

between TCNE molecules along this axis is 10.23 (1) Å. Electrical conduction measurements along the charge-transfer axis did not lead to an observable value. A resistivity higher than 1.5 GΩ cm<sup>-1</sup> was found.

In (II), each of the two TCNE molecules related by a centre of symmetry is associated with one of the two non-symmetrically equivalent benzene rings of the paracyclophane molecule (*B* in Fig. 3). This leads to a one-dimensional sandwich-type stacking along a face diagonal, *a* + *b* (Fig. 3). The shortest TCNE–TCNE distance along this axis is 14.15 Å. This sandwich arrangement is identical to that observed in [3.3]-paracyclophane–TCNE (Bernstein & Trueblood, 1971). Contrary to this previous study, no disorder of the TCNE molecules was found in the present compounds. Both of them show normal intermolecular distances involving van der Waals interactions. Other structure studies are in progress.

The authors are indebted to Professor J. Lajzéróvicz for having suggested this study and for fruitful discussions. Thanks are due to Professor J. L. Pierre and Dr P. Chautemps for contribution in the synthesis of the compounds, G. d'Assenza for technical assistance and J. Dumas for electrical measurements. This work received financial support from CNRS (ATP 'Chimie Fine', 'Matériaux Originaux').

#### References

BERNSTEIN, J. & TRUEBLOOD, K. N. (1971). *Acta Cryst.* **B27**, 2078–2088.

- BUSING, W. R. & LEVY, H. A. (1962). *ORXFLS3*. Report ORNL-TM-271. Oak Ridge National Laboratory, Tennessee.
- COHEN-ADDAD, C., BARET, P., CHAUTEUPS, P. & PIERRE, J. L. (1983). *Acta Cryst.* **C39**, 1346–1349.
- CRAM, J. & BAUER, H. R. (1959). *J. Am. Chem. Soc.* **81**, 5971–5977.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HOLDER, D. D. & THOMPSON, C. C. (1972). *J. Chem. Soc. Chem. Commun.* pp. 277–279.
- IMASHIRO, F., YOSHIDA, Z. & TABUSHI, I. (1973). *Tetrahedron*, **29**, 3521–3526.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- IRNGARTINGER, H. & GOLDMAN, A. (1979). *Kristallografiya*, **149**, 97.
- KEEHN, P. M. & ROSENFELD, M. S. (1983). *Cyclophanes in Organic Chemistry*, 45–I. New York: Academic Press.
- KURODA, H., AMANO, T., IKEMOTO, I. & AKAMATU, H. (1967). *J. Am. Chem. Soc.* **89**, 6056–6063.
- LJUNGSTRÖM, E., LINDQVIST, O. & WENNERSTRÖM, O. (1978). *Acta Cryst.* **B34**, 1889–1893.
- MOBLEY, M. J., RIECKHOFF, K. E. & VOIGT, E. M. (1977). *J. Phys. Chem.* **81**, 809–810.
- OLSSON, T., TANNER, D., THULIN, B., WENNERSTRÖM, O. & LILJEFORS, T. (1981). *Tetrahedron*, **37**, 3473–3483.
- PIERRE, J. L., BARET, P., CHAUTEUPS, P. & ARMAND, M. (1981). *J. Am. Chem. Soc.* **103**, 2986–2988.
- PROUT, C. K. & KAMENAR, B. (1973). *Molecular Complexes*, edited by R. FOSTER, pp. 4–207. London: Elek Science.
- ROLLETT, J. S. (1965). *Computing Methods in Crystallography*, p. 114. Oxford: Pergamon Press.
- TABUSHI, I., YAMADA, H. & KURODA, Y. (1975). *J. Org. Chem.* **40**, 1946.
- TABUSHI, I., YAMADA, H., YOSHIDA, Z. & ODA, R. (1971). *Tetrahedron*, **27**, 4845–4853.
- THULIN, B., WENNERSTRÖM, O. & HÖGBERG, H. E. (1975). *Acta Chem. Scand. Ser. B*, **29**, 138–139.
- TROUGHTON, P. G. H. (1969). PhD Thesis, Chemical Crystallography Laboratory, Imperial College, London.

