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# Benzylation and nitrosation of 4-amino-2-(methylsulfanyl)pyrimidin-6(1*H*)-one: two $P2_1/c$ polymorphs of 4-amino-1-benzyl-2-(methylsulfanyl)-pyrimidin-6(1*H*)-one with $Z'$ = 1 and 2, 4-amino-6-benzyloxy-2-(methylsulfanyl)pyrimidine and 4-amino-1-benzyl-2-(methylsulfanyl)-5-nitrosopyrimidin-6(1*H*)-one all give different hydrogen-bonded supramolecular structures

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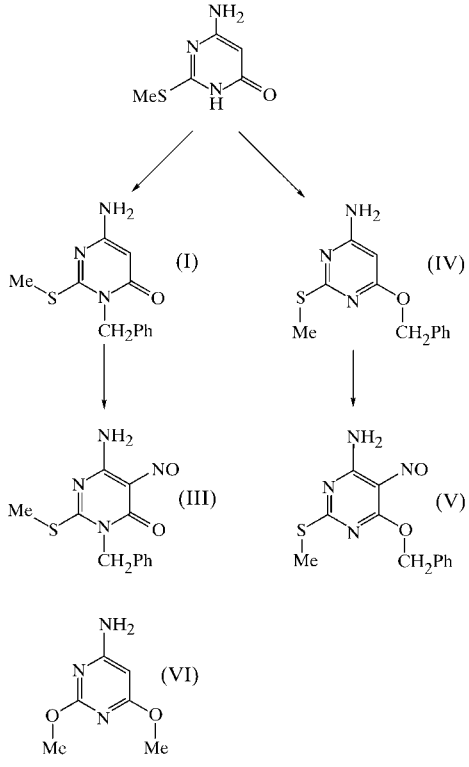
4-Amino-1-benzyl-2-(methylsulfanyl)pyrimidin-6(1*H*)-one, $C_{12}H_{13}N_3OS$, crystallizes in two polymorphic forms, both having space group $P2_1/c$, with $Z'$ = 1 for form (I) and $Z'$ = 2 for form (II). In (I), the molecules are linked by a single N—H···O hydrogen bond into simple $C(6)$ chains, which are themselves linked into sheets by aromatic $\pi$–$\pi$ interactions, while in (II), chains of edge-fused $R_4^2(8)$ and $R_4^4(24)$ rings are generated by four distinct N—H···O hydrogen bonds. In 4-amino-1-benzyl-2-(methylsulfanyl)-5-nitrosopyrimidin-6(1*H*)-one, $C_{12}H_{12}N_4O_2S$, (III), where $Z'$ = 2, two independent three-centre N—H···(N,O) hydrogen bonds generate a $C(5)C(6)[R_1^2(5)]$ chain of rings. In 4-amino-6-benzyloxy-2-(methylsulfanyl)pyrimidine, $C_{12}H_{13}N_3OS$, (IV), which is isomeric with (I) and (II), a combination of N—H···N and N—H···O hydrogen bonds generates a sheet of alternating $R_2^2(8)$ and $R_6^6(28)$ rings.

## Comment

Benzylation of 4-amino-2-(methylsulfanyl)pyrimidin-6(1*H*)-one using benzyl chloride yields a mixture of two isomeric benzyl derivatives, namely 4-amino-1-benzyl-2-(methylsulfanyl)pyrimidin-6(1*H*)-one, (I), and 4-amino-6-benzyloxy-2-(methylsulfanyl)pyrimidine, (IV), which result from *N*- and *O*-benzylation, respectively (see reaction *Scheme* below). Nitrosation of (I) and (IV) yields the corresponding 5-nitroso derivatives (III) and (V), respectively. We have reported previously the molecular and supramolecular structure of (V) (Low, Quesada, Marchal, Nogueras *et al.*, 2002) and report here on two polymorphs, (I) and (II), of 4-amino-1-benzyl-2-(methylsulfanyl)pyrimidin-6(1*H*)-one and on compounds (III) and (IV). The nitrosation of (I), which has $Z'$ = 1 in space group $P2_1/c$, yielded deep-blue (III) and a second pale-green product, (II). Compound (II) proved to be a polymorph of (I), having $Z'$ = 2 in $P2_1/c$, which had cocrystallized with a very small quantity (less than 3%) of (III).




