

## Triclinic

 $P\bar{1}$  $a = 7.0543 (7) \text{ \AA}$  $b = 8.8125 (9) \text{ \AA}$  $c = 15.016 (1) \text{ \AA}$  $\alpha = 72.980 (3)^\circ$  $\beta = 77.562 (3)^\circ$  $\gamma = 69.707 (3)^\circ$  $V = 830.4 (1) \text{ \AA}^3$  $Z = 2$  $D_x = 1.592 \text{ Mg m}^{-3}$  $D_m$  not measured

## Data collection

Siemens SMART CCD diffractometer

 $\omega$  rotation scans with narrow frames

Absorption correction:

empirical via  $\psi$  scans

(SHELXTL; Sheldrick, 1994)

 $T_{\min} = 0.65, T_{\max} = 0.89$ 

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.039$  $wR(F^2) = 0.099$  $S = 1.118$ 

2554 reflections

266 parameters

Only coordinates of H atoms refined

 $w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 1.0763P]$ where  $P = (F_o^2 + 2F_c^2)/3$ 

Cell parameters from 510 reflections

 $\theta = 7.0\text{--}24.1^\circ$  $\mu = 0.711 \text{ mm}^{-1}$  $T = 150 (2) \text{ K}$ 

Rectangular

 $0.50 \times 0.42 \times 0.16 \text{ mm}$ 

Colourless

3487 measured reflections

2560 independent reflections

2429 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.032$  $\theta_{\text{max}} = 25.14^\circ$  $h = -8 \rightarrow 7$  $k = -10 \rightarrow 7$  $l = -17 \rightarrow 17$  $(\Delta/\sigma)_{\text{max}} = 0.001$  $\Delta\rho_{\text{max}} = 0.295 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.390 \text{ e \AA}^{-3}$ 

Extinction correction:

SHELXL

Extinction coefficient:

0.072 (5)

Scattering factors from

International Tables for

Crystallography (Vol. C)

## References

- Geich, H., Grimme, W. & Proske, K. (1992). *J. Am. Chem. Soc.* **114**, 1492–1493.
- Hagenbuch, J.-P., Stampfli, B. & Vogel, P. (1981). *J. Am. Chem. Soc.* **103**, 3934–3935.
- Mackenzie, K., Howard, J. A. K., Mason, S. A., Gravett, E. C., Astin, K. B., Shi-Xiong, L., Batsanov, A. B., Vlaovic, D., Maher, J. P., Murray, M., Kendrew, D., Wilson, C., Johnson, R. E., Preiß, T. & Gregory, R. J. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 1211–1228.
- Mackenzie, K., Howard, J. A. K., Siedlecka, R., Astin, K. B., Gravett, E. C., Wilson, C., Cole, J., Gregory, R. G. & Tomlins, A. S. (1996). *J. Chem. Soc. Perkin Trans. 2*, pp. 1749–1760.
- Mackenzie, K., Proctor, G. & Woodnutt, D. J. (1987). *Tetrahedron*, **43**, 5981–5993.
- Molecular Structure Corporation (1991). *MSCI/AFD Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- O'Doherty, G. A., Rogers, R. D. & Paquette, L. A. (1994). *J. Am. Chem. Soc.* **116**, 10883–10894.
- Paquette, L. A., Kesselmayr, M. A. & Rogers, R. D. (1990). *J. Am. Chem. Soc.* **112**, 284–291.
- Paquette, L. A., O'Doherty, G. A. & Rogers, R. D. (1991). *J. Am. Chem. Soc.* **113**, 7761–7762.
- Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wilson, C. (1995). PhD thesis, University of Durham, England.

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Table 2. Selected bond lengths (Å) for (2D)

C2—C7	1.395 (3)	C12—C11	1.530 (4)
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Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1991) for (1D); *SMART* (Siemens, 1995) for (2D). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1992) for (1D); *SMART* for (2D). Data reduction: *TEXSAN* for (1D); *SAINT* (Siemens, 1995) for (2D). For both compounds, program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank Dr K. Mackenzie who conceived the research programme, executed preparative and kinetic work, and provided excellent quality crystals. Dr R. Siedlecka is thanked for the preparation of compound (2D). CW thanks the Institut Laue-Langevin for a studentship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1209). Services for accessing these data are described at the back of the journal.

