Donohue, 1962), but is substantially longer than in P_2, 1·89 Å (Douglas & Rao, 1958). The P–P linkage appears therefore to be essentially a single bond. In this case the MoP_2H_2 group would be expected to be non-coplanar like the phosphines above and to have angles at P markedly less than the tetrahedral value. Of the possible non-coplanar forms of the phosphine ligand, the *cis* form is consistent with the fact that the Mo–P_2 plane does not bisect the angle formed by the normals to the mean planes of the η-cyclopentadienyl rings, as both H atoms on the same side repulse some C atoms of the corresponding cyclopentadienyl ring, thereby increasing the angle.

Thermal ellipsoids are represented, in projection down **b**, in Fig. 3. The large difference between the two P thermal ellipsoids might have the following explanation. From the estimated H atom positions of the η-C_5H_5 group, Fig. 2, it appears that the surroundings of the P atoms are quite different, and distances from P(2) to H(1) and H(2), 3·35 and 3·00 Å, are longer than those from P(1) to H(1) and H(2), 3·00 and 2·45 Å. The vibration of P(1) is, therefore, restricted while P(2) is free to move.

References

CALHOUN, H. P. & TROTTER, J. (1974). *J. Chem. Soc.* (*D*), pp. 382–386.

CARRUTHERS, J. R. (1976). *CRYSTALS User Manual*, Oxford Univ. Computing Laboratory.

DALY, J. J. (1964). *J. Chem. Soc.* pp. 6147–6166.

DAVIES, J. E. & GATEHOUSE, B. M. (1974). *J. Chem. Soc.* (*D*), pp. 184–187.

DOUGLAS, A. E. & RAO, K. S. (1958). *Canad. J. Phys.* **36**, 565–570.

GREEN, J. C., GREEN, M. L. H. & MORRIS, G. E. (1974). *Chem. Commun.* pp. 212–213.

KARLE, J. & HAUPTMAN, H. (1953). In *The Solution of the Phase Problem*, ACA Monograph No. 3. Ann Arbor, Michigan: Edwards.

LARSON, A. C. (1970). *Crystallographic Computing*, pp. 291–294. Copenhagen: Munksgaard.

LEUNG, Y. C. & WASER, J. (1956). *J. Phys. Chem.* **60**, 539–543.

PALENIK, G. J. & DONOHUE, J. (1962). *Acta Cryst.* **15**, 564–569.

PROUT, C. K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* B**30**, 2290–2304.

PROUT, C. K., CRITCHLEY, S. R. & REES, G. V. (1974). *Acta Cryst.* B**30**, 2305–2311.

ROGERS, D., HOWELLS, E. R. & PHILLIPS, D. C. (1950). *Acta Cryst.* **3**, 210–214.

ROLLETT, J. S. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, p. 40. Oxford: Pergamon Press.

ROLLETT, J. S. & CARRUTHERS, J. R. (1975). Private communication.

WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.

Acta Cryst. (1977). B**33**, 2611–2614

Stacking Patterns of Thiopyrimidines: The Crystal Structure of 2-Thiocytosine Picrate

BY LAWRENCE J. DELUCAS, RICHARD A. HEARN AND CHARLES E. BUGG

Institute of Dental Research, University of Alabama in Birmingham, University Station, Birmingham, Alabama 35294, *USA*

(*Received* 16 *September* 1976; *accepted* 31 *December* 1976)

$C_4H_6N_3S.C_6H_2N_3O_7$, monoclinic, $P2_1/c$, $a = 12{\cdot}430\ (1)$, $b = 15{\cdot}594\ (1)$, $c = 7{\cdot}239\ (3)$ Å, $\beta = 99{\cdot}81\ (3)°$, $Z = 4$, $D_x = 1{\cdot}713$, $D_m = 1{\cdot}71$ g cm^{-3}. The structure was solved by use of 2305 symmetry-independent reflections measured on a diffractometer, and was refined by least squares to $R = 0{\cdot}091$. The crystal structure consists of ribbons of stacked thiocytosine cations hydrogen-bonded to the picrate anions and to neighboring thiocytosine moieties. No stacking interactions were observed between thiocytosine cations and picrate anions.