In the molecule of (I) (Fig. 1), the C2—N3 and N3—C4 distances (Table 1) are typical of those for double and single bonds of these types (Allen *et al.*, 1987). On the other hand, the C4—C5 distance is very long for a double bond of this type (mean value = 1.326 Å and upper quartile value = 1.334 Å) and the C5—C6 distance is correspondingly short (mean value = 1.464 Å and lower quartile value = 1.453 Å; Allen *et al.*, 1987); at the same time, the C4—N4 bond is shorter than typical Ar—$NH_2$ bonds (mean value = 1.355 Å and lower quartile value = 1.340 Å), while the C6—O6 distance is longer than is typical for C=O conjugated with C=C (mean value = 1.222 Å and upper quartile value = 1.229 Å). The two independent C—S distances differ as expected. Finally, the

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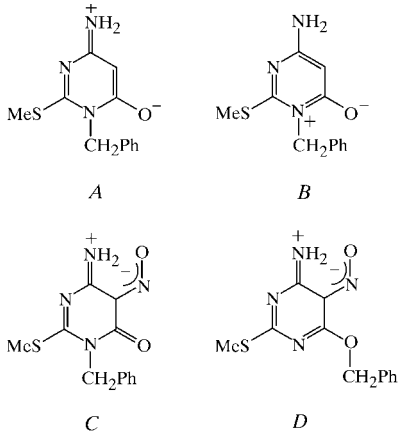
N1—C6 distance is much longer than is usual in amides (mean value = 1.346 Å and upper quartile value = 1.356 Å). All of these observations point to the importance of the delocalized form *A* as a significant contributor to the overall molecular–electronic structure, while effectively ruling out any significant contribution from form *B* (see *Scheme* below).




In polymorph (II), molecule 1 (Fig. 2*a*) contains no trace of a 5-nitroso substituent, but there is an approximate 5% occupancy by a 5-nitroso substituent in molecule 2 (Fig. 2*b*). Accordingly, the pattern of the bond distances in both molecules (Table 3) is very similar to that in (I), which is again consistent with form *A* being a significant contributor to the overall molecular–electronic structure. In (III), which also crystallizes with $Z' = 2$ (Fig. 3), the bond lengths in the two independent molecules are similar (Table 5) but differ from those in (I) and (II) in several important respects. Firstly, the C*n*4—C*n*5 and C*n*5—C*n*6 bonds ($n = 1$ or 2) are both significantly longer than the corresponding bonds in (I) and (II), while the C*n*4—N*n*4 and C*n*6—O*n*6 bonds are both shorter, implying that form *C* is an important contributor to the molecular–electronic structure of (III). This result is consistent with deductions, on geometrical grounds, of the importance of the analogous form *D* in the isomeric compound (V) (Low, Quesada, Marchal, Nogueras *et al.*, 2002).

The development of form *A* in both (I) and (II), and of form *C* in (III), such that both the potential hydrogen-bond donor (atom N4) and the potential acceptors [atom O6 in (I) and (II), and atom O5 in (III)] carry significant partial charges, suggests that the intermolecular hydrogen bonding may be dominated by these two components in the formation of so-called resonance-assisted hydrogen bonds (Gilli *et al.*, 1989, 1994, 2000; Bertolasi *et al.*, 1991).

The crystal quality of (IV) (Fig. 4) was consistently very poor, giving very poor diffraction characteristics, with poor resolution and precision. Accordingly, we do not comment

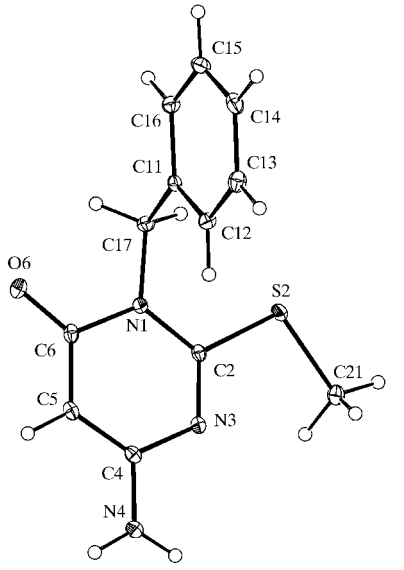



**Figure 1**
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

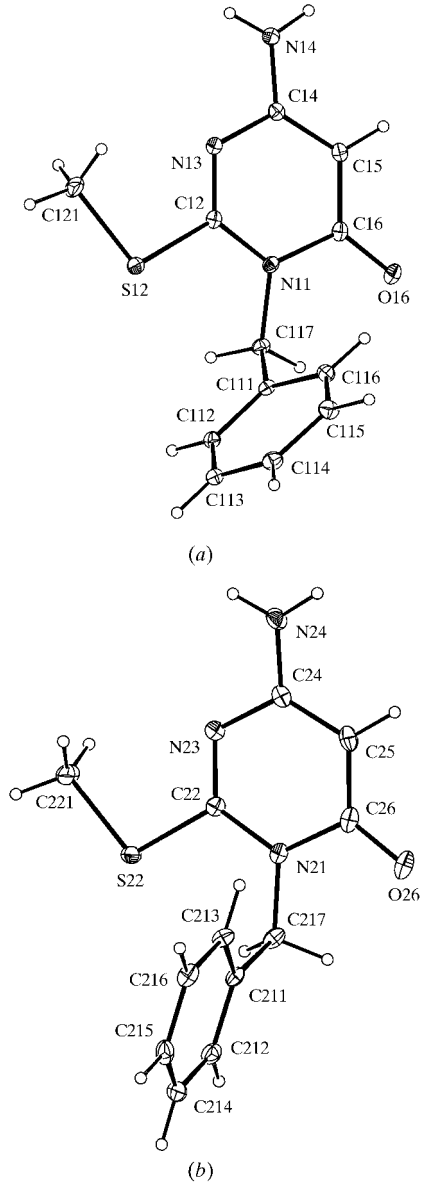



**Figure 2**
The two independent molecules of (II), showing the atom-labelling schemes for (*a*) molecule 1 and (*b*) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.

