

Ethyl (4-benzyloxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate and a redetermination of ethyl (4*RS*)-4-(4-methoxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate, as its 0.105-hydrate, both at 200 K: subtly different hydrogen-bonded ribbons

Balladka K. Sarojini,^a Hemmige S. Yathirajan,^b Eric C. Hosten,^c Richard Betz^{c*} and Christopher Glidewell^{d*}

^aIndustrial Chemistry Section, Department of Chemistry, Mangalore University, Mangalagangothri 574 199, India, ^bDepartment of Studies in Chemistry, University of Mysore, Manasagangothri, Mysore 570 006, India, ^cDepartment of Chemistry, Nelson Mandela Metropolitan University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, and ^dSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: richard.betz@nmmu.ac.za, cg@st-andrews.ac.uk

Received 24 November 2014

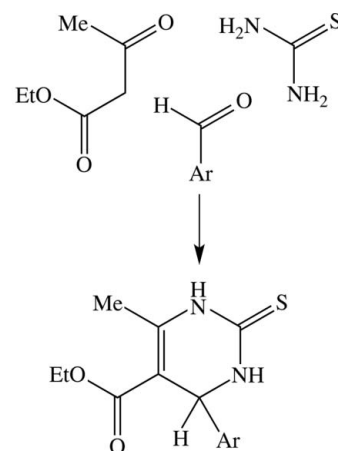
Accepted 5 December 2014

Two sulfanylidene-1,2,3,4-tetrahydropyrimidine derivatives have been synthesized using acid-catalysed cyclocondensation reactions between thiourea, ethyl 3-oxobutanoate and substituted benzaldehydes. In each of ethyl (4*RS*)-4-(4-benzyloxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate, C₂₁H₂₂N₂O₃S, (I), where Z' = 2, and ethyl (4*RS*)-4-(4-methoxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate 0.105-hydrate, C₁₅H₁₈N₂O₃S·0.105H₂O, (II), the reduced pyrimidine ring adopts a conformation intermediate between the boat, screw-boat and twist-boat forms. In (I) and (II), a combination of N—H···O and N—H···S hydrogen bonds links the organic molecules into ribbons containing alternating R₂²(8) and R₄⁴(20) rings. In (I), the ribbon contains three types of ring, *viz.* two different R₂²(8) rings which are both centrosymmetric and R₄⁴(20) rings which are not centrosymmetric. In (II), the ribbon contains two types of ring, both of which are centrosymmetric. In compound (II), the ribbons enclose continuous channels which run along the twofold rotation axes in the space group C2/c, and the partial-occupancy water molecules lie within these channels. Structural comparisons are made with a number of related compounds.

Keywords: racemic 1,2,3,4-tetrahydropyrimidine-5-carboxylate esters; cyclocondensation reaction; N—H···O and N—H···S hydrogen bonding; crystal structure; multicomponent reactions.

1. Introduction

Multicomponent reactions are of importance in synthetic chemistry because of their ability to produce quite complex molecular products from simple precursors in a single step. The multicomponent synthesis of 3,4-dihydropyrimidones or 3,4-dihydropyrimidinethiones using urea or thiourea, a keto ester and an aldehyde, catalysed by mineral acids, as developed by Biginelli (1893), is of considerable importance mainly because of the various biological activities shown by pyrimidine derivatives, such as antiviral (Hurst & Hull, 1961), anti-tumour (El-Hashash *et al.*, 1993) and antimicrobial activities (Karale *et al.*, 2002), as well as herbicidal and plant growth regulator activities (Chambhare *et al.*, 2003), and action as calcium channel blockers (Manjula *et al.*, 2004). A number of variations of the original Biginelli protocol have been developed in recent years, including the use of ionic liquids as the reaction solvent, which also act as the catalytic agent (Peng & Deng, 2001), of ultrasound irradiation (Li *et al.*, 2003), of simple metal salts as the catalytic agent (Maiti *et al.*, 2003) or of microwave irradiation (Youssef & Amin, 2012).

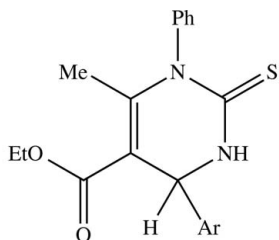


- (I) Ar = 4-PhCH₂OC₆H₄
 (II) Ar = 4-MeOC₆H₄ 0.105-hydrate
 (III) Ar = C₆H₅
 (IV) Ar = 4-FC₆H₄
 (V) Ar = 4-ClC₆H₄
 (VI) Ar = 4-MeC₆H₄
 (VII) Ar = 4-Me₂NC₆H₄
 (VIII) Ar = 3-ClC₆H₄
 (IX) Ar = 2-ClC₆H₄
 (X) Ar = 3-MeOC₆H₄
 (XI) Ar = 3-O₂NC₆H₄
 (XII) Ar = 4-NCC₆H₄
 (XIII) Ar = 3,4-(MeO)₂C₆H₃
 (XIV) Ar = 3,4,5-(MeO)₃C₆H₂ (methyl ester)

Scheme 1

We report here the molecular structures and supramolecular assembly of ethyl (4*RS*)-4-(4-benzyloxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate, (I) (Fig. 1), which was synthesized in good yields using three-component cyclocondensation reactions between thiourea, ethyl 3-oxobutanoate and 4-benzyloxybenzaldehyde, catalysed by silicon tetrachloride acting as a Lewis acid. We have also taken the opportunity to redetermine the structure

of the closely related ethyl (4*RS*)-4-(4-methoxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate, (II) (Fig. 2), using diffraction data collected at 200 K. The structure of (II) has been reported recently (Nayak *et al.*, 2010) using data collected at 292 K, but in our hands this compound crystallized as a 0.105-hydrate, whereas the previous report made no mention of any water component.



- (XV) Ar = 2-O₂N-4,5-(MeO)₂C₆H₂
 (XVI) Ar = 2-Br-5-FC₆H₃
 (XVII) Ar = 2,4-F₂C₆H₃

Scheme 2

The redetermination, as the partial hydrate, reported here converged with significantly lower *R* values (*R*₁ and *wR*₂ = 0.0359 and 0.0958, respectively, as opposed to 0.0468 and 0.1376), despite the use of a substantially larger data set (4023 unique reflections, as opposed to 2907). More importantly, however, our re-analysis of the supramolecular assembly in (II) has revealed some interesting features which appear to have been overlooked in the earlier report. The structures of a number of related compounds (see Scheme 1) have been reported in recent years; some of these have been the subject

of short single-structure reports which usually contain only a very brief structural description and, in general, no detailed analysis of the hydrogen bonding. Consequently, it seemed worthwhile to draw together these scattered results for comparative purposes in the hope that some general patterns may be discernible. The purposes of the present study are: (i) the determination of the molecular and supramolecular structure of compound (I); (ii) the re-interpretation of the supramolecular assembly in compound (II); (iii) the comparison of the supramolecular assembly in compounds (III)–(XIV) (see Scheme 1) with that in (I) and (II); (iv) to consider the differences in supramolecular assembly in some analogues, *i.e.* (XV)–(XVII) (see Scheme 2), in which only one N–H bond is present in each molecule.

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of compounds (I) and (II), a mixture of thiourea and ethyl 3-oxobutanoate (0.01 mol of each) was added at ambient temperature to a solution of the appropriately substituted benzaldehyde (0.01 mol) in acetonitrile–*N,N*-dimethylformamide (2:1 *v/v*, 50 ml). The reaction mixtures were cooled to 273 K, silicon tetrachloride (0.9 mmol) was added dropwise and the mixtures were stirred at ambient temperature for 24 h. Ice-cold water (100 ml) was added and each mixture was stirred for a further 30 min. The resulting solid products were collected by filtration, washed with water and dried under reduced pressure. Compound (I): yield 73%,

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₂₁ H ₂₂ N ₂ O ₃ S	C ₁₅ H ₁₈ N ₂ O ₃ S·0.105H ₂ O
<i>M_r</i>	382.47	308.26
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>C2/c</i>
Temperature (K)	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.0094 (4), 12.7915 (5), 14.5418 (5)	18.1455 (6), 7.3171 (2), 25.0493 (8)
α , β , γ (°)	85.567 (2), 83.815 (2), 69.150 (2)	90, 102.008 (1), 90
<i>V</i> (Å ³)	1900.96 (12)	3253.08 (17)
<i>Z</i>	4	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.19	0.21
Crystal size (mm)	0.46 × 0.45 × 0.35	0.52 × 0.48 × 0.19
Data collection		
Diffractometer	Bruker APEXII CCD diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.833, 0.935	0.906, 0.961
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	33717, 9456, 7596	14922, 4023, 3447
<i>R_{int}</i>	0.020	0.015
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.669	0.667
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.118, 1.04	0.036, 0.101, 1.04
No. of reflections	9456	4023
No. of parameters	503	202
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.55, -0.32	0.35, -0.23

Computer programs: *APEX2* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *SHELXL2014* (Sheldrick, 2015).

m.p. 433–435 K; analysis found: C 65.9, H 5.7, N 7.4%; $C_{21}H_{22}N_2O_3S$ requires: C 65.9, H 5.8, N 7.3%. Compound (II): yield 70%, m.p. 413–415 K; analysis found: C 58.8, H 5.8, N 9.1%; $C_{15}H_{18}N_2O_3S$ requires: C 58.8, H 5.9, N 9.1%. Colourless crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, from solutions in chloroform–methanol (9:1 v/v).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps. H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic C–H) and $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms. For H atoms bonded to N atoms, the atomic coordinates were refined with $U_{iso}(H) = 1.2U_{eq}(N)$, giving the N–H distances shown in Table 3. For compound (I), three low-angle reflections (001, $\bar{1}11$ and 121), and for compound (II), one low-angle reflection (002), which had all been attenuated by the beam stop, were omitted from the refinements. Examination of the refined structure of (I) showed that this structure contained no solvent-accessible voids. However, the structure of (II) contains a total void volume of 350.7 Å³ per unit cell, *ca* 10.8% of the total cell volume, arranged in the form of continuous channels aligned along the twofold rotation axes. The largest peak in the difference map, *i.e.* 0.88 e Å⁻³, was located on a twofold rotation axis within the channel and distant by *ca* 2.97 Å from the two symmetry-related atoms of type O441. Using the CIF and .fcf files from this refinement, the SQUEEZE tool (Spek, 2015) within PLATON (Spek, 2009) identified a total of 11.4 additional electrons per unit cell located in the solvent-accessible voids, equivalent to *ca* 0.14 molecules of water per molecule of the organic component. Hence, this residual peak was modelled as the O atom, denoted O71, of a partial-occupancy water molecule which was refined isotropically; the H atoms associated with this O atom could not be located in difference maps but were placed in calculated positions, with O–H = 0.935 Å and $U_{iso}(H) = 1.5U_{iso}(O)$. Inclusion of this water molecule in the refinement then gave a value of 0.105 (5) molecules of water per molecule of the organic component, close to the value indicated by SQUEEZE, and there were no significant features in the final difference map. A further application of the SQUEEZE procedure at this point indicated that essentially all of the additional electron density had been accounted for by the partially occupied water molecule. It should be emphasized here that both applications of the SQUEEZE procedure referred to above were intended only to estimate the number of electrons not yet accounted for at those stages of the refinement, and that the refinements at every stage were undertaken with the original data, independent of SQUEEZE.