## Two New Structures of 5-Nitrouracil

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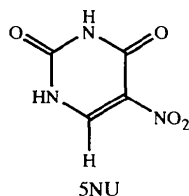
## Abstract

The structure of monoclinic anhydrous 5-nitrouracil,  $C_4H_3N_3O_4$ , and of the solvate 5-nitrouracil dimethyl sulfoxide,  $C_4H_3N_3O_4 \cdot C_2H_6OS$ , are presented and compared with the previously known structures of the orthorhombic anhydrous form and the monohydrate.

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### Comment

5-Nitouracil (5NU) is currently of prime interest to the non-linear optical community (Puccetti *et al.*, 1993; Youping *et al.*, 1992) and is also of relevance to the biological and pharmaceutical sciences (Rao *et al.*, 1995; Perrier & Byrn, 1982). Interest in the manufacture and desolvation processes of 5NU led us to investigate the crystal growth and stability of the 5NU system from its favoured industrial solvents, water and dimethyl sulfoxide (DMSO). Two crystalline forms had previously been reported, namely, an optically active orthorhombic anhydrate, (I) (Pierce & Wing, 1986), and a monoclinic monohydrate, (II) (Craven, 1967). We found that aqueous solution growth gave a mixture not only of these known polymorphs but also of a third, a monoclinic anhydrate, (III). In addition, growth from DMSO and aqueous DMSO solutions gave a DMSO-solvated form, (IV). The structures of these new polymorphs are discussed as are the relationships between all four forms.



The crystal structures exhibit extensive hydrogen-bonding networks (Tables 3 and 6; Figs. 1 and 2) and it is here that the major differences between the polymorphs lie. In 5NU.DMSO, formal hydrogen bonding exists only between the N—H moieties of 5NU and the sulfoxide of the solvent; there are

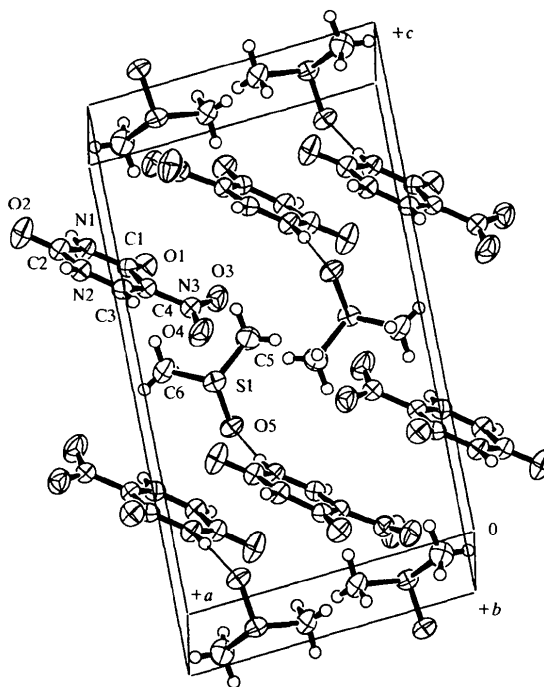


Fig. 2. Packing diagram and hydrogen bonding of 5NU.DMSO, (IV), with 50% probability ellipsoids.

no 5NU to 5NU bonds, for example. This leads to the layered structure shown in Fig. 2. In contrast, the hydrated structure has dimeric hydrogen-bonded 5NU units linked in sheets by both 5NU···H<sub>2</sub>O and 5NU···5NU interactions. In (III), hydrogen bonding occurs about inversion centres, such that each 5NU molecule has four individual hydrogen bonds involving two adjacent molecules. This contrasts with (I), where each 5NU molecule is hydrogen bonded to four adjacent molecules.

The differing intermolecular interactions seem to have little effect on the molecular structures of the 5NU moiety, with all bond lengths and angles being in good agreement. The main conformational difference is evident in the large twist of the NO<sub>2</sub> group away from the plane of the ring in 5NU.DMSO, whereas it approaches coplanarity in the other three forms [dihedral angle between the least-squares planes of the ring and the NO<sub>2</sub> group: 4.7, 2.0, 7.0(1) and 16.8(1)° for (I), (II), (III) and (IV), respectively].

The solvated forms lose solvent on heating. DSC studies, in combination with powder diffraction studies of the desolvated products, indicate that in both cases, the resulting material was of the newly reported anhydrous monoclinic form (III). Form (II) is observed to lose water at 373 K and (IV) to lose DMSO in a multi-stage process from 393 to 423 K. In addition, form (I) is also observed to transform to (III) at 538 K, with (III) melting at 578 K (Okoth *et al.*, 1997).