here on the intramolecular geometry, except to note that the conformation of the MeS substituent differs from that in (I) and (II).

The importance of form *A* in (I) is emphasized by the fact that the molecules of (I) are linked into simple *C*(6) chains (Fig. 5) by a single N—H···O hydrogen bond (Table 2). Amino atom N4 acts as a hydrogen-bond donor, *via* atom H4*B*, to atom O6 in the molecule at $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, and propagation of this hydrogen bond produces a chain running parallel to the [010] direction, generated by the $2_1$ screw axis along $(\frac{1}{2}, y, \frac{1}{4})$. An antiparallel chain is generated by the screw axis along $(\frac{1}{2}, -y, \frac{3}{4})$. However, the N4—H4*A* bond participates neither in any conventional hydrogen bond nor in an N—H···$\pi$(arene) hydrogen bond. Although an adjacent phenyl ring is available, the H4*A*···*Cg*1$(x, -1+y, z)$ distance is ∼3.42 Å (*Cg*1 is the centroid of the C11–C16 ring), and atom N3 does not act as a hydrogen-bond acceptor, although such behaviour is commonly observed in compounds of this type (Low, Quesada, Marchal, Melguizo *et al.*, 2002; Low, Quesada, Marchal, Nogueras *et al.*, 2002).

The chains generated by the N—H···O hydrogen bonds are, however, linked by means of aromatic $\pi$–$\pi$-stacking interactions. The phenyl rings in the molecules at $(x, y, z)$ and

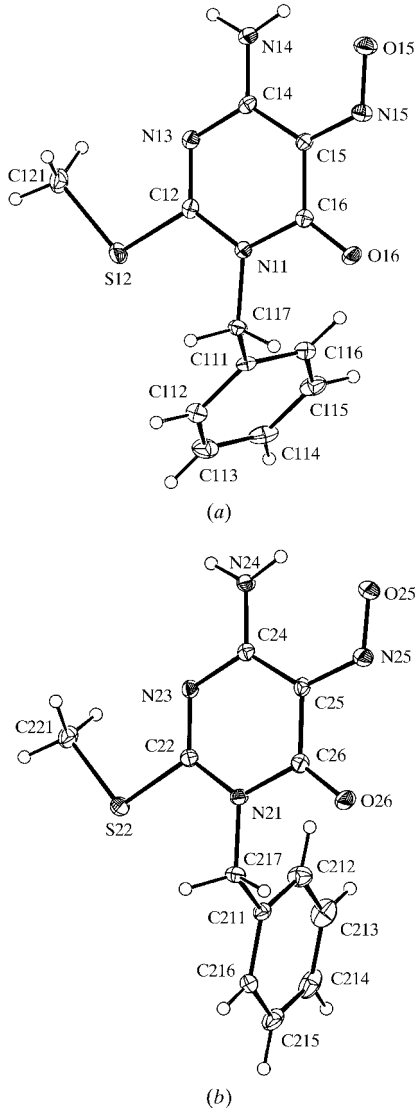



**Figure 3**
The two independent molecules of (III), showing the atom-labelling schemes for (*a*) molecule 1 and (*b*) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.

