

verfeinert. Die Zeichnungen wurden anhand der Programme *PLUTO* (Motherwell & Clegg, 1978) und *ORTEPII* (Johnson, 1976) angefertigt.

Die Listen der Strukturparameter, anisotropen Verschiebungsparameter, H-Atom Koordinaten, und vollständigen geometrischen Daten sind bei der IUCr (Aktenzeichen: SH1093) hinterlegt. Kopien sind erhältlich durch: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Literatur

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Gzella, A. (1993). Doktorarbeit, Medizinische Karol-Marcinkowski-Akademie Poznań, Polen, und dort zitierte Literatur.
 Gzella, A. & Wrzeciono, U. (1990). *Acta Cryst.* **C46**, 2107–2109.
 Gzella, A. & Wrzeciono, U. (1991a). *Acta Cryst.* **C47**, 599–602.
 Gzella, A. & Wrzeciono, U. (1991b). *Acta Cryst.* **C47**, 980–982.
 Gzella, A. & Wrzeciono, U. (1995). *Acta Cryst.* **C51**. Im Druck.
 Gzella, A., Wrzeciono, U. & Borowiak, T. (1989). *Acta Cryst.* **C45**, 644–647.
 Gzella, A., Wrzeciono, U. & Łukaszewski, Z. (1994). *Pharmazie*, **49**, 319–322.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, VStA.
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. York, England, und Louvain, Belgien.
 Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. Cambridge, England.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. Cambridge, England.
 Wrzeciono, U. & Linkowska, E. (1980). *Pharmazie*, **35**, 593–596.

Acta Cryst. (1995). **C51**, 487–489

A 1:1 Adduct of 4,6-Dimethylpyrimidine-2(1H)-thione and Thiourea

SHYAMAL SETH

Department of Physics, X-ray Laboratory,
 Presidency College, College Street,
 Calcutta 700 073, West Bengal, India

H. SUR

Department of Physics, B. N. Mahavidyalaya,
 Itachuna, Hooghly 712 147, West Bengal, India

(Received 17 January 1994; accepted 8 August 1994)

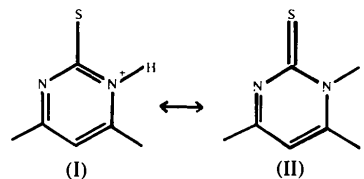
Abstract

In the 1:1 molecular adduct of 4,6-dimethylpyrimidine-2(1H)-thione and thiourea, $C_6H_8N_2S \cdot CH_4N_2S$, the pyrimidine ring is planar to within $0.037(5) \text{ \AA}$ and is

protonated at the N atom rather than at the S atom. It is linked to two other thiourea molecules by $N \cdots H-N$ and $S \cdots H-N$ hydrogen bonds. Each thiourea molecule couples with two adjacent thiourea molecules through hydrogen bonds, thereby forming a polymeric chain extending along the *c* axis.

Comment

The 4,6-dimethylpyrimidine-2(1H)-thione (dtm) molecule displays bond lengths and angles close to expected values and is almost planar [maximum deviation: C(6) $0.037(5) \text{ \AA}$]. The pyrimidine ring itself is planar to within $\pm 0.012(3) \text{ \AA}$ and its geometry is similar to that found in both thiocytosine (Furberg & Jensen, 1970) and metal complexes (Seth, 1994; Cartwright, Langguth & Skapski, 1979; Cotton, Niswander & Sekutowski, 1979), with the exception of the C(1)—N(1)—C(2) angle [$124.0(2)^\circ$]. The ring is protonated at N(1) and seems to have significant contributions from both resonance structures (I) and (II) (see below). The S(1) atom is coplanar with the pyrimidine ring, as indicated by the torsion angle C(2)—N(1)—C(1)—S(1) of $179.4(2)^\circ$. The C(1)—S(1) bond length [$1.685(3) \text{ \AA}$] is at the lower end of the range reported for other thio-substituted structures (Saenger & Suck, 1971) and may be compared with the value of 1.677 \AA in thiouridine (Hawkinson, 1977).



The thiourea (tu) molecule, excluding the amido H atoms, is planar to within $0.004(3) \text{ \AA}$. It has normal configuration and dimensions (see, e.g., Mak & Lau, 1978; Truter, 1967; Elcombe & Taylor, 1968). The dihedral angle between the dtm and tu molecular planes is $145.1(1)^\circ$.