Introduction

The ability of thiopyrimidine residues to stabilize the secondary structure of polynucleotides has been attributed to enhanced base-stacking interactions induced by the sulfur substituents (Faerber, Scheit & Sommer, 1972; Scheit & Gaertner, 1969; Bahr, Faerber & Scheit, 1973). Recent reviews have suggested that the bases in crystal structures of thiopyrimidines generally exhibit characteristic stacking patterns that involve intimate contacts between the sulfur substituent of one base and the ring systems of neighboring bases (Saenger, 1973; Saenger & Suck, 1973). We determined the crystal structure of 2-thiocytosine picrate to

obtain additional information about the base-stacking patterns of thiopyrimidines.

Rectangular plates were grown by evaporating an aqueous solution that contained an approximately equimolar mixture of 2-thiocytosine and picric acid. The space group is $P2_1/c$, as indicated by the systematic absence of the reflections $0k0$ when k is odd and $h0l$ when l is odd. Cell constants were obtained by a least-squares analysis of 2θ values for 12 high-angle reflections (Cu $K\alpha_1$, $\lambda = 1{\cdot}54051$ Å) measured on the diffractometer. The density was measured by flotation in a tetrabromoethane–carbon tetrachloride mixture.

A crystal fragment with approximate dimensions 0·2 × 0·1 × 0·05 mm was mounted on a Picker FACS-1 diffractometer with its c axis slightly inclined to the φ axis of the goniostat. Three-dimensional intensity data for the 2305 symmetry-independent reflections with $2\theta < 128°$ were obtained with the diffractometer (Ni-filtered Cu radiation, a scintillation counter, and a θ–2θ scan mode). The scanning speed was 1 ° min^{-1} and a 20 s background measurement was performed at each terminus of the scans. Three strong reflections (102, 200, 020), which were monitored periodically, exhibited no significant variation of intensity during data collection. Those reflections with scan counts below background level (negative intensities) were assigned intensities of 0·0 and were retained in all subsequent calculations; this procedure introduces a bias in the refinement on F^2, but probably has negligible effects on the final parameters. Intensities were assigned variances, $\sigma^2(I)$, according to counting statistics plus the additional term $(0{\cdot}03S)^2$, S being the scan count. The intensities and their variances were corrected for Lorentz and polarization effects, and absorption corrections were applied with the program *ORABS* (Wehe, Busing & Levy, 1962). The data were scaled by a Wilson (1942) plot.

We arrived at a suitable trial structure by the heavy-atom method. H atoms were located in difference Fourier maps during the later stages of refinement. A modified version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962; Busing, 1971) was used to refine coordinates for all atoms, anisotropic temperature factors for the nonhydrogen atoms, isotropic temperature factors for the H atoms, and Zachariasen's (1963) isotropic extinction parameter g [as formulated by Coppens & Hamilton (1970)]. The quantity minimized was $\Sigma\, w(F_o^2 - F_c^2/k^2)^2$, where k is a scale factor and the weight w is $1/\sigma^2(F_o^2)$. Scattering factors for the non-hydrogen atoms were from *International Tables for X-ray Crystallography* (1962), and anomalous-dispersion correction factors for these atoms were from Cromer & Liberman (1970). Scattering factors for the H atoms were from Stewart, Davidson & Simpson (1965). Because of the limited core-storage capacity of the computer it was impractical to refine all parameters simultaneously; consequently, the atoms were divided into two overlapping blocks which were refined in alternate cycles. During the last cycles of refinement no parameter shifted more than one-quarter of its standard deviation. Considering all reflections, the R_1 index $(\Sigma \| F_o| - |F_c \| / \Sigma |F_o|)$ is 0·091, R_2 $(\Sigma |F_o^2 - F_c^2| / \Sigma F_o^2)$ is 0·063, wR $\{[\Sigma w|F_o^2 - |F_c|^2|^2/(\Sigma wF_o^4)]^{1/2}\}$ is 0·091, and the goodness-of-fit $\{[\Sigma w(F_o^2 - F_c^2)/(m - s)]^{1/2}$, where m is the number of reflections and s the number of parameters refined$\}$ is 1·10. Considering only the 1785 reflections for which $I > \sigma(I)$, $R_1 = 0{\cdot}062$, $R_2 = 0{\cdot}059$, $wR = 0{\cdot}087$ and goodness-of-fit = 1·21.* A final three-dimensional difference Fourier map showed no fluctuations exceeding 0·3 e Å^{-3}.