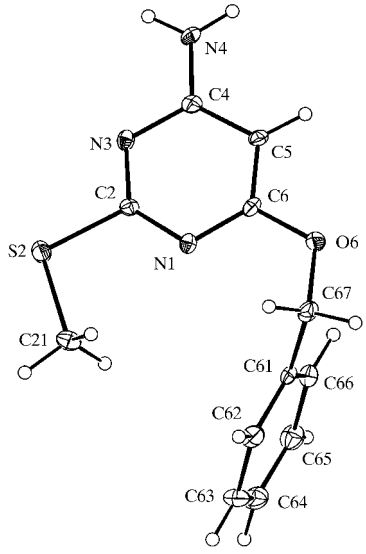



**Figure 4**
The molecule of (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

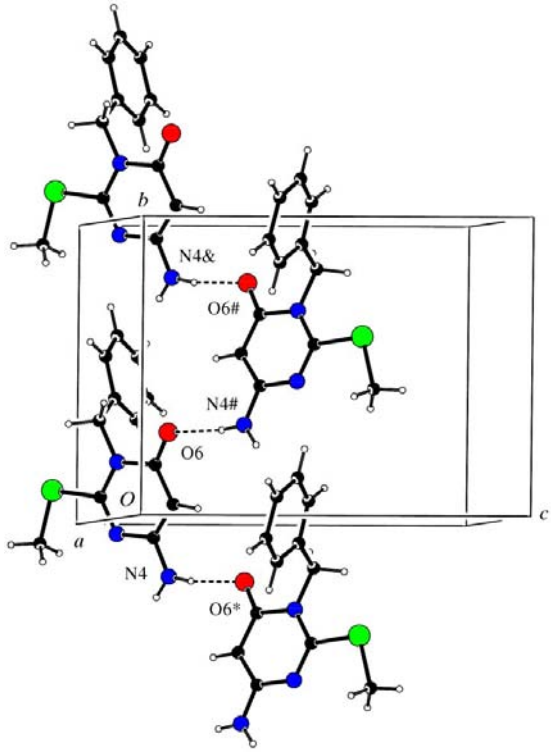



**Figure 5**
Part of the crystal structure of (I), showing the formation of a *C*(6) chain along [010]. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ and $(x, 1+y, z)$, respectively.

$(2 - x, 1 - y, -z)$ are parallel, with an interplanar spacing of 3.488 (2) Å and a centroid separation of 3.675 (2) Å, corresponding to a centroid offset of 1.157 (2) Å. These two molecules lie in the chains along $(\frac{1}{2}, y, \frac{1}{4})$ and $(\frac{3}{2}, -y, -\frac{1}{4})$, respectively. Similarly, the molecule at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, which also lies in the $(\frac{1}{2}, y, \frac{1}{4})$ chain, forms a $\pi$–$\pi$-stacking interaction with the molecule at $(-1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$, which lies in the chain along $(-\frac{1}{2}, -y, \frac{3}{4})$. In this manner, the hydrogen-bonded chains are linked to form a (102) sheet (Fig. 6).

The two independent molecules in (II) are also linked by three N—H···O hydrogen bonds (Table 4). Amino atom N14 of molecule 1 acts as a hydrogen-bond donor, *via* atom H14*B*, to atom O26 of molecule 2 in the asymmetric unit. Atom N14 also acts as a donor, *via* atom H14*A*, to atom O26 in the molecule at $(1 - x, 1 - y, 1 - z)$, and these two interactions generate a centrosymmetric $R_4^2(8)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 7). At the same time, amino atom N24 in molecule 2 at $(x, y, z)$ acts as a donor to atom O16 in the type 1 molecule at $(-x, 1 - y, 1 - z)$, so generating an $R_4^4(24)$ ring centred at $(0, \frac{1}{2}, \frac{1}{2})$. The combined effect of these hydrogen bonds is the formation of a chain of edge-fused rings running parallel to the [100] direction, with $R_4^2(8)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ($n$ = zero or integer) alternating with $R_4^4(24)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ ($n$ = zero or integer) (Fig. 7). The formation of this chain is reinforced by the overlap of centrosymmetrically related pairs of highly polarized pyrimidinone rings (Fig. 8). The interplanar spacing between these rings in the type 2 molecules at $(x, y, z)$ and $(-x, 1 - y, 1 - z)$ is 3.444 (2) Å, and the centroid separation is 3.514 (2) Å, corresponding to a centroid offset of only 0.698 (2) Å.

Each of the two independent molecules of (III) contains an intramolecular N—H···O hydrogen bond, defining an $S(6)$ motif, as is usual in molecules of this type with adjacent amino and nitroso substituents. The molecules of (III) are linked into chains by two independent three-centre N—H···(N,O) hydrogen bonds, each of which is asymmetric but essentially planar (Table 6). In the asymmetric unit, amino atom N14 in the type 1 molecule acts as a hydrogen-bond donor, *via* atom H14*A*, to both atom N25 and atom O26 in the type 2 molecule. Similarly, atom N24 in the type 2 molecule at $(x, y, z)$ acts as a hydrogen-bond donor, *via* atom H24*A*, to atoms N15 and O16 in the type 1 molecule at $(x, y, -1 + z)$. In this manner, a $C(5)C(6)[R_1^2(5)]$ chain of rings is generated by translation along [001] (Fig. 9). Two chains of this type run through each unit cell, but there are no direction-specific interactions between adjacent chains. The supramolecular structure of (III) may be contrasted with that of the isomeric compound (V); in (V), which also crystallizes with $Z' = 2$, two independent $R_2^2(8)$ dimers are formed by paired N—H···N hydrogen bonds, and these dimers are linked into chains by means of aromatic $\pi$–$\pi$-stacking interactions (Low, Quesada, Marchal, Nogueras *et al.*, 2002).

