

Three hexahydropyridopyrimidine-spiro-cyclohexanetriones: supra-molecular 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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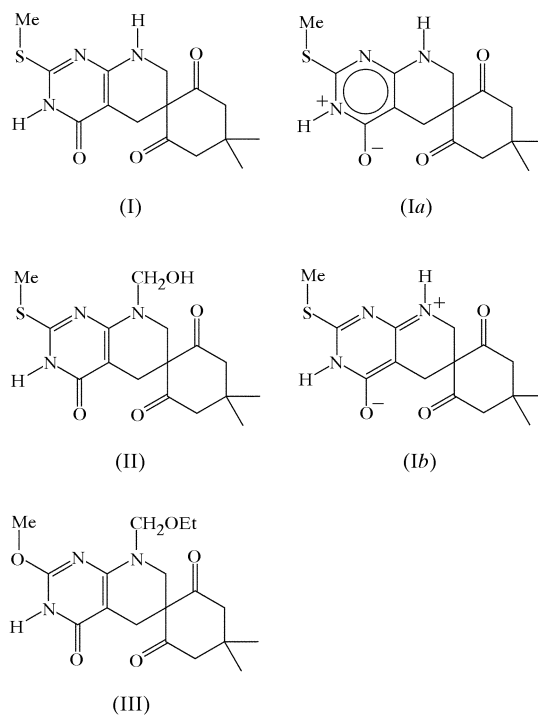
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4',4'-Dimethyl-2-methylsulfanyl-3,4,5,6,7,8-hexahydropyrido[2,3-*d*]pyrimidine-6-spiro-1'-cyclohexane-2',4,6'-trione, C₁₅H₁₉N₃O₃S, (I), has a markedly polarized molecular–electronic structure, and the molecules are linked into a three-dimensional framework 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, C₁₆H₂₁N₃O₄S, (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, C₁₈H₂₅N₃O₅, (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.

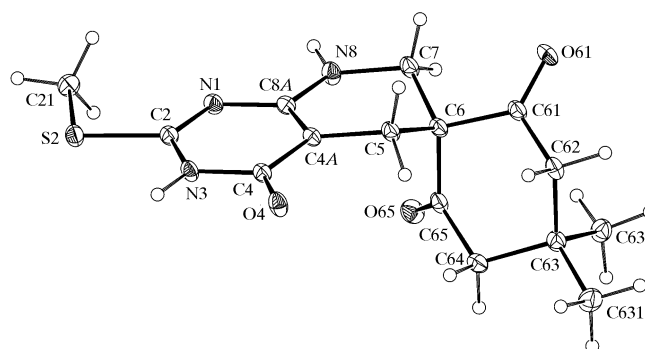
Comment

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 $P\bar{1}$ and hence are racemic. The structure of (II) is complicated by the disorder of the –CH₂OH 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.



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–C4A and C4A–C8A bonds are too similar in length to be characterized as single and double bonds, respectively, and the C8A–N8 bond, involving a three-coordinate N atom, is much shorter than the C8A–N1 bond, which involves a two-coordinate N atom. These observations, taken together, effectively preclude the polarized form (Ia) as an effective contributor to the overall molecular–electronic structure, instead pointing to the importance of the polarized vinylogous amide form (Ib).

Compounds (II) and (III) (Figs. 2 and 3) both show a much smaller degree of electronic polarization. For example, the difference between the C8A–N1 and C8A–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° .

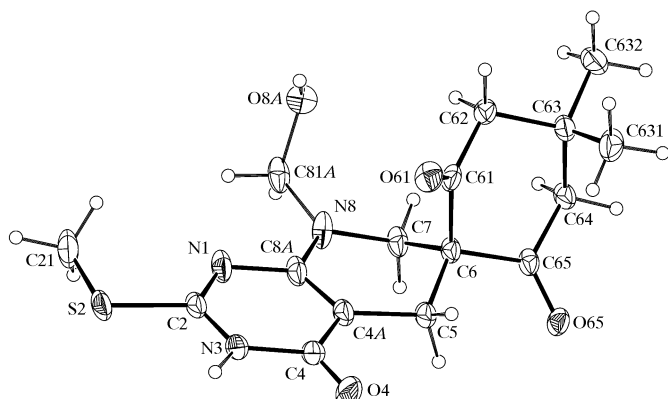


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only one orientation of the disordered $-\text{CH}_2\text{OH}$ substituent is shown.

