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Three hexahydropyridopyrimidine-spiro-cyclohexanetriones: supramolecular structures generated by O—H···O, N—H···O, C—H···O and C—H···π hydrogen bonds, and π–π stacking interactions

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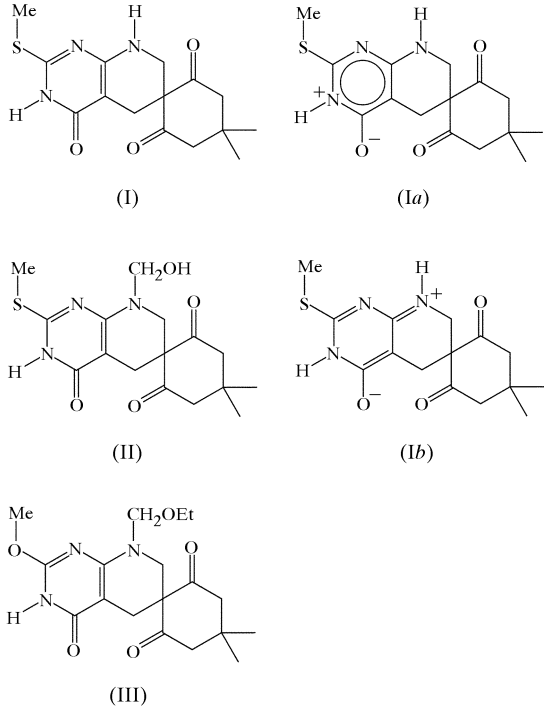
4′,4′-Dimethyl-2-methylsulfanyl-3,4,5,6,7,8-hexahydropyrido-[2,3-*d*]pyrimidine-6-spiro-1′-cyclohexane-2′,4,6′-trione, $C_{15}H_{19}N_3O_3S$, (I), has a markedly polarized molecular–electronic structure, and the molecules are linked into a three-dimensional framework by a combination of N—H···O, C—H···O and C—H···π hydrogen bonds. 8-Hydroxymethyl-4′,4′-dimethyl-2-methylsulfanyl-3,4,5,6,7,8-hexahydropyrido[2,3-*d*]pyrimidine-6-spiro-1′-cyclohexane-2′,4,6′-trione, $C_{16}H_{21}N_3O_4S$, (II), where the hydroxymethyl substituent is disordered over two sets of sites, has a much less polarized structure than (I); the molecules are linked by a combination of O—H···O and N—H···O hydrogen bonds into chains containing alternating $R_2^2(8)$ and $R_2^2(16)$ rings, and these chains are linked into sheets by a combination of a π–π stacking interaction and a C—H···O hydrogen bond. 8-Ethoxymethyl-2-methoxy-4′,4′-dimethyl-3,4,5,6,7,8-hexahydropyrido[2,3-*d*]-pyrimidine-6-spiro-1′-cyclohexane-2′,4,6′-trione, $C_{18}H_{25}N_3O_5$, (III), has an unpolarized electronic structure, and a combination of N—H···O, C—H···O and C—H···π hydrogen bonds links the molecules into sheets.

Comment

Dihydropyridine systems are of current interest because of their exceptional properties as calcium antagonists (Bossert & Vater, 1989) and as powerful arteriolar vasodilators (Kazda & Towart, 1981). As part of a search for new fused heterocyclic systems containing dihydropyridine units, we have been exploring the use of three-component cyclocondensation



reactions between 4-aminopyrimidin-4(3*H*)-ones, dimedone (5,5-dimethyl-1,3-cyclohexanedione) and simple aliphatic aldehydes, in the expectation of forming pyrimidinoquinolines. In the event, reactions of this type, using an excess of formaldehyde in the presence of triethylamine, have led to the formation of spiro compounds rather than the expected pyrimidinoquinolines, and we report here the molecular and supramolecular structures of three such compounds, (I)–(III). All of the molecules are chiral, but the compounds studied all crystallize in the centrosymmetric space group $P\overline{1}$ and hence are racemic. The structure of (II) is complicated by the disorder of the –CH_2OH substituent at atom N8, which was modelled using sets of sites, each with an occupancy of 0.5, corresponding to two distinct orientations for this group.

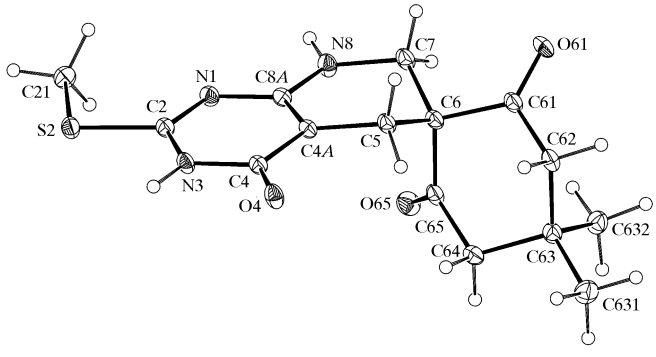


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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The bond lengths in (I) (Fig. 1 and Table 1) show some discrepancies when compared with typical values for bonds of similar types (Allen *et al.*, 1987). For example, the N3—C4 and C4—O4 bonds are both long for their types, the C4—C4*A* and C4*A*—C8*A* bonds are too similar in length to be characterized as single and double bonds, respectively, and the C8*A*—N8 bond, involving a three-coordinate N atom, is much shorter than the C8*A*—N1 bond, which involves a two-coordinate N atom. These observations, taken together, effectively preclude the polarized form (I*a*) as an effective contributor to the overall molecular–electronic structure, instead pointing to the importance of the polarized vinylogous amide form (I*b*).

Compounds (II) and (III) (Figs. 2 and 3) both show a much smaller degree of electronic polarization. For example, the difference between the C8*A*—N1 and C8*A*—N8 bond lengths (Tables 3 and 5) is much smaller in (II) and (III) than in (I). Hence, for these compounds, the classically localized forms are the most appropriate representations. We also note here the much greater difference between the C2—O2 and O2—C21 distances in (III) (∼0.11 Å) than between the corresponding C2—S2 and S2—C21 distances in (I) and (II) (∼0.04 and ∼0.02 Å, respectively). In each compound, the exocyclic bond angles at atom C2 are very different from 120°.

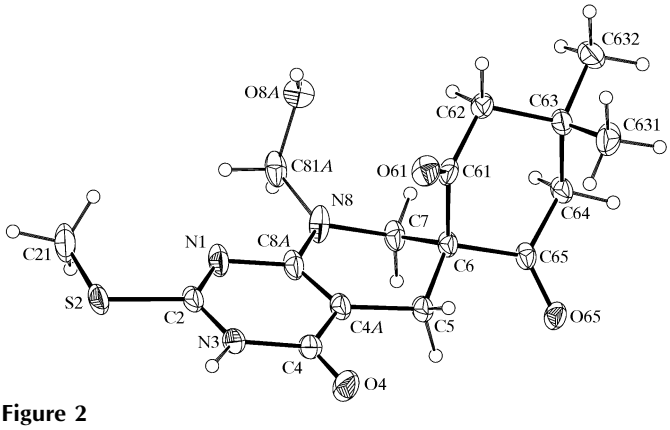


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only one orientation of the disordered –CH_2OH substituent is shown.

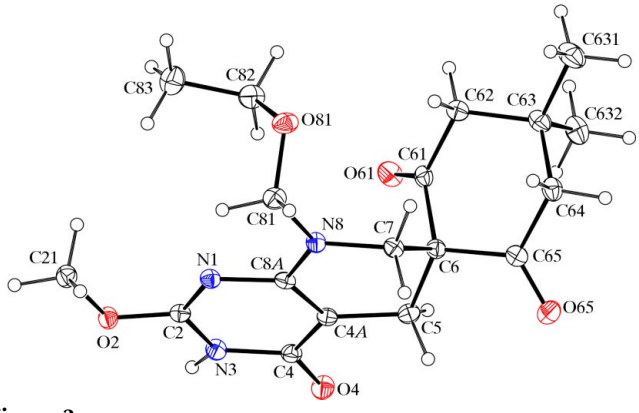


Figure 3
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

In each of (I)–(III), the ring containing atoms N1 and N3 is effectively planar, but for the ring containing atom N8, the ring-puckering parameters (Cremer & Pople, 1975) corresponding to the atom sequence N8—C7—C6—C5—C4*A*—C8*A* [θ = 129.2 (2)° and φ = 304.5 (3)° in (I), θ = 51.3 (3)° and φ = 98.5 (3)° in (II), and θ = 126.5 (3)° and φ = 283.2 (4)° in (III)] indicate that, in each compound, the conformation of this ring is best described as an envelope form, itself dominated by a combination of boat and chair forms (Evans & Boeyens, 1989). The carbocyclic rings adopt almost perfect chair conformations, with local pseudo-mirror symmetry defined by the plane through atoms C6, C63, C631 and C632. The conformations of the pendent CH_3X substituents [*X* = S in (I) and (II), and O in (III)] are similar in (I)–(III), while the –CH_2OEt unit in (III) exhibits some unusual torsion angles (Table 5).

The molecules of (I) are linked into a three-dimensional framework by a combination of N—H···O, C—H···O and C—H···π hydrogen bonds (Table 2). Two independent N—H···O hydrogen bonds generate a one-dimensional substructure in the form of a chain of rings; these chains are linked into sheets by the C—H···O hydrogen bonds, and the sheets are linked by C—H···π hydrogen bonds. Atom N3 in the molecule at (*x*, *y*, *z*) acts as a donor to atom O4 in the molecule at (1 − *x*, 1 − *y*, 1 − *z*), so forming a centrosymmetric $R_2^2(8)$ ring, centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 4). Similarly, atom N8 at (*x*, *y*, *z*) acts as a donor to atom O65 in the molecule at (−*x*, 1 − *y*, −*z*), forming a centrosymmetric $R_2^2(12)$ motif, this time centred at (0, $\frac{1}{2}$, 0). The propagation by inversion of these two motifs generates a chain running parallel to the [101] direction. Atom C5 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O61 in the molecule at (−*x*,

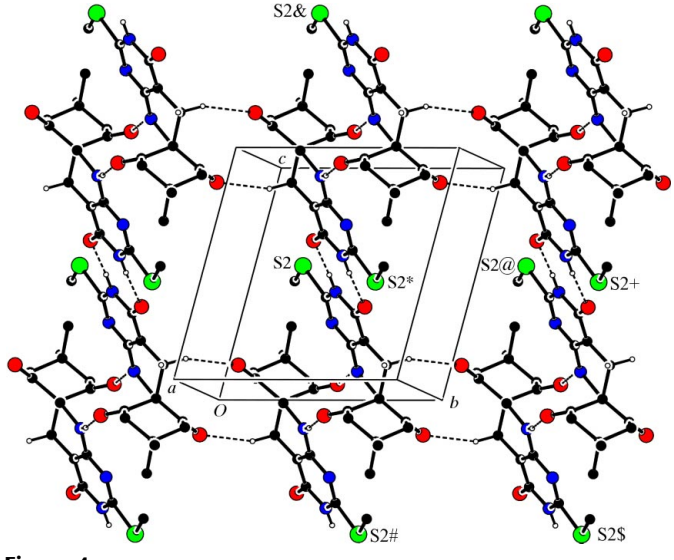


Figure 4
Part of the crystal structure of (I), showing the formation of a (10$\bar{1}$) sheet containing four types of centrosymmetric ring. For clarity, H atoms bonded to atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), an ampersand (&), a plus sign (+), an 'at' sign (@), a dollar sign ($) or a hash (#) are at the symmetry positions (1 − *x*, 1 − *y*, 1 − *z*), (1 + *x*, *y*, 1 + *z*), (1 − *x*, 2 − *y*, 1 − *z*), (*x*, 1 + *y*, *z*), (−*x*, 2 − *y*, −*z*) and (−*x*, 1 − *y*, −*z*), respectively.