In compound (IV), the molecules are linked into centrosymmetric dimer units by pairs of strong N—H···N hydrogen bonds (Table 7), and these units are linked into sheets by a weaker N—H···O hydrogen bond. Amino atom N4 in the molecule at $(x, y, z)$ acts as a hydrogen-bond donor, *via* atom H4*A*, to ring atom N3 in the molecule at $(1 - x, 1 - y, 1 - z)$,

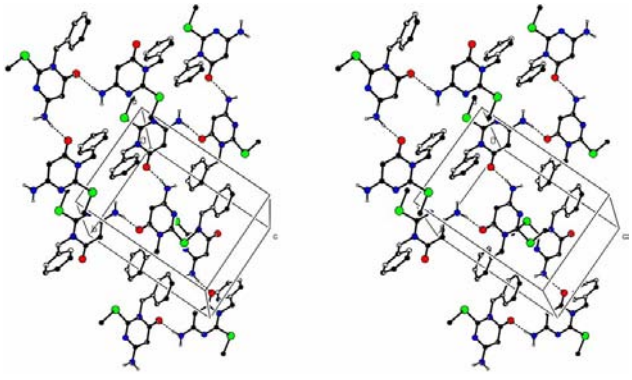


**Figure 6**
A stereoview of part of the crystal structure of (I), showing the linking of the [010] chains into a (102) sheet by means of aromatic $\pi$–$\pi$-stacking interactions. For clarity, H atoms bonded to C atoms have been omitted.

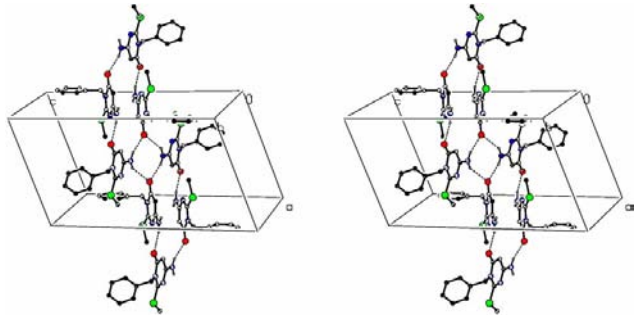


**Figure 7**
A stereoview of part of the crystal structure of (II), showing the formation of a chain of edge-fused rings along [100]. For clarity, H atoms bonded to C atoms have been omitted.

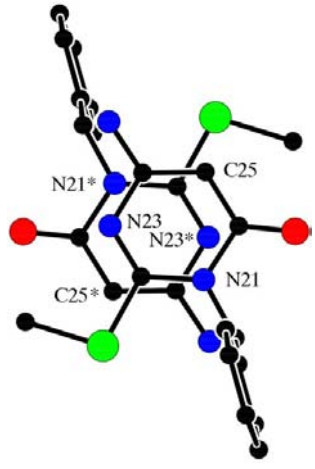



**Figure 8**
Part of the crystal structure of (II), showing the overlap of pairs of type 2 molecules. Atoms marked with an asterisk (*) are at the symmetry position $(-x, 1 - y, 1 - z)$. For clarity, the unit-cell box and H atoms bonded to C atoms have been omitted.

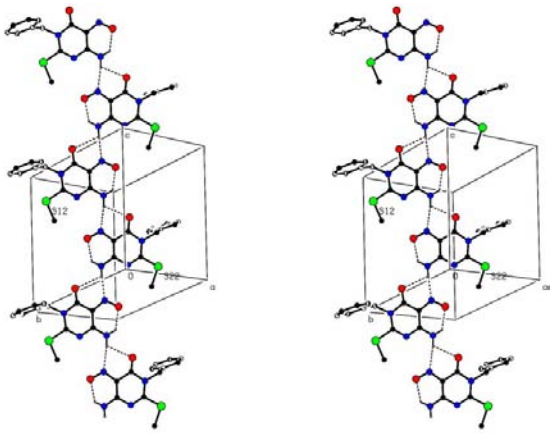


**Figure 9**
A stereoview of part of the crystal structure of (III), showing the formation of a chain of rings along [001]. For clarity, H atoms bonded to C atoms have been omitted.