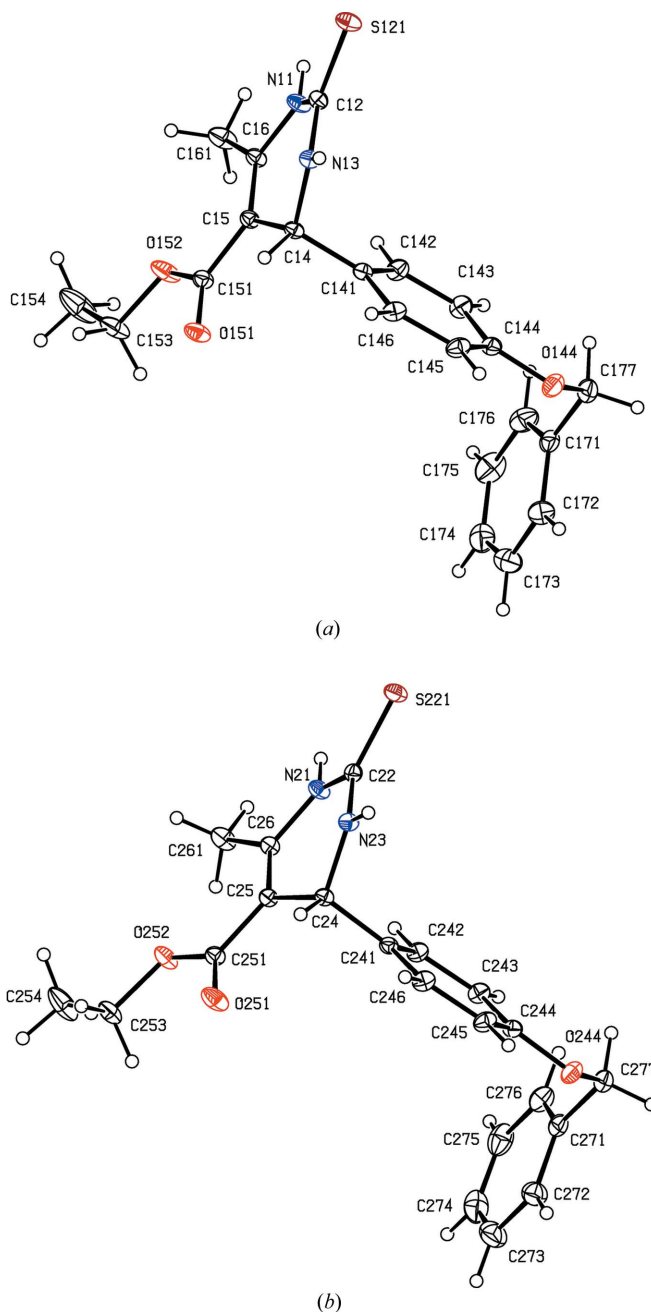
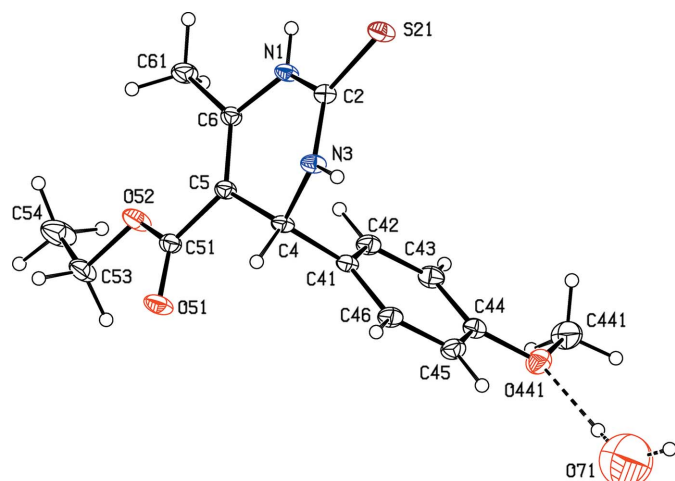


Figure 1

The molecular structures of the *R* enantiomers of the two independent molecules in compound (I), showing the atom-labelling schemes for (a) a type 1 molecule and (b) a type 2 molecule. Displacement ellipsoids are drawn at the 30% probability level.

3. Results and discussion

Compound (I) crystallizes in the space group $P\bar{1}$ with $Z' = 2$. It will be convenient to refer to the molecules of compound (I) which contain atoms S121 and S221 (*cf.* Fig. 1) as types 1 and 2, respectively. The two independent molecules in the selected asymmetric unit for (I) are related by an approximate translation of $c/2$. However, the minor but significant differences between the corresponding pairs of geometrical parameters for the two molecules (Tables 2 and 3) appear to preclude the


Figure 2

The molecular structure of the *R* enantiomer of compound (II), showing the partial-occupancy water molecule and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

possibility of them being geometrically identical, and a detailed comparison of the atomic coordinates for corresponding pairs of atoms shows that the translational relationship is, indeed, approximate but not exact. The ADDSYM routine within *PLATON* (Spek, 2009) confirms that the present reduced cell is the correct one. Nonetheless, of the reflections labelled ‘observed’ for (I), those having odd values of l are in general significantly weaker than those having even values of l .

Each of the independent molecules in compounds (I) and (II) contains a stereogenic centre, at atoms C x 4 ($x = 1$ or 2 hereafter) in (I) and at atom C4 in (II). The reference molecules were all selected at those having the *R* configuration at these atoms, but the centrosymmetric space groups confirm that compounds (I) and (II) both crystallize as racemic mixtures.

The reduced pyrimidine rings are all nonplanar and all have very similar ring-puckering (Cremer & Pople, 1975) parameters (Table 2), which indicate ring conformations intermediate between the boat, screw-boat and twist-boat forms. The ideal values of the ring-puckering angles for these three forms (Boeyens, 1978) are $\theta = 90.0$, 67.5 and 90.0° , respectively, and $\varphi = (60k)^\circ$ for the boat form and $\varphi = (60k + 30)^\circ$ for the other two forms, where k represents an integer. The conformations adopted by the ester units are also similar, as indicated by the relevant torsion angles, as are the orientations of the aryl rings bonded to the reduced pyrimidine rings (Table 2).

The alkoxy C atoms, *i.e.* C x 77 in (I) and C441 in (II), are nearly coplanar with the C41–C46 and C x 41–C x 46 aryl rings, respectively, with displacements from these ring planes of 0.148 (2) and 0.048 (2) Å for atoms C177 and C277, respectively, in (I), and of 0.220 (2) Å in (II). Associated with this near coplanarity, the corresponding pairs of exocyclic C–C–O angles in (II) and (III) all differ by *ca* 10° , as is often observed in such circumstances (Seip & Seip, 1973; Ferguson *et al.*, 1996).

Table 2

Selected geometrical parameters (Å, °).

Ring-puckering parameters are calculated for the atom sequence N x 1–C x 2–N x 3–C x 4–C x 5–C x 6, where $x = 1$ or 2 for (I) and $x = \text{nil}$ for (II).

Parameter	(I) (molecule 1, $x = 1$)	(I) (molecule 2, $x = 2$)	(II)
Ring-puckering parameters			
Q	0.3166 (13)	0.3078 (13)	0.3050 (13)
θ	75.9 (2)	74.2 (2)	69.4 (2)
φ	176.0 (2)	173.6 (3)	165.7 (3)
Torsion angles			
N x 3–C x 4–C x 41–C x 42	–93.55 (14)	–84.06 (14)	–96.71 (13)
C x 4–C x 5–C x 51–O x 51	3.35 (19)	1.32 (19)	18.17 (18)
C x 4–C x 5–C x 51–O x 52	–177.69 (12)	–179.32 (11)	–159.64 (11)
C x 5–C x 51–O x 52– x C53	–176.06 (13)	–177.45 (12)	178.66 (12)
C x 51–O x 52–C x 53–C x 54	177.87 (17)	–179.34 (15)	–175.52 (14)
C x 43–C x 44–O x 44–C x 77	–4.2 (2)	1.89 (19)	
C x 44–C x 44–C x 77–C x 71	–75.78 (16)	–71.53 (15)	
O x 44–C x 77–C x 71–C x 72	–59.75 (18)	–53.53 (18)	
C x 43–C x 44–O x 441–C x 441			7.0 (2)
Bond angles			
C x 43–C x 44–O x 44	124.95 (13)	124.95 (12)	
C x 45–C x 44–O x 44	115.74 (12)	115.44 (11)	
C x 43–C x 44–O x 441			124.56 (13)
C x 45–C x 44–O x 441			115.64 (12)

The supramolecular assembly in compounds (I) and (II) is determined by a combination of N–H \cdots O and N–H \cdots S hydrogen bonds (Table 3), where in all cases the N–H \cdots O hydrogen bonds utilize the carbonyl O atom of the ester unit as the acceptor. However, the structures contain neither any aromatic π – π stacking interactions nor any significant C–H \cdots π (arene) interactions. The only reasonably short C–H \cdots π (arene) contacts either involve a methyl C–H bond or they have a C–H \cdots C g angle less than 135° (where C g represents the ring centroid concerned); in neither case are these contacts likely to be of structural significance (Riddell & Rogerson, 1996, 1997; Wood *et al.*, 2009).

