–C acetal fragments [19,1,2], but, to our knowledge, only one X-ray investigation has been reported for the C–S–C–S–C arrangement [3]. The valence angles τ (C-1–S-1–C-6) (**1A**: 104.9°; **1B**: 104.1°) are larger than the mean value of 102.5° reported for 1,5-dithio-β-D-pyranosides [12,3]. For **2**, the valence angles C-1–O-1–C-6 (**2A**: 117.5°; **2B**: 121.2°) are in reasonable agreement with the range of 117° and 120° reported for aryl pyranosides [19], which is greater than the mean value of 116° reported for alkyl glucosides and disaccharides [18,20]. For **1**, the orientation of the phenyl substituent with respect to the xylopyranose residue is described by the torsion angles Φ (S-5–C-1–S-1–C-6) and Ψ (C-1–S-1–C-6–C-7). These angles have respective values of **1A**: −99.4°; **1B**: −102.1° and **1A**: 153.4°; **1B**: 154.2°. These values do not fall within the respective ranges of −65° to −85° and 180 ± 20° observed in aryl pyranoside structures [19]. The orientation of the phenyl substituent with respect to the xylopyranose residue in **2** is described by the torsion angles Φ (S-5-C-1-O-1-C-6) and Ψ (C-1-O-1-C-6-C-7). These angles have respective values of **2A**: −79.4°; **2B**: −130.2° and **2A**: 172.1°; **2B**: −178.4°. Only the Φ torsion angle of molecule A is in agreement with the range reported for aryl pyranosides. This is not the case for the Ψ torsion angles, which values are located in the range of 180 ± 20° expected for such structures. In this case, the orientation of the aromatic rings is nearly coplanar with respect to the anomeric carbon atom C-1. This con-

Table 8
Torsion angles (°) of **1A** and **1B**

Atom 1	Atom 2	Atom 3	Atom 4	Angle (°)	
				1A	**1B**
O-5	S-5	C-1	O-1	−64.7(6)	−71.1(7)
O-5	S-5	C-1	C-2	50.1(7)	50.0(7)
S-5	C-1	O-1	C-6	−79.4(8)	−130.2(6)
C-1	O-1	C-6	C-7	172.1(7)	−178.4(7)
S-5	C-1	C-2	C-3	63.5(9)	64.9(8)
C-1	C-2	C-3	C-4	−61.9(11)	−58.4(9)
C-2	C-3	C-4	C-5	60.7(10)	55.3(9)
C-3	C-4	C-5	S-5	−62.2(9)	−61.6(9)
C-4	C-5	S-5	C-1	58.5(7)	59.1(7)
C-5	S-5	C-1	C-2	−58.7(7)	−60.0(6)
C-5	S-5	C-1	O-1	−173.6(6)	178.8(5)
S-1	C-1	C-2	O-2	−63.1(9)	−59.3(8)
O-2	C-2	C-3	O-3	63.0(10)	62.9(8)
O-3	C-3	C-4	O-4	−58.1(10)	−65.9(8)

formation favours the delocalization of the electrons from the lone-pair orbitals of the glycosidic O atoms to the π orbitals of the phenyl ring. This may explain the significant opening of the τ valence angle observed for both molecules. Another relevant geometric parameter of **2** is the O-1–C-6 bond length (**2**A: 1.391 Å; **2**B: 1.374 Å). These values are intermediate between those taken respectively by a O–C single (1.42 Å) and double bond (1.22 Å). Such a partial double-bond character could reflect the resonance of the glycosidic oxygen lone pairs with the aromatic ring. This behaviour is not adopted by **1** for which the two independent molecules show glycosidic valence angles greater than the mean value reported for 1,5-dithio-β-D-pyranosides [12,3] but for which the glycosidic torsion angles do not follow the trends observed in aryl pyranosides.

The S–O bond distances of **1** (**1**A: 1.519 Å; **1**B: 1.478 Å) and **2** (**2**A: 1.413 Å; **2**B: 1.486 Å) are significantly different from each other and smaller than the values of 1.502 and 1.524 Å reported by Miler–Srenger et al. for methyl 5-thio-β-D-(*S*) and -(*R*) ribopyranoside S oxides [15]. The geometries and conformations of compounds **1** and **2**, which respectively illustrate the acetal fragments C–S(O)–C–S–C and C–S(O)–C–O–C are very close to the structural data available on the C–S–C–S–C and C–S–C–O–C sequences, showing that the sulfoxide groups do not influence significantly the molecular geometries and conformation of these molecules.

