

O(40')—H(40')...O(120<sup>b</sup>) exist which connect symmetry-related molecules mainly in the  $y$  direction.

Fig. 3, representing a projection of the unit cell in the  $y$  direction, shows that at  $x = 0, 1/2, \dots$  relatively empty spaces are present, forming channels in the  $y$  direction with diameters of about 6 Å. Inside the channels there are only the half-populated methanol molecules, on the border there are the half-populated water molecules. Both of these solvent molecules take part in one hydrogen bond each [the water molecule O(1 $W$ ) as donor, the methanol oxygen O(2 $M$ ) as acceptor, see Table 3]. Since both molecules are not engaged in any further hydrogen bonding (although they have free donor groups) and since they are located at rather empty sites of the crystal lattice it becomes understandable that they are less strongly integrated in the crystal packing and may get out quite easily. If, however, a considerable amount of methanol is withdrawn from the channels the crystal lattice is no longer stable which then causes the rapid decomposition of the crystal, when removed from the solvent. So the microscopic properties of this crystal lattice may serve as an explanation for the macroscopically observed decay of the crystal. Also in connection with this the unusual low density, close to  $1 \text{ g cm}^{-3}$ , should be

mentioned. In comparable organic compounds the density is between 1.2 and  $1.3 \text{ g cm}^{-3}$ , for example 1.20 for dirithromycin or  $1.24 \text{ g cm}^{-3}$  for erythromycin A carbonate (Hempel, 1978). This is a further hint of the instability of the crystals.

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## A New Crystal Structure of 3,6-Diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dithione

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**Abstract.**  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{S}_2$ ,  $M_r = 320.426$ , monoclinic,  $C2/c$ ,  $a = 27.008$  (4),  $b = 6.982$  (1),  $c = 7.935$  (1) Å,  $\beta = 100.64$  (1)°,  $V = 1470.6$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.447$ ,  $D_m = 1.436 \text{ Mg m}^{-3}$ , graphite-monochromatized Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å,  $\mu = 3.18 \text{ mm}^{-1}$ ,  $T = 293 \text{ K}$ ,  $F(000) = 664$ ,  $R = 0.064$  for 1496 reflec-

tions. The molecule has  $C_2$  symmetry. Both phenyl rings are twisted, in opposite directions, out of the plane of the heterocyclic ring system by  $30.1$  (2)°. The heterocyclic ring system is not quite planar, as the two five-membered rings form a dihedral angle of  $5.4$  (1)°. Along the stacking axis, alternate molecules lie directly above each other, forming columns. The molecules in adjacent columns overlap only at the S—C(1), C(1)—N, N—C(3) and N—H bonds in one

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stack, and the S—C(4), C(4)—N, N—C(6) and N—H bonds in the other. The stacking arrangement can be compared to the bricks in a brick wall.

**Introduction.** The solid-state properties of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dithione (abbreviated to DPPT, Fig. 1) have been extensively studied, especially in connection with photoconductive behavior (Mizuguchi & Rochat, 1988; Mizuguchi & Homma, 1989; Mizuguchi, 1989). It has been recognized that the solvent-vapor treatment of an evaporated film of DPPT induces a large spectral shift in the visible and near-IR region towards longer wavelengths. This vapor treatment also brings about a great increase in photoconductivity (of two orders of magnitude). Because of the enhanced absorption and photoconduction in the near-IR region, DPPT was found to be an excellent photoconductor for the electrophotographic photoreceptor for laser printers. Another application for information storage has also recently been reported (Mizuguchi & Rochat, 1991).

The near-IR absorption caused by the vapor treatment is characteristic of an intermolecular interaction such as charge transfer (Mizuguchi & Rochat, 1988). The supposition of charge transfer is based on the notion that in the DPPT molecule the space around the S atom is the acceptor and the rest the donor part. Detailed studies by means of Fourier transform infrared spectrometry and X-ray photoelectron spectroscopy revealed that a large intermolecular interaction operates along the molecular stacking axis *via*  $\pi$  electrons of C, N and S atoms (Mizuguchi & Homma, 1989). The solvent vapor causes a rearrangement of the molecules so that the donor part of one molecule and the acceptor part of the other lie directly above one another. This greatly facilitates an intermolecular electron transfer in the excited state.