The dtm molecule is linked to two tu molecules by $N(2) \cdots H(42)-N(4)$, $N(1)-H(1) \cdots S(2)(x, y+1, z)$ and $S(1) \cdots H(31)-N(3)$ hydrogen bonds (Fig. 2 and Table 2). The tu molecules are held together by pairs of equivalent $N(4)-H(41) \cdots S(2)(-x, -y-1, 1-z)$ and $N(3)-H(32) \cdots S(2)(1-x, -y-1, 2-z)$ interactions (Table 2). Thus, each tu molecule, besides being hydrogen bonded to two dtm molecules, couples with two adjacent centrosymmetrically related tu molecules forming a polymeric chain extending along the *c* axis. All four amido H atoms take part in hydrogen bonding, as was also observed in orthorhombic thiourea (Truter, 1967). The network of $N-H \cdots N$ and $N-H \cdots S$ hydrogen bonds connects the two molecular components of the adduct into corrugated layers elongated along the *c* axis. Thus,

tu forms a channel in this adduct. Molecules of dtm are packed in layers but are displaced with respect to one another in order to relieve short intermolecular contacts; as a result, packing forces are unlikely to influence the geometry of dtm to any appreciable extent. The closest intermolecular non-H atom contact in the structure is S(2)···N(1)(x, y-1, z) of 3.277 (3) Å.

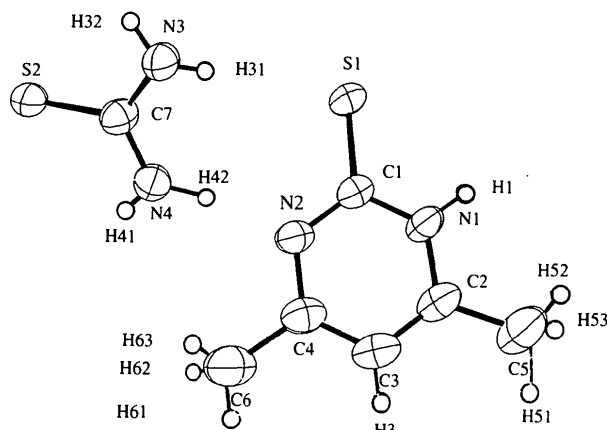


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound showing the atom-numbering scheme. H atoms are represented by spheres of arbitrary size and other atoms by 50% probability ellipsoids.

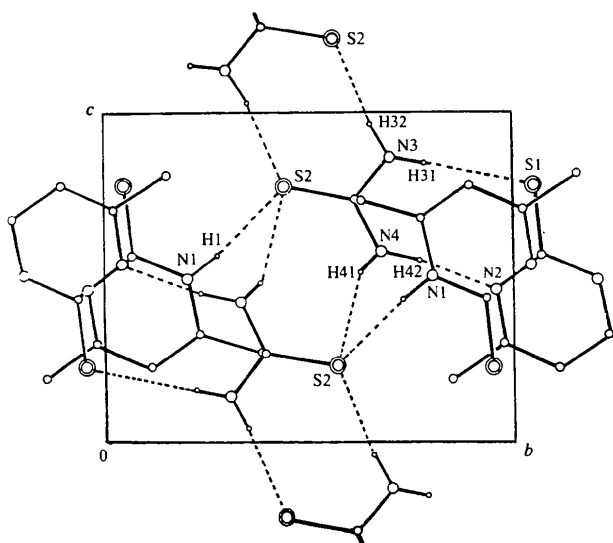


Fig. 2. The packing of the molecules viewed down the *a* axis.

Experimental

A hot alcoholic solution (100 ml) of thiourea (0.004 ml) was added to acetylacetone (0.004 ml) and the resulting solution refluxed on a water bath for about 10 min. Equimolar concentrated HCl was then added and the solution was refluxed for a further 2 h, after which a crystalline product separated

out. This product was filtered, dried and recrystallized from hot water. The reddish brown plate-like crystals, obtained by slow evaporation of a solution in a mixture of acetone and alcohol at room temperature, were investigated in this work. The investigation of yellow acicular crystals obtained from hot water is in progress. The result of the elemental analysis of the title compound is in agreement with the formula C₆H₈N₂S·(NH₂)₂CS. Analysis: calculated C 38.9, H 5.6, N 25.9, S 29.6%; found C 38.8, H 5.7, N 26.0, S 29.5%. The free ligand exhibits a characteristic C=S IR band at 1080 cm⁻¹, indicating the absence of a thiolate group.

