

Triclinic	Cell parameters from 510 reflections
$P\bar{1}$	$\theta = 7.0\text{--}24.1^\circ$
$a = 7.0543 (7) \text{ \AA}$	$\mu = 0.711 \text{ mm}^{-1}$
$b = 8.8125 (9) \text{ \AA}$	$T = 150 (2) \text{ K}$
$c = 15.016 (1) \text{ \AA}$	Rectangular
$\alpha = 72.980 (3)^\circ$	$0.50 \times 0.42 \times 0.16 \text{ mm}$
$\beta = 77.562 (3)^\circ$	Colourless
$\gamma = 69.707 (3)^\circ$	
$V = 830.4 (1) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.592 \text{ Mg m}^{-3}$	
D_m not measured	
Data collection	
Siemens SMART CCD diffractometer	3487 measured reflections
ω rotation scans with narrow frames	2560 independent reflections
Absorption correction: empirical via ψ scans (SHELXTL; Sheldrick, 1994)	2429 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.65, T_{\max} = 0.89$	$R_{\text{int}} = 0.032$
	$\theta_{\max} = 25.14^\circ$
	$h = -8 \rightarrow 7$
	$k = -10 \rightarrow 7$
	$l = -17 \rightarrow 17$
Refinement	
Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{\max} = 0.295 \text{ e \AA}^{-3}$
$wR(F^2) = 0.099$	$\Delta\rho_{\min} = -0.390 \text{ e \AA}^{-3}$
$S = 1.118$	Extinction correction: SHELXL
2554 reflections	Extinction coefficient: 0.072 (5)
266 parameters	Scattering factors from International Tables for Crystallography (Vol. C)
Only coordinates of H atoms refined	
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 1.0763P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 2. Selected bond lengths (\AA) for (2D)

C2—C7	1.395 (3)	C12—C11	1.530 (4)
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Data collection: *MSCIAFC 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.

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). *MSCIAFC 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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Two New Structures of 5-Nitrouracil

ALAN R. KENNEDY, MAURICE O. OKOTH,† DAVID B. SHEEN, JOHN N. SHERWOOD AND RANKO M. VRCELJ

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

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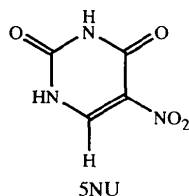
Abstract

The structure of monoclinic anhydrous 5-nitrouracil, $\text{C}_4\text{H}_3\text{N}_3\text{O}_4$, and of the solvate 5-nitrouracil dimethyl sulfoxide, $\text{C}_4\text{H}_3\text{N}_3\text{O}_4 \cdot \text{C}_2\text{H}_6\text{OS}$, are presented and compared with the previously known structures of the orthorhombic anhydrous form and the monohydrate.

† Present address: Department of Chemistry, Moi University, PO Box 1125, Eldoret, Kenya.

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

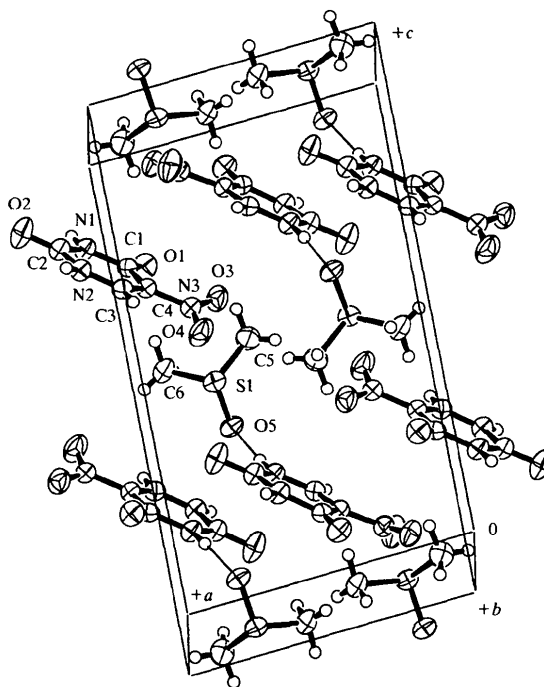


Fig. 2. Packing diagram and hydrogen bonding of 5NU.DMSO, (IV), with 50% probability ellipsoids.

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···H₂O 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 NO₂ 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 NO₂ 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).