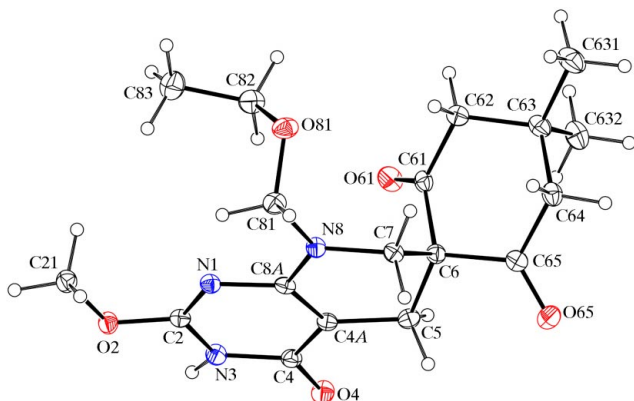


Figure 3
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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–C4A–C8A [$\theta = 129.2$ (2) $^\circ$ and $\varphi = 304.5$ (3) $^\circ$ in (I), $\theta = 51.3$ (3) $^\circ$ and $\varphi = 98.5$ (3) $^\circ$ in (II), and $\theta = 126.5$ (3) $^\circ$ and $\varphi = 283.2$ (4) $^\circ$ 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 [$\text{X} = \text{S}$ in (I) and (II), and O in (III)] are similar in (I)–(III), while the $-\text{CH}_2\text{OEt}$ 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 $\text{N}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ hydrogen bonds (Table 2). Two independent $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds generate a one-dimensional substructure in the form of a chain of rings; these chains are linked into sheets by the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, and the sheets are linked by $\text{C}-\text{H}\cdots\pi$ 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 $(-x,$

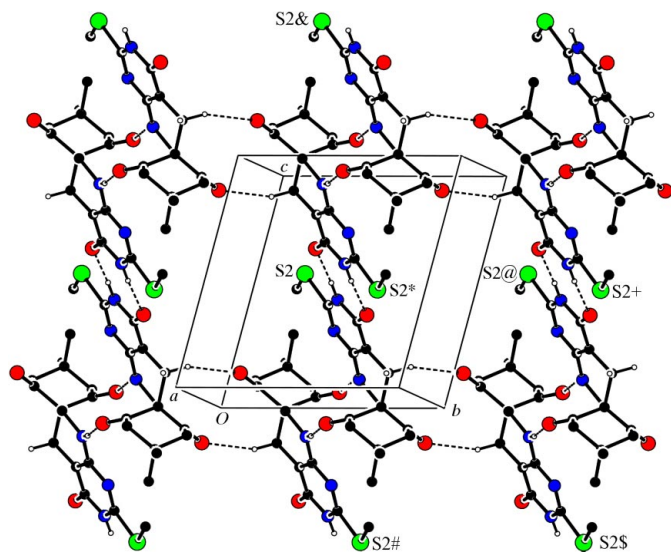


Figure 4
Part of the crystal structure of (I), showing the formation of a $(10\bar{1})$ sheet containing four types of centrosymmetric ring. For clarity, H atoms bonded to atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), an ampersand (&), a plus sign (+), an '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 $R_6^0(34)$ 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* H64A, to the N1/C2/N3/C4/C4A/C8A 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

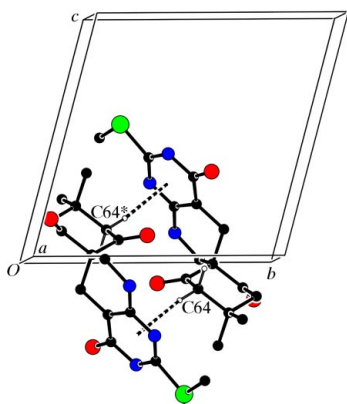


Figure 5

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 $(1 - x, 1 - y, -z)$.