$2 - y, -z$), so forming a third centrosymmetric ring motif, of $R_2^2(10)$ type, centred at (0, 1, 0). The combination of this motif with the [101] chains generates a $(10\bar{1})$ sheet (Fig. 4) containing four distinct types of ring, all centrosymmetric; in addition to the $R_2^2(8)$, $R_2^2(10)$ and $R_2^2(12)$ types already described, the sheet also contains $R_6^6(34)$ rings. Finally, atom C64 in the molecule at (x, y, z), which lies in the sheet passing through $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor, *via* H64*A*, to the N1/C2/N3/C4/C4*A*/C8*A* ring in the molecule at $(1 - x, 1 - y, -z)$, which lies in the sheet passing through $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$. The formation of this further centrosymmetric motif (Fig. 5) thus serves to link all of the centrosymmetric sheets into a single framework.

The molecules of (II) are linked by a combination of N—H···O and O—H···O hydrogen bonds (Table 4) into chains, and these chains are linked into sheets by a combination of a C—H···O hydrogen bond and a π–π stacking interaction. The description of the supramolecular aggregation is complicated by the disorder of the pendent –CH_2OH unit. Atom N3 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O4 in the molecule at $(2 - x, 1 - y, 1 - z)$, so forming a fully ordered $R_2^2(8)$ motif centred at $(1, \frac{1}{2}, \frac{1}{2})$. In addition, the partially occupied O8*A* site at (x, y, z) acts as a donor to carboxyl atom O61 in the molecule at $(1 - x, 1 - y, -z)$. There is also a much longer, and hence presumably weaker, O—H···O interaction involving the alternative atom site, O8*B*, as a donor and the same O61 atom as an acceptor. Hence, regardless of which site, O8*A* or O8*B*, is occupied, there will be two O—H···O linkages between the pair of molecules in question, forming an $R_2^2(16)$ ring. If the O8*A* sites were occupied in both molecules, the ring would be centrosymmetric. At the local level, such pairs of molecules can, in fact, be linked by zero, one or two strong O—H···O hydrogen bonds, with a mean of one such bond. In any event, the combination of the N—H···O and O—H···O hydrogen bonds generates a chain of rings running parallel to the [101] direction (Fig. 6).

Two weaker interactions combine to link the [101] chains into sheets. The N1/C2/N3/C4/C4*A*/C8*A* rings in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are parallel, with an interplanar spacing of 3.583 (2) Å; the ring-centroid separation is 3.878 (2) Å, corresponding to a centroid offset of 1.484 (2) Å (Fig. 7). The molecules involved lie in adjacent

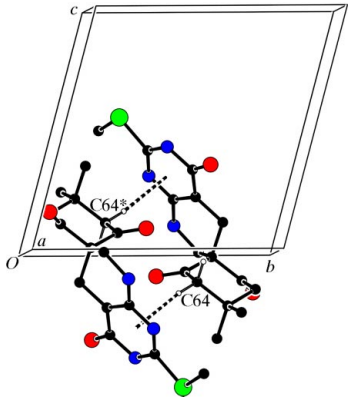


Figure 5
Part of the crystal structure of (I), showing the centrosymmetric linking of the molecules by pairs of C—H···π hydrogen bonds. For clarity, H atoms bonded to atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, -z)$.

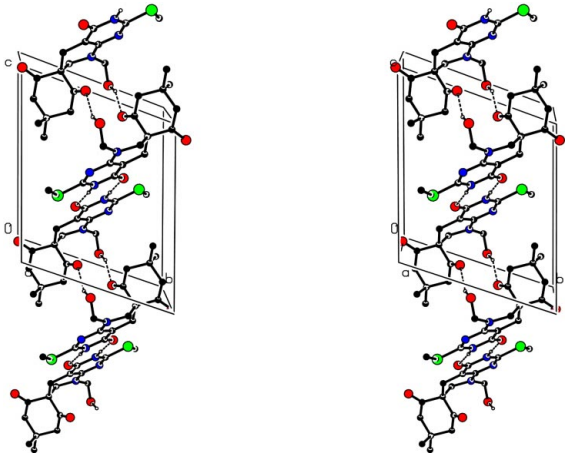


Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a chain of rings along [101]. For clarity, H atoms bonded to C atoms have been omitted and only one orientation of the disordered –CH_2OH group is shown.

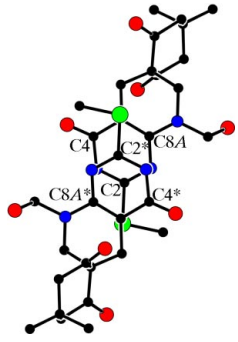


Figure 7
Part of the crystal structure of (II), showing the π–π stacking interaction that links the [101] chains into sheets. For clarity, H atoms bonded to C atoms have been omitted, the unit-cell box has been omitted and only one orientation of the disordered –CH_2OH group is shown.

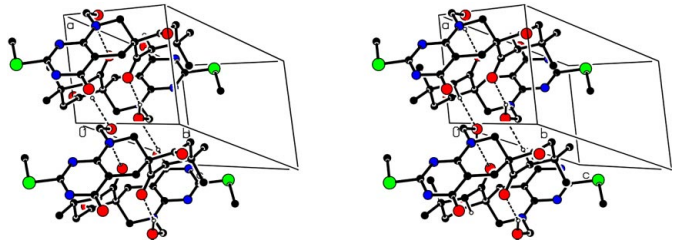


Figure 8
A stereoview of part of the crystal structure of (II), showing the action of the C—H···O hydrogen bond in linking adjacent [101] chains. For clarity, H atoms bonded to C atoms but not involved in the motif shown have been omitted, and only one orientation of the disordered –CH_2OH group is shown.

[101] chains, separated by a unit translation along [100]. This interaction is reinforced by a single C—H···O hydrogen bond; atom C62 in the molecule at (x, y, z) acts as a donor, *via* H62*B*, to the partially occupied O8*A* site in the molecule at ($-x$, $1-y$, $-z$) (Fig. 8).

In (III), the molecules are linked into sheets by a combination of N—H···O, C—H···O and C—H···π hydrogen bonds (Table 6). Pairs of N—H···O and of C—H···O hydrogen bonds generate a chain containing two types of centrosymmetric ring, and these chains are linked by C—H···π hydrogen bonds. Amine atom N3 in the molecule at (x, y, z) acts as a hydrogen-bond donor to amide atom O4 in the molecule at ($1-x$, $1-y$, $1-z$), thereby generating a centrosymmetric $R_2^2(8)$ motif centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). In addition, ring atom C7 at (x, y, z) acts as a donor, *via* H7*B*, to the exocyclic atom O81 in the molecule at ($3-x$, $-y$, $1-z$), so forming an $R_2^2(10)$ ring centred at ($\frac{3}{2}$, 0, $\frac{1}{2}$). Propagation by inversion of these two hydrogen bonds then generates a chain running parallel to the [2$\bar{1}$0] direction, in which $R_2^2(8)$ and $R_2^2(10)$ rings alternate (Fig. 9). Finally, atom C7 in the molecule at (x, y, z), which is part of the [2$\bar{1}$0] chain passing through ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), acts as a hydrogen-bond donor, *via* H7*A*, to the N1/C2/N3/C4/C4*A*/C8*A* ring in the molecule at ($2-x$, $-y$, $1-z$), which itself lies in the [2$\bar{1}$0] chain passing through ($-\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The resulting centrosymmetric motif (Fig. 10) thus serves to link [2$\bar{1}$0] chains into a (001) sheet. Although the structures of both (I) and (III) contain C—H···π hydrogen bonds, they differ in that the donor atoms lie in different rings in the two compounds.

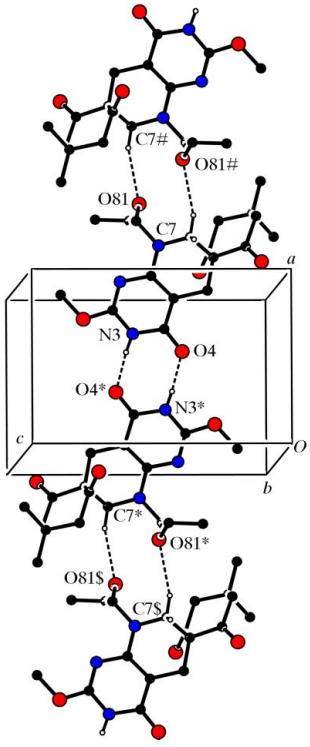


Figure 9
Part of the crystal structure of (III), showing the formation of a [2$\bar{1}$0] chain of centrosymmetric $R_2^2(8)$ and $R_2^2(10)$ rings. For clarity, H atoms bonded to atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions ($1-x$, $1-y$, $1-z$), ($3-x$, $-y$, $1-z$) and ($-2+x$, $1+y$, z), respectively.