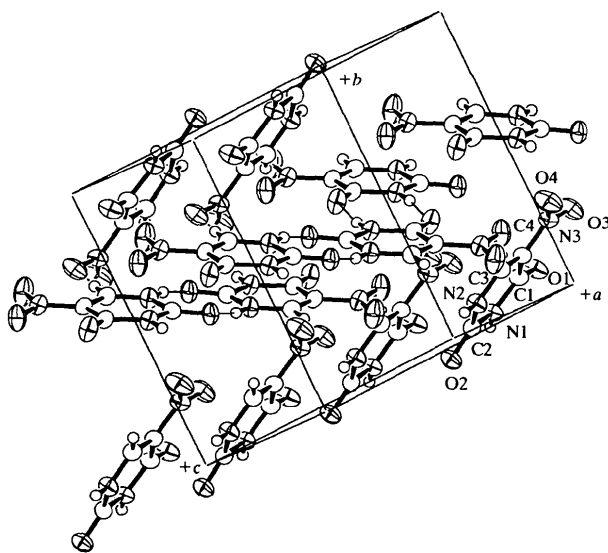


Fig. 1. Packing diagram and hydrogen bonding of anhydrous 5NU, (III), with 50% probability ellipsoids.

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*C₄H₃N₃O₄M_r = 157.09

Monoclinic

P2₁/n

a = 5.873 (1) Å

b = 9.693 (1) Å

c = 10.4561 (9) Å

β = 104.07 (1)°

V = 577.4 (1) Å³

Z = 4

D_x = 1.807 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 22.3–24.9°

μ = 0.164 mm⁻¹

T = 295 K

Cut needle

0.60 × 0.40 × 0.10 mm

Colourless

Data collection

Rigaku AFC-7S diffractometer

ω/2θ scans

Absorption correction: none

1770 measured reflections

1627 independent reflections

1154 reflections with

I > 2σ(I)

R_{int} = 0.012θ_{max} = 29.0°

h = 0 → 8

k = 0 → 13

l = -14 → 13

3 standard reflections

every 150 reflections

intensity decay: none

Refinement

Refinement on F

R = 0.036

wR = 0.051

S = 1.950

1154 reflections

113 parameters

All H atoms refined

w = 1/σ²(F)(Δ/σ)_{max} = 0.0002Δρ_{max} = 0.31 e Å⁻³Δρ_{min} = -0.19 e Å⁻³

Extinction correction:

Zachariasen (1968) type

2, Gaussian isotropic

Extinction coefficient:

1.00 (14) × 10⁻⁵Scattering factors from *International Tables for X-ray**Crystallography* (Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)

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

	x	y	z	U _{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 (Å, °) 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 (Å, °) for (III)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O1 ⁱ	0.89 (2)	2.01 (2)	2.890 (2)	170 (2)
N2—H2...O2 ⁱⁱ	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*C₄H₃N₃O₄·C₂H₆OSM_r = 235.21

Monoclinic

P2₁/n

a = 8.858 (1) Å

b = 6.9619 (6) Å

c = 15.822 (1) Å

β = 95.823 (8)°

V = 970.7 (1) Å³

Z = 4

D_x = 1.609 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 25.1–27.5°

μ = 0.341 mm⁻¹

T = 295 K

Cut block

0.80 × 0.60 × 0.40 mm

Colourless

Data collection

Rigaku AFC-7S diffractometer

ω/2θ scans

Absorption correction: none

2651 measured reflections

2496 independent reflections

2042 reflections with

I > 2σ(I)

R_{int} = 0.009θ_{max} = 28.01°

h = 0 → 11

k = 0 → 9

l = -20 → 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/σ²(F)(Δ/σ)_{max} = 0.002Δρ_{max} = 0.27 e Å⁻³Δρ_{min} = -0.22 e Å⁻³

Extinction correction:

Zachariasen (1968) type

2, Gaussian isotropic

Extinction coefficient:

2.3 (4) × 10⁻⁶Scattering factors from *International Tables for X-ray**Crystallography* (Vol. IV)

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) 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 _{eq}
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 ⁱ	0.88 (2)	1.98 (2)	2.859 (2)	171 (2)
N2—H2...O5 ⁱⁱ	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: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSCI/AFD 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). *MSCI/AFD 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.

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

MICHAEL H. PALMER,^a SIMON PARSONS,^a SUSAN SMITH,^a
 ALEXANDER J. BLAKE^b AND MARTYN F. GUEST^c

^aDepartment of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland,

^bDepartment of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England, and

^cTCS Division, CCLRC Daresbury Laboratory, Warrington WA4 4AD, England. E-mail: s.parsons@ed.ac.uk

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Abstract

The theoretical equilibrium and X-ray crystallographic structures of 3-methyl-1,2,4-triazine, C₄H₅N₃S, 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),