so generating a dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and containing an $R_2^2(8)$ ring. Amino atom N4 at $(x, y, z)$ also acts as a hydrogen-bond donor, this time *via* atom H4*B*, to atom O6 in the molecule at $(1 - z, \frac{1}{2} + y, \frac{1}{2} - z)$, which lies in the dimer centred at $(\frac{1}{2}, 1, 0)$, while atom O6 at $(x, y, z)$ accepts a hydrogen bond from atom N4 at $(1 - z, -\frac{1}{2} + y, \frac{1}{2} - z)$, which lies in the dimer centred at $(\frac{1}{2}, 0, 0)$. At the same time, atom N4 at $(1 - x, 1 - y, 1 - z)$ acts as a donor to atom O6 at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$, which lies in the dimer centred at $(\frac{1}{2}, 0, 1)$, while atom O6 at $(1 - x, 1 - y, 1 - z)$ acts as an acceptor from atom N4 at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, part of the dimer centred at $(\frac{1}{2}, 1, 1)$. In this manner, the molecules are linked into a (100) sheet built from $R_2^2(8)$ and $R_6^6(28)$ rings alternating in a checkerboard fashion (Fig. 10). If the individual molecules are regarded as the nodes of the resulting net then this is a (6,3)-net, while if the $R_2^2(8)$ dimers are taken as the nodes it is a (4,4)-net (Batten & Robson, 1998). Thus, although the supramolecular structure of (IV) is entirely different from those of (I) and (II), it is, in fact, similar to that of 4-amino-2,6-dimethoxypyrimidine, (VI) (Glidewell *et al.*, 2003), as indeed the overall conformation of (IV) is similar to that of both (V) and (VI).

Thus, in summary, no two isomeric or polymorphic compounds in this series adopt the same pattern of supramolecular aggregation. The two polymorphs (I) and (II) form $\pi$-stacked chains and chains of edge-fused rings, respectively, while the isomeric compound (IV) forms sheets. Compound (III) forms a simple chain of rings, while its isomer (V) forms chains of $\pi$-stacked dimers.

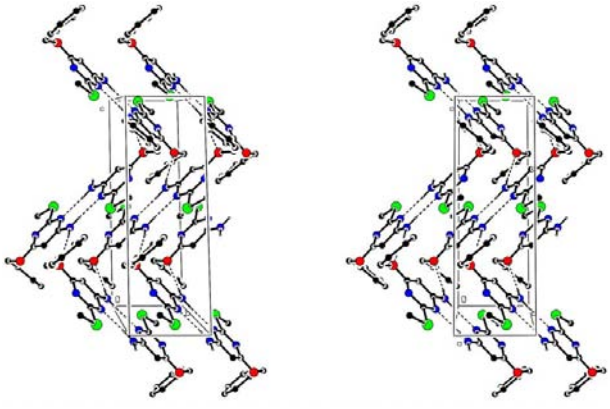


**Figure 10**
A stereoview of part of the crystal structure of (IV), showing the formation of a (100) sheet of $R_2^2(8)$ and $R_6^6(28)$ rings. For clarity, H atoms bonded to C atoms have been omitted.

## Experimental

A suspension of 6-amino-2-(methylsulfanyl)pyrimidin-4(3*H*)-one (10.00 g, 63.62 mmol) and finely ground $K_2CO_3$ (11.89 g, 86 mmol) in dimethyl sulfoxide (90 ml) was stirred at room temperature for 1 h. Benzyl chloride (10 ml, 86 mmol) was then added and the mixture was stirred at room temperature for 9 h. Cold water (270 ml) was added to the mixture, with continuous stirring, to precipitate the water-insoluble reaction products. The resulting mixture was stirred for a further 2 h, and a white solid was then collected by filtration, washed with water and dried *in vacuo*. The dried solid was suspended in diethyl ether (300 ml) and stirred for 24 h. The solid in suspension was collected by filtration, washed with diethyl ether and recrystallized from ethanol to afford the pure *N*-benzyl isomer (I) (2.23 g, 9.02 mmol, 14%). The ethereal fitrate was evaporated under reduced pressure and the residue was chromatographed on silica gel with mixed dichloromethane–acetone to afford the corresponding *O*-benzyl isomer (IV) (5.42 g, 22.4 mmol, 35%) and further crystals of (I) (0.378 g, 1.53 mmol, 2.4%). Crystals of (I) and (IV) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of solutions in ethyl acetate for (I) (m.p. 478 K) and in *tert*-butanol for (IV) [m.p.: 397 K; literature value for (IV): 396–397 K (Ward & Baker, 1977)]. The nitrosation methodology described by Low, Quesada, Marchal, Nogueras *et al.* (2002), using (I) as starting material, provided a mixture of green (II) and blue (III). Crystals of (II) and (III) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in acetone–water (1:1 *v*/*v*) and manual separation.

### Compound (I)

*Crystal data*

$C_{12}H_{13}N_3OS$
$M_r = 247.31$
Monoclinic, $P2_1/c$
$a = 9.7139\ (2)$ Å
$b = 9.5846\ (2)$ Å
$c = 12.6431\ (2)$ Å
$\beta = 103.4465\ (13)^\circ$
$V = 1144.85\ (4)$ Å$^3$
$Z = 4$
$D_x = 1.435$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2600 reflections
$\theta = 3.0$–$27.5^\circ$
$\mu = 0.27$ mm$^{-1}$
$T = 120\ (1)$ K
Block, colourless
0.30 × 0.26 × 0.20 mm

*Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.902$, $T_{max} = 0.943$
7564 measured reflections
2600 independent reflections
2249 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5^\circ$
$h = -12 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -14 \rightarrow 16$