Two orthogonal views of the packing of the molecules of **1** and **2** in the unit cell are respectively displayed in Figs. 4 and 5. They help to illustrate the respective roles of hydrogen-bond and hydrophobic

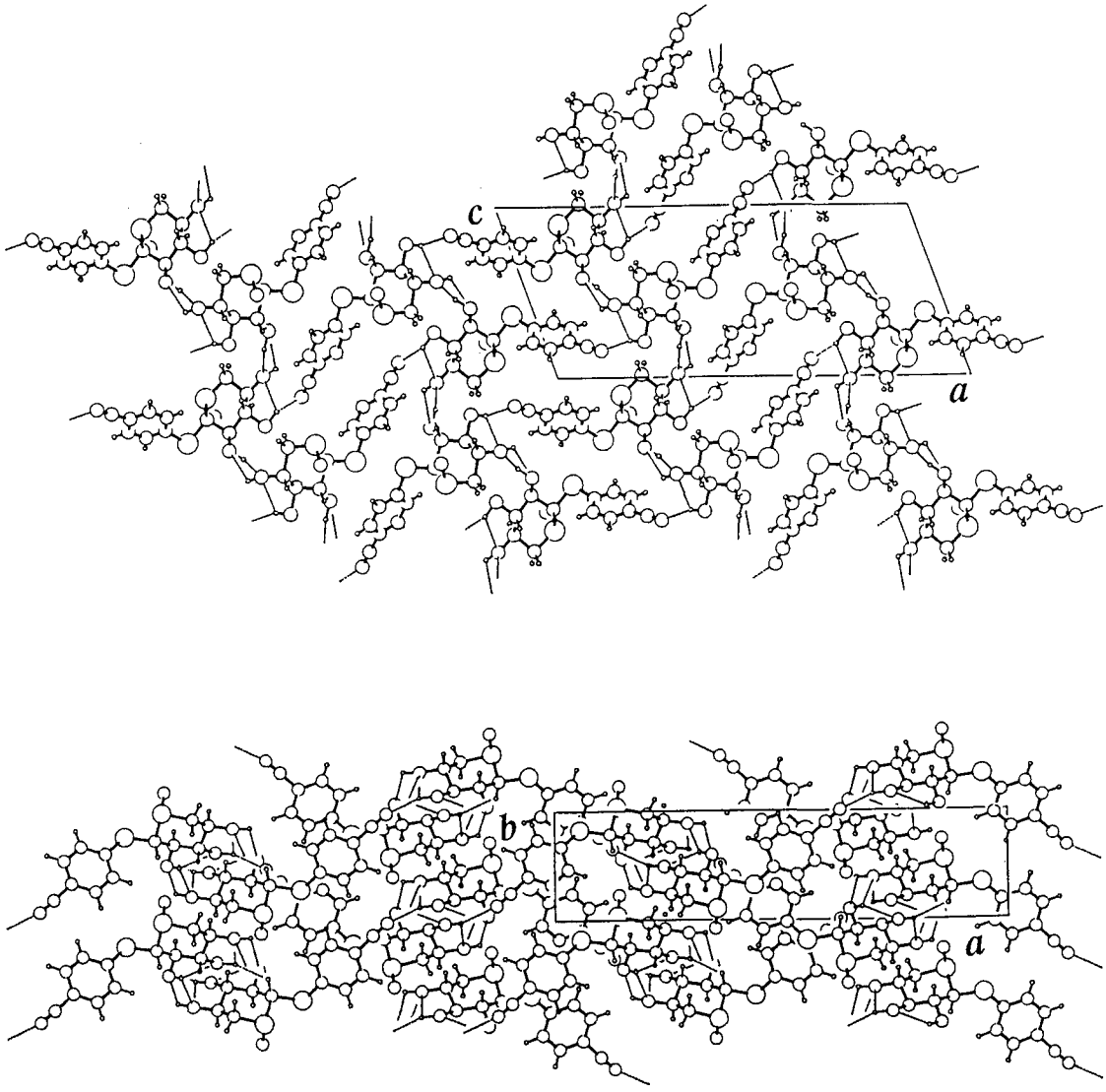


Fig. 4. Packing of the molecules of 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide. Hydrogen bonds are shown by dashed lines. (Top) View down the *b* axis; (bottom) view down the *c* axis.