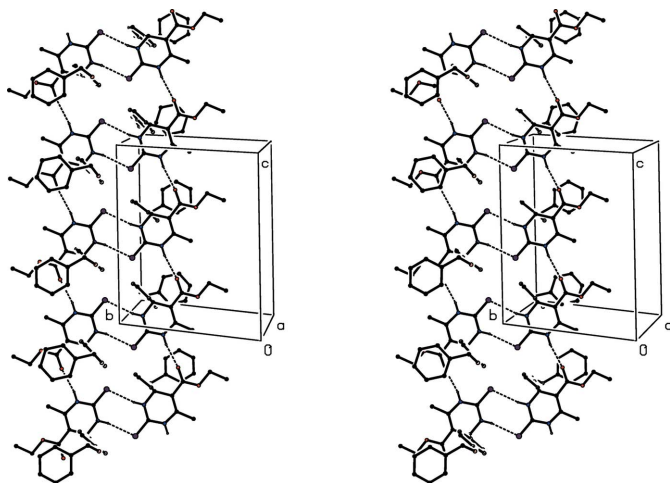
Within the selected asymmetric unit of (I), the two molecules are linked by an N–H \cdots O hydrogen bond (Table 3), and these two-molecule units are linked by a second N–H \cdots O hydrogen bond to form a C $_2^2$ (12) (Bernstein *et al.*, 1995) chain running parallel to the [001] direction (Fig. 3). Inversion-related pairs of these chains are linked by the two independent N–H \cdots S hydrogen bonds to form a ribbon. Within the ribbon, R $_2^2$ (8) rings involving only type 1 molecules are centred at $(0, 1, n + \frac{1}{2})$ and R $_2^2$ (8) rings involving only type 2 molecules

Table 3

Hydrogen bond parameters (Å, °).

	D –H \cdots A	D –H	H \cdots A	$D\cdots A$	D –H \cdots A
(I)	N11–H11 \cdots O251	0.828 (17)	2.173 (17)	2.9786 (14)	164.4 (17)
	N13–H13 \cdots S121 ⁱ	0.863 (17)	2.479 (17)	3.3254 (11)	167.2 (15)
	N21–H21 \cdots O151 ⁱⁱ	0.839 (17)	2.159 (17)	2.9818 (14)	166.4 (16)
	N23–H23 \cdots S221 ⁱⁱⁱ	0.856 (17)	2.531 (17)	3.3682 (11)	166.2 (15)
(II)	N1–H1 \cdots O51 ^{iv}	0.836 (15)	2.125 (15)	2.9552 (15)	172.2 (16)
	N3–H3 \cdots S21 ^v	0.847 (16)	2.477 (16)	3.3108 (12)	168.1 (13)
	O71–H71 \cdots O441	0.935	2.02	2.949 (1)	178

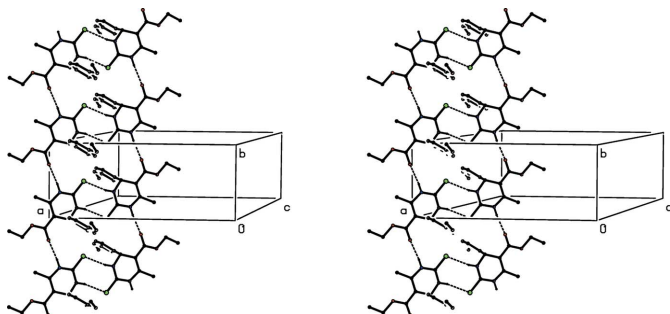
Symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $x, y, z - 1$; (iii) $-x, -y + 2, -z$; (iv) $x, y - 1, z$; (v) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z$.

**Figure 3**

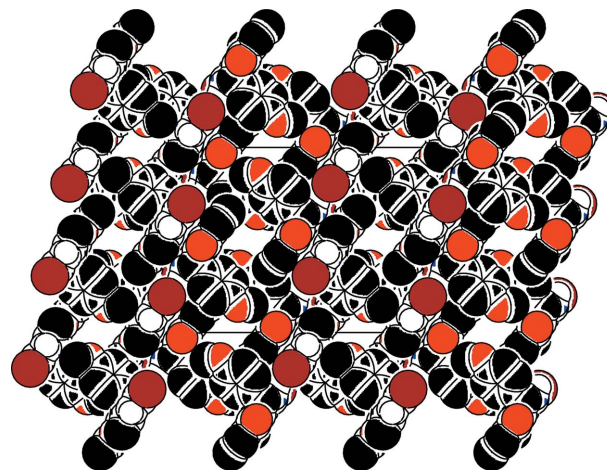
A stereoview of part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded ribbon parallel to the [001] direction containing two types of centrosymmetric $R_2^2(8)$ ring and a single type of $R_4^4(20)$ ring, which is noncentrosymmetric. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms bonded to C atoms have been omitted.

are centred at $(0, 1, n)$, where n represents an integer (Fig. 3). Between each pair of $R_2^2(8)$ rings there is a noncentrosymmetric $R_4^4(20)$ ring which involves four molecules, two of type 1 and two of type 2. The mid-points of the $R_4^4(20)$ rings are close to $(0, 1, \frac{n}{2} + \frac{1}{4})$, but these points are not crystallographic centres of inversion, merely the mid-points between pairs of genuine inversion centres. The centrosymmetric nature of both types of $R_2^2(8)$ ring confirms that only one type of $R_4^4(20)$ ring is present, giving a ribbon containing three types of ring in total.

Molecules of (II) which are related by translation are linked by $N-H \cdots O$ hydrogen bonds to form a $C(6)$ (Bernstein *et al.*, 1995) chain running parallel to the [010] direction (Fig. 4). Inversion-related pairs of such chains are linked by the $N-H \cdots S$ hydrogen bonds to form a ribbon containing edge-fused centrosymmetric rings in which $R_2^2(8)$ rings are centred at $(\frac{3}{4}, n + \frac{1}{4}, 0)$ and $R_4^4(20)$ rings are centred at $(\frac{3}{4}, n - \frac{1}{4}, 0)$, where n again represents an integer. Four ribbons of this type pass

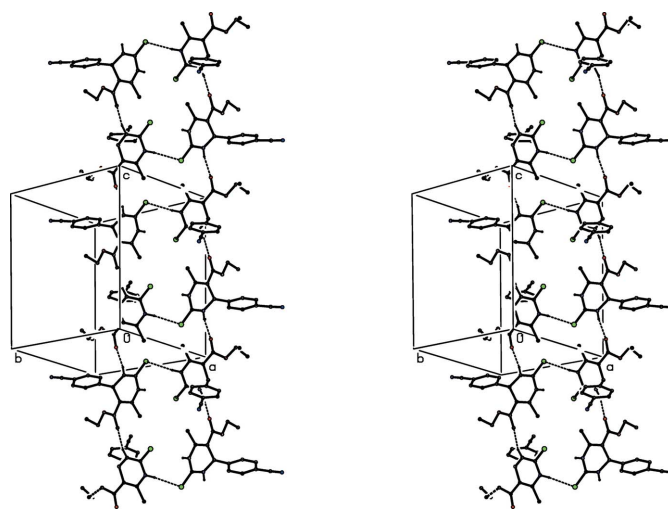
**Figure 4**

A stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded ribbon parallel to the [010] direction in which centrosymmetric $R_2^2(8)$ and $R_4^4(20)$ rings alternate. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms bonded to C atoms have been omitted.

**Figure 5**

A space-filling representation of part of the crystal structure of compound (II), viewed in projection along the [010] direction, showing the continuous channels along the twofold rotation axes. The origin is at the lower left-hand corner of the unit-cell projection with the c axis vertical. For the sake of clarity, the partial-occupancy water molecules have been omitted. (Colour key: white = C, black = H, blue = N, red = O and brown = S atoms.)

through each unit cell and they are arranged such that they enclose continuous channels, four per unit cell, running along the twofold rotation axes and having a mean diameter of *ca* 3.9 Å (Fig. 5). The partial-occupancy water molecules are located in these channels, weakly linked to the organic components by $O-H \cdots O$ hydrogen bonds (Table 3). The earlier report (Nayak *et al.*, 2010) on compound (II) did not mention the presence of the stereogenic centre, nor were the graph-set motifs defining the hydrogen bonding specified. The supramolecular structure was described as 'sheet-like' when,

**Figure 6**

A stereoview of part of the crystal structure of compound (XII), showing the formation of a hydrogen-bonded ribbon parallel to the [001] direction containing alternating $R_4^4(20)$ and $R_4^4(24)$ rings. The original atomic coordinates (Wu *et al.*, 2009) have been used. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms bonded to C atoms have been omitted.

in fact, it takes the form of a ribbon, as in compound (I). More importantly, the earlier report contains no mention of the mutual arrangement of the ribbons, forming the channels (Fig. 5), even though these are clearly apparent in the ambient-temperature structure.

We turn now to a comparison of the supramolecular assembly in some related compounds (III)–(XIV) (see Scheme 1) with the assemblies reported here for compounds (I) and (II). Compounds (III)–(VI) are all isostructural (Qin *et al.*, 2006; Nayak *et al.*, 2009, 2010) and all form ribbons containing alternating $R_2^2(8)$ and $R_4^4(20)$ rings, just as in (II). Entirely similar ribbons are present also in the structures of compounds (VII) and (VIII) (Nayak *et al.*, 2010), (XI) (Begum & Vasundhara, 2006), (XIII) (Begum & Vasundhara, 2009) and (XIV) (Li *et al.*, 2007), although those in (XII) are weakly linked into sheets by C–H...O hydrogen bonds in which one of the nitro-group O atoms acts as the acceptor. The supramolecular assembly in compounds (I)–(VIII), (XI), (XIII) and (XIV) thus involves, in every case, the linkage of inversion-related pairs of molecules by N–H...S hydrogen bonds and the linkage of molecules related by translation by means of N–H...O hydrogen bonds, to give ribbons containing alternating $R_2^2(8)$ and $R_4^4(20)$ rings.

Exceptions to this pattern are found in compounds (IX) and (X) (Nayak *et al.*, 2010), where re-analysis of the structures shows that N–H...O hydrogen bonds are absent and the structures contain ribbons of edge-fused $R_2^2(8)$ rings built only from N–H...S hydrogen bonds. Another exception is provided by 4-cyano derivative (XII), which crystallizes with $Z' = 2$ (Wu *et al.*, 2009). The original structure report described the supramolecular assembly as three-dimensional, but re-analysis of this structure using the deposited atomic coordinates shows that it is, in fact, one-dimensional. Each of the two independent molecular types forms a $C(6)$ chain built from N–H...O hydrogen bonds linking molecules related by translation, but only one N–H...S hydrogen bond is present, leading to the formation of a ribbon in which $R_4^4(20)$ rings alternate with $R_4^4(24)$ rings, although $R_2^2(8)$ rings are absent (Fig. 6); it is of interest that the cyano groups play no part in the hydrogen bonding.