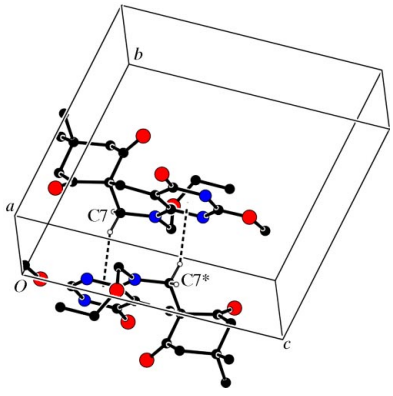
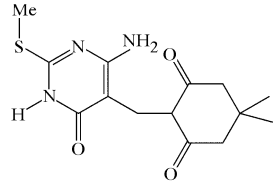
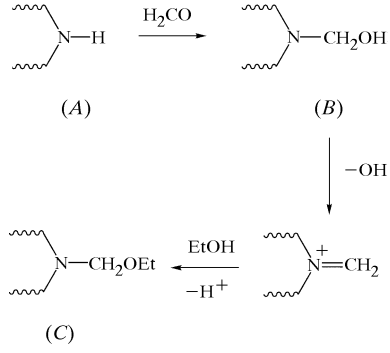


Figure 10
Part of the crystal structure of (III), showing the centrosymmetric linking of the molecules by pairs of C—H···π hydrogen bonds. For clarity, H atoms bonded to atoms not involved in the motif shown have been omitted. The atom marked with an asterisk (*) is at the symmetry position ($2-x$, $-y$, $1-z$).

The formation of (I) from the precursor aminopyrimidine, dimedone and two molecules of formaldehyde is straightforward, proceeding *via* the intermediate (IV); we have recently reported the structure of the N^3-methyl analogue of (IV) (Low *et al.*, 2004). Further reaction at the secondary amine atom N8 of the primary product of type (*A*) with another molecule of formaldehyde in the presence of ethanol can lead, *via* a hydroxymethyl derivative, (*B*) [*cf.* compound (II)], to an ethoxymethyl product, (*C*) [*cf.* compound (III)].



(IV)



Experimental

For the preparation of (I), dimedone (2 mmol), a large excess of an aqueous solution (37% *w*/*w*) of formaldehyde (30 mmol formaldehyde) and triethylamine (0.5 mmol) were added to a solution of 6-amino-2-methylsulfanyl-3,4-dihydropyrimidin-4-one (2 mmol) in

ethanol, and this mixture was heated under reflux for 90 min. After cooling the mixture, the resulting white product, (I), was filtered off and washed with ethanol (m.p. 563–567 K). Analysis found: C 55.7, H 5.8, N 12.8, S 10.0%; $C_{15}H_{19}N_3O_3S$ requires: C 13.1, H 6.0, N 13.1, S 10.0%. Compound (II) was an occasional and erratic by-product of this reaction. For the preparation of (III), dimedone (2 mmol) and a large excess of an aqueous solution (37% *w*/*w*) of formaldehyde (30 mmol) were added to a solution of 6-amino-2-methoxy-3,4-dihydropyrimidin-4-one (2 mmol) in ethanol, and this mixture was heated under reflux for 90 min. After cooling the mixture, the resulting white product, (III), was filtered off and washed with ethanol (m.p. 533–536 K). For (I) and (II), crystals suitable for single-crystal X-ray diffraction were grown from solutions in wet dimethyl sulfoxide; crystals of (III) suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

Compound (I)

Crystal data

$C_{15}H_{19}N_3O_3S$
M_r = 321.39
Triclinic, $P\overline{1}$
a = 7.8990 (3) Å
b = 10.0386 (3) Å
c = 10.0500 (3) Å
α = 74.938 (2)°
β = 84.271 (2)°
γ = 81.842 (2)°
V = 760.10 (4) Å^3
Z = 2
D_x = 1.404 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3462 reflections
θ = 3.2–27.5°
μ = 0.23 mm^{-1}
T = 120 (2) K
Block, colourless
0.42 × 0.38 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.921, T_{max} = 0.956
15 364 measured reflections
3462 independent reflections
2923 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 27.5°
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.125
S = 1.04
3462 reflections
202 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.5301P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C2	1.300 (2)	C8*A*—N8	1.342 (2)
C2—N3	1.356 (2)	C7—N8	1.455 (2)
N3—C4	1.395 (2)	C2—S2	1.7547 (18)
C4—C4*A*	1.409 (2)	S2—C21	1.7983 (19)
C4*A*—C8*A*	1.391 (2)	C61—O61	1.216 (2)
C8*A*—N1	1.379 (2)	C65—O65	1.219 (2)
C4—O4	1.253 (2)		
N1—C2—N3	125.04 (16)	N3—C2—S2	113.71 (13)
N1—C2—S2	121.25 (14)	C2—S2—C21	100.96 (9)
C4*A*—C5—C6—C7	51.41 (18)	C6—C61—C62—C63	58.5 (2)
C5—C6—C7—N8	−50.4 (2)	C61—C62—C63—C64	−56.58 (18)
C6—C7—N8—C8*A*	26.8 (3)	C62—C63—C64—C65	54.3 (2)
C7—N8—C8*A*—C4*A*	−2.5 (3)	C63—C64—C65—C6	−53.2 (2)
N8—C8*A*—C4*A*—C5	4.8 (3)	C64—C65—C6—C61	49.58 (19)
C8*A*—C4*A*—C5—C6	−30.3 (2)	C65—C6—C61—C62	−52.5 (2)

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

*Cg*1 is the centroid of the N1/C2/N3/C4/C4*A*/C8*A* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O4^{i}	0.88	1.84	2.715 (2)	176
N8—H8···O65^{ii}	0.88	2.10	2.965 (2)	166
C5—H5*B*···O61^{iii}	0.99	2.46	3.389 (2)	155
C64—H64*A*···*Cg*1^{iv}	0.99	2.87	3.854 (2)	173

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$; (iii) $-x, 2-y, -z$; (iv) $1-x, -y, -z$.

Compound (II)

Crystal data

$C_{16}H_{21}N_3O_4S$
M_r = 351.42
Triclinic, $P\overline{1}$
a = 6.6682 (2) Å
b = 11.0319 (3) Å
c = 12.3449 (4) Å
α = 109.2678 (18)°
β = 99.8329 (18)°
γ = 101.227 (2)°
V = 813.32 (5) Å^3
Z = 2
D_x = 1.435 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3737 reflections
θ = 3.2–27.5°
μ = 0.23 mm^{-1}
T = 120 (2) K
Plate, colourless
0.15 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.976, T_{max} = 0.994
18 379 measured reflections
3737 independent reflections
2502 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.5°
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.140
S = 1.03
3737 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.2491P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C2	1.294 (3)	C8*A*—N8	1.362 (3)
C2—N3	1.334 (3)	C7—N8	1.456 (2)
N3—C4	1.395 (3)	C2—S2	1.756 (2)
C4—C4*A*	1.414 (3)	S2—C21	1.779 (3)
C4*A*—C8*A*	1.374 (3)	C61—O61	1.212 (2)
C8*A*—N1	1.379 (3)	C65—O65	1.206 (2)
C4—O4	1.239 (3)		
N1—C2—N3	124.60 (19)	N3—C2—S2	114.25 (17)
N1—C2—S2	121.14 (19)	C2—S2—C21	99.74 (12)
C4*A*—C5—C6—C7	−46.1 (2)	C6—C61—C62—C63	−55.9 (2)
C5—C6—C7—N8	59.0 (2)	C61—C62—C63—C64	56.3 (2)
C6—C7—N8—C8*A*	−42.4 (3)	C62—C63—C64—C65	−55.6 (3)
C7—N8—C8*A*—C4*A*	12.1 (3)	C63—C64—C65—C6	52.5 (2)
N8—C8*A*—C4*A*—C5	1.0 (3)	C64—C65—C6—C61	−45.7 (2)
C8*A*—C4*A*—C5—C6	18.1 (3)	C65—C6—C61—C62	48.1 (2)
C6—C7—N8—C81*A*	139.6 (4)	C6—C7—N8—C81*B*	158.5 (4)
C7—N8—C81*A*—O8*A*	−61.9 (14)	C7—N8—C81*B*—O8*B*	−113.3 (9)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O4^{v}	0.88	1.83	2.709 (3)	176
O8A—H8A···O61^{vi}	0.84	2.00	2.767 (3)	152
O8B—H8B···O61^{vi}	0.84	2.35	3.036 (4)	139
C62—H62B···O8A^{ii}	0.99	2.33	3.314 (4)	173

Symmetry codes: (ii) $-x, 1-y, -z$; (v) $2-x, 1-y, 1-z$; (vi) $1-x, 1-y, -z$.

Compound (III)

Crystal data

$C_{18}H_{25}N_3O_5$
M_r = 363.41
Triclinic, $P\overline{1}$
a = 8.9219 (5) Å
b = 9.9806 (5) Å
c = 11.3542 (7) Å
α = 75.662 (3)°
β = 85.580 (3)°
γ = 66.526 (3)°
V = 898.22 (9) Å^3
Z = 2
D_x = 1.344 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4082 reflections
θ = 2.9–27.6°
μ = 0.10 mm^{-1}
T = 120 (2) K
Prism, colourless
0.15 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.967, T_{max} = 0.990
17 797 measured reflections
4082 independent reflections
2026 reflections with $I > 2\sigma(I)$
R_{int} = 0.088
θ_{max} = 27.6°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Table 5
Selected geometric parameters (Å, °) for (III).

N1—C2	1.292 (3)	C8A—N8	1.370 (3)
C2—N3	1.343 (3)	C7—N8	1.451 (3)
N3—C4	1.388 (3)	C2—O2	1.334 (3)
C4—C4A	1.412 (3)	O2—C21	1.447 (3)
C4A—C8A	1.378 (3)	C61—O61	1.213 (3)
C8A—N1	1.375 (3)	C65—O65	1.210 (3)
C4—O4	1.250 (3)		
N1—C2—N3	125.1 (2)	N3—C2—O2	113.1 (2)
N1—C2—O2	121.8 (2)	C2—O2—C21	115.51 (18)
C4A—C5—C6—C7	47.6 (3)	C6—C61—C62—C63	55.5 (3)
C5—C6—C7—N8	−58.7 (2)	C61—C62—C63—C64	−56.8 (3)
C6—C7—N8—C8A	39.4 (3)	C62—C63—C64—C65	55.1 (3)
C7—N8—C8A—C4A	−7.4 (3)	C63—C64—C65—C6	−51.0 (3)
N8—C8A—C4A—C5	−3.4 (4)	C64—C65—C6—C61	44.1 (3)
C8A—C4A—C5—C6	−18.9 (3)	C65—C6—C61—C62	−46.8 (3)
C6—C7—N8—C81	−142.4 (2)	N8—C81—O81—C82	71.3 (3)
C7—N8—C81—O81	74.4 (3)	C81—O81—C82—C83	82.4 (3)

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

$Cg1$ is the centroid of the N1/C2/N3/C4/C4A/C8A ring.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O4^{i}	0.88	1.89	2.769 (2)	173
C7—H7B···O81^{vii}	0.99	2.49	3.414 (3)	155
C7—H7A···$Cg1^{viii}$	0.99	2.62	3.535 (3)	155

Symmetry codes: (i) $1-x, 1-y, 1-z$; (vii) $3-x, -y, 1-z$; (viii) $2-x, -y, 1-z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.164
S = 0.95
4082 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Crystals of (I)–(III) are triclinic; space group $P\overline{1}$ was selected for each and confirmed by the subsequent structure analyses. In (II), the hydroxymethyl substituent is disordered; it was modelled using two sets of atom sites (C81A/O8A for one orientation and C81B/O8B for the other), all atoms having an occupancy of 0.50. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.98 (CH_3) or 0.99 Å (CH_2), N—H distances of 0.88 Å and O—H distances of 0.84 Å, and with U_{iso}(H) values of $1.2U_{eq}(X)$ (X = C, N and O) [$1.5U_{eq}$(C) for the methyl groups].