The near-IR photoactive phase is crystallographically characterized by the X-ray diffraction patterns at 6.6 and 25.40° in  $2\theta$  for Cu  $K\alpha$  (Mizuguchi & Rochat, 1988). In order to gain more insight into the correlation between the crystal structure and the physical properties, we carried out a crystal structure analysis of DPPT (Mizuguchi, Rochat & Rihs, 1990). Single crystals have been grown from the vapor phase. Two types of single crystals have been obtained, both of which are monoclinic and very similar in structure. Neither of these modifications, however, coincides with that of the photoactive phase. Specifically, these modifications gave no characteristic diffraction pattern at  $2\theta = 6.6^\circ$ . In addition, reflection spectrum measurements of these single crystals showed no near-IR absorption.

In the present investigation, a new single crystal-line phase that exhibits near-IR absorption has been

found. This modification does, indeed, give the diffraction patterns at  $2\theta = 6.6$  and  $25.40^\circ$ .

**Experimental.** DPPT was prepared from 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione (Iqbal, Cassar, Rochat, Pfenninger & Wallquist, 1988) by using a Lawesson's reagent as the thionation agent (Mizuguchi & Rochat, 1988). The product synthesized was identified by means of mass spectroscopy, NMR and elemental analysis. The blue-black DPPT powder was then recrystallized from *N*-methylpyrrolidone for purification. The powder was further purified four times by sublimation in an argon atmosphere using an apparatus which has been described previously (Mizuguchi, 1981).

The single crystal was grown from the vapor phase using argon as the carrier gas in the same sublimation apparatus described above. DPPT was sublimated at about 573 K, and the argon flow rate was controlled to  $33 \text{ mm}^3 \text{ s}^{-1}$  using a mass flow meter (F-100/200, Bronkhorst BV) so as to transport DPPT at a rate of about  $33 \mu\text{g s}^{-1}$ . After 24 h of vapor growth, a number of scale-like and tetragonal-shaped single crystals were obtained in the sublimation tube.

The dimensions of the single crystal under investigation were  $0.4 \times 0.4 \times 0.08 \text{ mm}$  (scale-like crystal). The crystal structure was analyzed at 293 K using a Nonius CAD-4 four-circle diffractometer with graphite-monochromatized Cu  $K\alpha$  radiation.  $\theta$ - $2\theta$  scans. Unit-cell dimensions from 25 reflections ( $20 < 2\theta < 35^\circ$ ). 1496 independent reflections obtained in the range  $4 < 2\theta < 150^\circ$ ,  $-33 \leq h \leq 33$ ,  $0 \leq k \leq 8$ ,  $0 \leq l \leq 9$ . Among these, 1372 reflections with  $I > 3\sigma(I)$  were used for structure refinement. Corrections for absorption and secondary extinction were not applied. Three standard reflections monitored every 2 h during data collection showed no significant change in intensity. The density of the single crystals was measured by flotation in a mixture of benzene and carbon tetrachloride. Crystallographic data are given in the *Abstract*.

#### *Structure determination and refinement*

The structure was determined by direct methods using *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The structures were refined on *F* by full-matrix least-squares calculations using the *SDP* package (Frenz, 1985) with anisotropic atomic displacement parameters, neglecting H atoms, up to  $R = 0.073$ . Six H atoms were then located in difference electron density maps. Final  $R = 0.064$  and  $wR = 0.073$ ,  $S = 1.40$ . Weights of each reflection in the refinement were  $w = 1/\sigma^2(F_o)$ ,  $\sigma(F_o)$  being the e.s.d based on counting statistics.  $(\Delta/\sigma)_{\text{max}} = 0.06$ . The maximum weights in the final difference electron density maps were

0.178 e Å<sup>-3</sup>. Atomic scattering factors for C, N and S were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic positional and equivalent isotropic displacement parameters are given in Table 1.\*

## Discussion.

### Molecular geometry

The conformation and the intermolecular hydrogen bonds of DPPT are given in Fig. 1, where the atoms are represented by displacement ellipsoids according to *ORTEP* (Johnson, 1971). The interatomic distances and bond angles together with their e.s.d.'s are listed in Table 2. The molecule has C<sub>2</sub> symmetry. Both phenyl rings are twisted, in opposite directions, out of the plane of the heterocyclic ring system by 30.1 (2)°. The heterocyclic ring system is not quite planar, as the two five-membered rings form a dihedral angle of 5.4 (1)°.

### Arrangement of the molecules

Fig. 2 shows the projection of the crystal structure onto the *ac* plane. The dotted molecules are located in the same molecular plane, whereas the undotted ones are in the plane below.