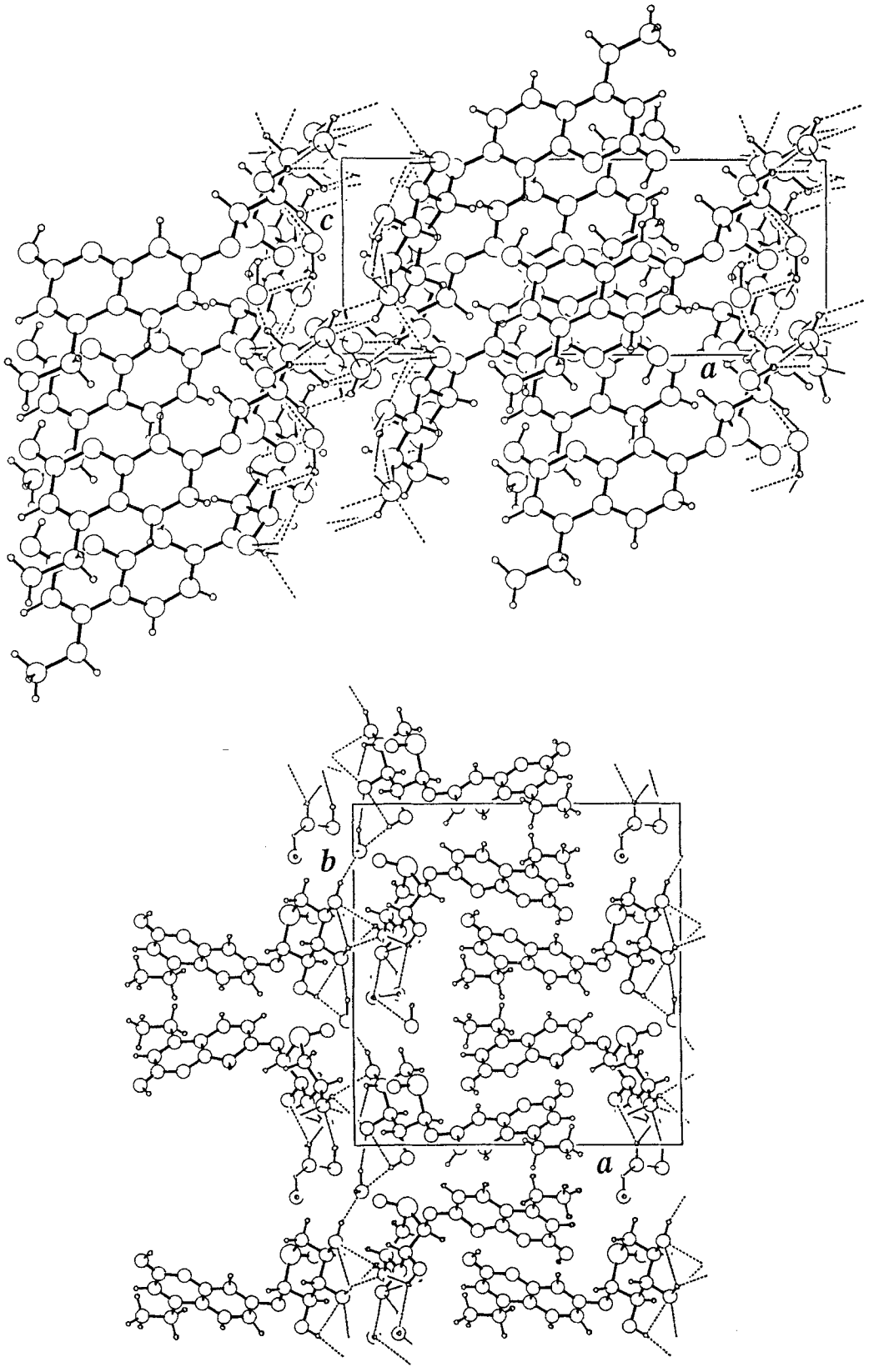


Fig. 5. Packing of the molecules of 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide. Hydrogen bonds are shown by dashed lines. (Top) View down the *b* axis; (bottom) view down the *c* axis.