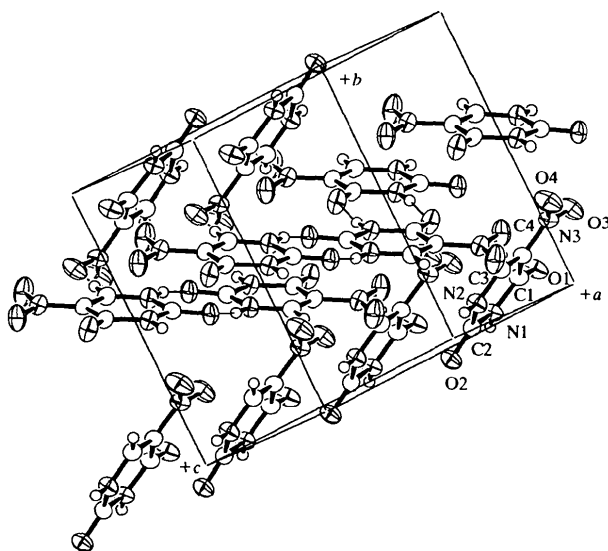
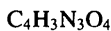


Fig. 1. Packing diagram and hydrogen bonding of anhydrous 5NU, (III), with 50% probability ellipsoids.

**Experimental**

Crystals of (III) were grown by slow cooling of an aqueous solution and those of (IV) by cooling of a DMSO solution. Both crystal forms grew as very large entities and were cut to size for X-ray analysis.

**Compound (III)***Crystal data* $M_r = 157.09$ 

Monoclinic

 $P2_1/n$  $a = 5.873 (1) \text{ \AA}$  $b = 9.693 (1) \text{ \AA}$  $c = 10.4561 (9) \text{ \AA}$  $\beta = 104.07 (1)^\circ$  $V = 577.4 (1) \text{ \AA}^3$  $Z = 4$  $D_x = 1.807 \text{ Mg m}^{-3}$  $D_m$  not measured*Data collection*

Rigaku AFC-7S diffractometer

 $\omega/2\theta$  scans

Absorption correction: none

1770 measured reflections

1627 independent reflections

1154 reflections with

 $I > 2\sigma(I)$ *Refinement*Refinement on  $F$  $R = 0.036$  $wR = 0.051$  $S = 1.950$ 

1154 reflections

113 parameters

All H atoms refined

 $w = 1/\sigma^2(F)$  $(\Delta/\sigma)_{\max} = 0.0002$ Mo  $K\alpha$  radiation $\lambda = 0.71069 \text{ \AA}$ 

Cell parameters from 25 reflections

 $\theta = 22.3\text{--}24.9^\circ$  $\mu = 0.164 \text{ mm}^{-1}$  $T = 295 \text{ K}$ 

Cut needle

 $0.60 \times 0.40 \times 0.10 \text{ mm}$ 

Colourless

 $R_{\text{int}} = 0.012$  $\theta_{\max} = 29.0^\circ$  $h = 0 \rightarrow 8$  $k = 0 \rightarrow 13$  $l = -14 \rightarrow 13$ 

3 standard reflections

every 150 reflections

intensity decay: none

 $\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$ 

Extinction correction:

Zachariasen (1968) type

2, Gaussian isotropic

Extinction coefficient:

 $1.00 (14) \times 10^{-5}$ Scattering factors from *International Tables for X-ray**Crystallography* (Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (III)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	$x$	$y$	$z$	$U_{\text{eq}}$
O1	0.7137 (2)	0.0960 (1)	-0.03325 (10)	0.0439 (5)
O2	0.7134 (2)	-0.0428 (1)	0.38079 (10)	0.0396 (5)
O3	1.1109 (2)	0.2276 (1)	-0.0552 (1)	0.0486 (6)
O4	1.3560 (2)	0.2892 (2)	0.1233 (1)	0.0588 (8)
N1	0.7180 (2)	0.0324 (1)	0.1753 (1)	0.0325 (5)
N2	1.0188 (2)	0.0896 (1)	0.3539 (1)	0.0349 (6)
N3	1.1750 (2)	0.2317 (1)	0.0650 (1)	0.0346 (6)
C1	0.8159 (2)	0.0979 (1)	0.0833 (1)	0.0300 (6)
C2	0.8087 (2)	0.0218 (1)	0.3085 (1)	0.0301 (6)
C3	1.1290 (3)	0.1561 (1)	0.2747 (1)	0.0319 (6)
C4	1.0389 (2)	0.1621 (1)	0.1428 (1)	0.0286 (6)