Results and discussion

Tables 1 and 2 list the parameters and their estimated standard deviations for the nonhydrogen and hydrogen atoms respectively. Estimated errors in positional parameters are about 0·001 Å for S, 0·004 Å for C, N and O, and 0·04 Å for H. Fig. 1 shows bond lengths, bond angles and thermal ellipsoids. The thiocytosine

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32535 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional parameters and their estimated standard deviations*

Values for the S atoms have been multiplied by 10^5, and all other values by 10^4. The final value of the isotropic extinction parameter is $g = 0{\cdot}018$ (3).

	X	Y	Z
S	90318(6)	57798(5)	29324(12)
C2	9796(2)	4941(2)	2594(4)
N3	9403(2)	4117(1)	2687(3)
C4	9997(2)	3395(2)	2476(5)
C6	11426(2)	4292(2)	1915(4)
C5	11047(3)	3497(2)	2045(5)
N1	10815(2)	4988(2)	2208(4)
N4	9544(2)	2652(2)	2687(4)
C1'	6718(2)	2966(2)	3944(4)
C2'	6389(2)	2083(2)	4169(4)
C3'	5378(2)	1846(2)	4514(4)
C4'	4614(2)	2469(2)	4684(4)
C6'	4848(2)	3332(2)	4486(5)
C5'	5860(2)	3550(2)	4171(4)
O1'	7621(2)	3206(1)	3592(3)
N1'	7147(2)	1387(2)	4051(4)
O2'	6924(2)	676(1)	4562(4)
O3'	8000(2)	1523(1)	3486(4)
N2'	3557(2)	2218(2)	5100(4)
O4'	2900(2)	2780(2)	5308(4)
O5'	3388(2)	1454(2)	5294(4)
N3'	6080(2)	4476(2)	4032(4)
O6'	6898(2)	4763(1)	4980(4)
O7'	5407(2)	4903(1)	3011(4)

Table 2. *Hydrogen-atom parameters*

Values have been multiplied by 10^3. The U values ($U = B/8\pi^2$) correspond to isotropic temperature factors and are in units of Å^2.

	X	Y	Z	U
HN1	111(3)	551(2)	213(4)	61(11)
HN3	872(2)	405(2)	303(4)	39(9)
HN4	986(3)	219(2)	249(5)	54(11)
HN4'	879(3)	266(2)	313(4)	69(11)
HC5	1145(2)	302(2)	175(4)	52(10)
HC6	1216(2)	441(1)	163(3)	24(7)
HC3'	520(2)	128(2)	471(4)	34(8)
HC5'	432(2)	374(2)	461(4)	50(10)

cation is nearly planar: S, N(4) and C(2) deviate by 0·01, 0·06 and 0·01 Å, respectively, from a least-squares plane through the six atoms of the pyrimidine ring. The central benzene ring of the picrate anion is planar, but N(1′), N(2′) and N(3′) deviate from this plane by 0·03, 0·04, and 0·04 Å respectively. The N(1′), N(2′) and N(3′) nitro groups are twisted out of the benzene plane by 12, 2 and 51 ° respectively.

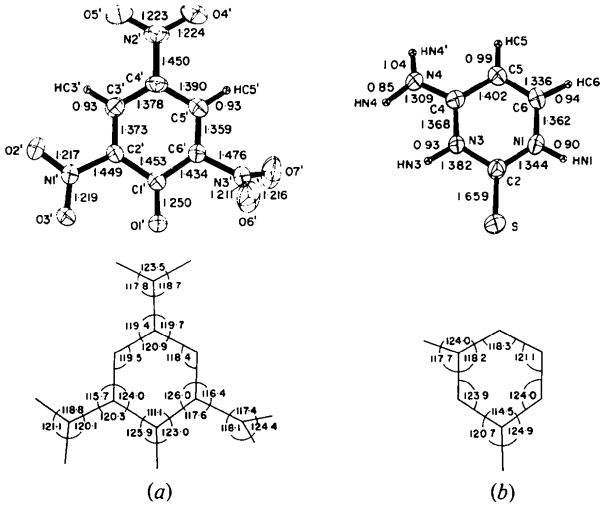

Fig. 1. Bond distances (Å) and angles (°) for (*a*) the picrate anion and (*b*) the 2-thiocytosine cation. Non-hydrogen atoms are represented by thermal ellipsoids scaled to include 50% probability. Hydrogen atoms are represented by spheres of 0·1 Å radius. Estimated standard deviations in bond lengths and angles are 0·006 Å and 0·4° respectively. This drawing and Fig. 2 were prepared with the program *ORTEP* (Johnson, 1965).