Crystal data

C₆H₈N₂S·CH₄N₂S

M_r = 216.32

Triclinic

P $\bar{1}$

a = 7.511 (3) Å

b = 9.468 (5) Å

c = 8.142 (2) Å

α = 88.26 (4)°

β = 112.69 (2)°

γ = 92.23 (4)°

V = 533.7 (4) Å³

Z = 2

D_x = 1.346 Mg m⁻³

D_m = 1.36 Mg m⁻³

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 10.4–17.8°

μ = 0.46 mm⁻¹

T = 295 K

Plate

0.125 × 0.030 × 0.025 mm

Reddish brown

Data collection

Enraf–Nonius CAD-4F diffractometer

$\omega/2\theta$ scans

Absorption correction: none

1975 measured reflections

1794 independent reflections

1463 observed reflections

[*I* > 3 σ (*I*)]

*R*_{int} = 0.025

θ_{\max} = 25°

h = -8 → 8

k = -11 → 11

l = 0 → 9

3 standard reflections

frequency: 60 min

intensity decay: 3.1%

Refinement

Refinement on *F*²

R = 0.034

wR = 0.038

S = 1.13

1463 reflections

167 parameters

All H-atom parameters refined

w = 2.1521/[$\sigma^2(F_o)$

+ 0.000148*F_o*²]

(Δ/σ)_{max} = 0.07

$\Delta\rho_{\max}$ = 0.1 e Å⁻³

$\Delta\rho_{\min}$ = -0.2 e Å⁻³

Extinction correction:

SHELX76 (Sheldrick, 1976)

Extinction coefficient:

0.001 (1)

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S(1)	0.2911 (1)	0.0497 (1)	0.7821 (1)	0.0534 (3)
S(2)	0.2430 (1)	-0.5611 (1)	0.7731 (1)	0.0497 (3)
N(1)	0.2662 (3)	0.2022 (2)	0.4971 (3)	0.0468 (9)
N(2)	0.2521 (3)	-0.0421 (2)	0.4648 (2)	0.0441 (7)
N(3)	0.3807 (3)	-0.3020 (3)	0.8648 (3)	0.0530 (10)
N(4)	0.1706 (4)	-0.3231 (3)	0.5799 (3)	0.0577 (10)

C(1)	0.2678 (3)	0.0693 (3)	0.5685 (3)	0.0413 (9)
C(2)	0.2500 (4)	0.2288 (3)	0.3278 (3)	0.0492 (11)
C(3)	0.2371 (4)	0.1159 (3)	0.2253 (4)	0.0527 (12)
C(4)	0.2356 (3)	-0.0200 (3)	0.2967 (3)	0.0465 (11)
C(5)	0.2479 (7)	0.3801 (4)	0.2702 (6)	0.0734 (17)
C(6)	0.2117 (6)	-0.1486 (4)	0.1893 (4)	0.0660 (16)
C(7)	0.2666 (3)	-0.3844 (3)	0.7365 (3)	0.0427 (9)

Table 2. Selected geometric parameters (Å, °)

S(1)—C(1)	1.685 (3)	S(2)—C(7)	1.705 (3)	
N(1)—C(1)	1.369 (4)	N(1)—C(2)	1.353 (4)	
N(2)—C(1)	1.344 (3)	N(2)—C(4)	1.337 (3)	
N(3)—C(7)	1.320 (3)	N(4)—C(7)	1.327 (3)	
C(2)—C(3)	1.354 (4)	C(2)—C(5)	1.493 (5)	
C(3)—C(4)	1.397 (4)	C(4)—C(6)	1.485 (5)	
C(1)—N(1)—C(2)	124.0 (2)	C(1)—N(2)—C(4)	119.4 (2)	
N(1)—C(1)—N(2)	118.4 (2)	S(1)—C(1)—N(2)	122.1 (2)	
S(1)—C(1)—N(1)	119.6 (2)	N(1)—C(2)—C(5)	117.2 (3)	
N(1)—C(2)—C(3)	117.2 (2)	C(3)—C(2)—C(5)	125.6 (3)	
C(2)—C(3)—C(4)	119.0 (3)	N(2)—C(4)—C(3)	122.0 (2)	
C(3)—C(4)—C(6)	122.0 (3)	N(2)—C(4)—C(6)	115.9 (2)	
N(3)—C(7)—N(4)	117.0 (2)	S(2)—C(7)—N(4)	122.1 (2)	
S(2)—C(7)—N(3)	121.0 (2)			
<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>
N(3)—H(31)...S(1)	0.87 (3)	2.58 (3)	3.418 (3)	164 (3)
N(4)—H(42)...N(2)	0.95 (3)	1.97 (3)	2.915 (4)	172 (3)
N(1)—H(1)...S(2 ⁱ)	0.89 (3)	2.40 (3)	3.277 (3)	167 (2)
N(3)—H(32)...S(2 ⁱⁱ)	0.90 (3)	2.60 (2)	3.462 (3)	161 (2)
N(4)—H(41)...S(2 ⁱⁱⁱ)	0.80 (3)	2.75 (2)	3.486 (3)	154 (3)