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) [for (I) and (II)] and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1722). Services for accessing these data are described at the back of the journal.

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Three hexahydropyridopyrimidine-spiro-cyclohexanetriones: supramolecular structures generated by O—H···O, N—H···O, C—H···O and C—H···π hydrogen bonds, and π–π stacking interactions

John N. Low, George Ferguson, Justo Cobo, Manuel Nogueras, Silvia Cruz, Jairo Quiroga and Christopher Glidewell

Computing details

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO*–SMN (Otwinowski & Minor, 1997); data reduction: *DENZO*–SMN. Program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997) for (I); *OSCAIL*,(McArdle, 2003) and *SHELXS97* (Sheldrick, 1997) for (II); *SHELXS97* (Sheldrick, 1997) for (III). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

(I) 4′,4′-Dimethyl-2-methylsulfanyl-3,4,5,6,7,8-hexahydropyrido[2,3-*d*]pyrimidine- 6-spiro-1′-cyclohexane-2′,4,6′-trione

Crystal data

$C_{15}H_{19}N_3O_3S$
$M_r = 321.39$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.8990\ (3)$ Å
$b = 10.0386\ (3)$ Å
$c = 10.0500\ (3)$ Å
$\alpha = 74.938\ (2)°$
$\beta = 84.271\ (2)°$
$\gamma = 81.842\ (2)°$
$V = 760.10\ (4)$ Å^3
$Z = 2$
$F(000) = 340$
$D_x = 1.404$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3462 reflections
$\theta = 3.2–27.5°$
$\mu = 0.23$ mm^{-1}
$T = 120$ K
Block, colourless
0.42 × 0.38 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: rotating anode
Graphite monochromator
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.921$, $T_{max} = 0.956$
15364 measured reflections
3462 independent reflections
2923 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = -10\rightarrow10$
$k = -12\rightarrow12$
$l = -12\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.125$
$S = 1.04$
3462 reflections
202 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.5301P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.00$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S2	0.15187 (6)	0.24922 (5)	0.56484 (5)	0.02612 (15)
O4	0.46653 (17)	0.64675 (14)	0.36030 (13)	0.0279 (3)
O61	0.05306 (17)	0.96763 (14)	−0.15486 (15)	0.0331 (3)
O65	0.28955 (18)	0.55478 (14)	−0.09297 (15)	0.0323 (3)
N1	0.07802 (19)	0.43116 (16)	0.32602 (16)	0.0244 (3)
N3	0.31142 (19)	0.46290 (15)	0.43867 (15)	0.0233 (3)
N8	0.0050 (2)	0.58608 (17)	0.12273 (16)	0.0273 (4)
C2	0.1785 (2)	0.39542 (18)	0.42755 (18)	0.0222 (4)
C4	0.3459 (2)	0.58565 (18)	0.34291 (18)	0.0216 (4)
C4A	0.2356 (2)	0.63152 (18)	0.23395 (18)	0.0209 (4)
C5	0.2533 (2)	0.76576 (18)	0.12915 (18)	0.0227 (4)
C6	0.1928 (2)	0.75976 (18)	−0.01135 (18)	0.0223 (4)
C7	0.0142 (2)	0.71174 (19)	0.01191 (19)	0.0256 (4)
C8A	0.1081 (2)	0.55127 (19)	0.22779 (18)	0.0226 (4)
C21	−0.0302 (2)	0.1891 (2)	0.5149 (2)	0.0291 (4)
C61	0.1869 (2)	0.90528 (19)	−0.10925 (18)	0.0240 (4)
C62	0.3564 (2)	0.96031 (18)	−0.14977 (19)	0.0250 (4)
C63	0.4792 (2)	0.86132 (19)	−0.22051 (19)	0.0249 (4)
C64	0.4979 (2)	0.71366 (19)	−0.1225 (2)	0.0260 (4)
C65	0.3253 (2)	0.66308 (18)	−0.07575 (18)	0.0243 (4)
C631	0.6538 (3)	0.9146 (2)	−0.2529 (2)	0.0335 (4)
C632	0.4043 (3)	0.8563 (2)	−0.35318 (19)	0.0294 (4)
H21A	−0.1256	0.2642	0.5013	0.044*
H21B	−0.0645	0.1097	0.5875	0.044*
H21C	0.0002	0.1606	0.4285	0.044*
H3	0.3806	0.4296	0.5062	0.028*
H5A	0.3746	0.7838	0.1174	0.027*
H5B	0.1837	0.8428	0.1615	0.027*
H7A	−0.0703	0.7868	0.0343	0.031*
H7B	−0.0171	0.6944	−0.0746	0.031*
H8	−0.0872	0.5443	0.1285	0.033*
H62A	0.4072	0.9689	−0.0667	0.030*
H62B	0.3397	1.0538	−0.2139	0.030*
H63A	0.7317	0.8529	−0.2990	0.050*

H63B	0.7008	0.9164	−0.1668	0.050*
H63C	0.6412	1.0087	−0.3136	0.050*
H63D	0.3819	0.9509	−0.4116	0.044*
H63E	0.2968	0.8146	−0.3303	0.044*
H63F	0.4860	0.8003	−0.4028	0.044*
H64A	0.5686	0.6487	−0.1709	0.031*
H64B	0.5577	0.7147	−0.0409	0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0244 (2)	0.0256 (3)	0.0252 (2)	−0.00489 (18)	−0.00546 (17)	0.00175 (17)
O4	0.0283 (7)	0.0269 (7)	0.0275 (7)	−0.0075 (5)	−0.0132 (5)	0.0015 (5)
O61	0.0260 (7)	0.0301 (7)	0.0347 (8)	0.0065 (6)	−0.0093 (6)	0.0043 (6)
O65	0.0327 (7)	0.0239 (7)	0.0405 (8)	−0.0050 (6)	−0.0044 (6)	−0.0069 (6)
N1	0.0208 (8)	0.0267 (8)	0.0240 (8)	−0.0027 (6)	−0.0058 (6)	−0.0017 (6)
N3	0.0221 (7)	0.0235 (8)	0.0219 (7)	−0.0023 (6)	−0.0091 (6)	0.0010 (6)
N8	0.0228 (8)	0.0307 (9)	0.0263 (8)	−0.0077 (6)	−0.0101 (6)	0.0022 (6)
C2	0.0206 (8)	0.0219 (9)	0.0225 (8)	−0.0019 (7)	−0.0035 (7)	−0.0023 (7)
C4	0.0203 (8)	0.0216 (8)	0.0215 (8)	−0.0007 (6)	−0.0041 (6)	−0.0028 (6)
C4A	0.0188 (8)	0.0222 (8)	0.0201 (8)	0.0001 (6)	−0.0052 (6)	−0.0021 (7)
C5	0.0220 (8)	0.0230 (9)	0.0214 (8)	−0.0004 (7)	−0.0069 (7)	−0.0018 (7)
C6	0.0202 (8)	0.0216 (9)	0.0225 (9)	0.0007 (7)	−0.0063 (7)	−0.0008 (7)
C7	0.0244 (9)	0.0254 (9)	0.0248 (9)	−0.0008 (7)	−0.0096 (7)	−0.0004 (7)
C8A	0.0182 (8)	0.0259 (9)	0.0218 (8)	−0.0001 (7)	−0.0046 (6)	−0.0026 (7)
C21	0.0258 (9)	0.0288 (10)	0.0322 (10)	−0.0073 (7)	−0.0007 (8)	−0.0049 (8)
C61	0.0256 (9)	0.0234 (9)	0.0204 (8)	0.0032 (7)	−0.0063 (7)	−0.0025 (7)
C62	0.0279 (9)	0.0213 (9)	0.0238 (9)	−0.0011 (7)	−0.0085 (7)	−0.0002 (7)
C63	0.0223 (9)	0.0266 (9)	0.0239 (9)	−0.0027 (7)	−0.0049 (7)	−0.0017 (7)
C64	0.0216 (9)	0.0250 (9)	0.0289 (9)	0.0017 (7)	−0.0050 (7)	−0.0033 (7)
C65	0.0261 (9)	0.0217 (9)	0.0219 (8)	0.0010 (7)	−0.0069 (7)	0.0003 (7)
C631	0.0262 (10)	0.0396 (12)	0.0349 (11)	−0.0091 (8)	−0.0030 (8)	−0.0064 (9)
C632	0.0278 (10)	0.0356 (11)	0.0239 (9)	−0.0060 (8)	−0.0037 (7)	−0.0041 (8)

Geometric parameters (Å, º)

N1—C2	1.300 (2)	C6—C61	1.532 (2)
C2—N3	1.356 (2)	C6—C65	1.536 (2)
N3—C4	1.395 (2)	C61—C62	1.499 (3)
C4—C4A	1.409 (2)	C62—C63	1.546 (3)
C4A—C8A	1.391 (2)	C62—H62A	0.99
C8A—N1	1.379 (2)	C62—H62B	0.99
C4—O4	1.253 (2)	C63—C631	1.525 (3)
C8A—N8	1.342 (2)	C63—C632	1.527 (3)
C7—N8	1.455 (2)	C63—C64	1.548 (3)
C2—S2	1.7547 (18)	C631—H63A	0.98
S2—C21	1.7983 (19)	C631—H63B	0.98
C61—O61	1.216 (2)	C631—H63C	0.98

C65—O65	1.219 (2)	C632—H63D	0.98
C21—H21A	0.98	C632—H63E	0.98
C21—H21B	0.98	C632—H63F	0.98
C21—H21C	0.98	C64—C65	1.511 (3)
N3—H3	0.88	C64—H64A	0.99
C4A—C5	1.494 (2)	C64—H64B	0.99
C5—C6	1.554 (2)	C7—H7A	0.99
C5—H5A	0.99	C7—H7B	0.99
C5—H5B	0.99	N8—H8	0.88
C6—C7	1.532 (2)		