Fig. 2 shows the crystal-packing and hydrogen-bonding schemes, and Table 3 lists the lengths and angles for the postulated hydrogen bonds. The thiocytosine cations form ribbons running parallel to **b**. Within these ribbons, adjacent thiocytosine moieties are joined by N(4)–H(N4)···S hydrogen bonds with N···S distances of 3·483 Å. The ribbons of thiocytosine bases are hydrogen bonded to picrate anions, which are clustered in stacked columns which run in the **c** direction. The thiocytosine–picrate hydrogen-bonding scheme involves a bifurcated hydrogen bond between a H atom from the amino group of thiocytosine and two O atoms of a picrate anion. N(1) and N(3) both donate hydrogen bonds to picrate anions. In addition H(C6), the H atom from C(6) of the pyrimidine ring, forms two close contacts which may be considered hydrogen bonds.

The ribbons of thiocytosine cations are stacked in the **c** direction. The stacking pattern for the pair of thiocytosine cations with the closest contacts is shown in Fig. 3, and the cytosine–picrate hydrogen-bonding scheme is depicted in Fig. 4. The bases are stacked across inversion centers, with a separation of about 3·4 Å between thiocytosine planes. The stacking pattern involves no direct overlap of pyrimidine rings, but the S substituents are positioned in contact with atoms of neighboring pyrimidine rings. The S substituent forms three contacts that are about equal to van der Waals distances (Pauling, 1960). This type of stacking pattern, wherein S substituents are in intimate contact

Table 3. *Hydrogen-bond distances and angles*

D	H	*A*	*D*···*A*	H···*A*	∠*DHA*
C(6)	H(C6)	O(5′)^{iv}	3·107 Å	2·4 Å	132°
C(6)	H(C6)	O(2′)^{iii}	3·278	2·5	135
N(4)	H(N4)	S^{ii}	3·483	2·6	176
N(4)	H(N4′)	O(1′)^{i}	2·724	1·8	151
N(4)	H(N4′)	O(3′)^{i}	2·738	2·1	121
N(3)	H(N3)	O(1′)^{i}	2·801	2·0	145
N(1)	H(N1)	O(3′)^{v}	2·899	2·0	165

Symmetry code

(i)	x, y, z	(iv)	$1 + x, \frac{1}{2} - y, z - \frac{1}{2}$
(ii)	$2 - x, y - \frac{1}{2}, \frac{1}{2} - z$	(v)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(iii)	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$		

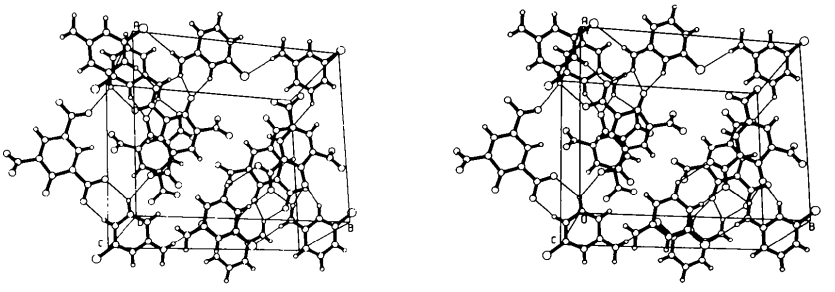

Fig. 2. Stereo drawing of the crystal packing and the hydrogen-bonding scheme. Hydrogen bonds are represented by thinner lines.

with atoms of the ring systems from adjacent bases, has now been observed in several crystal structures of thiopyrimidines (Saenger, 1973; Saenger & Suck, 1973) and thiopurines (Bugg & Thewalt, 1975; Bugg & Sternglanz, 1974). However, this type of stacking interaction is somewhat unusual; protonated pyrimidines are almost never found to stack either in crystal structures or in aqueous solution (Bugg, Thomas, Sundaralingam & Rao, 1971).

The thiocytosine picrate salt was of interest since we felt that the crystal structure might involve charge-transfer interactions between the thiocytosine and picrate moieties. We had no spectroscopic data to indicate that a charge-transfer complex was formed, but we suspected this possibility on the basis of data suggesting that thiopyrimidines (Fulton & Lyons, 1968) and other organic sulfur compounds (Bent, 1968; Hassel, 1970; Prout & Wright, 1968) are capable of acting as electron donors, whereas picric acid is a good electron acceptor (Gartland, Freeman & Bugg, 1974, and references therein). Our expectation that the structure might display π–π complexes in stacks of alternating thiocytosine and picrate ions (as found in many crystal structures of aromatic donor–acceptor complexes) was not realized; instead, both the thiocytosine residues and picrate ions are self-stacked.