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.4958P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.035$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $wR(F^2) = 0.091$ | $\Delta\rho_{max} = 0.24$ e Å$^{-3}$ |
| $S = 1.06$ | $\Delta\rho_{min} = -0.31$ e Å$^{-3}$ |
| 2600 reflections | |
| 155 parameters | |
| H-atom parameters constrained | |

**Table 1**
Selected bond lengths (Å) for (I).

| | | | |
|---|---|---|---|
| N1—C2 | 1.364 (2) | N1—C17 | 1.463 (2) |
| C2—N3 | 1.303 (3) | C2—S2 | 1.757 (2) |
| N3—C4 | 1.375 (2) | C21—S2 | 1.798 (2) |
| C4—C5 | 1.376 (2) | C4—N4 | 1.344 (2) |
| C5—C6 | 1.401 (2) | C6—O6 | 1.241 (2) |
| C6—N1 | 1.424 (2) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H4$B$···O6$^{i}$ | 0.88 | 1.95 | 2.823 (2) | 170 |

Symmetry code: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

## Compound (II)

*Crystal data*

| | |
|---|---|
| $C_{12}H_{13}N_3OS$ | $D_x = 1.400$ Mg m$^{-3}$ |
| $M_r = 247.31$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 5325 reflections |
| $a = 11.4629$ (2) Å | $\theta = 3.1$–$27.5°$ |
| $b = 10.2603$ (2) Å | $\mu = 0.26$ mm$^{-1}$ |
| $c = 20.9303$ (4) Å | $T = 120$ (1) K |
| $\beta = 107.0920$ (14)° | Block, green |
| $V = 2352.95$ (8) Å$^3$ | 0.47 × 0.22 × 0.14 mm |
| $Z = 8$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 5325 independent reflections |
| $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets | 4389 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997) | $R_{int} = 0.064$ |
| | $\theta_{max} = 27.5°$ |
| $T_{min} = 0.887$, $T_{max} = 0.957$ | $h = -14 \rightarrow 14$ |
| 21 205 measured reflections | $k = -13 \rightarrow 12$ |
| | $l = -27 \rightarrow 27$ |

**Table 3**
Selected bond lengths (Å) for (II).

| | | | |
|---|---|---|---|
| N11—C12 | 1.366 (2) | N21—C22 | 1.376 (2) |
| C12—N13 | 1.304 (2) | C22—N23 | 1.311 (3) |
| N13—C14 | 1.374 (2) | N23—C24 | 1.373 (3) |
| C14—C15 | 1.390 (3) | C24—C25 | 1.381 (3) |
| C15—C16 | 1.401 (3) | C25—C26 | 1.400 (3) |
| C16—N11 | 1.435 (2) | C26—N21 | 1.420 (3) |
| N11—C117 | 1.469 (2) | N21—C217 | 1.464 (3) |
| C12—S12 | 1.759 (2) | C22—S22 | 1.747 (2) |
| S12—C121 | 1.794 (2) | S22—C221 | 1.791 (2) |
| C14—N14 | 1.342 (2) | C24—N24 | 1.353 (3) |
| C16—O16 | 1.245 (2) | C26—O26 | 1.246 (3) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N14—H14$A$···O26$^{ii}$ | 0.88 | 2.28 | 3.029 (2) | 143 |
| N14—H14$B$···O26 | 0.88 | 2.10 | 2.896 (2) | 151 |
| N24—H24$A$···O16$^{iii}$ | 0.88 | 2.29 | 3.124 (2) | 157 |
| N24—H24$B$···O16$^{iv}$ | 0.88 | 2.62 | 3.330 (2) | 138 |

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

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 1.7296P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $wR(F^2) = 0.119$ | $\Delta\rho_{max} = 0.51$ e Å$^{-3}$ |
| $S = 1.06$ | $\Delta\rho_{min} = -0.41$ e Å$^{-3}$ |
| 5325 reflections | |
| 318 parameters | |
| H-atom parameters constrained | |

## Compound (III)

*Crystal data*

| | |
|---|---|
| $C_{12}H_{12}N_4O_2S$ | $Z = 4$ |
| $M_r = 276.33$ | $D_x = 1.461$ Mg m$^{-3}$ |
| Triclinic, $P\overline{1}$ | Mo $K\alpha$ radiation |
| $a = 10.5035$ (3) Å | Cell parameters from 4417 reflections |
| $b = 10.8741$ (3) Å | $\theta = 3.0$–$25.0°$ |
| $c = 11.8261$ (4) Å | $\mu = 0.26$ mm$^{-1}$ |
| $\alpha = 109.6510$ (13)° | $T = 120$ (1) K |
| $\beta = 96.4203$ (14)° | Plate, blue |
| $\gamma = 93.7181$ (14)° | 0.30 × 0.22 × 0.04 mm |
| $V = 1256.49$ (7) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 4417 independent reflections |
| $\varphi$ scans, and $\omega$ scans with $\kappa$ offsets | 3498 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997) | $R_{int} = 0.094$ |
| | $\theta_{max} = 25.0°$ |
| $T_{min} = 0.920$, $T_{max} = 0.991$ | $h = -12 \rightarrow 12$ |
| 24 784 measured reflections | $k = -12 \rightarrow 12$ |
| | $l = -14 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.5677P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $wR(F^2) = 0.107$ | $\Delta\rho_{max} = 0.21$ e Å$^{-3}$ |
| $S = 1.05$ | $\Delta\rho_{min} = -0.31$ e Å$^{-3}$ |
| 4417 reflections | |
| 345 parameters | |
| H-atom parameters constrained | |