C2—N1—C8A	115.44 (15)	H62A—C62—H62B	108.2
N1—C2—N3	125.04 (16)	C631—C63—C632	110.35 (16)
N1—C2—S2	121.25 (14)	C631—C63—C62	109.14 (16)
N3—C2—S2	113.71 (13)	C632—C63—C62	108.96 (15)
C2—S2—C21	100.96 (9)	C631—C63—C64	109.67 (15)
S2—C21—H21A	109.5	C632—C63—C64	109.27 (15)
S2—C21—H21B	109.5	C62—C63—C64	109.43 (15)
H21A—C21—H21B	109.5	C63—C631—H63A	109.5
S2—C21—H21C	109.5	C63—C631—H63B	109.5
H21A—C21—H21C	109.5	H63A—C631—H63B	109.5
H21B—C21—H21C	109.5	C63—C631—H63C	109.5
C2—N3—C4	121.61 (15)	H63A—C631—H63C	109.5
C2—N3—H3	120.9	H63B—C631—H63C	109.5
C4—N3—H3	117.5	C63—C632—H63D	109.5
O4—C4—N3	119.22 (15)	C63—C632—H63E	109.5
O4—C4—C4A	125.53 (16)	H63D—C632—H63E	109.5
N3—C4—C4A	115.24 (15)	C63—C632—H63F	109.5
C8A—C4A—C4	118.83 (16)	H63D—C632—H63F	109.5
C8A—C4A—C5	120.88 (15)	H63E—C632—H63F	109.5
C4—C4A—C5	120.27 (15)	C65—C64—C63	111.36 (14)
C4A—C5—C6	110.13 (14)	C65—C64—H64A	109.4
C4A—C5—H5A	109.6	C63—C64—H64A	109.4
C6—C5—H5A	109.6	C65—C64—H64B	109.4
C4A—C5—H5B	109.6	C63—C64—H64B	109.4
C6—C5—H5B	109.6	H64A—C64—H64B	108.0
H5A—C5—H5B	108.1	O65—C65—C64	122.40 (17)
C7—C6—C61	110.16 (14)	O65—C65—C6	121.37 (17)
C7—C6—C65	112.50 (15)	C64—C65—C6	116.15 (15)
C61—C6—C65	107.40 (14)	N8—C7—C6	112.53 (14)
C7—C6—C5	109.13 (14)	N8—C7—H7A	109.1
C61—C6—C5	108.56 (14)	C6—C7—H7A	109.1
C65—C6—C5	109.02 (14)	N8—C7—H7B	109.1
O61—C61—C62	123.16 (17)	C6—C7—H7B	109.1
O61—C61—C6	121.12 (17)	H7A—C7—H7B	107.8
C62—C61—C6	115.64 (14)	C8A—N8—C7	122.57 (15)
C61—C62—C63	110.06 (15)	C8A—N8—H8	120.0
C61—C62—H62A	109.6	C7—N8—H8	115.9

C63—C62—H62A	109.6	N8—C8A—N1	114.84 (16)
C61—C62—H62B	109.6	N8—C8A—C4A	121.46 (16)
C63—C62—H62B	109.6	N1—C8A—C4A	123.70 (16)
C8A—N1—C2—N3	−3.3 (3)	C4A—C5—C6—C65	−71.82 (18)
C8A—N1—C2—S2	177.39 (13)	C7—C6—C61—O61	1.4 (2)
N1—C2—S2—C21	−0.46 (18)	C65—C6—C61—O61	124.28 (19)
N3—C2—S2—C21	−179.84 (14)	C5—C6—C61—O61	−117.99 (19)
N1—C2—N3—C4	4.2 (3)	C7—C6—C61—C62	−175.34 (15)
S2—C2—N3—C4	−176.43 (13)	C5—C6—C61—C62	65.23 (19)
C2—N3—C4—O4	177.52 (16)	O61—C61—C62—C63	−118.25 (19)
C2—N3—C4—C4A	−1.3 (2)	C61—C62—C63—C631	−176.60 (15)
O4—C4—C4A—C8A	179.34 (17)	C61—C62—C63—C632	62.84 (19)
N3—C4—C4A—C8A	−2.0 (2)	C631—C63—C64—C65	173.96 (16)
O4—C4—C4A—C5	−2.1 (3)	C632—C63—C64—C65	−65.0 (2)
N3—C4—C4A—C5	176.63 (15)	C63—C64—C65—O65	123.80 (19)
C4—C4A—C5—C6	151.19 (16)	C7—C6—C65—O65	−6.0 (2)
C4A—C5—C6—C7	51.41 (18)	C61—C6—C65—O65	−127.42 (18)
C5—C6—C7—N8	−50.4 (2)	C5—C6—C65—O65	115.15 (18)
C6—C7—N8—C8A	26.8 (3)	C7—C6—C65—C64	170.96 (15)
C7—N8—C8A—C4A	−2.5 (3)	C5—C6—C65—C64	−67.85 (19)
N8—C8A—C4A—C5	4.8 (3)	C61—C6—C7—N8	−169.50 (15)
C8A—C4A—C5—C6	−30.3 (2)	C65—C6—C7—N8	70.72 (19)
C6—C61—C62—C63	58.5 (2)	C7—N8—C8A—N1	177.95 (16)
C61—C62—C63—C64	−56.58 (18)	C2—N1—C8A—N8	179.23 (16)
C62—C63—C64—C65	54.3 (2)	C2—N1—C8A—C4A	−0.3 (3)
C63—C64—C65—C6	−53.2 (2)	C4—C4A—C8A—N8	−176.60 (17)
C64—C65—C6—C61	49.58 (19)	C4—C4A—C8A—N1	2.9 (3)
C65—C6—C61—C62	−52.5 (2)	C5—C4A—C8A—N1	−175.72 (16)
C4A—C5—C6—C61	171.49 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O4^{i}	0.88	1.84	2.715 (2)	176
N8—H8···O65^{ii}	0.88	2.10	2.965 (2)	166
C5—H5*B*···O61^{iii}	0.99	2.46	3.389 (2)	155
C64—H64*A*···*Cg*1^{iv}	0.99	2.87	3.854 (2)	173

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*; (iii) −*x*, −*y*+2, −*z*; (iv) −*x*+1, −*y*, −*z*.

(II) 8-Hydroxymethyl-4′,4′-dimethyl-2-methylsulfanyl-3,4,5,6,7,8- hexahydropyrido[2,3-*d*]pyrimidine-6-spiro-1′-cyclohexane-2′,4,6′-trione

Crystal data

$C_{16}H_{21}N_3O_4S$	*a* = 6.6682 (2) Å
M_r = 351.42	*b* = 11.0319 (3) Å
Triclinic, $P\overline{1}$	*c* = 12.3449 (4) Å
Hall symbol: -P 1	α = 109.2678 (18)°

β = 99.8329 (18)°
γ = 101.227 (2)°
V = 813.32 (5) Å^3
Z = 2
F(000) = 372
D_x = 1.435 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 3737 reflections
θ = 3.2–27.5°
μ = 0.23 mm^{-1}
T = 120 K
Plate, colourless
0.15 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: rotating anode
Graphite monochromator
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.976, T_{max} = 0.994

18379 measured reflections
3737 independent reflections
2502 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 27.5°, θ_{min} = 3.2°
h = −8→8
k = −14→14
l = −15→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.140
S = 1.03
3737 reflections
238 parameters
4 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 0.2491P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S2	0.73487 (11)	0.77931 (5)	0.56516 (5)	0.0559 (2)	
O4	0.8658 (3)	0.35113 (16)	0.36896 (15)	0.0701 (6)	
O8A	0.0777 (5)	0.5505 (3)	0.0734 (3)	0.0474 (8)	0.50
O8B	0.1860 (5)	0.6134 (4)	0.1656 (3)	0.0500 (8)	0.50
O61	0.6178 (2)	0.37648 (14)	0.03689 (14)	0.0461 (4)	
O65	0.2484 (2)	−0.00235 (13)	0.00947 (12)	0.0382 (4)	
N1	0.4772 (3)	0.59074 (17)	0.36624 (16)	0.0460 (5)	
N3	0.7797 (4)	0.54542 (17)	0.45024 (15)	0.0522 (6)	
N8	0.2429 (3)	0.43269 (17)	0.19453 (17)	0.0472 (5)	
C2	0.6503 (4)	0.6233 (2)	0.44750 (18)	0.0431 (6)	
C4	0.7391 (4)	0.4187 (2)	0.36314 (19)	0.0491 (6)	
C4A	0.5490 (3)	0.37791 (19)	0.27379 (17)	0.0393 (5)	
C5	0.4922 (3)	0.24252 (19)	0.17519 (17)	0.0374 (5)	
C6	0.3324 (3)	0.23534 (18)	0.06839 (16)	0.0325 (5)	
C7	0.1552 (3)	0.29491 (19)	0.11179 (18)	0.0393 (5)	
C8A	0.4264 (3)	0.4653 (2)	0.27876 (18)	0.0405 (5)	
C21	0.5183 (5)	0.8446 (2)	0.5328 (2)	0.0681 (8)	
C61	0.4339 (3)	0.31261 (18)	−0.00039 (18)	0.0342 (5)	
C62	0.3010 (3)	0.29784 (19)	−0.11717 (18)	0.0369 (5)	