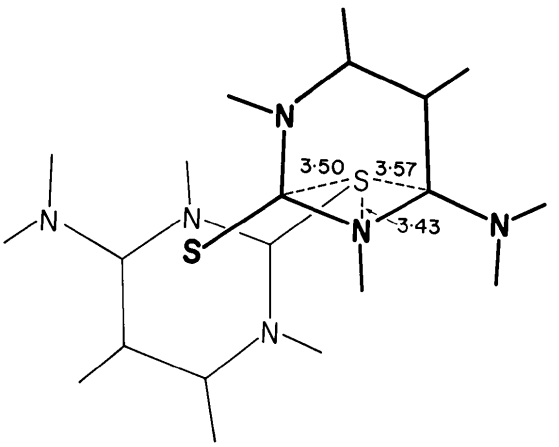

Fig. 3. Base stacking pattern for the pair of thiocytosine cations with the closest stacking contacts. A second stacking pattern, which displays no close contacts, would be obtained by shifting the lower base up through the c translation. The view is perpendicular to the pyrimidine ring.

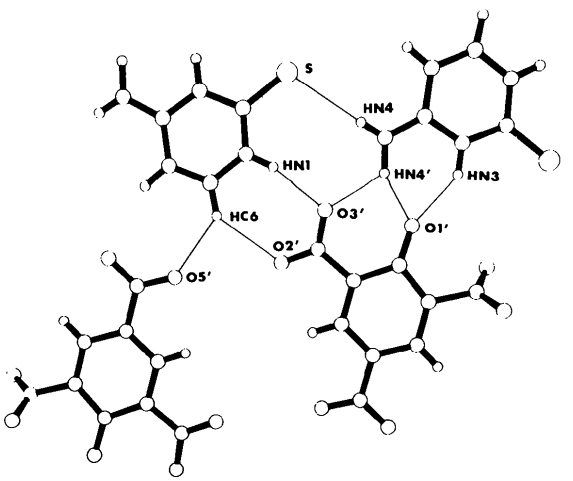

Fig. 4. Cytosine–picrate hydrogen-bonding scheme.

We thank Miss Catherine Sims and Miss Mary Ann Comer for assistance with the preparation of this manuscript. This work was supported by NIH grants CA-12159, CA-13148 and DE-02670.

References

BAHR, W., FAERBER, P. & SCHEIT, K.-H. (1973). *Eur. J. Biochem.* **33**, 535–544.

BENT, H. A. (1968). *Chem. Rev.* **68**, 587–648.

BUGG, C. E. & STERNGLANZ, H. (1974). *Molecular and Quantum Pharmacology, Structural Properties of Purine and Pyrimidine Analogs*, edited by E. D. BERGMAN & B. PULLMAN, pp. 473–500. Dordrecht, Holland: Reidel.

BUGG, C. E. & THEWALT, U. (1975). *Acta Cryst.* B**31**, 121–127.

BUGG, C. E., THOMAS, J. M., SUNDARALINGAM, M. & RAO, S. T. (1971). *Biopolymers*, **10**, 175–219.

BUSING, W. R. (1971). *Acta Cryst.* A**27**, 683–684.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

FAERBER, P., SCHEIT, K. H. & SOMMER, H. (1972). *Eur. J. Biochem.* **27**, 109–115.

FULTON, A. & LYONS, L. E. (1968). *Aust. J. Chem.* **21**, 419–423.

GARTLAND, G. L., FREEMAN, G. R. & BUGG, C. E. (1974). *Acta Cryst.* B**30**, 1841–1849.

HASSEL, O. (1970). *Science*, **170**, 497–502.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–211. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.

PROUT, C. K. & WRIGHT, J. D. (1968). *Angew. Chem. Int. Ed.* **7**, 659–667.

SAENGER, W. (1973). *Angew. Chem. Int. Ed.* **12**, 591–601.

SAENGER, W. & SUCK, D. (1973). *Eur. J. Biochem.* **32**, 473–478.

SCHEIT, K. H. & GAERTNER, E. (1969). *Biochim. Biophys. Acta*, **182**, 10–16.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.