interactions in the three-dimensional arrangement. In both structures, all secondary hydroxyl groups are involved in hydrogen bonding with neighbouring secondary hydroxyl groups in intra- or inter-molecular interactions; each acts both as a donor and an acceptor, except O-2–HO-2 of molecule **2**A which is only involved as a donor. The geometric characteristics of these interactions are given in Table 9 (**1**) and Table 10. (**2**), respectively. Such a use of the hydrogen-bonding potential gives rise to two bifurcated hydrogen bonds (three centers) for each independent molecule of **1**. In **2**, the presence of four water molecules in the asymmetric unit of the crystal contributes to the formation of seven bifurcated and one trifurcated hydrogen-bonds interactions (Table 10). All the water molecules use their hydrogen-bonding capacities except O-31 which uses only one hydrogen as a donor and O-34 which uses only one lone pair as an acceptor. These factors give rise to the formation of several hydrogen-bond cyclic interactions at 4, 5, and 6 rings. In none of these structures, the hydrogen-acceptor capacities of the oxygen atoms of the sulfoxides groups, the ring sulfurs and bridged sulfur (**1**) or oxygen (**2**) atoms are utilized. In **1**, the nitrogen atom of the nitrile group, which forms the end of the hydrophobic part of the molecule, utilizes its hydrogen acceptor capacity. In **2**, the hydrogen-bonding potential of the oxygen atoms of the hydrophobic part of the molecules is not used.

The crystal packing is characterized by an alternation of hydrophilic and hydrophobic regions (Figs. 4 and 5). The neighbouring molecules are arranged so as to maximize their hydrophilic interactions through the network of hydrogen-bonds interactions. These arrangements occur preferentially along the *b* and *c* crystallographic axes. They stack in columns in which hydrophobic contacts between the aromatic rings are favored; these contacts also involve the most hydrophobic moiety of xylopyranose, around C-5–S-5(O) and C-1–S-1 (**1**) or C-1–O-1 (**2**). As already observed [1–3], these hydrophobic interactions occur preferentially along the longest axis (*a*) of the crystalline unit cells. As observed for the crystal structures of methyl 1-thio-α- [21], 5-thio-α-, and 5-thio-β-D-ribopyranosides [13], the molecular packing in thiopyranosides is such that there is a distinct segregation between the polar and non-polar groups. Another common feature already reported for methyl 1,5-dithio-α- [12] and 5-thio-β-D-ribopyranosides [15] is the fact that the hydrogen-bonding network links

Table 9
Hydrogen bonding in **1**

Donor-H	Acceptor [a]	D ··· A (Å)	D–H (Å)	H ··· A (Å)	D–H ··· A (°)
O-2A–H–O-2A	↗ O-3A *intra*	2.75(1)	1.00(2)	2.35(5)	102(3)
	↘ O-4B *intra*	2.89(1)	1.00(2)	2.06(5)	138(3)
O-3A–H–O-3A	↗ O-4A *intra*	2.79(1)	1.08(2)	2.32(5)	104(3)
	↘ N-12B II ($a-b+2c$)	3.00(1)	1.08(2)	1.99(4)	153(3)
O-4A–H–O-4A	→ O-2B I (c)	2.89(1)	0.95(2)	2.54(6)	102(3)
O-2B–H–O-2B	↗ O-3B *intra*	2.73(1)	1.00(2)	2.33(5)	103(3)
	↘ O-4A I ($-c$)	2.89(1)	1.00(3)	2.07(5)	138(4)
O-3B–H–O-3B	↗ O-4B *intra*	2.80(1)	0.92(3)	2.34(4)	110(5)
	↘ N-12A II (c)	3.01(1)	0.92(2)	2.16(4)	153(5)
O-4B–H–O-4B	→ O-2A II ($-a-b+2c$)	2.88(1)	0.89(2)	2.395(4)	115.1(5)

[a] Equivalent positions: (I) x, y, z (II) $-x$, $y+1/2$, $-z$.
Short contacts assuming a cutoff O ··· O < 3.20 Å:

O-2A ··· O-5SA I	($-b$)	2.69(7)
O-2B ··· O-5SB I	($+b$)	2.68(6).

the molecules so that they are packed in columns with the hydrophobic parts at the exterior of the columns.

