

1,4-Dithiins are known to have the boat structure, as mentioned above. However, molecules *A* and *B* of this complex are planar with respective maximum shifts of 0.0736 Å [C(5)*A*] and 0.0303 Å [C(4)*B*] from their least-squares planes. The C=C–S angles of molecule *A* are larger than that of 1,4-dithiin (124°) (Howell, Curtis & Lipscomb, 1954). The C–S–C angles of molecule *A* are somewhat smaller than those of 1,4-dithiin (101°), thianthrene (100°) (Rowe & Post, 1956, 1958; Lynton & Cox, 1956) and 1,4-dithiane (99°) (Marsh, 1955). The C–S and C=C bond distances of molecule *A* are normal. The dithiin ring of molecule *A* is flattened out along the S...S direction by the face-to-face stacking of molecules *A* and *B*.

The intermolecular distances C(4)*A*...C(5)*B* and C(6)*A*...C(4)*B* are respectively 3.34 (2) and 3.38 (2) Å and are shorter than the van der Waals distance (3.40 Å). This suggests that π–π interactions between molecules *A* and *B* exist in these parts and the molecules form a paired molecular group. The dihedral angle between the least-squares planes of molecules *A* and *B* is 2.3°. Distances between paired groups are larger than the van der Waals distances. The minimum distance is 3.50 (1) Å [C(1)*A*...C(8)*B*]. The stacking of paired molecules is in accordance with the poor electrical conductivity of this complex (Hayakawa, Mibu, Ōsawa & Kanematsu, 1982).

Although the crystal structure of this complex is similar to those of charge-transfer complexes, the

interactions between molecules *A* and *B* in this complex seem to be fairly weak. No CT band could be observed in chloroform solution.

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Structure of 1-(*p*-Dimethylaminophenyl)-3-(mercaptoacetyl)urea, C₁₁H₁₅N₃O₂S

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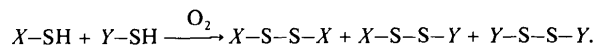
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Abstract. $M_r = 253.32$, monoclinic, $P2_1/n$, $a = 20.981$ (1), $b = 8.1402$ (4), $c = 7.2535$ (4) Å, $\beta = 94.375$ (6)°, $V = 1235.2$ (1) Å³, $D_m = 1.38$, $D_x = 1.363$ g cm⁻³, $Z = 4$, $T = 293$ K, $F(000) = 134$, $\mu(\text{Cu K}\alpha) = 21.40$ cm⁻¹, $\lambda = 1.54184$ Å, $R = 0.054$ for 1779 observed reflections. The molecule is roughly planar, except the SH group. Two molecules around an inversion center are connected by two N–H...O hydrogen bonds to form a dimer. Two molecules

around another inversion center are stacked, the distance between the central acylurea moieties being 3.392 (3) Å.

Introduction. It has been reported that in the following oxidation, the selectivity, defined by the ratio of the yield of the unsymmetrical disulfide ($X-S-S-Y$) to that of the symmetrical disulfides ($X-S-S-X$ and $Y-S-S-Y$), depends on the substituents, X and Y :



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When X is $\text{CH}_2(\text{CONH})_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ and Y is $\text{CH}_2\text{CH}_2(\text{NHCO})_2(\text{CH}_2)_m\text{CH}(\text{CH}_3)_2$, the selectivity reaches a maximum at $m = 2$ (Endo, Kuwahara, Tasai, Murata, Hashimoto & Ishigami, 1977). From chemical and spectroscopic experiments, it was proposed that a pair of thiols, $X\text{-SH}$ and $Y\text{-SH}$, would make a hydrogen-bonded dimeric complex and then the two dimers might be stacked to form a tetrameric complex in the intermediate stage of the oxidation (Endo, Takeda, Orii, Kaneko & Kondo, 1979; Endo, Takeda, Kamada, Kayama & Tasai, 1980). All attempts to crystallize the dimer and tetramer were in vain. The present work was undertaken to determine the structure of $X\text{-SH}$ and to examine the model of the hydrogen-bonded dimer.