*Acta Cryst.* (1984). **C40**, 1931–1934

## Structure of Bis(*o*-chlorophenylaminocarbonylmethyl) Disulphide,\* C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>

BY M. PIERROT,† A. BALDY† AND J. C. MAIRE

*Service de Cristallographie et Laboratoire des Organométalliques, Faculté des Sciences et Techniques de St-Jérôme, Université de Droit, d'Economie et des Sciences d'Aix-Marseille, rue Henri Poincaré, 13397 Marseille CEDEX 13, France*

AND R. C. MEHROTRA, T. S. KAPOOR AND B. P. BACHLAS

*Department of Chemistry, University of Rajasthan, Jaipur 302004, India*

(Received 19 March 1984; accepted 13 July 1984)

**Abstract.** *M<sub>r</sub>* = 401.33, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.394 (5), *b* = 17.84 (1), *c* = 10.576 (5) Å, β = 91.9 (1)°, *V* = 1771 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.5, *D<sub>x</sub>* =

1.495 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71073 Å, μ = 6.0 cm<sup>-1</sup>, *F*(000) = 824, *T* = 293 K. Final *R* = 0.031 for 1403 observed reflections. The molecules adopt a folded conformation with non-parallel phenyl rings and are arranged in columns along the screw axis as a result of intermolecular hydrogen bonds [N–H...O distances of

\* *N,N'*-Bis(*o*-chlorophenyl)-2,2'-dithiodiacetamide.

† Service de Cristallographie.

2.85 (2) and 2.88 (2) Å]. A comparison is made with analogous disulphide compounds. The S—S distance of 2.022 (2) Å indicates partial double-bond character.

**Introduction.** Recently there has been considerable activity in the field of disulphide chemistry. Certain organic disulphides exhibit anti-seizing and anti-friction properties (Meyer, 1977), and disulphide compounds have been intensively studied in order to assess their ligand potentials. In addition to their chemical interest the disulphides are of biological importance insofar as they determine the structure, and therefore the biological activity, of molecules ranging from insulin to ribonuclease (Dickerson & Geis, 1969). Ribonuclease contains four intrachain disulphide linkages, the reduction of which results in total loss of enzymatic activity. The two peptide chains of insulin are held together by disulphide bridges (Adams *et al.*, 1969).

In view of the importance of the disulphide ligand we describe here the crystal and molecular structure of bis(*o*-chlorophenylaminocarbonylmethyl) disulphide.

**Experimental.** Title compound prepared by mild oxidation of *N*-(*o*-chlorophenyl)-2-mercaptoacetamide with 30% (v/v) H<sub>2</sub>O<sub>2</sub> in 70% methanol–water mixture (Maire, Kapoor, Bachlas & Vincent, 1984). Product recrystallized from hot methanol solution to give needle-shaped white crystals, m.p. 413 K. Single crystals grown by slow evaporation of the methanolic solution of the above ligand at room temperature.

Crystal (0.1 × 0.2 × 0.4 mm) mounted on a CAD-4 Enraf–Nonius diffractometer (graphite monochromator for Mo K $\alpha$ ). Unit-cell parameters refined by least squares on 2sin $\theta$ / $\lambda$  values for 25 reflections (15 <  $\theta$  < 20°). Density obtained by flotation. Intensities measured using an  $\omega$ –2 $\theta$  scan of 0.91 to 10.06° min<sup>-1</sup>, range  $\Delta\omega = (0.6 + 0.35 \tan\theta)^\circ$ ,  $\theta_{\max} = 25^\circ$ . Intensities of three standard reflections measured every 5000 s throughout data collection, remained constant within 2%. A total of 1852 independent reflections obtained from which 1403 with  $I > 3\sigma(I)$  used in structure determination:  $h_{\max} = 10$ ,  $k_{\max} = 18$ ,  $l_{\max} = \pm 11$ .