4. Conclusion

The present work characterizes the molecular and crystalline structures of 4-cyanophenyl 1,5-dithio-β-D-xylopyranoside S-5 oxide (**1**) and 4-ethyl-2-oxo-2*H*-1-benzopyran-7-yl 5-thio-β-D-xylopyranoside S-5 oxide (**2**) by X-ray diffraction. For both compounds, two different conformers are observed in the crystalline state. The molecular geometries and conformations are very similar to their homologues non-oxydated at the ring sulfur. For one of them, however, (**1**), the conformation at the glycosidic linkage is not in agreement with the ones reported for aryl pyranosides. The present data have also illustrated the

Table 10
Hydrogen bonding in **2**

Donor-H	Acceptor [a]	D · · · A (Å)	D–H (Å)	H · · · A (Å)	D–H · · · A (°)
O-2A–H–O-2A	↗ O-31 I (−*b* + *c*)	2.82(1)	1.00(2)	1.88(4)	154(3)
	↘ O-3A *intra*	2.79(1)	1.00(2)	2.42(5)	100(3)
O-3A–H–O-3A	↗ O-4A *intra*	2.78(1)	1.08(2)	2.40(5)	101(3)
	↘ O-4B II (2*c*)	2.75(1)	1.00(2)	1.95(4)	134(3)
O-4A–H–O-4A	→ O-31 II (−*b* + *c*)	2.81(1)	0.98(2)	1.85(4)	163(3)
O-2B–H–O-2B	↗ O-3B *intra*	2.78(1)	1.00(2)	2.39(5)	102(3)
	↘ O-4B I (*c*)	2.71(1)	0.92(2)	2.20(5)	110(3)
O-3B–H–O-3B	↗ O-33 I (−*b* + *c*)	2.86(1)	1.00(2)	1.90(3)	158(3)
	↘ O-4B *intra*	2.80(1)	1.00(2)	2.41(4)	102(3)
O-4B–H–O-4B	↗ O-3A II (−*b* + 2*c*)	2.75(1)	0.99(2)	2.35(5)	103(4)
	↘ O-4A II (−*b* + 2*c*)	3.10(1)	0.99(2)	2.31(4)	135(3)
O-32-H321	→ O-33 *intra*	2.91(2)	1.06(3)	2.00(4)	143(3)
O-32-H322	→ O-3B I (*b* − 2*c*)	2.99(1)	1.07(3)	2.11(4)	136(3)
O-33-H331	↗ O-3B I (*b* − *c*)	2.86(1)	1.09(3)	2.45(4)	100(2)
	↘ O-34 II (*a* − *b* + *c*)	2.90(2)	1.09(3)	2.46(4)	102(3)
O-33-H332	→ O-4B I (*b* − *c*)	3.26(1)	1.09(3)	2.20(4)	162(3)
O-34-H341	→ O-33 II (*a* + *c*)	2.90(1)	1.09(3)	2.36(4)	108(3)
O-34-H342	→ O-32 II (*a*)	2.78(1)	1.15(3)	1.98(3)	123(3)

[a] Equivalent positions: (I) x, y, z (II) −x, y + 1/2, −z.
Short contacts assuming a cutoff O · · · O < 3.20 Å:

O-4A · · · O-5SA I	(−*c*)	2.72(1)	O-31 · · · O-5SB I	(*b* − 2*c*)	2.69(1)
O-3A · · · O-4B II	(+*c*)	2.75(1)	O-31 · · · O-32 II		2.86(1)
O-4A · · · O-34 II	(+*a* − *b* + *c*)	3.10(2)	O-32 · · · O-34 II	(*a* − *b*)	2.78(2)
O-3B · · · O-32 I	(−*b* + 2*c*)	2.99(1)	O-33 · · · O-5SB II	(2*c*)	2.87(1)
O-33 · · · O-3B I	(*b* − *c*)	2.86(1)			

lack of stabilizing influence arising from the exo-anomeric effect when such C–S(O)–C–S–C or C–S(O)–C–O–C sequences are involved. They also show the necessary compensation that must occur at the three-dimensional level to accommodate both the hydrophobic and hydrophilic moieties of such molecules. The neighboring molecules are first arranged so as to stack in columns to maximize their hydrophilic interactions through intermolecular hydrogen bonding. In the case of carbohydrate molecules bearing a bulky hydrophobic aglycon such an arrangement is most likely to require two independent molecules in the asymmetric unit.

Acknowledgements

The authors are very much indebted to Dr. B. Bachet from Laboratoire de Minéralogie Cristallographie, Université Pierre et Marie Curie, Paris for the data collection.

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