Finally, it is of interest to note the effect of substitution at one of the pyrimidine N atoms, as in compounds (XV)–(XVII) (see Scheme 2), so that there are now two good hydrogen-bond acceptors present in each molecule, *viz.* the doubly-bonded O and S atoms, but only one N–H donor. In each of compounds (XV) (Kumaradhas *et al.*, 2007) and (XVI) (Fun *et al.*, 2008), inversion-related pairs of molecules are linked by N–H...S hydrogen bonds into $R_2^2(8)$ dimers. Compound (XVII) (Fun *et al.*, 2009) crystallizes with $Z' = 4$; two of the four independent molecules are linked by N–H...S hydrogen bonds to form a noncentrosymmetric $R_2^2(8)$ dimer, while each of the other two molecules forms a centrosymmetric $R_2^2(8)$

dimer with an inversion-related analogue. Thus, in each of compounds (XV)–(XVII), N–H...S hydrogen bonds are present forming exactly the same type of motif as in compounds (I)–(XIV), but N–H...O hydrogen bonds are absent, so that they resemble compounds (IX) and (X), rather than compounds (I)–(VIII), (XI), (XIII) and (XIV).

One of the authors (BKS) gratefully acknowledges the Department of Atomic Energy (DAE)/BRNS, Government of India, for providing financial assistance through BRNS Project No. 2011/34/20-BRNS/0846.

References

- Begum, N. S. & Vasundhara, D. E. (2006). *Acta Cryst.* **E62**, o5796–o5798.
 Begum, N. S. & Vasundhara, D. E. (2009). *J. Chem. Res. (S)*, pp. 201–204.
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Biginelli, P. (1893). *Gazz. Chim. Ital.* **23**, 360–413.
 Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
 Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Chambhare, R. V., Khadse, B. G., Bobde, A. S. & Bahekar, R. H. (2003). *Eur. J. Med. Chem.* **38**, 89–100.
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 El-Hashash, M. A., Mahmoud, M. R. & Madboli, S. A. (1993). *Indian J. Chem.* **32**, 449–551.
 Ferguson, G., Glidewell, C. & Patterson, I. L. J. (1996). *Acta Cryst.* **C52**, 420–423.
 Fun, H.-K., Jebas, S. R., Babu, M. & Kalluraya, B. (2009). *Acta Cryst.* **E65**, o981–o982.
 Fun, H.-K., Jebas, S. R., Babu, M., Patil, P. S., Kalluraya, B. & Dharmaparakash, S. M. (2008). *Acta Cryst.* **E64**, o1526–o1527.
 Hurst, E. W. & Hull, R. (1961). *J. Med. Pharm. Chem.* **3**, 215–229.
 Karale, B. K., Gill, C. H., Khan, M., Chavan, V. P., Mane, A. S. & Shingare, M. S. (2002). *Indian J. Chem. Sect. B*, **41**, 1957–1959.
 Kumaradhas, P., David Stephen, A., Satheesh Rai, N., Kalluraya, B. & Sridar, B. (2007). *Acta Cryst.* **E63**, o3403.
 Li, J. T., Han, J. F., Yang, J. H. & Li, T. S. (2003). *Ultrason. Sonochem.* **10**, 119–122.
 Li, W., Long, Q.-Y. & Liu, H.-W. (2007). *Acta Cryst.* **E63**, o1745–o1746.
 Maiti, G., Kundu, P. & Guin, C. (2003). *Tetrahedron Lett.* **44**, 2757–2758.
 Manjula, A., Rao, B. V. & Neelakantan, P. (2004). *Synth. Commun.* **34**, 2665–2671.
 Nayak, S. K., Venugopala, K. N., Chopra, D., Govender, T., Kruger, H. G., Maguire, G. E. M. & Guru Row, T. N. (2009). *Acta Cryst.* **E65**, o2518.
 Nayak, S. K., Venugopala, K. N., Chopra, D., Vasu & Guru Row, T. N. (2010). *CrystEngComm*, **12**, 1205–1216.
 Peng, J. J. & Deng, Y. Q. (2001). *Tetrahedron Lett.* **42**, 5917–5919.
 Qin, Y.-Q., Ren, X.-Y., Liang, T.-L. & Jian, F.-F. (2006). *Acta Cryst.* **E62**, o5215–o5216.
 Riddell, F. G. & Rogerson, M. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 493–504.
 Riddell, F. G. & Rogerson, M. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 249–256.
 Seip, H. M. & Seip, R. (1973). *Acta Chem. Scand.* **27**, 4024–4027.
 Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Spek, A. L. (2015). *Acta Cryst.* **C71**, 9–18.
 Wood, P. A., Allen, F. H. & Pidcock, E. (2009). *CrystEngComm*, **11**, 1563–1571.
 Wu, D.-H., Zhang, Y.-H. & Li, Z.-F. (2009). *Acta Cryst.* **E65**, o1733.
 Youssef, M. M. & Amin, M. A. (2012). *Molecules*, **17**, 9652–9667.

supporting information

Acta Cryst. (2015). C71, 59-64 [doi:10.1107/S2053229614026758]

Ethyl (4-benzyloxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydro-pyrimidine-5-carboxylate and a redetermination of ethyl (4*RS*)-4-(4-methoxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate, as its 0.105-hydrate, both at 200 K: subtly different hydrogen-bonded ribbons

Balladka K. Sarojini, Hemmige S. Yathirajan, Eric C. Hosten, Richard Betz and Christopher Glidewell

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009) and *SHELXL2014* (Sheldrick, 2015).

(I) Ethyl (4*RS*)-4-(4-benzyloxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate

Crystal data

$C_{21}H_{22}N_2O_3S$	$Z = 4$
$M_r = 382.47$	$F(000) = 808$
Triclinic, $P\bar{1}$	$D_x = 1.336 \text{ Mg m}^{-3}$
$a = 11.0094 (4) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 12.7915 (5) \text{ \AA}$	Cell parameters from 9459 reflections
$c = 14.5418 (5) \text{ \AA}$	$\theta = 1.4\text{--}28.4^\circ$
$\alpha = 85.567 (2)^\circ$	$\mu = 0.19 \text{ mm}^{-1}$
$\beta = 83.815 (2)^\circ$	$T = 200 \text{ K}$
$\gamma = 69.150 (2)^\circ$	Block, colourless
$V = 1900.96 (12) \text{ \AA}^3$	$0.46 \times 0.45 \times 0.35 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	9456 independent reflections
Radiation source: sealed tube	7596 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.020$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$\theta_{\text{max}} = 28.4^\circ$, $\theta_{\text{min}} = 2.1^\circ$
$T_{\text{min}} = 0.833$, $T_{\text{max}} = 0.935$	$h = -14 \rightarrow 14$
33717 measured reflections	$k = -17 \rightarrow 17$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$wR(F^2) = 0.118$
Least-squares matrix: full	$S = 1.04$
$R[F^2 > 2\sigma(F^2)] = 0.040$	9456 reflections

503 parameters
 0 restraints
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.7328P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N11	0.21431 (12)	0.71459 (9)	0.43348 (7)	0.0238 (2)
H11	0.2173 (16)	0.6941 (14)	0.3804 (12)	0.029*
C12	0.13365 (12)	0.82098 (10)	0.45360 (8)	0.0200 (2)
S121	0.04251 (3)	0.90348 (3)	0.37186 (2)	0.02719 (9)
N13	0.13064 (11)	0.85040 (9)	0.53884 (7)	0.0199 (2)
H13	0.0773 (16)	0.9155 (14)	0.5548 (11)	0.024*
C14	0.22348 (12)	0.78615 (10)	0.60637 (8)	0.0189 (2)
H14	0.1767	0.7980	0.6697	0.023*
C15	0.26548 (12)	0.66310 (10)	0.58756 (8)	0.0199 (2)
C16	0.26515 (13)	0.63180 (10)	0.50101 (8)	0.0216 (2)
C141	0.33708 (12)	0.82781 (10)	0.60311 (8)	0.0199 (2)
C142	0.45216 (14)	0.77920 (11)	0.54866 (9)	0.0265 (3)
H142	0.4608	0.7173	0.5131	0.032*
C143	0.55523 (14)	0.81832 (12)	0.54454 (10)	0.0296 (3)
H143	0.6335	0.7829	0.5071	0.035*
C144	0.54337 (13)	0.90929 (11)	0.59525 (9)	0.0251 (3)
C145	0.42779 (14)	0.96038 (11)	0.64912 (10)	0.0280 (3)
H145	0.4181	1.0239	0.6830	0.034*
C146	0.32672 (13)	0.91929 (11)	0.65367 (9)	0.0252 (3)
H146	0.2490	0.9540	0.6919	0.030*
O144	0.63842 (10)	0.95429 (8)	0.59768 (8)	0.0328 (2)
C177	0.76374 (15)	0.90049 (13)	0.54925 (11)	0.0345 (3)
H17A	0.8118	0.9533	0.5411	0.041*
H17B	0.7511	0.8820	0.4870	0.041*
C171	0.84438 (14)	0.79534 (12)	0.59897 (10)	0.0289 (3)
C172	0.87700 (16)	0.80058 (13)	0.68762 (11)	0.0353 (3)
H172	0.8465	0.8704	0.7166	0.042*
C173	0.95335 (17)	0.70546 (15)	0.73430 (12)	0.0421 (4)
H173	0.9751	0.7104	0.7949	0.051*
C174	0.99774 (16)	0.60387 (15)	0.69327 (13)	0.0435 (4)
H174	1.0492	0.5384	0.7257	0.052*
C175	0.96750 (18)	0.59740 (15)	0.60544 (15)	0.0491 (4)
H175	0.9987	0.5273	0.5768	0.059*
C176	0.89194 (17)	0.69214 (15)	0.55836 (12)	0.0419 (4)