The overlap of the molecules along the stacking axis is shown in Fig. 3. The molecule designated by *C* is directly under molecule *A*, separated by double the intermolecular layer. Molecule *B* lies between molecules *A* and *C* with overlap occurring only at the S—C, C—N, N—C and N—H bonds, where the first and second C atoms are of the thiocarbonyl group and the third one connects to the phenyl ring. The alternate C (which connects to the phenyl ring) and S atoms form one column along the stacking axis, and the alternate N and thiocarbonyl C atoms, which are aligned, form the other column. The interatomic distance between the nitrogen in molecule *A* and the thiocarbonyl carbon in molecule *B* [3.518 (8) Å] is slightly longer than that between molecules *B* and *C* [3.496 (8) Å]. These features are characteristic of the new phase found in the present investigation.

### Hydrogen bonding

Intermolecular hydrogen bonds of the type NH...S are depicted by dotted lines in Figs. 1 and 2. One can see that there are chains of hydrogen bonds along the *c* axis. The angle NH/S is 174 (4)°, and the distances between S/H, N/H and N/S are 2.50 (8), 0.88 (8) and 3.359 (5) Å, respectively.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54041 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic displacement parameters with e.s.d.'s in parentheses*

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (Å <sup>2</sup> )
S1	0.06966 (5)	0.2421 (3)	0.1479 (2)	0.043 (1)
N2	-0.0266 (2)	0.2531 (7)	-0.0187 (5)	0.033 (1)
C3	0.0246 (2)	0.2453 (8)	-0.0244 (7)	0.030 (1)
C4	0.0250 (2)	0.2376 (9)	-0.2058 (6)	0.032 (1)
C5	-0.0579 (2)	0.2472 (8)	-0.1765 (7)	0.033 (1)
C6	-0.1118 (2)	0.2498 (9)	-0.1956 (7)	0.034 (1)
C7	-0.1419 (2)	0.159 (1)	-0.3332 (8)	0.042 (1)
C8	-0.1935 (2)	0.158 (1)	-0.3485 (9)	0.054 (2)
C9	-0.2161 (2)	0.249 (1)	-0.224 (1)	0.061 (2)
C10	-0.1866 (2)	0.339 (1)	-0.0876 (8)	0.054 (1)
C11	-0.1346 (2)	0.342 (1)	-0.0691 (7)	0.045 (1)

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

S1—C3	1.654 (5)	C7—C8	1.376 (9)
N2—C3	1.392 (7)	C7—H13	0.9 (1)
N2—C5	1.376 (6)	C8—C9	1.41 (1)
N2—H12	0.86 (8)	C8—H14	0.96 (8)
C3—C4	1.442 (8)	C9—C10	1.37 (1)
C4—C4	1.401 (6)	C9—H15	1.0 (1)
C4—C5	1.405 (8)	C10—C11	1.384 (8)
C5—C6	1.437 (7)	C10—H16	0.9 (1)
C6—C7	1.387 (8)	C11—H17	0.91 (9)
C6—C11	1.423 (9)		
C3—N2—C5	114.6 (5)	C6—C7—C8	120.6 (6)
C3—N2—H12	118. (5)	C6—C7—H13	120. (5)
C5—N2—H12	127. (5)	C8—C7—H13	120. (5)
S1—C3—N2	123.9 (4)	C7—C8—C9	119.8 (6)
S1—C3—C4	133.2 (4)	C7—C8—H14	123. (6)
N2—C3—C4	102.9 (4)	C9—C8—H14	117. (6)
C3—C4—C4	108.5 (4)	C8—C9—C10	119.9 (6)
C3—C4—C5	141.6 (4)	C8—C9—H15	118. (6)
C4—C4—C5	109.6 (4)	C10—C9—H15	122. (6)
N2—C5—C4	104.4 (4)	C9—C10—C11	121.2 (7)
N2—C5—C6	122.4 (5)	C9—C10—H16	116. (6)
C4—C5—C6	133.2 (5)	C11—C10—H16	122. (6)
C5—C6—C7	120.8 (6)	C6—C11—C10	118.8 (5)
C5—C6—C11	119.6 (5)	C6—C11—H17	118. (6)
C7—C6—C11	119.6 (5)	C10—C11—H17	123. (6)

### Comparison with the known crystal structures

Table 3 shows the known crystal structures of DPPT and their crystal data (Mizuguchi, Rochat & Rihs, 1990). Modifications (I) and (II) are very similar, but differ slightly in the following ways: both phenyl rings are twisted out of plane to the heterocyclic ring system by 13.3 (5)° in modification (I), and by only 6 (1)° in modification (II). In the projection along the stacking axis, all the molecules are arranged in parallel in modification (I), and in a zigzag fashion in modification (II). The intermolecular hydrogen-bond parameters of NH...S are: the angle NH...S is 162 (3)°, and the distances between S/H, N/H and N/S are 2.53 (5), 0.94 (5) and 3.435 (3) Å, respectively, in modification (I). The angle NH...S is 150 (4)°, and the distances between S/H, N/H and N/S are 2.59 (5), 0.95 (5) and 3.440 (5) Å, respectively, in modification (II).