Experimental. Pale-yellow crystals obtained from an acetonitrile solution, density measured by flotation in $n\text{-C}_6\text{H}_{12}/\text{CCl}_4$; systematic absences $h0l: h + l = 2n + 1, 0k0: k = 2n + 1$; approximate dimensions of crystal $0.3 \times 0.2 \times 0.1$ mm, Rigaku AFC-4 diffractometer, graphite monochromator; cell parameters refined by least-squares method on the basis of 19 independent 2θ values, $\text{Cu K}\alpha$ radiation ($37^\circ < 2\theta < 62^\circ$); intensity measurement performed up to $2\theta = 125^\circ$ ($\pm h + k + l$ set), $\theta\text{-}2\theta$ scan technique, scan speed 4°min^{-1} (θ); 1977 reflections measured, 1779 intensities with $|F_o| > 3\sigma(|F_o|)$ considered as observed and used for the structure determination; corrections for Lorentz and polarization, absorption ignored; direct method (MULTAN78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); block-diagonal least squares (HBL5, Ohashi, 1975) with anisotropic thermal parameters for all non-H atoms, H atoms located on difference map, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + (C|F_o|)^2]^{-1}$, $C (= 0.015)$ adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ were obtained in the different $|F_o|$ and $\sin\theta$ intervals; final $R = 0.054$, $R_w = 0.058$ for 1779 observed reflections; $(\Delta/\sigma)_{\text{max}} = 0.5$; difference-map excursions $< 0.2 \text{ e } \text{\AA}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); no correction for secondary extinction; calculations carried out on the FACOM-HITAC system M-180 computer at this Institute.

Discussion. The final atomic parameters for non-H atoms are in Table 1.* The crystal structure viewed along the c axis is shown in Fig. 1. The SH group makes no hydrogen bonds with the neighboring atoms. Two molecules around the inversion center $(\frac{1}{2}, \frac{1}{2}, 0)$ are

linked by two $\text{N}(13)\text{-H}(13)\cdots\text{O}(12)$ hydrogen bonds to form a dimer. The $\text{N}(13)\cdots\text{O}(12)$ and $\text{H}(13)\cdots\text{O}(12)$ distances are $2.856(3)$ and $1.98(2)$ \AA, respectively. Two molecules around another inversion center $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, on the other hand, are stacked as shown in Fig. 2.

Table 1. Final atomic coordinates ($\times 10^4$, for S $\times 10^5$) with their estimated standard deviations and equivalent isotropic thermal parameters

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	2329 (1)	1291 (4)	6588 (4)	6.3
C(2)	2837 (1)	-693 (4)	4639 (4)	6.1
N(3)	2267 (1)	199 (3)	5014 (3)	5.4
C(4)	1823 (1)	580 (3)	3550 (3)	4.1
C(5)	1801 (1)	-280 (3)	1888 (3)	4.6
C(6)	1345 (1)	49 (3)	440 (3)	4.4
C(7)	894 (1)	1267 (3)	622 (3)	3.8
C(8)	911 (1)	2121 (3)	2273 (3)	4.3
C(9)	1360 (1)	1797 (3)	3702 (3)	4.4
N(10)	415 (1)	1720 (2)	-764 (3)	4.3
C(11)	274 (1)	1001 (3)	-2403 (3)	4.1
O(12)	549 (1)	-191 (2)	-2994 (2)	5.0
N(13)	-237 (1)	1688 (2)	-3492 (2)	4.3
C(14)	-625 (1)	2964 (3)	-3104 (3)	4.5
O(15)	-567 (1)	3751 (2)	-1660 (2)	5.7
C(16)	-1133 (1)	3353 (3)	4619 (4)	5.0
S(17)	-8263 (4)	44556 (10)	-65099 (10)	5.9

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

C(1)-N(3)	1.445 (4)	C(8)-C(9)	1.372 (4)
C(2)-N(3)	1.443 (4)	N(10)-C(11)	1.338 (3)
N(3)-C(4)	1.392 (3)	C(11)-O(12)	1.224 (3)
C(4)-C(5)	1.392 (3)	C(11)-N(13)	1.399 (3)
C(4)-C(9)	1.398 (4)	N(13)-C(14)	1.362 (3)
C(5)-C(6)	1.392 (4)	C(14)-O(15)	1.226 (3)
C(6)-C(7)	1.385 (3)	C(14)-C(16)	1.505 (4)
C(7)-C(8)	1.382 (3)	C(16)-S(17)	1.799 (3)
C(7)-N(10)	1.416 (3)		
C(1)-N(3)-C(2)	115.6 (2)	C(7)-C(8)-C(9)	122.0 (2)
C(1)-N(3)-C(4)	118.7 (2)	C(4)-C(9)-C(8)	121.2 (2)
C(2)-N(3)-C(4)	118.9 (2)	C(7)-N(10)-C(11)	127.9 (2)
N(3)-C(4)-C(5)	121.6 (2)	N(10)-C(11)-O(12)	125.4 (2)
N(3)-C(4)-C(9)	121.7 (2)	N(10)-C(11)-N(13)	115.8 (2)
C(5)-C(4)-C(9)	116.6 (2)	O(12)-C(11)-N(13)	118.8 (2)
C(4)-C(5)-C(6)	122.2 (2)	C(11)-N(13)-C(14)	129.2 (2)
C(5)-C(6)-C(7)	120.1 (2)	N(13)-C(14)-O(15)	123.6 (2)
C(6)-C(7)-C(8)	118.0 (2)	N(13)-C(14)-C(16)	114.2 (2)
C(6)-C(7)-N(10)	124.9 (2)	O(15)-C(14)-C(16)	122.2 (2)
C(8)-C(7)-N(10)	117.0 (2)	C(14)-C(16)-S(17)	112.8 (2)