H176	0.8722	0.6866	0.4973	0.050*
C151	0.30497 (13)	0.58793 (11)	0.66841 (9)	0.0228 (3)
O151	0.29911 (11)	0.62057 (8)	0.74539 (6)	0.0313 (2)
O152	0.34668 (12)	0.47914 (8)	0.65164 (7)	0.0381 (3)
C153	0.37915 (19)	0.40045 (13)	0.73079 (10)	0.0397 (4)
H13A	0.3028	0.4147	0.7771	0.048*
H13B	0.4520	0.4084	0.7606	0.048*
C154	0.4174 (3)	0.28690 (15)	0.69562 (13)	0.0701 (7)
H14A	0.4326	0.2318	0.7478	0.105*
H14B	0.4976	0.2714	0.6542	0.105*
H14C	0.3475	0.2822	0.6616	0.105*
C161	0.31257 (17)	0.51619 (11)	0.46509 (10)	0.0350 (4)
H16A	0.2531	0.4774	0.4902	0.053*
H16B	0.4002	0.4746	0.4842	0.053*
H16C	0.3155	0.5209	0.3974	0.053*
N21	0.22339 (11)	0.71506 (9)	-0.06713 (7)	0.0220 (2)
H21	0.2321 (16)	0.6960 (13)	-0.1221 (12)	0.026*
C22	0.13871 (12)	0.82050 (10)	-0.04733 (8)	0.0194 (2)
S221	0.05673 (4)	0.90568 (3)	-0.13169 (2)	0.02650 (9)
N23	0.12534 (11)	0.84730 (9)	0.04004 (7)	0.0199 (2)
H23	0.0713 (16)	0.9119 (14)	0.0548 (11)	0.024*
C24	0.21315 (12)	0.78351 (10)	0.11050 (8)	0.0184 (2)
H24	0.1613	0.7922	0.1721	0.022*
C25	0.26335 (12)	0.66080 (10)	0.08851 (8)	0.0189 (2)
C26	0.27199 (12)	0.63140 (10)	0.00015 (8)	0.0201 (2)
C241	0.32089 (12)	0.83063 (10)	0.11486 (8)	0.0187 (2)
C242	0.43286 (13)	0.79839 (11)	0.05446 (9)	0.0228 (3)
H242	0.4448	0.7422	0.0118	0.027*
C243	0.52799 (13)	0.84623 (11)	0.05485 (9)	0.0247 (3)
H243	0.6037	0.8233	0.0126	0.030*
C244	0.51157 (13)	0.92773 (11)	0.11736 (9)	0.0230 (3)
C245	0.39908 (14)	0.96204 (11)	0.17751 (9)	0.0262 (3)
H245	0.3866	1.0190	0.2195	0.031*
C246	0.30527 (13)	0.91367 (11)	0.17641 (9)	0.0245 (3)
H246	0.2291	0.9373	0.2182	0.029*
O244	0.60001 (10)	0.97809 (8)	0.12656 (7)	0.0294 (2)
C277	0.71754 (14)	0.94740 (12)	0.06555 (10)	0.0307 (3)
H27A	0.7615	1.0019	0.0702	0.037*
H27B	0.6944	0.9521	0.0011	0.037*
C271	0.81097 (14)	0.83195 (12)	0.08616 (10)	0.0289 (3)
C272	0.85152 (16)	0.79980 (14)	0.17437 (11)	0.0378 (3)
H272	0.8195	0.8510	0.2228	0.045*
C273	0.93913 (18)	0.69246 (16)	0.19196 (14)	0.0485 (4)
H273	0.9663	0.6702	0.2525	0.058*
C274	0.98655 (17)	0.61835 (15)	0.12150 (16)	0.0502 (5)
H274	1.0454	0.5448	0.1339	0.060*
C275	0.94917 (17)	0.65027 (15)	0.03352 (14)	0.0461 (4)
H275	0.9833	0.5994	-0.0150	0.055*

C276	0.86178 (15)	0.75666 (14)	0.01583 (12)	0.0372 (3)
H276	0.8362	0.7786	-0.0451	0.045*
C251	0.29512 (13)	0.58390 (10)	0.16949 (8)	0.0214 (2)
O251	0.28022 (12)	0.61566 (8)	0.24779 (7)	0.0362 (3)
O252	0.34081 (11)	0.47541 (8)	0.15133 (6)	0.0297 (2)
C253	0.36861 (16)	0.39552 (11)	0.22972 (9)	0.0305 (3)
H23A	0.2883	0.4053	0.2713	0.037*
H23B	0.4345	0.4065	0.2654	0.037*
C254	0.4194 (2)	0.28144 (13)	0.19146 (12)	0.0538 (5)
H24A	0.4349	0.2249	0.2425	0.081*
H24B	0.5013	0.2714	0.1532	0.081*
H24C	0.3552	0.2732	0.1535	0.081*
C261	0.32595 (16)	0.51656 (11)	-0.03761 (9)	0.0305 (3)
H26A	0.2606	0.4804	-0.0257	0.046*
H26B	0.4046	0.4719	-0.0073	0.046*
H26C	0.3480	0.5223	-0.1045	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N11	0.0324 (6)	0.0195 (5)	0.0140 (5)	-0.0017 (5)	-0.0027 (4)	-0.0028 (4)
C12	0.0200 (6)	0.0200 (6)	0.0181 (5)	-0.0051 (5)	0.0003 (5)	-0.0012 (4)
S121	0.02919 (19)	0.02468 (17)	0.02029 (16)	0.00067 (13)	-0.00590 (13)	-0.00103 (12)
N13	0.0200 (5)	0.0177 (5)	0.0186 (5)	-0.0018 (4)	-0.0016 (4)	-0.0037 (4)
C14	0.0217 (6)	0.0171 (5)	0.0159 (5)	-0.0038 (5)	-0.0021 (4)	-0.0019 (4)
C15	0.0239 (6)	0.0176 (6)	0.0171 (5)	-0.0059 (5)	-0.0021 (5)	-0.0012 (4)
C16	0.0267 (6)	0.0180 (6)	0.0176 (6)	-0.0046 (5)	-0.0023 (5)	-0.0012 (4)
C141	0.0229 (6)	0.0183 (6)	0.0176 (5)	-0.0056 (5)	-0.0043 (5)	-0.0004 (4)
C142	0.0274 (7)	0.0264 (7)	0.0265 (6)	-0.0094 (6)	0.0000 (5)	-0.0091 (5)
C143	0.0256 (7)	0.0350 (7)	0.0283 (7)	-0.0110 (6)	0.0022 (5)	-0.0069 (6)
C144	0.0267 (7)	0.0243 (6)	0.0258 (6)	-0.0099 (5)	-0.0098 (5)	0.0044 (5)
C145	0.0302 (7)	0.0220 (6)	0.0318 (7)	-0.0063 (5)	-0.0094 (6)	-0.0055 (5)
C146	0.0239 (7)	0.0224 (6)	0.0269 (6)	-0.0033 (5)	-0.0046 (5)	-0.0074 (5)
O144	0.0289 (5)	0.0302 (5)	0.0434 (6)	-0.0141 (4)	-0.0092 (5)	0.0008 (4)
C177	0.0294 (8)	0.0407 (8)	0.0372 (8)	-0.0184 (7)	-0.0045 (6)	0.0069 (6)
C171	0.0241 (7)	0.0361 (8)	0.0300 (7)	-0.0157 (6)	0.0002 (5)	-0.0013 (6)
C172	0.0347 (8)	0.0354 (8)	0.0344 (8)	-0.0092 (7)	-0.0037 (6)	-0.0067 (6)
C173	0.0378 (9)	0.0509 (10)	0.0334 (8)	-0.0105 (8)	-0.0050 (7)	0.0016 (7)
C174	0.0309 (8)	0.0394 (9)	0.0567 (11)	-0.0096 (7)	-0.0051 (7)	0.0071 (8)
C175	0.0416 (10)	0.0353 (9)	0.0683 (12)	-0.0082 (8)	-0.0055 (9)	-0.0144 (8)
C176	0.0398 (9)	0.0480 (10)	0.0404 (9)	-0.0159 (8)	-0.0042 (7)	-0.0130 (7)
C151	0.0281 (7)	0.0206 (6)	0.0190 (6)	-0.0073 (5)	-0.0039 (5)	-0.0010 (5)
O151	0.0468 (6)	0.0272 (5)	0.0173 (4)	-0.0081 (5)	-0.0075 (4)	-0.0024 (4)
O152	0.0681 (8)	0.0191 (5)	0.0203 (5)	-0.0049 (5)	-0.0129 (5)	0.0008 (4)
C153	0.0618 (11)	0.0275 (7)	0.0221 (7)	-0.0051 (7)	-0.0121 (7)	0.0040 (5)
C154	0.129 (2)	0.0265 (9)	0.0356 (9)	-0.0049 (11)	-0.0058 (11)	0.0046 (7)
C161	0.0575 (10)	0.0190 (6)	0.0224 (6)	-0.0036 (6)	-0.0087 (6)	-0.0053 (5)
N21	0.0288 (6)	0.0192 (5)	0.0145 (5)	-0.0037 (4)	-0.0024 (4)	-0.0022 (4)

C22	0.0200 (6)	0.0183 (5)	0.0204 (6)	-0.0070 (5)	-0.0025 (5)	-0.0009 (4)
S221	0.03222 (19)	0.02175 (16)	0.02254 (16)	-0.00391 (13)	-0.00978 (13)	0.00005 (12)
N23	0.0199 (5)	0.0169 (5)	0.0203 (5)	-0.0023 (4)	-0.0032 (4)	-0.0036 (4)
C24	0.0199 (6)	0.0184 (5)	0.0156 (5)	-0.0049 (5)	-0.0012 (4)	-0.0026 (4)
C25	0.0215 (6)	0.0171 (5)	0.0171 (5)	-0.0051 (5)	-0.0019 (4)	-0.0017 (4)
C26	0.0223 (6)	0.0182 (6)	0.0181 (5)	-0.0049 (5)	-0.0018 (5)	-0.0014 (4)
C241	0.0210 (6)	0.0176 (5)	0.0169 (5)	-0.0054 (5)	-0.0037 (4)	-0.0012 (4)
C242	0.0246 (7)	0.0240 (6)	0.0205 (6)	-0.0081 (5)	-0.0015 (5)	-0.0065 (5)
C243	0.0229 (6)	0.0291 (7)	0.0227 (6)	-0.0096 (5)	-0.0003 (5)	-0.0044 (5)
C244	0.0236 (6)	0.0217 (6)	0.0248 (6)	-0.0080 (5)	-0.0085 (5)	0.0016 (5)
C245	0.0278 (7)	0.0238 (6)	0.0275 (6)	-0.0074 (5)	-0.0048 (5)	-0.0093 (5)
C246	0.0243 (6)	0.0260 (6)	0.0220 (6)	-0.0065 (5)	-0.0001 (5)	-0.0084 (5)
O244	0.0266 (5)	0.0284 (5)	0.0376 (5)	-0.0134 (4)	-0.0060 (4)	-0.0050 (4)
C277	0.0289 (7)	0.0321 (7)	0.0359 (8)	-0.0170 (6)	-0.0063 (6)	0.0056 (6)
C271	0.0237 (7)	0.0316 (7)	0.0354 (7)	-0.0152 (6)	-0.0030 (6)	0.0023 (6)
C272	0.0345 (8)	0.0405 (9)	0.0372 (8)	-0.0120 (7)	-0.0065 (7)	0.0042 (7)
C273	0.0377 (9)	0.0497 (10)	0.0540 (11)	-0.0121 (8)	-0.0115 (8)	0.0184 (8)
C274	0.0298 (9)	0.0330 (8)	0.0824 (14)	-0.0077 (7)	-0.0010 (9)	0.0088 (9)
C275	0.0333 (9)	0.0391 (9)	0.0667 (12)	-0.0146 (7)	0.0055 (8)	-0.0110 (8)
C276	0.0305 (8)	0.0418 (9)	0.0429 (9)	-0.0168 (7)	-0.0018 (7)	-0.0048 (7)
C251	0.0242 (6)	0.0204 (6)	0.0183 (6)	-0.0059 (5)	-0.0021 (5)	-0.0021 (4)
O251	0.0590 (7)	0.0257 (5)	0.0175 (5)	-0.0055 (5)	-0.0070 (5)	-0.0032 (4)
O252	0.0483 (6)	0.0176 (4)	0.0176 (4)	-0.0045 (4)	-0.0047 (4)	0.0004 (3)
C253	0.0440 (9)	0.0230 (6)	0.0195 (6)	-0.0061 (6)	-0.0040 (6)	0.0035 (5)
C254	0.0954 (16)	0.0224 (7)	0.0287 (8)	-0.0043 (9)	-0.0006 (9)	0.0019 (6)
C261	0.0457 (9)	0.0192 (6)	0.0203 (6)	-0.0026 (6)	-0.0039 (6)	-0.0051 (5)