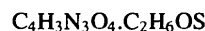
Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (III)

O1—C1	1.221 (2)	N2—C2	1.377 (2)
O2—C2	1.218 (2)	N2—C3	1.335 (2)
O3—N3	1.222 (2)	N3—C4	1.439 (2)
O4—N3	1.224 (2)	C1—C4	1.447 (2)
N1—C1	1.389 (2)	C3—C4	1.353 (2)
N1—C2	1.368 (2)		
C1—N1—C2	127.9 (1)	O2—C2—N1	123.1 (1)
C2—N2—C3	123.0 (1)	O2—C2—N2	122.7 (1)
O3—N3—O4	122.7 (1)	N1—C2—N2	114.2 (1)
O3—N3—C4	119.4 (1)	N2—C3—C4	121.7 (1)
O4—N3—C4	117.8 (1)	N3—C4—C1	121.9 (1)
O1—C1—N1	119.9 (1)	N3—C4—C3	117.5 (1)
O1—C1—C4	127.6 (1)	C1—C4—C3	120.6 (1)
N1—C1—C4	112.5 (1)		
O3—N3—C4—C3	172.8 (1)	O4—N3—C4—C3	-4.9 (2)

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (III)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1 $\cdots$ O1 <sup>i</sup>	0.89 (2)	2.01 (2)	2.890 (2)	170 (2)
N2—H2 $\cdots$ O2 <sup>ii</sup>	0.88 (2)	2.01 (2)	2.873 (2)	167 (2)

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

**Compound (IV)***Crystal data* $M_r = 235.21$ 

Monoclinic

 $P2_1/n$  $a = 8.858 (1) \text{ \AA}$  $b = 6.9619 (6) \text{ \AA}$  $c = 15.822 (1) \text{ \AA}$  $\beta = 95.823 (8)^\circ$  $V = 970.7 (1) \text{ \AA}^3$  $Z = 4$  $D_x = 1.609 \text{ Mg m}^{-3}$  $D_m$  not measuredMo  $K\alpha$  radiation $\lambda = 0.71069 \text{ \AA}$ 

Cell parameters from 25 reflections

 $\theta = 25.1\text{--}27.5^\circ$  $\mu = 0.341 \text{ mm}^{-1}$  $T = 295 \text{ K}$ 

Cut block

 $0.80 \times 0.60 \times 0.40 \text{ mm}$ 

Colourless

*Data collection*

Rigaku AFC-7S diffractometer

 $\omega/2\theta$  scans

Absorption correction: none

2651 measured reflections

2496 independent reflections

2042 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.009$  $\theta_{\max} = 28.01^\circ$  $h = 0 \rightarrow 11$  $k = 0 \rightarrow 9$  $l = -20 \rightarrow 20$ 

3 standard reflections

every 150 reflections

intensity decay: 20.4%

*Refinement*Refinement on  $F$  $R = 0.030$  $wR = 0.049$  $S = 2.132$ 

2042 reflections

173 parameters

All H atoms refined

 $w = 1/\sigma^2(F)$  $(\Delta/\sigma)_{\max} = 0.002$  $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$ 

Extinction correction:

Zachariasen (1968) type

2, Gaussian isotropic

Extinction coefficient:

 $2.3 (4) \times 10^{-6}$ Scattering factors from *International Tables for X-ray**Crystallography* (Vol. IV)