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

The thermal motion of the molecule is strongly anisotropic with U_{22} larger than the other components for most of the atoms.

Program systems used: XRAYARC (Vickery, Bright & Mallinson, 1971) for Patterson synthesis; NORMAL, EXFFT and SEARCH sequences of MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) for weighted Fourier syntheses, SHELX76 (Sheldrick, 1976) for refinement, and ORTEPII (Johnson, 1976) for molecular graphics.

The authors thank Professors Siddhartha Ray and Saktiprosad Ghosh, IACS, Jadavpur, Calcutta, for their valuable suggestions and discussions. Financial assistance from the University Grants Commission, New Delhi, is also gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: MU1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Cartwright, B. A., Langguth, P. O. Jr & Skapski, A. C. (1979). *Acta Cryst.* B35, 63–67.
 Cotton, F. A., Niswander, R. H. & Sekutowski, J. C. (1979). *Inorg. Chem.* 18, 1149–1151.
 Elcombe, M. M. & Taylor, J. C. (1968). *Acta Cryst.* A24, 410–420.
 Furberg, S. & Jensen, L. H. (1970). *Acta Cryst.* B26, 1260–1269.
 Hawkinson, S. W. (1977). *Acta Cryst.* B33, 80–85.
 Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

Mak, T. C. W. & Lau, O. W. (1978). *Acta Cryst.* B34, 1290–1294.
 Saenger, W. & Suck, D. (1971). *Acta Cryst.* B27, 1178–1186.

Seth, S. (1994). *Acta Cryst.* C50, 1196–1199.

Sheldrick, G. M. (1976). SHELX76. Program for Crystal Structure Determination. Univ. of Cambridge, England.

Truter, M. R. (1967). *Acta Cryst.* 22, 556–559.

Vickery, B. L., Bright, D. & Mallinson, P. R. (1971). XRAYARC. IBM1130 program system, modified for a Cyber Computer. Agricultural Research Council, Univ. College, London.

Acta Cryst. (1995). C51, 489–491

1-Diphenylmethylene-4-(triphenylmethyl)-cyclohexa-2,5-diene Benzene Solvate

LEONID N. BOCHKAREV AND NATALIA E. MOLOSNOVA

Department of Chemistry, Nizhny Novgorod State Pedagogical University, Ulyanova 1, Nizhny Novgorod 603600, Russia

LEV N. ZAKHAROV AND GEORGY K. FUKIN

Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, Nizhny Novgorod 603600, Russia

ALEXANDER I. YANOVSKY AND YURI T. STRUCHKOV

Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow 117813, Russia

(Received 18 May 1994; accepted 2 August 1994)

Abstract

The crystal structure of the benzene solvate of 1-diphenylmethylene-4-(triphenylmethyl)cyclohexa-2,5-diene, $C_{38}H_{30} \cdot C_6H_6$, has been determined by X-ray diffraction.

Comment

After the discovery of the Ph_3C^* radical there was lengthy discussion about the structure of its dimer (McBride, 1974). The correct structure of this dimer, 1-diphenylmethylene-4-(triphenylmethyl)cyclohexa-2,5-diene, (I), was first established by an NMR study (Staab, Brettschneider & Brunner, 1970) and was later confirmed by X-ray analysis of the ethyl acetate solvate and unsolvated crystals (Allemand & Gerdil, 1978;