Geometric parameters (Å, °)

N11—C12	1.3681 (16)	N21—C22	1.3705 (16)
N11—C16	1.3910 (16)	N21—C26	1.3899 (15)
N11—H11	0.828 (17)	N21—H21	0.840 (17)
C12—N13	1.3167 (16)	C22—N23	1.3208 (16)
C12—S121	1.6859 (13)	C22—S221	1.6849 (12)
N13—C14	1.4757 (15)	N23—C24	1.4741 (15)
N13—H13	0.863 (17)	N23—H23	0.856 (17)
C14—C15	1.5124 (16)	C24—C25	1.5144 (16)
C14—C141	1.5193 (17)	C24—C241	1.5184 (17)
C14—H14	1.0000	C24—H24	1.0000
C15—C16	1.3507 (17)	C25—C26	1.3507 (17)
C15—C151	1.4607 (17)	C25—C251	1.4634 (16)
C16—C161	1.4978 (17)	C26—C261	1.4986 (17)
C141—C142	1.3849 (18)	C241—C242	1.3863 (17)
C141—C146	1.3938 (17)	C241—C246	1.3937 (17)
C142—C143	1.3880 (19)	C242—C243	1.3890 (18)
C142—H142	0.9500	C242—H242	0.9500
C143—C144	1.3852 (19)	C243—C244	1.3867 (18)
C143—H143	0.9500	C243—H243	0.9500

C144—O144	1.3666 (16)	C244—O244	1.3670 (15)
C144—C145	1.390 (2)	C244—C245	1.3894 (19)
C145—C146	1.3834 (19)	C245—C246	1.3820 (19)
C145—H145	0.9500	C245—H245	0.9500
C146—H146	0.9500	C246—H246	0.9500
O144—C177	1.4362 (19)	O244—C277	1.4355 (18)
C177—C171	1.503 (2)	C277—C271	1.499 (2)
C177—H17A	0.9900	C277—H27A	0.9900
C177—H17B	0.9900	C277—H27B	0.9900
C171—C172	1.388 (2)	C271—C272	1.387 (2)
C171—C176	1.388 (2)	C271—C276	1.390 (2)
C172—C173	1.384 (2)	C272—C273	1.392 (2)
C172—H172	0.9500	C272—H272	0.9500
C173—C174	1.374 (3)	C273—C274	1.380 (3)
C173—H173	0.9500	C273—H273	0.9500
C174—C175	1.370 (3)	C274—C275	1.373 (3)
C174—H174	0.9500	C274—H274	0.9500
C175—C176	1.381 (3)	C275—C276	1.382 (2)
C175—H175	0.9500	C275—H275	0.9500
C176—H176	0.9500	C276—H276	0.9500
C151—O151	1.2121 (15)	C251—O251	1.2134 (15)
C151—O152	1.3342 (16)	C251—O252	1.3340 (15)
O152—C153	1.4558 (16)	O252—C253	1.4526 (15)
C153—C154	1.477 (2)	C253—C254	1.493 (2)
C153—H13A	0.9900	C253—H23A	0.9900
C153—H13B	0.9900	C253—H23B	0.9900
C154—H14A	0.9800	C254—H24A	0.9800
C154—H14B	0.9800	C254—H24B	0.9800
C154—H14C	0.9800	C254—H24C	0.9800
C161—H16A	0.9800	C261—H26A	0.9800
C161—H16B	0.9800	C261—H26B	0.9800
C161—H16C	0.9800	C261—H26C	0.9800
C12—N11—C16	123.20 (11)	C22—N21—C26	123.52 (11)
C12—N11—H11	117.7 (12)	C22—N21—H21	117.2 (11)
C16—N11—H11	117.2 (11)	C26—N21—H21	117.6 (11)
N13—C12—N11	115.96 (11)	N23—C22—N21	115.84 (11)
N13—C12—S121	124.37 (10)	N23—C22—S221	124.15 (10)
N11—C12—S121	119.64 (9)	N21—C22—S221	120.00 (9)
C12—N13—C14	124.61 (11)	C22—N23—C24	124.53 (11)
C12—N13—H13	118.4 (10)	C22—N23—H23	117.9 (11)
C14—N13—H13	116.6 (10)	C24—N23—H23	116.5 (11)
N13—C14—C15	108.45 (10)	N23—C24—C25	108.55 (9)
N13—C14—C141	110.70 (10)	N23—C24—C241	109.96 (9)
C15—C14—C141	113.20 (10)	C25—C24—C241	113.44 (10)
N13—C14—H14	108.1	N23—C24—H24	108.3
C15—C14—H14	108.1	C25—C24—H24	108.3
C141—C14—H14	108.1	C241—C24—H24	108.3

C16—C15—C151	125.99 (11)	C26—C25—C251	126.04 (11)
C16—C15—C14	119.56 (11)	C26—C25—C24	119.65 (11)
C151—C15—C14	114.45 (10)	C251—C25—C24	114.28 (10)
C15—C16—N11	118.49 (11)	C25—C26—N21	118.57 (11)
C15—C16—C161	128.68 (12)	C25—C26—C261	128.47 (11)
N11—C16—C161	112.82 (11)	N21—C26—C261	112.94 (11)
C142—C141—C146	117.73 (12)	C242—C241—C246	118.11 (12)
C142—C141—C14	121.86 (11)	C242—C241—C24	121.55 (11)
C146—C141—C14	120.38 (11)	C246—C241—C24	120.20 (11)
C141—C142—C143	121.90 (12)	C241—C242—C243	121.58 (12)
C141—C142—H142	119.1	C241—C242—H242	119.2
C143—C142—H142	119.1	C243—C242—H242	119.2
C144—C143—C142	119.64 (13)	C244—C243—C242	119.51 (12)
C144—C143—H143	120.2	C244—C243—H243	120.2
C142—C143—H143	120.2	C242—C243—H243	120.2
O144—C144—C143	124.95 (13)	O244—C244—C243	124.95 (12)
O144—C144—C145	115.74 (12)	O244—C244—C245	115.44 (11)
C143—C144—C145	119.31 (13)	C243—C244—C245	119.60 (12)
C146—C145—C144	120.36 (12)	C246—C245—C244	120.25 (12)
C146—C145—H145	119.8	C246—C245—H245	119.9
C144—C145—H145	119.8	C244—C245—H245	119.9
C145—C146—C141	121.05 (13)	C245—C246—C241	120.93 (12)
C145—C146—H146	119.5	C245—C246—H246	119.5
C141—C146—H146	119.5	C241—C246—H246	119.5
C144—O144—C177	118.67 (11)	C244—O244—C277	118.17 (11)
O144—C177—C171	112.86 (12)	O244—C277—C271	113.46 (11)
O144—C177—H17A	109.0	O244—C277—H27A	108.9
C171—C177—H17A	109.0	C271—C277—H27A	108.9
O144—C177—H17B	109.0	O244—C277—H27B	108.9
C171—C177—H17B	109.0	C271—C277—H27B	108.9
H17A—C177—H17B	107.8	H27A—C277—H27B	107.7
C172—C171—C176	117.95 (15)	C272—C271—C276	119.03 (15)
C172—C171—C177	119.63 (14)	C272—C271—C277	120.86 (14)
C176—C171—C177	122.39 (14)	C276—C271—C277	120.07 (14)
C173—C172—C171	120.86 (15)	C271—C272—C273	120.00 (17)
C173—C172—H172	119.6	C271—C272—H272	120.0
C171—C172—H172	119.6	C273—C272—H272	120.0
C174—C173—C172	120.19 (16)	C274—C273—C272	120.01 (17)
C174—C173—H173	119.9	C274—C273—H273	120.0
C172—C173—H173	119.9	C272—C273—H273	120.0
C175—C174—C173	119.70 (16)	C275—C274—C273	120.39 (17)
C175—C174—H174	120.1	C275—C274—H274	119.8
C173—C174—H174	120.1	C273—C274—H274	119.8
C174—C175—C176	120.35 (16)	C274—C275—C276	119.78 (17)
C174—C175—H175	119.8	C274—C275—H275	120.1
C176—C175—H175	119.8	C276—C275—H275	120.1
C175—C176—C171	120.94 (16)	C275—C276—C271	120.77 (16)
C175—C176—H176	119.5	C275—C276—H276	119.6