The most striking difference between the known modifications [(I) and (II)] and the new modification

(III) is in the molecular stacking. In modifications (I) and (II), the heterocyclic ring system of one molecule overlaps with the phenyl ring of the other located directly above or below. On the other hand, in modification (III), the molecules overlap only at the S—C, C—N, N—C and N—H bonds which form two kinds of stacking columns along the *b* axis. This stacking suggests that the intermolecular interaction between the thiocarbonyl C and N atoms as well as

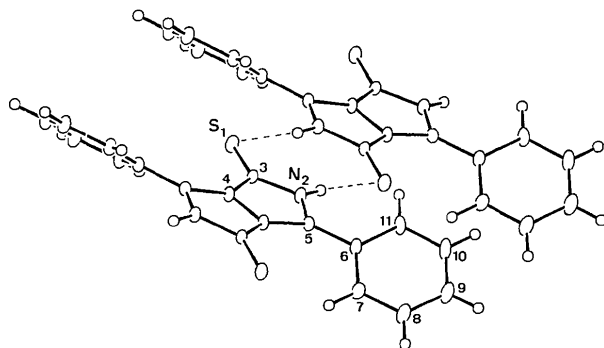


Fig. 1. Conformation and the intermolecular hydrogen bonds of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dithione.

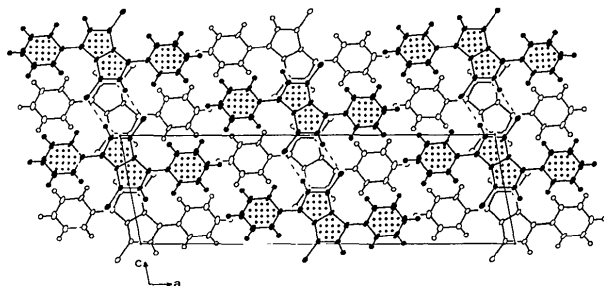


Fig. 2. Projection of the crystal structure on the *ac* plane. The dotted and undotted molecules are located on the plane above and below, respectively.

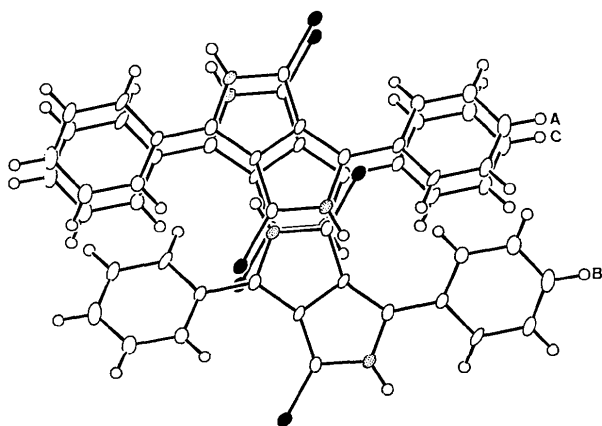


Fig. 3. Overlap of the molecules along the stacking axis.

Table 3. *Crystallographic data for modifications (I) and (II)*

	Modification (I)*	Modification (II)*
Chemical formula		C <sub>18</sub> H <sub>12</sub> N <sub>2</sub> S <sub>2</sub>
Molecular symmetry		C <sub>i</sub>
Formula weight		320.426
Z		2
Space group		P2 <sub>1</sub> /n
<i>a</i> (Å)	7.986 (1)	4.873 (1)
<i>b</i> (Å)	4.757 (1)	18.613 (2)
<i>c</i> (Å)	19.685 (3)	7.995 (1)
β (°)	99.18 (2)	95.76 (2)
<i>V</i> (Å <sup>3</sup> )	738.2 (5)	721.5 (5)
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.441	1.475
<i>D<sub>m</sub></i> (Mg m <sup>-3</sup> )	1.432	1.465

\* Mizuguchi, Rochat & Rihs (1990).

the C atom which connects to the phenyl ring and the S atom is much stronger in modification (III) than in modifications (I) and (II).

The diffraction pattern at  $2\theta = 6.6^\circ$  characterized by the near-IR photoactive phase is given only by modification (III). This diffraction corresponds to (200).

A further difference is seen in the intermolecular hydrogen bond. The distance NH...S is slightly shorter in modification (III) than in modifications (I) and (II). Since the angle NH...S in modification (III) is very close to  $180^\circ$ , the N, H and S atoms are almost aligned. These facts indicate that the hydrogen bond in modification (III) is stronger than in modifications (I) and (II), because the hydrogen-bond-forming power increases as the atoms become closer and are arranged in a linear fashion (Pauling, 1967).