C63	0.2179 (4)	0.1500 (2)	−0.19984 (18)	0.0427 (6)	
C64	0.0954 (4)	0.0723 (2)	−0.13757 (17)	0.0414 (5)	
C65	0.2261 (3)	0.09007 (19)	−0.01856 (17)	0.0338 (5)	
C81A	0.117 (2)	0.5262 (14)	0.1814 (11)	0.0454 (15)	0.50
C81B	0.106 (2)	0.5204 (14)	0.2135 (11)	0.0454 (15)	0.50
C631	0.4024 (5)	0.0939 (2)	−0.2260 (2)	0.0611 (8)	
C632	0.0690 (5)	0.1399 (2)	−0.3135 (2)	0.0606 (8)	
H3	0.8944	0.5750	0.5090	0.063*	
H5A	0.4327	0.1731	0.2040	0.045*	
H5B	0.6214	0.2246	0.1516	0.045*	
H7A	0.0497	0.2911	0.0429	0.047*	
H7B	0.0825	0.2414	0.1513	0.047*	
H8A	0.1924	0.5880	0.0643	0.057*	0.50
H8B	0.2429	0.5775	0.1123	0.060*	0.50
H21A	0.4913	0.8373	0.4500	0.102*	
H21B	0.5519	0.9385	0.5852	0.102*	
H21C	0.3922	0.7940	0.5452	0.102*	
H62A	0.3862	0.3478	−0.1548	0.044*	
H62B	0.1803	0.3358	−0.1042	0.044*	
H63A	0.0162	0.0463	−0.3680	0.091*	
H63B	0.1458	0.1922	−0.3514	0.091*	
H63C	−0.0503	0.1745	−0.2939	0.091*	
H63D	0.4905	0.0976	−0.1521	0.092*	
H63E	0.4871	0.1468	−0.2606	0.092*	
H63F	0.3489	0.0011	−0.2820	0.092*	
H64A	−0.0325	0.1029	−0.1270	0.050*	
H64B	0.0489	−0.0237	−0.1887	0.050*	
H81A	−0.0222	0.4938	0.1949	0.054*	0.50
H81B	0.1877	0.6134	0.2467	0.054*	0.50
H81C	−0.0428	0.4713	0.1713	0.054*	0.50
H81D	0.1163	0.5646	0.2990	0.054*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0910 (5)	0.0289 (3)	0.0278 (3)	−0.0058 (3)	0.0162 (3)	−0.0023 (2)
O4	0.1007 (15)	0.0337 (9)	0.0459 (10)	0.0158 (10)	−0.0274 (10)	0.0014 (8)
O8A	0.0405 (18)	0.053 (2)	0.050 (2)	0.0121 (15)	0.0125 (16)	0.0217 (17)
O8B	0.0458 (19)	0.052 (2)	0.049 (2)	0.0127 (16)	0.0105 (17)	0.0153 (17)
O61	0.0399 (9)	0.0370 (8)	0.0523 (9)	−0.0035 (7)	0.0111 (7)	0.0135 (7)
O65	0.0424 (8)	0.0238 (7)	0.0403 (8)	0.0019 (6)	0.0094 (6)	0.0064 (6)
N1	0.0558 (12)	0.0291 (9)	0.0366 (10)	−0.0028 (8)	0.0171 (9)	−0.0030 (8)
N3	0.0835 (15)	0.0260 (9)	0.0257 (9)	−0.0010 (10)	−0.0074 (9)	0.0025 (7)
N8	0.0381 (10)	0.0312 (9)	0.0515 (11)	0.0037 (8)	0.0110 (9)	−0.0074 (8)
C2	0.0669 (15)	0.0244 (10)	0.0259 (10)	−0.0048 (10)	0.0126 (11)	0.0033 (8)
C4	0.0777 (17)	0.0262 (11)	0.0285 (11)	0.0008 (11)	−0.0020 (11)	0.0069 (9)
C4A	0.0529 (13)	0.0263 (10)	0.0270 (10)	−0.0017 (9)	0.0091 (9)	0.0029 (8)
C5	0.0474 (12)	0.0257 (10)	0.0285 (10)	0.0003 (9)	0.0057 (9)	0.0042 (8)

C6	0.0375 (11)	0.0226 (9)	0.0281 (10)	−0.0009 (8)	0.0084 (8)	0.0026 (8)
C7	0.0401 (12)	0.0291 (10)	0.0347 (11)	−0.0021 (9)	0.0117 (9)	−0.0002 (9)
C8A	0.0491 (13)	0.0275 (10)	0.0313 (11)	−0.0034 (9)	0.0142 (10)	−0.0004 (8)
C21	0.099 (2)	0.0377 (13)	0.0507 (15)	0.0092 (14)	0.0320 (15)	−0.0057 (11)
C61	0.0409 (12)	0.0189 (9)	0.0384 (11)	0.0032 (8)	0.0149 (9)	0.0054 (8)
C62	0.0459 (12)	0.0252 (10)	0.0361 (11)	0.0023 (9)	0.0139 (9)	0.0095 (8)
C63	0.0663 (15)	0.0267 (10)	0.0290 (10)	0.0023 (10)	0.0178 (10)	0.0057 (8)
C64	0.0556 (14)	0.0267 (10)	0.0272 (10)	−0.0070 (9)	0.0069 (9)	0.0038 (8)
C65	0.0379 (11)	0.0248 (10)	0.0309 (10)	−0.0023 (8)	0.0146 (9)	0.0039 (8)
C81A	0.0417 (18)	0.0393 (16)	0.045 (6)	0.0019 (15)	0.029 (4)	−0.001 (3)
C81B	0.0417 (18)	0.0393 (16)	0.045 (6)	0.0019 (15)	0.029 (4)	−0.001 (3)
C631	0.095 (2)	0.0367 (12)	0.0580 (16)	0.0164 (13)	0.0463 (15)	0.0136 (12)
C632	0.096 (2)	0.0394 (13)	0.0308 (12)	−0.0069 (13)	0.0099 (12)	0.0104 (10)

Geometric parameters (Å, º)

N1—C2	1.294 (3)	C63—C632	1.531 (3)
C2—N3	1.334 (3)	C63—C64	1.540 (3)
N3—C4	1.395 (3)	C631—H63D	0.98
C4—C4A	1.414 (3)	C631—H63E	0.98
C4A—C8A	1.374 (3)	C631—H63F	0.98
C8A—N1	1.379 (3)	C632—H63A	0.98
C4—O4	1.239 (3)	C632—H63B	0.98
C8A—N8	1.362 (3)	C632—H63C	0.98
C7—N8	1.456 (2)	C64—C65	1.504 (3)
C2—S2	1.756 (2)	C64—H64A	0.99
S2—C21	1.779 (3)	C64—H64B	0.99
C61—O61	1.212 (2)	C7—H7A	0.99
C65—O65	1.206 (2)	C7—H7B	0.99
C21—H21A	0.98	N8—C81B	1.445 (8)
C21—H21B	0.98	N8—C81A	1.482 (7)
C21—H21C	0.98	C81A—O8A	1.436 (8)
N3—H3	0.88	C81A—H81A	0.99
C6—C5	1.516 (3)	C81A—H81B	0.99
C6—C61	1.535 (3)	O8A—H8A	0.84
C6—C65	1.544 (2)	C81B—O8B	1.407 (9)
C6—C7	1.550 (3)	C81B—H81C	0.99
C61—C62	1.498 (3)	C81B—H81D	0.99
C62—C63	1.538 (3)	O8B—H8B	0.84
C62—H62A	0.99	C4A—C5	1.509 (3)
C62—H62B	0.99	C5—H5A	0.99
C63—C631	1.517 (4)	C5—H5B	0.99
C2—N1—C8A	115.9 (2)	H63A—C632—H63C	109.5
N1—C2—N3	124.60 (19)	H63B—C632—H63C	109.5
N1—C2—S2	121.14 (19)	C65—C64—C63	112.38 (17)
N3—C2—S2	114.25 (17)	C65—C64—H64A	109.1
C2—S2—C21	99.74 (12)	C63—C64—H64A	109.1

S2—C21—H21A	109.5	C65—C64—H64B	109.1
S2—C21—H21B	109.5	C63—C64—H64B	109.1
H21A—C21—H21B	109.5	H64A—C64—H64B	107.9
S2—C21—H21C	109.5	O65—C65—C64	122.99 (17)
H21A—C21—H21C	109.5	O65—C65—C6	120.79 (18)
H21B—C21—H21C	109.5	C64—C65—C6	116.22 (18)
C2—N3—C4	122.2 (2)	N8—C7—C6	110.54 (16)
C2—N3—H3	118.9	N8—C7—H7A	109.5
C4—N3—H3	118.9	C6—C7—H7A	109.5
O4—C4—N3	119.6 (2)	N8—C7—H7B	109.5
O4—C4—C4A	125.2 (2)	C6—C7—H7B	109.5
N3—C4—C4A	115.1 (2)	H7A—C7—H7B	108.1
C5—C6—C61	111.79 (16)	C8A—N8—C81B	118.4 (7)
C5—C6—C65	111.91 (17)	C8A—N8—C7	119.01 (19)
C61—C6—C65	107.97 (15)	C81B—N8—C7	119.2 (7)
C5—C6—C7	108.64 (16)	C8A—N8—C81A	125.2 (7)
C61—C6—C7	109.28 (17)	C7—N8—C81A	115.8 (7)
C65—C6—C7	107.13 (15)	O8A—C81A—N8	120.5 (6)
O61—C61—C62	122.43 (19)	O8A—C81A—H81A	107.2
O61—C61—C6	120.23 (19)	N8—C81A—H81A	107.2
C62—C61—C6	117.22 (16)	O8A—C81A—H81B	107.2
C61—C62—C63	110.53 (17)	N8—C81A—H81B	107.2
C61—C62—H62A	109.5	H81A—C81A—H81B	106.8
C63—C62—H62A	109.5	O8B—C81B—N8	102.7 (6)
C61—C62—H62B	109.5	O8B—C81B—H81C	111.2
C63—C62—H62B	109.5	N8—C81B—H81C	111.2
H62A—C62—H62B	108.1	O8B—C81B—H81D	111.2
C631—C63—C632	111.5 (2)	N8—C81B—H81D	111.2
C631—C63—C62	109.62 (19)	H81C—C81B—H81D	109.1
C632—C63—C62	108.29 (19)	C81B—O8B—H8B	109.5
C631—C63—C64	108.88 (19)	C8A—C4A—C4	118.29 (19)
C632—C63—C64	109.54 (18)	C8A—C4A—C5	122.70 (19)
C62—C63—C64	108.98 (16)	C4—C4A—C5	119.0 (2)
C63—C631—H63D	109.5	C4A—C5—C6	111.07 (18)
C63—C631—H63E	109.5	C4A—C5—H5A	109.4
H63D—C631—H63E	109.5	C6—C5—H5A	109.4
C63—C631—H63F	109.5	C4A—C5—H5B	109.4
H63D—C631—H63F	109.5	C6—C5—H5B	109.4
H63E—C631—H63F	109.5	H5A—C5—H5B	108.0
C63—C632—H63A	109.5	N8—C8A—C4A	121.15 (18)
C63—C632—H63B	109.5	N8—C8A—N1	115.0 (2)
H63A—C632—H63B	109.5	C4A—C8A—N1	123.9 (2)
C63—C632—H63C	109.5		

C8A—N1—C2—N3	1.0 (3)	C6—C61—C62—C63	−55.9 (2)
C8A—N1—C2—S2	−179.61 (15)	C61—C62—C63—C64	56.3 (2)
N1—C2—S2—C21	3.4 (2)	C62—C63—C64—C65	−55.6 (3)
N3—C2—S2—C21	−177.13 (17)	C63—C64—C65—C6	52.5 (2)