C171—C176—H176	119.5	C271—C276—H276	119.6
O151—C151—O152	121.90 (12)	O251—C251—O252	121.98 (11)
O151—C151—C15	123.31 (12)	O251—C251—C25	122.90 (12)
O152—C151—C15	114.78 (11)	O252—C251—C25	115.12 (10)
C151—O152—C153	117.11 (11)	C251—O252—C253	117.29 (10)
O152—C153—C154	107.07 (12)	O252—C253—C254	106.93 (11)
O152—C153—H13A	110.3	O252—C253—H23A	110.3
C154—C153—H13A	110.3	C254—C253—H23A	110.3
O152—C153—H13B	110.3	O252—C253—H23B	110.3
C154—C153—H13B	110.3	C254—C253—H23B	110.3
H13A—C153—H13B	108.6	H23A—C253—H23B	108.6
C153—C154—H14A	109.5	C253—C254—H24A	109.5
C153—C154—H14B	109.5	C253—C254—H24B	109.5
H14A—C154—H14B	109.5	H24A—C254—H24B	109.5
C153—C154—H14C	109.5	C253—C254—H24C	109.5
H14A—C154—H14C	109.5	H24A—C254—H24C	109.5
H14B—C154—H14C	109.5	H24B—C254—H24C	109.5
C16—C161—H16A	109.5	C26—C261—H26A	109.5
C16—C161—H16B	109.5	C26—C261—H26B	109.5
H16A—C161—H16B	109.5	H26A—C261—H26B	109.5
C16—C161—H16C	109.5	C26—C261—H26C	109.5
H16A—C161—H16C	109.5	H26A—C261—H26C	109.5
H16B—C161—H16C	109.5	H26B—C261—H26C	109.5
C16—N11—C12—N13	15.90 (19)	C26—N21—C22—N23	13.56 (18)
C16—N11—C12—S121	-162.13 (10)	C26—N21—C22—S221	-165.00 (10)
N11—C12—N13—C14	11.75 (18)	N21—C22—N23—C24	13.70 (17)
S121—C12—N13—C14	-170.32 (9)	S221—C22—N23—C24	-167.80 (9)
C12—N13—C14—C15	-31.89 (16)	C22—N23—C24—C25	-32.41 (16)
C12—N13—C14—C141	92.86 (14)	C22—N23—C24—C241	92.22 (13)
N13—C14—C15—C16	27.72 (16)	N23—C24—C25—C26	27.10 (16)
C141—C14—C15—C16	-95.54 (14)	C241—C24—C25—C26	-95.45 (14)
N13—C14—C15—C151	-152.93 (11)	N23—C24—C25—C251	-151.24 (11)
C141—C14—C15—C151	83.82 (13)	C241—C24—C25—C251	86.22 (13)
C151—C15—C16—N11	174.77 (12)	C251—C25—C26—N21	172.47 (12)
C14—C15—C16—N11	-5.95 (19)	C24—C25—C26—N21	-5.65 (18)
C151—C15—C16—C161	-4.8 (2)	C251—C25—C26—C261	-6.0 (2)
C14—C15—C16—C161	174.49 (14)	C24—C25—C26—C261	175.90 (13)
C12—N11—C16—C15	-18.5 (2)	C22—N21—C26—C25	-17.22 (19)
C12—N11—C16—C161	161.15 (13)	C22—N21—C26—C261	161.46 (12)
N13—C14—C141—C142	-93.55 (14)	N23—C24—C241—C242	-84.06 (14)
C15—C14—C141—C142	28.47 (16)	C25—C24—C241—C242	37.70 (15)
N13—C14—C141—C146	84.68 (14)	N23—C24—C241—C246	91.67 (13)
C15—C14—C141—C146	-153.31 (11)	C25—C24—C241—C246	-146.56 (11)
C146—C141—C142—C143	0.7 (2)	C246—C241—C242—C243	0.39 (19)
C14—C141—C142—C143	178.98 (12)	C24—C241—C242—C243	176.21 (11)
C141—C142—C143—C144	-0.7 (2)	C241—C242—C243—C244	0.4 (2)
C142—C143—C144—O144	179.12 (13)	C242—C243—C244—O244	177.66 (12)

C142—C143—C144—C145	−0.4 (2)	C242—C243—C244—C245	−1.3 (2)
O144—C144—C145—C146	−178.12 (12)	O244—C244—C245—C246	−177.69 (12)
C143—C144—C145—C146	1.4 (2)	C243—C244—C245—C246	1.3 (2)
C144—C145—C146—C141	−1.4 (2)	C244—C245—C246—C241	−0.5 (2)
C142—C141—C146—C145	0.35 (19)	C242—C241—C246—C245	−0.33 (19)
C14—C141—C146—C145	−177.95 (12)	C24—C241—C246—C245	−176.21 (12)
C143—C144—O144—C177	−4.2 (2)	C243—C244—O244—C277	1.89 (19)
C145—C144—O144—C177	175.36 (12)	C245—C244—O244—C277	−179.15 (11)
C144—O144—C177—C171	−75.78 (16)	C244—O244—C277—C271	−71.53 (15)
O144—C177—C171—C172	−59.75 (18)	O244—C277—C271—C272	−53.53 (18)
O144—C177—C171—C176	122.39 (16)	O244—C277—C271—C276	128.72 (14)
C176—C171—C172—C173	−0.7 (2)	C276—C271—C272—C273	−1.7 (2)
C177—C171—C172—C173	−178.68 (14)	C277—C271—C272—C273	−179.50 (14)
C171—C172—C173—C174	−0.2 (3)	C271—C272—C273—C274	0.6 (3)
C172—C173—C174—C175	0.8 (3)	C272—C273—C274—C275	0.9 (3)
C173—C174—C175—C176	−0.5 (3)	C273—C274—C275—C276	−1.1 (3)
C174—C175—C176—C171	−0.5 (3)	C274—C275—C276—C271	−0.1 (2)
C172—C171—C176—C175	1.1 (2)	C272—C271—C276—C275	1.5 (2)
C177—C171—C176—C175	178.98 (15)	C277—C271—C276—C275	179.28 (14)
C16—C15—C151—O151	−177.35 (14)	C26—C25—C251—O251	−176.89 (14)
C14—C15—C151—O151	3.35 (19)	C24—C25—C251—O251	1.32 (19)
C16—C15—C151—O152	1.6 (2)	C26—C25—C251—O252	2.5 (2)
C14—C15—C151—O152	−177.67 (12)	C24—C25—C251—O252	−179.32 (11)
O151—C151—O152—C153	2.9 (2)	O251—C251—O252—C253	1.9 (2)
C15—C151—O152—C153	−176.06 (13)	C25—C251—O252—C253	−177.45 (12)
C151—O152—C153—C154	177.87 (17)	C251—O252—C253—C254	−179.34 (15)

Hydrogen-bond 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>
N11—H11...O251	0.828 (17)	2.173 (17)	2.9786 (14)	164.4 (17)
N13—H13...S121 ⁱ	0.863 (17)	2.479 (17)	3.3254 (11)	167.2 (15)
N21—H21...O151 ⁱⁱ	0.839 (17)	2.159 (17)	2.9818 (14)	166.4 (16)
N23—H23...S221 ⁱⁱⁱ	0.856 (17)	2.531 (17)	3.3682 (11)	166.2 (15)

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $x, y, z-1$; (iii) $-x, -y+2, -z$.**(II) Ethyl (4*RS*)-4-(4-methoxyphenyl)-6-methyl-2-sulfanylidene-1,2,3,4-tetrahydropyrimidine-5-carboxylate****0.105-hydrate***Crystal data*C₁₅H₁₈N₂O₃S·0.105H₂O*M_r* = 308.26Monoclinic, *C*2/*c**a* = 18.1455 (6) Å*b* = 7.3171 (2) Å*c* = 25.0493 (8) Å β = 102.008 (1)°*V* = 3253.08 (17) Å³*Z* = 8*F*(000) = 1304.4*D_x* = 1.259 Mg m^{−3}Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 4024 reflections

 θ = 1.7–28.3° μ = 0.21 mm^{−1}*T* = 200 K

Plate, colourless

0.52 × 0.48 × 0.19 mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.906$, $T_{\max} = 0.961$

14922 measured reflections

4023 independent reflections

3447 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -16 \rightarrow 24$

$k = -9 \rightarrow 9$

$l = -33 \rightarrow 33$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.101$

$S = 1.04$

4023 reflections

202 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 2.7236P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.58395 (6)	0.14175 (15)	0.05939 (4)	0.0243 (2)	
H1	0.5704 (9)	0.033 (2)	0.0609 (7)	0.029*	
C2	0.64611 (7)	0.17583 (17)	0.03842 (5)	0.0227 (2)	
S21	0.69387 (2)	0.00082 (4)	0.01780 (2)	0.03111 (11)	
N3	0.66379 (6)	0.35016 (14)	0.03425 (4)	0.0247 (2)	
H3	0.7022 (9)	0.371 (2)	0.0209 (6)	0.030*	
C4	0.63694 (7)	0.49796 (16)	0.06557 (5)	0.0223 (2)	
H4	0.6356	0.6144	0.0445	0.027*	
C5	0.55778 (7)	0.45320 (16)	0.07152 (5)	0.0225 (2)	
C6	0.53519 (7)	0.27681 (16)	0.07031 (5)	0.0228 (2)	
C41	0.69191 (7)	0.52154 (16)	0.12017 (5)	0.0224 (2)	
C42	0.68044 (8)	0.44080 (18)	0.16797 (5)	0.0269 (3)	
H42	0.6348	0.3766	0.1676	0.032*	
C43	0.73407 (8)	0.45151 (19)	0.21645 (5)	0.0302 (3)	
H43	0.7248	0.3968	0.2488	0.036*	
C44	0.80118 (8)	0.54267 (18)	0.21714 (5)	0.0284 (3)	
C45	0.81305 (8)	0.62852 (19)	0.16998 (6)	0.0299 (3)	
H45	0.8584	0.6943	0.1706	0.036*	
C46	0.75898 (7)	0.61814 (17)	0.12227 (5)	0.0272 (3)	
H46	0.7675	0.6776	0.0904	0.033*	
O441	0.85890 (6)	0.55694 (15)	0.26190 (4)	0.0383 (2)	
C441	0.85197 (12)	0.4539 (3)	0.30910 (7)	0.0516 (5)	