**Table 5**
Selected bond lengths (Å) for (III).

| | | | |
|---|---|---|---|
| N11—C12 | 1.372 (3) | N21—C22 | 1.372 (3) |
| C12—N13 | 1.306 (3) | C22—N23 | 1.305 (3) |
| N13—C14 | 1.362 (3) | N23—C24 | 1.368 (3) |
| C14—C15 | 1.433 (3) | C24—C25 | 1.422 (3) |
| C15—C16 | 1.452 (3) | C25—C26 | 1.445 (3) |
| C16—N11 | 1.419 (3) | C26—N21 | 1.420 (3) |
| N11—C117 | 1.483 (3) | N21—C217 | 1.466 (3) |
| C12—S12 | 1.743 (2) | C22—S22 | 1.747 (2) |
| S12—C121 | 1.804 (2) | S22—C221 | 1.796 (2) |
| C14—N14 | 1.312 (3) | C24—N24 | 1.316 (3) |
| C15—N15 | 1.353 (3) | C25—N25 | 1.352 (3) |
| N15—O15 | 1.273 (2) | N25—O25 | 1.272 (2) |
| C16—O16 | 1.218 (3) | C26—O26 | 1.223 (3) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N14—H14$A$···N25 | 0.88 | 2.23 | 3.100 (3) | 168 |
| N14—H14$A$···O26 | 0.88 | 2.40 | 2.879 (2) | 114 |
| N14—H14$B$···O15 | 0.88 | 2.01 | 2.642 (2) | 128 |
| N24—H24$A$···N15$^{v}$ | 0.88 | 2.09 | 2.970 (3) | 177 |
| N24—H24$A$···O16$^{v}$ | 0.88 | 2.50 | 2.938 (2) | 112 |
| N24—H24$B$···O25 | 0.88 | 2.01 | 2.631 (2) | 127 |

Symmetry code: (v) $x, y, z-1$.

### Compound (IV)

*Crystal data*

$C_{12}H_{13}N_3OS$
$M_r = 247.31$
Monoclinic, $P2_1/c$
$a = 15.747$ (2) Å
$b = 5.1044$ (7) Å
$c = 15.501$ (3) Å
$\beta = 105.286$ (5)°
$V = 1201.9$ (3) Å$^3$
$Z = 4$
$D_x = 1.367$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1177 reflections
$\theta = 2.7$–20.5°
$\mu = 0.26$ mm$^{-1}$
$T = 120$ (1) K
Needle, colourless
0.60 × 0.04 × 0.03 mm

*Data collection*

Nonius KappaCCD diffractometer
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.862$, $T_{max} = 0.992$
9738 measured reflections
1177 independent reflections
1006 reflections with $I > 2\sigma(I)$
$R_{int} = 0.147$
$\theta_{max} = 20.5°$
$h = -15 \rightarrow 15$
$k = -5 \rightarrow 5$
$l = -14 \rightarrow 15$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.077$
$wR(F^2) = 0.155$
$S = 1.22$
1177 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 5.5293P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.35$ e Å$^{-3}$

**Table 7**
Hydrogen-bonding geometry (Å, °) for (IV).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H4$A$···N3$^{ii}$ | 0.88 | 2.16 | 3.044 (8) | 177 |
| N4—H4$B$···O6$^{vi}$ | 0.88 | 2.40 | 3.209 (7) | 154 |

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

For (I), (II) and (IV), the space group $P2_1/c$ was determined uniquely from the systematic absences. Crystals of (III) are triclinic, and space group $P\overline{1}$ was selected and confirmed by successful structure analysis. For (IV), it proved extremely difficult to obtain single crystals; those obtained were always of extremely poor quality and very fine hair-like habit, giving no detectable diffraction beyond a $\theta$ value of 20°, so that the overall resolution was poor. Nonetheless, the overall conformation and supramolecular structure of (IV) were determined as being clearly different from those of the isomeric (I) and (II). For each compound, all H atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 ($CH_3$) or 0.99 Å ($CH_2$), and N—H distances of 0.88 Å.

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: *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: GG1172). Services for accessing these data are described at the back of the journal.

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