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (IV)
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U <sub>eq</sub>
S1	0.74755 (4)	1.37225 (5)	0.46078 (2)	0.0376 (3)
O1	0.9045 (1)	0.3331 (2)	0.70742 (7)	0.0476 (5)
O2	1.2742 (1)	0.6491 (2)	0.87107 (9)	0.0612 (6)
O3	0.6784 (1)	0.5690 (2)	0.63578 (8)	0.0553 (6)
O4	0.7438 (2)	0.8616 (2)	0.61533 (9)	0.0671 (8)
O5	0.7210 (1)	1.3437 (1)	0.36490 (6)	0.0399 (5)
N1	1.0838 (1)	0.4962 (2)	0.79035 (7)	0.0367 (5)
N2	1.0999 (1)	0.8284 (2)	0.79110 (7)	0.0359 (5)
N3	0.7666 (1)	0.7034 (2)	0.64869 (7)	0.0408 (6)
C1	0.9561 (1)	0.4872 (2)	0.73185 (8)	0.0334 (6)
C2	1.1617 (2)	0.6558 (2)	0.82096 (9)	0.0382 (6)
C3	0.9760 (2)	0.8389 (2)	0.73547 (8)	0.0344 (6)
C4	0.9014 (1)	0.6783 (2)	0.70557 (8)	0.0332 (6)
C5	0.6146 (2)	1.2221 (3)	0.5061 (1)	0.0529 (9)
C6	0.9134 (2)	1.2380 (4)	0.4937 (1)	0.0596 (10)

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

O1—C1	1.214 (2)	N2—C2	1.384 (2)
O2—C2	1.210 (2)	N2—C3	1.337 (2)
O3—N3	1.223 (2)	N3—C4	1.432 (2)
O4—N3	1.229 (2)	C1—C4	1.462 (2)
N1—C1	1.389 (2)	C3—C4	1.359 (2)
N1—C2	1.370 (2)		
C1—N1—C2	128.2 (1)	O2—C2—N1	123.5 (1)
C2—N2—C3	122.8 (1)	O2—C2—N2	121.9 (1)
O3—N3—O4	122.7 (1)	N1—C2—N2	114.6 (1)
O3—N3—C4	119.3 (1)	N2—C3—C4	121.5 (1)
O4—N3—C4	118.0 (1)	N3—C4—C1	121.4 (1)
O1—C1—N1	120.5 (1)	N3—C4—C3	117.6 (1)
O1—C1—C4	127.6 (1)	C1—C4—C3	121.0 (1)
N1—C1—C4	111.9 (1)		
O3—N3—C4—C3	-163.4 (1)	O4—N3—C4—C3	15.9 (2)

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O5 <sup>i</sup>	0.88 (2)	1.98 (2)	2.859 (2)	171 (2)
N2—H2...O5 <sup>ii</sup>	0.83 (2)	1.90 (2)	2.733 (2)	175 (2)

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

Measurement of azimuthal scans showed insignificant absorption variations, so no corrections were applied.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program used to solve structure: *SIR* (Burla *et al.*, 1989). Program used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1206). Services for accessing these data are described at the back of the journal.

## References

- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.  
 Craven, B. M. (1967). *Acta Cryst.* **23**, 376–383.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Crystal Structure Analysis Package*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Okoth, M. O., Sheen, D. B., Sherwood, J. N. & Vrcelj, R. M. (1997). Unpublished results.

Perrier, P. R. & Byrn, S. R. (1982). *J. Org. Chem.* **47**, 4671–4676.

Pierce, B. P. & Wing, R. M. (1986). *Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications. Proc. Soc. Photo-Opt. Instrum. Eng.* **682**, 27–35.

Puccetti, G., Perigaud, A., Badan, J., Ledoux, I. & Zyss, J. (1993). *J. Opt. Soc. Am. B*, **10**, 733–744.

Rao, T. S., Rando, R. F., Huffman, J. H. & Revankar, G. R. (1995). *Nucleosides Nucleotides*, **14**, 1997–2008.

Youping, H., Genbo, S., Bochang, W. & Rihong, J. (1992). *J. Cryst. Growth*, **119**, 393–398.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

*Acta Cryst.* (1998). **C54**, 550–553

## 3-Methylthio-1,2,4-triazine: a Comparison of Experimental and Theoretical Structures

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## Abstract

The theoretical equilibrium and X-ray crystallographic structures of 3-methyl-1,2,4-triazine, C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>S, show a high level of agreement. The calculated charge distributions are analysed for each of four conformers; that with lowest energy is present both in the solid and in mesitylene solution, as shown by dipole-moment measurements.

## Comment

Although the Cambridge Structural Database (Allen & Kennard, 1993) contains about 70 crystal structures of molecules containing triazine moieties, there are no simple 1,2,4-triazine molecules. In recent work, we reported (Palmer *et al.*, 1995) an experimental and theoretical study of the parent compound (1). The synthesis of (1) proceeds *via* *S*-methylthiosemicarbazide and glyoxal, giving the 3-methylthio- derivative (2),