H44A	0.8414	0.3258	0.2988	0.077*	
H44B	0.8106	0.5035	0.3244	0.077*	
H44C	0.8991	0.4616	0.3364	0.077*	
C51	0.51321 (7)	0.61165 (17)	0.08256 (5)	0.0250 (3)	
O51	0.52961 (6)	0.76801 (13)	0.07394 (5)	0.0373 (2)	
O52	0.45486 (6)	0.56864 (13)	0.10456 (5)	0.0370 (2)	
C53	0.40870 (9)	0.71759 (19)	0.11794 (7)	0.0368 (3)	
H53A	0.3833	0.7819	0.0844	0.044*	
H53B	0.4402	0.8066	0.1424	0.044*	
C54	0.35186 (11)	0.6335 (2)	0.14581 (9)	0.0540 (5)	
H54A	0.3173	0.7281	0.1535	0.081*	
H54B	0.3776	0.5772	0.1801	0.081*	
H54C	0.3234	0.5400	0.1221	0.081*	
C61	0.46201 (8)	0.20188 (19)	0.07949 (7)	0.0352 (3)	
H61A	0.4208	0.2831	0.0626	0.053*	
H61B	0.4637	0.1934	0.1188	0.053*	
H61C	0.4537	0.0801	0.0631	0.053*	
O71	1.0000	0.737 (3)	0.2500	0.158 (11)*	0.210 (11)
H71A	0.9550	0.6822	0.2540	0.238*	0.105 (5)
H71B	1.0450	0.6822	0.2460	0.238*	0.105 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0278 (5)	0.0146 (5)	0.0332 (5)	-0.0028 (4)	0.0128 (4)	0.0008 (4)
C2	0.0258 (6)	0.0206 (6)	0.0226 (5)	-0.0019 (5)	0.0072 (4)	-0.0011 (4)
S21	0.03462 (19)	0.02042 (16)	0.0433 (2)	-0.00156 (12)	0.01972 (15)	-0.00386 (13)
N3	0.0294 (6)	0.0197 (5)	0.0294 (5)	-0.0050 (4)	0.0159 (4)	-0.0029 (4)
C4	0.0268 (6)	0.0149 (5)	0.0273 (6)	-0.0029 (4)	0.0104 (5)	-0.0005 (4)
C5	0.0243 (6)	0.0176 (5)	0.0267 (6)	-0.0017 (4)	0.0075 (5)	0.0006 (4)
C6	0.0231 (6)	0.0191 (5)	0.0269 (6)	-0.0011 (5)	0.0069 (5)	0.0008 (4)
C41	0.0258 (6)	0.0151 (5)	0.0279 (6)	-0.0012 (4)	0.0092 (5)	-0.0018 (4)
C42	0.0293 (6)	0.0221 (6)	0.0312 (6)	-0.0048 (5)	0.0110 (5)	0.0004 (5)
C43	0.0385 (7)	0.0249 (6)	0.0286 (6)	-0.0026 (5)	0.0102 (5)	0.0032 (5)
C44	0.0318 (7)	0.0217 (6)	0.0311 (6)	0.0013 (5)	0.0048 (5)	-0.0036 (5)
C45	0.0279 (6)	0.0261 (6)	0.0367 (7)	-0.0064 (5)	0.0092 (5)	-0.0026 (5)
C46	0.0305 (6)	0.0228 (6)	0.0307 (6)	-0.0051 (5)	0.0120 (5)	0.0003 (5)
O441	0.0399 (6)	0.0367 (5)	0.0341 (5)	-0.0038 (5)	-0.0020 (4)	-0.0007 (4)
C441	0.0671 (12)	0.0435 (9)	0.0359 (8)	-0.0066 (9)	-0.0084 (8)	0.0059 (7)
C51	0.0260 (6)	0.0192 (6)	0.0304 (6)	-0.0008 (5)	0.0069 (5)	0.0000 (5)
O51	0.0404 (6)	0.0166 (4)	0.0603 (7)	-0.0019 (4)	0.0226 (5)	0.0007 (4)
O52	0.0373 (5)	0.0189 (4)	0.0628 (7)	0.0028 (4)	0.0283 (5)	0.0022 (4)
C53	0.0372 (8)	0.0220 (6)	0.0559 (9)	0.0057 (6)	0.0205 (7)	-0.0009 (6)
C54	0.0538 (10)	0.0326 (8)	0.0868 (13)	0.0011 (7)	0.0407 (10)	-0.0058 (9)
C61	0.0277 (7)	0.0221 (6)	0.0593 (9)	-0.0048 (5)	0.0173 (6)	-0.0030 (6)

Geometric parameters (Å, °)

N1—C2	1.3627 (16)	C45—C46	1.3818 (19)
N1—C6	1.3910 (16)	C45—H45	0.9500
N1—H1	0.836 (17)	C46—H46	0.9500
C2—N3	1.3248 (16)	O441—C441	1.430 (2)
C2—S21	1.6864 (13)	C441—H44A	0.9800
N3—C4	1.4771 (15)	C441—H44B	0.9800
N3—H3	0.848 (16)	C441—H44C	0.9800
C4—C5	1.5106 (17)	C51—O51	1.2128 (15)
C4—C41	1.5256 (17)	C51—O52	1.3291 (16)
C4—H4	1.0000	O52—C53	1.4555 (16)
C5—C6	1.3525 (16)	C53—C54	1.493 (2)
C5—C51	1.4724 (17)	C53—H53A	0.9900
C6—C61	1.4980 (17)	C53—H53B	0.9900
C41—C42	1.3892 (17)	C54—H54A	0.9800
C41—C46	1.3989 (17)	C54—H54B	0.9800
C42—C43	1.3915 (19)	C54—H54C	0.9800
C42—H42	0.9500	C61—H61A	0.9800
C43—C44	1.385 (2)	C61—H61B	0.9800
C43—H43	0.9500	C61—H61C	0.9800
C44—O441	1.3699 (16)	O71—H71A	0.9351
C44—C45	1.3936 (19)	O71—H71B	0.9351
C2—N1—C6	123.86 (11)	C44—C45—H45	120.0
C2—N1—H1	117.9 (12)	C45—C46—C41	121.06 (12)
C6—N1—H1	117.5 (12)	C45—C46—H46	119.5
N3—C2—N1	116.10 (11)	C41—C46—H46	119.5
N3—C2—S21	123.97 (9)	C44—O441—C441	116.92 (12)
N1—C2—S21	119.90 (9)	O441—C441—H44A	109.5
C2—N3—C4	123.44 (10)	O441—C441—H44B	109.5
C2—N3—H3	116.1 (12)	H44A—C441—H44B	109.5
C4—N3—H3	117.7 (11)	O441—C441—H44C	109.5
N3—C4—C5	108.62 (9)	H44A—C441—H44C	109.5
N3—C4—C41	109.42 (10)	H44B—C441—H44C	109.5
C5—C4—C41	113.20 (10)	O51—C51—O52	122.92 (12)
N3—C4—H4	108.5	O51—C51—C5	123.00 (12)
C5—C4—H4	108.5	O52—C51—C5	114.04 (11)
C41—C4—H4	108.5	C51—O52—C53	117.67 (11)
C6—C5—C51	125.45 (11)	O52—C53—C54	106.60 (12)
C6—C5—C4	119.64 (11)	O52—C53—H53A	110.4
C51—C5—C4	114.74 (10)	C54—C53—H53A	110.4
C5—C6—N1	118.70 (11)	O52—C53—H53B	110.4
C5—C6—C61	128.31 (12)	C54—C53—H53B	110.4
N1—C6—C61	112.99 (11)	H53A—C53—H53B	108.6
C42—C41—C46	117.88 (12)	C53—C54—H54A	109.5
C42—C41—C4	122.50 (11)	C53—C54—H54B	109.5
C46—C41—C4	119.49 (11)	H54A—C54—H54B	109.5

C41—C42—C43	121.69 (12)	C53—C54—H54C	109.5
C41—C42—H42	119.2	H54A—C54—H54C	109.5
C43—C42—H42	119.2	H54B—C54—H54C	109.5
C44—C43—C42	119.43 (12)	C6—C61—H61A	109.5
C44—C43—H43	120.3	C6—C61—H61B	109.5
C42—C43—H43	120.3	H61A—C61—H61B	109.5
O441—C44—C43	124.56 (13)	C6—C61—H61C	109.5
O441—C44—C45	115.64 (12)	H61A—C61—H61C	109.5
C43—C44—C45	119.80 (13)	H61B—C61—H61C	109.5
C46—C45—C44	120.08 (12)	H71A—O71—H71B	128.7
C46—C45—H45	120.0		
C6—N1—C2—N3	7.45 (18)	C46—C41—C42—C43	-1.22 (19)
C6—N1—C2—S21	-170.69 (9)	C4—C41—C42—C43	174.71 (12)
N1—C2—N3—C4	19.96 (18)	C41—C42—C43—C44	-0.9 (2)
S21—C2—N3—C4	-161.98 (9)	C42—C43—C44—O441	-177.83 (13)
C2—N3—C4—C5	-35.56 (16)	C42—C43—C44—C45	2.5 (2)
C2—N3—C4—C41	88.46 (14)	O441—C44—C45—C46	178.37 (12)
N3—C4—C5—C6	26.59 (15)	C43—C44—C45—C46	-1.9 (2)
C41—C4—C5—C6	-95.15 (13)	C44—C45—C46—C41	-0.3 (2)
N3—C4—C5—C51	-157.92 (10)	C42—C41—C46—C45	1.81 (19)
C41—C4—C5—C51	80.34 (13)	C4—C41—C46—C45	-174.24 (12)
C51—C5—C6—N1	-179.85 (11)	C43—C44—O441—C441	7.0 (2)
C4—C5—C6—N1	-4.87 (18)	C45—C44—O441—C441	-173.34 (14)
C51—C5—C6—C61	0.1 (2)	C6—C5—C51—O51	-166.64 (14)
C4—C5—C6—C61	175.04 (13)	C4—C5—C51—O51	18.17 (18)
C2—N1—C6—C5	-14.65 (18)	C6—C5—C51—O52	15.55 (19)
C2—N1—C6—C61	165.42 (12)	C4—C5—C51—O52	-159.64 (11)
N3—C4—C41—C42	-96.71 (13)	O51—C51—O52—C53	0.9 (2)
C5—C4—C41—C42	24.58 (16)	C5—C51—O52—C53	178.66 (12)
N3—C4—C41—C46	79.16 (13)	C51—O52—C53—C54	-175.52 (14)
C5—C4—C41—C46	-159.55 (11)		

Hydrogen-bond 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>
N1—H1...O51 ⁱ	0.836 (15)	2.125 (15)	2.9552 (15)	172.2 (16)
N3—H3...S21 ⁱⁱ	0.847 (16)	2.477 (16)	3.3108 (12)	168.1 (13)
O71—H71A...O441	0.94	2.02	2.949 (10)	178

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+3/2, -y+1/2, -z$.