N1—C2—N3—C4	0.2 (3)	C64—C65—C6—C61	−45.7 (2)
S2—C2—N3—C4	−179.20 (17)	C65—C6—C61—C62	48.1 (2)
C2—N3—C4—O4	179.0 (2)	C6—C7—N8—C81B	158.5 (4)
C2—N3—C4—C4A	−1.4 (3)	C7—N8—C81B—O8B	−113.3 (9)
C5—C6—C61—O61	−4.5 (3)	C61—C6—C7—N8	−63.2 (2)
C65—C6—C61—O61	−128.0 (2)	C65—C6—C7—N8	−179.91 (17)
C7—C6—C61—O61	115.8 (2)	C8A—N8—C81A—O8A	120.2 (11)
C5—C6—C61—C62	171.59 (17)	C81B—N8—C81A—O8A	−168 (6)
C7—C6—C61—C62	−68.1 (2)	C8A—N8—C81B—O8B	87.5 (8)
O61—C61—C62—C63	120.1 (2)	C81A—N8—C81B—O8B	−31 (4)
C61—C62—C63—C631	−62.7 (2)	O4—C4—C4A—C8A	−179.1 (2)
C61—C62—C63—C632	175.42 (18)	N3—C4—C4A—C8A	1.4 (3)
C631—C63—C64—C65	64.0 (2)	O4—C4—C4A—C5	−0.9 (4)
C632—C63—C64—C65	−173.88 (19)	N3—C4—C4A—C5	179.61 (18)
C63—C64—C65—O65	−127.7 (2)	C4—C4A—C5—C6	−159.99 (19)
C5—C6—C65—O65	11.1 (3)	C61—C6—C5—C4A	74.5 (2)
C61—C6—C65—O65	134.5 (2)	C65—C6—C5—C4A	−164.23 (16)
C7—C6—C65—O65	−107.9 (2)	C81B—N8—C8A—C4A	171.3 (5)
C5—C6—C65—C64	−169.11 (17)	C81A—N8—C8A—C4A	−170.2 (4)
C7—C6—C65—C64	71.9 (2)	C81B—N8—C8A—N1	−9.2 (5)
C4A—C5—C6—C7	−46.1 (2)	C7—N8—C8A—N1	−168.49 (18)
C5—C6—C7—N8	59.0 (2)	C81A—N8—C8A—N1	9.3 (5)
C6—C7—N8—C8A	−42.4 (3)	C4—C4A—C8A—N8	179.14 (19)
C7—N8—C8A—C4A	12.1 (3)	C4—C4A—C8A—N1	−0.3 (3)
N8—C8A—C4A—C5	1.0 (3)	C5—C4A—C8A—N1	−178.39 (18)
C8A—C4A—C5—C6	18.1 (3)	C2—N1—C8A—N8	179.60 (18)
C6—C7—N8—C81A	139.6 (4)	C2—N1—C8A—C4A	−1.0 (3)
C7—N8—C81A—O8A	−61.9 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O4^{i}	0.88	1.83	2.709 (3)	176
O8*A*—H8*A*···O61^{ii}	0.84	2.00	2.767 (3)	152
O8*B*—H8*B*···O61^{ii}	0.84	2.35	3.036 (4)	139
C62—H62*B*···O8*A*^{iii}	0.99	2.33	3.314 (4)	173

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*; (iii) −*x*, −*y*+1, −*z*.

(III) 8-Ethoxymethyl-4′,4′-dimethyl-2-methoxy-3,4,5,6,7,8- hexahydropyrido[2,3-*d*]pyrimidine-6-spiro-1′-cyclohexane-2′,4,6′-trione

Crystal data

$C_{18}H_{25}N_3O_5$
M_r = 363.41
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.9219 (5) Å
b = 9.9806 (5) Å
c = 11.3542 (7) Å
α = 75.662 (3)°
β = 85.580 (3)°
γ = 66.526 (3)°
V = 898.22 (9) Å^3
Z = 2
F(000) = 388
D_x = 1.344 Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4082 reflections
$\theta = 2.9$–$27.6°$
$\mu = 0.10$ mm^{-1}
$T = 120$ K
Prism, colourless
0.15 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: rotating anode
Graphite monochromator
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.967$, $T_{max} = 0.990$
17797 measured reflections
4082 independent reflections
2026 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 27.6°$, $\theta_{min} = 2.9°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.164$
$S = 0.95$
4082 reflections
239 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.76490 (19)	0.29677 (18)	0.77260 (15)	0.0267 (4)
O4	0.60281 (19)	0.42536 (19)	0.37935 (16)	0.0307 (5)
O61	1.0648 (2)	0.45522 (19)	0.30859 (17)	0.0341 (5)
O65	1.0669 (2)	0.1427 (2)	0.09973 (17)	0.0366 (5)
O81	1.3916 (2)	0.11344 (19)	0.57305 (17)	0.0333 (5)
N1	0.9621 (2)	0.2004 (2)	0.63954 (19)	0.0220 (5)
N3	0.6927 (2)	0.3582 (2)	0.57622 (19)	0.0244 (5)
N8	1.1529 (2)	0.1062 (2)	0.49992 (18)	0.0219 (5)
C2	0.8137 (3)	0.2829 (3)	0.6605 (2)	0.0222 (6)
C4	0.7185 (3)	0.3526 (3)	0.4551 (2)	0.0235 (6)
C4A	0.8788 (3)	0.2631 (3)	0.4273 (2)	0.0214 (6)
C5	0.9216 (3)	0.2579 (3)	0.2974 (2)	0.0250 (6)
C6	1.1047 (3)	0.2140 (3)	0.2781 (2)	0.0226 (6)
C7	1.1958 (3)	0.0750 (3)	0.3809 (2)	0.0230 (6)
C8A	0.9942 (3)	0.1920 (3)	0.5206 (2)	0.0211 (6)
C21	0.8922 (3)	0.2250 (3)	0.8662 (2)	0.0291 (7)
C61	1.1592 (3)	0.3407 (3)	0.2821 (2)	0.0237 (6)
C62	1.3327 (3)	0.3162 (3)	0.2472 (2)	0.0272 (6)
C63	1.3671 (3)	0.2836 (3)	0.1202 (2)	0.0293 (7)
C64	1.3292 (3)	0.1471 (3)	0.1194 (2)	0.0284 (6)
C65	1.1581 (3)	0.1657 (3)	0.1582 (2)	0.0252 (6)

C81	1.2815 (3)	0.0402 (3)	0.5923 (2)	0.0285 (6)
C82	1.3228 (3)	0.2618 (3)	0.5964 (3)	0.0355 (7)
C83	1.3285 (4)	0.2592 (3)	0.7284 (3)	0.0424 (8)
C631	1.5468 (3)	0.2495 (3)	0.0911 (3)	0.0453 (8)
C632	1.2588 (4)	0.4201 (3)	0.0250 (3)	0.0404 (8)
H3	0.5981	0.4209	0.5960	0.029*
H5A	0.8609	0.3578	0.2436	0.030*
H5B	0.8878	0.1841	0.2749	0.030*
H7A	1.1679	−0.0097	0.3748	0.028*
H7B	1.3152	0.0444	0.3708	0.028*
H21A	0.9469	0.1177	0.8677	0.044*
H21B	0.8440	0.2369	0.9454	0.044*
H21C	0.9721	0.2716	0.8489	0.044*
H62A	1.4085	0.2305	0.3077	0.033*
H62B	1.3524	0.4068	0.2479	0.033*
H63A	1.5730	0.3339	0.0974	0.068*
H63B	1.5667	0.2345	0.0083	0.068*
H63C	1.6158	0.1581	0.1489	0.068*
H63D	1.1436	0.4423	0.0443	0.061*
H63E	1.2797	0.3982	−0.0556	0.061*
H63F	1.2837	0.5071	0.0254	0.061*
H64A	1.3444	0.1297	0.0364	0.034*
H64B	1.4080	0.0572	0.1746	0.034*
H81A	1.2320	0.0457	0.6729	0.034*
H81B	1.3426	−0.0673	0.5926	0.034*
H82A	1.2077	0.3126	0.5665	0.043*
H82B	1.3835	0.3214	0.5502	0.043*
H83A	1.2747	0.1952	0.7753	0.064*
H83B	1.2720	0.3616	0.7398	0.064*
H83C	1.4427	0.2192	0.7564	0.064*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0216 (10)	0.0335 (10)	0.0220 (11)	−0.0078 (8)	0.0001 (8)	−0.0065 (8)
O4	0.0180 (10)	0.0380 (11)	0.0297 (12)	−0.0032 (8)	−0.0046 (9)	−0.0085 (9)
O61	0.0357 (11)	0.0259 (10)	0.0400 (13)	−0.0113 (9)	0.0090 (9)	−0.0104 (9)
O65	0.0359 (11)	0.0463 (12)	0.0337 (12)	−0.0188 (9)	−0.0001 (9)	−0.0151 (10)
O81	0.0216 (10)	0.0365 (11)	0.0456 (13)	−0.0103 (8)	0.0025 (9)	−0.0186 (9)
N1	0.0173 (12)	0.0218 (11)	0.0253 (13)	−0.0057 (9)	0.0012 (9)	−0.0065 (9)
N3	0.0137 (11)	0.0269 (12)	0.0282 (14)	−0.0018 (9)	0.0016 (10)	−0.0098 (10)
N8	0.0150 (11)	0.0229 (11)	0.0229 (13)	−0.0025 (9)	−0.0008 (9)	−0.0050 (9)
C2	0.0215 (14)	0.0216 (13)	0.0246 (16)	−0.0100 (11)	0.0001 (12)	−0.0044 (11)
C4	0.0199 (14)	0.0253 (14)	0.0266 (17)	−0.0097 (11)	0.0012 (13)	−0.0074 (12)
C4A	0.0165 (13)	0.0222 (13)	0.0246 (15)	−0.0071 (11)	−0.0002 (12)	−0.0050 (11)
C5	0.0199 (14)	0.0251 (13)	0.0274 (16)	−0.0065 (11)	−0.0035 (12)	−0.0049 (12)
C6	0.0189 (13)	0.0256 (14)	0.0222 (15)	−0.0077 (11)	0.0007 (11)	−0.0057 (11)
C7	0.0213 (14)	0.0209 (13)	0.0253 (16)	−0.0071 (11)	0.0022 (12)	−0.0055 (11)