All computations performed on a PDP 11/44 computer (*SDP* software, Frenz, 1978). Structure solved by direct methods (*MULTAN77*, Main, Lesinger, Woolfson, Germain & Declercq, 1977) and completed by difference Fourier methods. Positions of H atoms defined on stereochemical grounds and introduced in the calculation before last refinement cycles. Full-matrix least-squares refinement included anisotropic thermal parameters for non-H atoms and minimized function  $\sum w(|F_o| - |F_c|)^2$ ,  $w = 1/\sigma^2(F_o)$ . Final refinements converged with  $R = 0.031$ ,  $R_w = 0.037$ ,  $S = 1.22$ ;  $(\Delta/\sigma)_{\max} = 0.21$ . A final difference Fourier synthesis did not reveal any peak of density > 0.35 e Å<sup>-3</sup>. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final atomic parameters are given in Table 1,\* bond distances and angles in Table 2.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39638 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Cl(1)	0.4723 (1)	0.2645 (8)	0.7832 (1)	4.64 (3)
Cl(2)	0.0466 (2)	0.7288 (8)	0.6741 (1)	5.16 (3)
S(1)	0.1270 (1)	0.4516 (8)	0.3294 (1)	4.29 (3)
S(2)	0.2433 (2)	0.5219 (8)	0.2243 (1)	4.15 (3)
C(1)	0.2612 (5)	0.4061 (3)	0.4306 (5)	4.1 (1)
C(2)	0.2009 (5)	0.3893 (3)	0.5571 (4)	3.2 (1)
N(1)	0.2977 (3)	0.3841 (2)	0.6533 (3)	3.19 (8)
C(3)	0.2649 (4)	0.3699 (3)	0.7808 (4)	3.0 (1)
C(4)	0.3393 (5)	0.3169 (3)	0.8518 (4)	3.3 (1)
C(5)	0.3077 (6)	0.3031 (3)	0.9760 (5)	4.5 (1)
C(6)	0.1993 (7)	0.3412 (4)	1.0286 (5)	6.0 (2)
C(7)	0.1245 (6)	0.3941 (4)	0.9614 (5)	5.2 (1)
C(8)	0.1564 (5)	0.4092 (3)	0.8375 (5)	4.2 (1)
C(9)	0.2311 (5)	0.6095 (3)	0.3086 (4)	3.4 (1)
C(10)	0.3008 (5)	0.6078 (3)	0.4391 (4)	3.3 (1)
N(2)	0.2122 (4)	0.6171 (2)	0.5339 (3)	3.32 (8)
C(11)	0.2508 (5)	0.6221 (3)	0.6634 (4)	3.3 (1)
C(12)	0.1778 (5)	0.6716 (3)	0.7400 (5)	3.8 (1)
C(13)	0.2113 (6)	0.6773 (4)	0.8665 (5)	5.5 (1)
C(14)	0.3191 (6)	0.6340 (4)	0.9192 (5)	6.4 (2)
C(15)	0.3923 (6)	0.5854 (4)	0.8461 (5)	5.2 (1)
C(16)	0.3594 (5)	0.5786 (3)	0.7179 (5)	4.1 (1)
O(1)	0.0743 (3)	0.3794 (2)	0.5712 (3)	4.77 (9)
O(2)	0.4289 (3)	0.5989 (2)	0.4542 (3)	5.20 (9)

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

S(1)–S(2)	2.022 (2)	S(2)–C(9)	1.804 (5)
S(1)–C(1)	1.817 (5)	C(9)–C(10)	1.508 (6)
C(1)–C(2)	1.500 (6)	C(10)–O(2)	1.219 (5)
C(2)–O(1)	1.216 (5)	C(10)–N(2)	1.335 (5)
C(2)–N(1)	1.345 (5)	N(2)–C(11)	1.408 (5)
N(1)–C(3)	1.416 (5)	C(11)–C(12)	1.394 (6)
C(3)–C(4)	1.383 (6)	C(12)–C(13)	1.368 (7)
C(4)–C(5)	1.378 (6)	C(13)–C(14)	1.377 (9)
C(5)–C(6)	1.359 (6)	C(14)–C(15)	1.363 (9)
C(6)–C(7)	1.363 (9)	C(15)–C(16)	1.386 (7)
C(7)–C(8)	1.380 (7)	C(16)–C(11)	1.390 (6)
C(8)–C(3)	1.389 (6)	Cl(2)–C(12)	1.729 (5)
Cl(1)–C(4)	1.739 (5)		
S(2)–S(1)–C(1)	103.0 (2)	S(1)–S(2)–C(9)	102.8 (2)
S(1)–C(1)–C(2)	109.8 (3)	S(2)–C(9)–C(10)	113.7 (4)
C(1)–C(2)–O(1)	122.6 (4)	C(9)–C(10)–O(2)	121.3 (4)
O(1)–C(2)–N(1)	122.4 (4)	N(2)–C(10)–O(2)	123.7 (4)
C(1)–C(2)–N(1)	115.0 (4)	C(9)–C(10)–N(2)	115.0 (4)
C(2)–N(1)–C(3)	124.7 (4)	C(10)–N(2)–C(11)	126.3 (4)
N(1)–C(3)–C(4)	121.2 (4)	N(2)–C(11)–C(12)	119.3 (4)
N(1)–C(3)–C(8)	120.5 (5)	N(2)–C(11)–C(16)	122.0 (4)
C(3)–C(4)–C(5)	121.2 (5)	C(11)–C(12)–C(13)	120.9 (5)
C(4)–C(5)–C(6)	119.3 (5)	C(12)–C(13)–C(14)	119.8 (6)
C(5)–C(6)–C(7)	120.9 (5)	C(13)–C(14)–C(15)	120.3 (6)
C(6)–C(7)–C(8)	120.4 (5)	C(14)–C(15)–C(16)	120.7 (6)
C(7)–C(8)–C(3)	119.8 (5)	C(11)–C(16)–C(15)	119.6 (5)
C(8)–C(3)–C(4)	118.4 (5)	C(16)–C(11)–C(12)	118.8 (4)
C(3)–C(4)–Cl(1)	119.9 (3)	C(11)–C(12)–Cl(2)	119.9 (4)
Cl(1)–C(4)–C(5)	118.8 (4)	Cl(2)–C(12)–C(13)	119.2 (5)