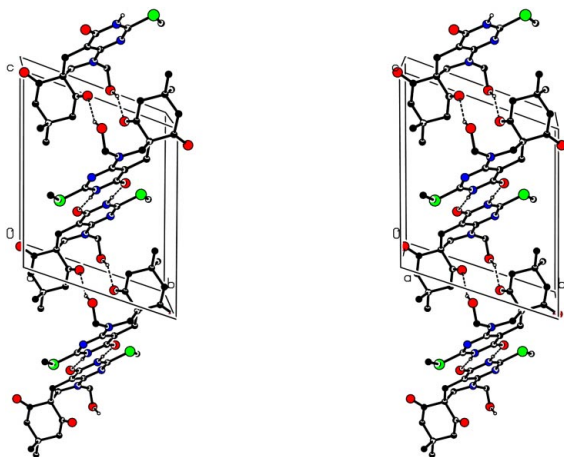


Figure 6

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 $-\text{CH}_2\text{OH}$ group is shown.

description of the supramolecular aggregation is complicated by the disorder of the pendent $-\text{CH}_2\text{OH}$ 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 O8A 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, O8B, as a donor and the same O61 atom as an acceptor. Hence, regardless of which site, O8A or O8B, 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 O8A 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/C4A/C8A 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

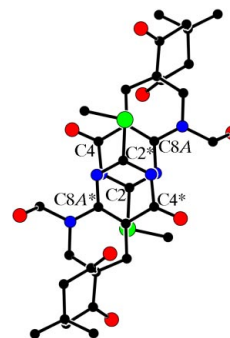


Figure 7

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 $-\text{CH}_2\text{OH}$ group is shown.

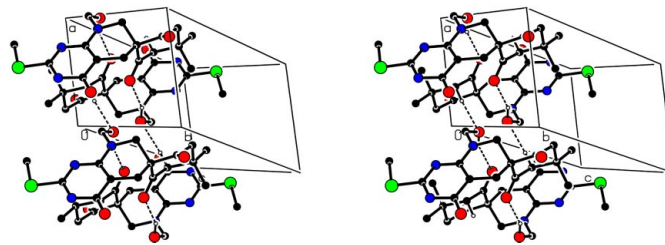


Figure 8

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 $-\text{CH}_2\text{OH}$ 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* H62B, to the partially occupied O8A 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

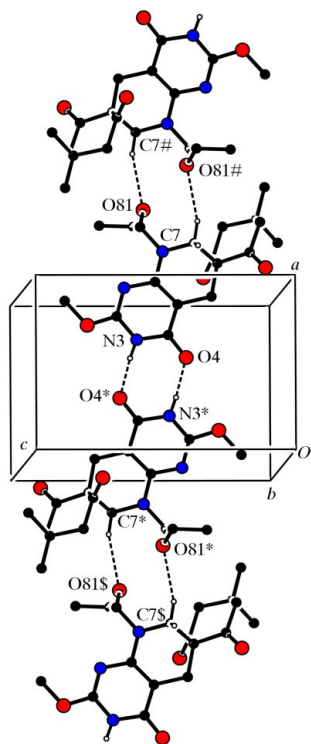


Figure 9

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.

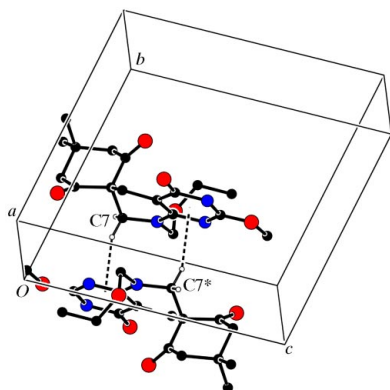
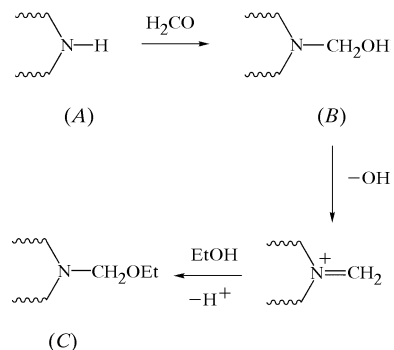
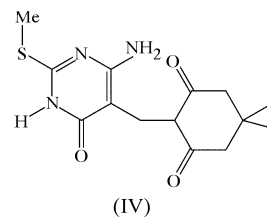


Figure 10

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 $(2 - x, -y, 1 - z)$.