#### Near-IR absorption and photoconduction

The near-IR absorption of the present crystal modification has been confirmed by measurements of the reflection spectra using a microscope spectrophotometer. As pointed out in the previous investigations (Mizuguchi & Rochat, 1988; Mizuguchi & Homma, 1989), the intermolecular charge-transfer transition may be operative for near-IR absorption. The existence of the two types of stacking column along the *b* axis provides strong support for this postulate.

As yet we have not been able to carry out meaningful photoconduction measurements as the single crystals are too small.

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## SHORT-FORMAT PAPERS

*Contributions intended for publication under this heading should follow the format given in the Checklist for Authors [Acta Cryst. (1985). C41, 1–4].*

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### Structures of RbD and CsD by Time-of-Flight Neutron Diffraction

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**Abstract.** Rubidium deuteride, RbD,  $M_r = 87.47$ , cubic,  $Fm\bar{3}m$ ,  $a = 5.9705(2) \text{ \AA}$  (10K),  $a = 6.0210(2) \text{ \AA}$  (300K),  $V = 212.83 \text{ \AA}^3$  (10K),  $V = 218.27(2) \text{ \AA}^3$  (300 K),  $Z = 4$ ,  $D_x = 2.66 \text{ g cm}^{-3}$  (300 K), neutron time-of-flight, Rietveld refinement,  $wR_p$ ,  $R_p$ , reduced  $\chi^2$  are 0.045, 0.031, 3.99 (10K), respectively, and 0.052, 0.037, 2.19 (300 K), respectively. Caesium deuteride, CsD,  $M_r = 134.92$ , cubic,  $Fm\bar{3}m$ ,  $a = 6.3741(3) \text{ \AA}$ ,  $V = 258.97(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 3.46 \text{ g cm}^{-3}$ , 300 K, neutron time-of-flight, Rietveld refinement,  $wR_p$ ,  $R_p$ , reduced  $\chi^2$  are 0.070, 0.048, 1.30, respectively. RbD and CsD were confirmed to have the B1 (rocksalt) structure.

**Experimental.** Rb metal (Alfa 99.9%) was melted into a copper crucible in an argon-filled drybox. The crucible was placed into a copper pipe which was lightly capped. The copper pipe was quickly transferred to an alumina tube fitted with ground-glass ends, evacuated and filled with D<sub>2</sub> (Matheson, 99.7%). The alumina tube was inside a tube furnace, but the copper pipe extended beyond the ends of the furnace. The D<sub>2</sub> was passed through a cold trap and over a boat of P<sub>2</sub>O<sub>5</sub>. The assembly was heated to 763 K under a very slow flow of D<sub>2</sub>. After 3 d, the furnace was cooled, and the copper pipe was quickly transferred to a drybox. Fluffy masses of white needles grew slightly downstream of the copper boat. CsD was prepared in an analogous fashion. The metals

and their hydrides are extremely pyrophoric. X-ray diffraction analysis confirmed the presence of single-phased materials.

Pulsed neutron diffraction data were collected at room temperature on the High Intensity Powder Diffractometer (HIPD) of the Manuel Lujan, Jr, Neutron Scattering Center at Los Alamos National Laboratory. The powder data were refined with use of the General Structure Analysis System (GSAS), a Rietveld profile analysis code which minimizes  $\sum w(I_o - I_c)^2$  (Larson & Von Dreele, 1990).

Data from the highest resolution detector banks ( $\pm 153.43^\circ$ ,  $-90^\circ$ ) were used. Collection times were kept to a minimum (2–4 h); this noisy data resulted in rather high residuals. The quality of the data determined the usable range. For RbD at 10 K and 300 K, 169 reflections in the range  $0.54 < d < 3.2 \text{ \AA}$  and 76 reflections in the range  $0.80 < d < 3.2 \text{ \AA}$  were used, respectively. For CsD, 78 reflections were available in the range  $0.8 < d < 3.3 \text{ \AA}$ .

The only possible structures for an AB compound with a face-centered cubic cell and with  $Z = 4$  are the B1 (rocksalt) (Bragg & Bragg, 1913) and B3 (sphalerite) (Bragg, 1912) ones. The neutron data clearly showed that the former was correct for both compounds.

The scattering lengths used were 7.08, 5.42 and 6.67 fm for Rb, Cs and D, respectively. Since these are all similar, the difference reflections ( $h, k, l$  all odd)