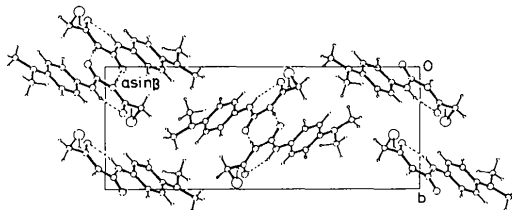


Fig. 1. The crystal structure viewed along the c axis. The hydrogen bonds are indicated by broken lines.

* Lists of structure factors, anisotropic thermal parameters for non-H atoms and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38847 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

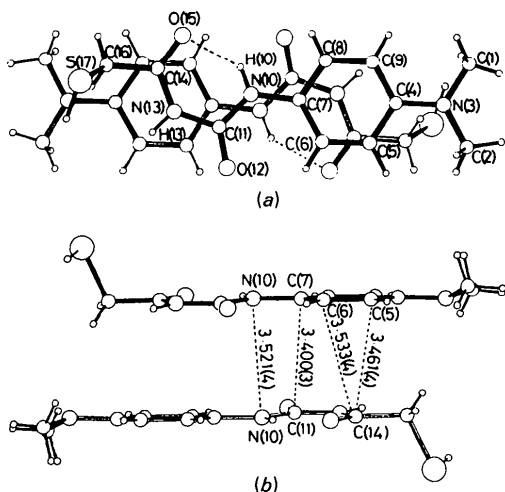


Fig. 2. The overlapping mode of the two molecules around the inversion center ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$): (a) projection along the normal to the mean plane of the acylurea moiety and (b) side view. Several contacts (Å) are given.

The acylurea moiety, $-\text{NHCONHCO}-$, is planar within ± 0.017 Å, the intramolecular hydrogen bond $\text{N}(10)\text{—H}(10)\cdots\text{O}(15)$ being formed. The $\text{N}(10)\cdots\text{O}(15)$ and $\text{H}(10)\cdots\text{O}(15)$ distances are 2.681 (3) and 1.96 (2) Å, respectively. The mean plane of the acylurea moiety makes an angle of 4.26 (8) $^\circ$ with the benzene ring of the *p*-dimethylaminophenyl group. The methyl groups deviate significantly from the mean plane of the benzene ring in the *p*-dimethylaminophenyl

group. The plane composed of C(1), C(2) and N(3) makes an angle of 23.5 (3) $^\circ$ with the benzene ring. Bond lengths and angles are given in Table 2. Five $\text{C}(sp^2)\text{—N}$ distances, C(4)—N(3), C(7)—N(10), C(11)—N(10), C(11)—N(13) and C(14)—N(13), are significantly different from each other; they range from 1.338 to 1.416 Å.

The acylurea moiety and the benzene ring of the *p*-dimethylaminophenyl group overlap each other as shown in Fig. 2, in which several short contacts between the two moieties are given. The distance between the mean planes of the acylurea moieties is 3.392 (3) Å. Since the present complex is colorless in an acetonitrile solution, the color of the crystal may be brought about by the weak charge-transfer interaction between the acylurea and *p*-dimethylaminophenyl groups in the crystalline field.

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Structure of 1-(*p*-Dimethylaminophenyl)-3-(phenylacetyl)urea, $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_2$

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Abstract. $M_r = 297.4$, monoclinic, $P2_1/a$, $a = 12.878$ (1), $b = 9.954$ (1), $c = 12.245$ (1) Å, $\beta = 94.92$ (1) $^\circ$, $V = 1563.8$ (3) Å³, $D_m = 1.26$, $D_x = 1.265$ g cm⁻³, $Z = 4$, $T = 293$ K, $F(000) = 148$, $\mu(\text{Cu K}\alpha) = 8.02$ cm⁻¹, $\lambda = 1.54184$ Å, $R = 0.049$ for

2160 observed reflections. The benzyl group is approximately at right angles to the remaining part of the molecule. The molecules form a symmetrical dimer structure linked by two $\text{N—H}\cdots\text{O}$ hydrogen bonds. The *p*-dimethylaminophenyl groups in the two molecules around another inversion center are stacked and the dimethylamino group of one molecule is capped by the benzyl group of the other.

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