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* H7B, 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* H7A, to the N1/C2/N3/C4/C4A/C8A 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.

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)].



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%; C₁₅H₁₉N₃O₃S 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

C₁₅H₁₉N₃O₃S
M_r = 321.39
 Triclinic, *P* $\bar{1}$
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) Å³

Z = 2
D_x = 1.404 Mg m⁻³
 Mo *K*α 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* > 2σ(*I*)
R_{int} = 0.057
 θ_{\max} = 27.5°
h = -10 → 10
k = -12 → 12
l = -12 → 13

Refinement

Refinement on *F*²
R[*F*² > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.00 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$

Table 1

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

N1—C2	1.300 (2)	C8A—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—C4A	1.409 (2)	S2—C21	1.7983 (19)
C4A—C8A	1.391 (2)	C61—O61	1.216 (2)
C8A—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)
C4A—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—C8A	26.8 (3)	C62—C63—C64—C65	54.3 (2)
C7—N8—C8A—C4A	-2.5 (3)	C63—C64—C65—C6	-53.2 (2)
N8—C8A—C4A—C5	4.8 (3)	C64—C65—C6—C61	49.58 (19)
C8A—C4A—C5—C6	-30.3 (2)	C65—C6—C61—C62	-52.5 (2)

Table 2

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

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

<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>
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—H5B...O61 ⁱⁱⁱ	0.99	2.46	3.389 (2)	155
C64—H64A...Cg1 ^{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

C₁₆H₂₁N₃O₄S
M_r = 351.42
 Triclinic, *P* $\bar{1}$
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) Å³
Z = 2

D_x = 1.435 Mg m⁻³
 Mo *K*α 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* > 2σ(*I*)
R_{int} = 0.047
 θ_{\max} = 27.5°
h = -8 → 8
k = -14 → 14
l = -15 → 16

Refinement

Refinement on *F*²
R[*F*² > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$

Table 3

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

N1—C2	1.294 (3)	C8A—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—C4A	1.414 (3)	S2—C21	1.779 (3)
C4A—C8A	1.374 (3)	C61—O61	1.212 (2)
C8A—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)
C4A—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—C8A	-42.4 (3)	C62—C63—C64—C65	-55.6 (3)
C7—N8—C8A—C4A	12.1 (3)	C63—C64—C65—C6	52.5 (2)
N8—C8A—C4A—C5	1.0 (3)	C64—C65—C6—C61	-45.7 (2)
C8A—C4A—C5—C6	18.1 (3)	C65—C6—C61—C62	48.1 (2)
C6—C7—N8—C81A	139.6 (4)	C6—C7—N8—C81B	158.5 (4)
C7—N8—C81A—O8A	-61.9 (14)	C7—N8—C81B—O8B	-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*

$C_{18}H_{25}N_3O_5$	$Z = 2$
$M_r = 363.41$	$D_x = 1.344 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.9219 (5) \text{ \AA}$	Cell parameters from 4082 reflections
$b = 9.9806 (5) \text{ \AA}$	$\theta = 2.9\text{--}27.6^\circ$
$c = 11.3542 (7) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\alpha = 75.662 (3)^\circ$	$T = 120 (2) \text{ K}$
$\beta = 85.580 (3)^\circ$	Prism, colourless
$\gamma = 66.526 (3)^\circ$	$0.15 \times 0.10 \times 0.10 \text{ mm}$
$V = 898.22 (9) \text{ \AA}^3$	

Data collection

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

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

Crystals of (I)–(III) are triclinic; space group $P\bar{1}$ 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 (CH₃) or 0.99 Å (CH₂), N—H distances of 0.88 Å and O—H distances of 0.84 Å, and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{X})$ (X = C, N and O) [$1.5U_{\text{eq}}(\text{C})$ 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 *SHELXS97* (Sheldrick, 1997); 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).

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