C8A	0.0170 (13)	0.0197 (13)	0.0274 (16)	−0.0080 (11)	0.0025 (12)	−0.0061 (11)
C21	0.0250 (15)	0.0356 (15)	0.0249 (16)	−0.0100 (12)	−0.0002 (12)	−0.0070 (12)
C61	0.0248 (14)	0.0248 (14)	0.0183 (15)	−0.0083 (12)	0.0002 (12)	−0.0017 (11)
C62	0.0260 (15)	0.0263 (14)	0.0292 (17)	−0.0113 (11)	0.0010 (12)	−0.0050 (12)
C63	0.0230 (14)	0.0313 (15)	0.0307 (17)	−0.0098 (12)	0.0036 (13)	−0.0044 (12)
C64	0.0246 (14)	0.0290 (14)	0.0275 (16)	−0.0058 (11)	0.0045 (12)	−0.0092 (12)
C65	0.0255 (15)	0.0200 (14)	0.0278 (16)	−0.0079 (11)	0.0004 (13)	−0.0031 (12)
C81	0.0198 (14)	0.0297 (15)	0.0327 (17)	−0.0055 (12)	−0.0015 (12)	−0.0083 (12)
C82	0.0318 (16)	0.0331 (16)	0.043 (2)	−0.0120 (13)	0.0025 (14)	−0.0125 (14)
C83	0.0497 (19)	0.0384 (17)	0.038 (2)	−0.0149 (14)	−0.0004 (15)	−0.0112 (14)
C631	0.0318 (17)	0.0550 (19)	0.049 (2)	−0.0189 (15)	0.0124 (15)	−0.0130 (16)
C632	0.0432 (18)	0.0406 (17)	0.0318 (18)	−0.0149 (14)	0.0058 (14)	−0.0030 (14)

Geometric parameters (Å, º)

N1—C2	1.292 (3)	C62—H62B	0.99
C2—N3	1.343 (3)	C63—C631	1.527 (4)
N3—C4	1.388 (3)	C63—C632	1.530 (4)
C4—C4A	1.412 (3)	C63—C64	1.531 (3)
C4A—C8A	1.378 (3)	C631—H63A	0.98
C8A—N1	1.375 (3)	C631—H63B	0.98
C4—O4	1.250 (3)	C631—H63C	0.98
C8A—N8	1.370 (3)	C632—H63D	0.98
C7—N8	1.451 (3)	C632—H63E	0.98
C2—O2	1.334 (3)	C632—H63F	0.98
O2—C21	1.447 (3)	C64—C65	1.507 (3)
C61—O61	1.213 (3)	C64—H64A	0.99
C65—O65	1.210 (3)	C64—H64B	0.99
C21—H21A	0.98	C7—H7A	0.99
C21—H21B	0.98	C7—H7B	0.99
C21—H21C	0.98	N8—C81	1.445 (3)
N3—H3	0.8798	C81—O81	1.417 (3)
C4A—C5	1.503 (3)	C81—H81A	0.99
C5—C6	1.527 (3)	C81—H81B	0.99
C5—H5A	0.99	O81—C82	1.444 (3)
C5—H5B	0.99	C82—C83	1.497 (4)
C6—C65	1.535 (3)	C82—H82A	0.99
C6—C61	1.535 (3)	C82—H82B	0.99
C6—C7	1.547 (3)	C83—H83A	0.98
C61—C62	1.505 (3)	C83—H83B	0.98
C62—C63	1.538 (3)	C83—H83C	0.98
C62—H62A	0.99		

C2—N1—C8A	115.7 (2)	C63—C631—H63C	109.5
N1—C2—N3	125.1 (2)	H63A—C631—H63C	109.5
N1—C2—O2	121.8 (2)	H63B—C631—H63C	109.5
N3—C2—O2	113.1 (2)	C63—C632—H63D	109.5
C2—O2—C21	115.51 (18)	C63—C632—H63E	109.5

O2—C21—H21A	109.5	H63D—C632—H63E	109.5
O2—C21—H21B	109.5	C63—C632—H63F	109.5
H21A—C21—H21B	109.5	H63D—C632—H63F	109.5
O2—C21—H21C	109.5	H63E—C632—H63F	109.5
H21A—C21—H21C	109.5	C65—C64—C63	113.06 (19)
H21B—C21—H21C	109.5	C65—C64—H64A	109.0
C2—N3—C4	121.5 (2)	C63—C64—H64A	109.0
C2—N3—H3	119.5	C65—C64—H64B	109.0
C4—N3—H3	118.6	C63—C64—H64B	109.0
O4—C4—N3	119.4 (2)	H64A—C64—H64B	107.8
O4—C4—C4A	124.9 (2)	O65—C65—C64	122.6 (2)
N3—C4—C4A	115.7 (2)	O65—C65—C6	121.0 (2)
C8A—C4A—C4	118.0 (2)	C64—C65—C6	116.4 (2)
C8A—C4A—C5	122.1 (2)	N8—C7—C6	111.47 (18)
C4—C4A—C5	119.6 (2)	N8—C7—H7A	109.3
C4A—C5—C6	111.4 (2)	C6—C7—H7A	109.3
C4A—C5—H5A	109.3	N8—C7—H7B	109.3
C6—C5—H5A	109.3	C6—C7—H7B	109.3
C4A—C5—H5B	109.3	H7A—C7—H7B	108.0
C6—C5—H5B	109.3	C8A—N8—C81	123.4 (2)
H5A—C5—H5B	108.0	C8A—N8—C7	119.2 (2)
C5—C6—C65	112.2 (2)	C81—N8—C7	117.39 (19)
C5—C6—C61	112.37 (19)	O81—C81—N8	112.3 (2)
C65—C6—C61	109.2 (2)	O81—C81—H81A	109.1
C5—C6—C7	107.7 (2)	N8—C81—H81A	109.1
C65—C6—C7	106.27 (18)	O81—C81—H81B	109.1
C61—C6—C7	108.9 (2)	N8—C81—H81B	109.1
O61—C61—C62	122.6 (2)	H81A—C81—H81B	107.9
O61—C61—C6	121.1 (2)	C81—O81—C82	113.65 (19)
C62—C61—C6	116.2 (2)	O81—C82—C83	112.9 (2)
C61—C62—C63	111.1 (2)	O81—C82—H82A	109.0
C61—C62—H62A	109.4	C83—C82—H82A	109.0
C63—C62—H62A	109.4	O81—C82—H82B	109.0
C61—C62—H62B	109.4	C83—C82—H82B	109.0
C63—C62—H62B	109.4	H82A—C82—H82B	107.8
H62A—C62—H62B	108.0	C82—C83—H83A	109.5
C631—C63—C632	109.6 (2)	C82—C83—H83B	109.5
C631—C63—C64	109.5 (2)	H83A—C83—H83B	109.5
C632—C63—C64	109.6 (2)	C82—C83—H83C	109.5
C631—C63—C62	109.8 (2)	H83A—C83—H83C	109.5
C632—C63—C62	109.7 (2)	H83B—C83—H83C	109.5
C64—C63—C62	108.7 (2)	N8—C8A—N1	114.8 (2)
C63—C631—H63A	109.5	N8—C8A—C4A	121.2 (2)
C63—C631—H63B	109.5	N1—C8A—C4A	124.0 (2)
H63A—C631—H63B	109.5		

C8A—N1—C2—O2	177.8 (2)	N8—C81—O81—C82	71.3 (3)
C8A—N1—C2—N3	0.2 (3)	C81—O81—C82—C83	82.4 (3)

N1—C2—O2—C21	5.5 (3)	C5—C6—C61—O61	5.9 (3)
N3—C2—O2—C21	−176.61 (19)	C65—C6—C61—O61	131.1 (2)
N1—C2—N3—C4	0.3 (4)	C7—C6—C61—O61	−113.3 (3)
O2—C2—N3—C4	−177.54 (19)	C5—C6—C61—C62	−172.0 (2)
C2—N3—C4—O4	−179.4 (2)	C7—C6—C61—C62	68.8 (3)
C2—N3—C4—C4A	0.0 (3)	O61—C61—C62—C63	−122.4 (3)
O4—C4—C4A—C8A	178.7 (2)	C61—C62—C63—C631	−176.4 (2)
N3—C4—C4A—C8A	−0.8 (3)	C61—C62—C63—C632	63.1 (3)
O4—C4—C4A—C5	3.4 (4)	C631—C63—C64—C65	174.9 (2)
N3—C4—C4A—C5	−176.1 (2)	C632—C63—C64—C65	−64.8 (3)
C4—C4A—C5—C6	156.1 (2)	C63—C64—C65—O65	129.8 (3)
C4A—C5—C6—C65	164.19 (19)	C5—C6—C65—O65	−11.4 (3)
C4A—C5—C6—C61	−72.3 (3)	C61—C6—C65—O65	−136.7 (2)
C4A—C5—C6—C7	47.6 (3)	C7—C6—C65—O65	106.0 (3)
C5—C6—C7—N8	−58.7 (2)	C5—C6—C65—C64	169.3 (2)
C6—C7—N8—C8A	39.4 (3)	C7—C6—C65—C64	−73.3 (3)
C7—N8—C8A—C4A	−7.4 (3)	C65—C6—C7—N8	−179.07 (19)
N8—C8A—C4A—C5	−3.4 (4)	C61—C6—C7—N8	63.4 (2)
C8A—C4A—C5—C6	−18.9 (3)	C8A—N8—C81—O81	−107.4 (2)
C6—C7—N8—C81	−142.4 (2)	C81—N8—C8A—N1	−5.5 (3)
C7—N8—C81—O81	74.4 (3)	C7—N8—C8A—N1	172.63 (19)
C6—C61—C62—C63	55.5 (3)	C81—N8—C8A—C4A	174.4 (2)
C61—C62—C63—C64	−56.8 (3)	C2—N1—C8A—N8	178.88 (19)
C62—C63—C64—C65	55.1 (3)	C2—N1—C8A—C4A	−1.1 (3)
C63—C64—C65—C6	−51.0 (3)	C4—C4A—C8A—N8	−178.56 (19)
C64—C65—C6—C61	44.1 (3)	C4—C4A—C8A—N1	1.4 (4)
C65—C6—C61—C62	−46.8 (3)	C5—C4A—C8A—N1	176.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O4^{i}	0.88	1.89	2.769 (2)	173
C7—H7*B*···O81^{ii}	0.99	2.49	3.414 (3)	155
C7—H7*A*···*Cg*1^{iii}	0.99	2.62	3.535 (3)	155

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+3, −*y*, −*z*+1; (iii) −*x*+2, −*y*, −*z*+1.