The most striking feature of the molecular structure is the folded conformation, shown in Fig. 1, which brings the two phenyl rings close to each other. Owing to the bend on both sides of the S—S bond the molecule appears to be asymmetric. In the limits of the experimental errors there is no significant discrepancy between the two halves of the molecule which are almost alike.

Some bond distances and angles found in analogous disulphide compounds are cited in Table 3. The S—S distance of 2.022 (2) Å indicates some partial double-bond character. The low value of the C—S—S angle of the title compound in comparison with  $(C_6H_5)_2S_2$  may be due to the attachment of S atoms to  $sp^3$  C atoms. The two N(1)—C(3) [1.416 (5) Å] and N(2)—C(11) [1.408 (5) Å] bond lengths are different from the C—N value calculated elsewhere (1.51 Å, Kagan, 1979). Both values correspond to a partial double-bond character in the C—N linkage with conjugation between the carbonyl group and the N atom. In both halves of the molecule the dihedral angles between the amide group and the corresponding phenyl ring are slightly different: 48.1 (8)° for the C(1)C(2)O(1)N(1)/C(3)—C(8) angle and 35.7 (8)° for the C(9)C(10)O(2)—N(2)/C(11)—C(16) angle.

We observe that the shorter N—C(O) bond, N(2)—C(10), is related to the more coplanar amide group/phenyl ring. The large values of the valency angles of the N atoms [C(2)—N(1)—C(3) 124.7 (4) and C(10)—N(2)—C(11) 126.3 (4)°] indicate deviation from trigonal N and could be due to the interplay of the electronic repulsion between the phenyl rings and the carbonyl O atoms.

The two phenyl rings are (almost) planar with a maximum deviation from the mean least-squares plane

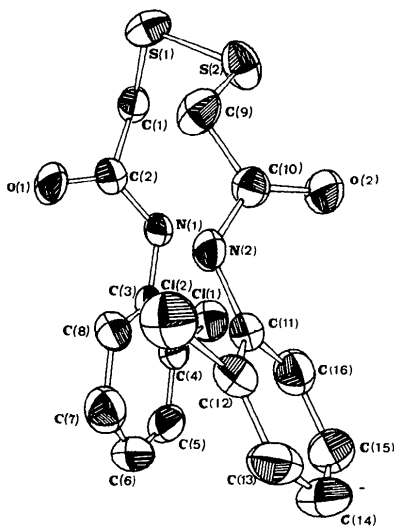


Fig. 1. ORTEP (Johnson, 1976) view of the molecule and labelling system used during the crystallographic study. The thermal parameters are shown as 50% probability envelopes.

of 0.009 (6) Å. The N and Cl atoms are nearly coplanar with the phenyl rings: the distances to the plane of their respective phenyl rings are: 0.014 (5) Å for N(1) and N(2) and 0.062 (4) and 0.065 (4) Å for Cl(1) and Cl(2). The Cl—C distances fall within the normal range for chlorophenyl compounds and the Cl—C—C angles do not indicate any steric hindrance.

Finally the two conjugated systems are not at all parallel. The observed dihedral angle between the two phenyl rings is 151 (1)°. Moreover, as can be seen on Fig. 1, the C(6)—C(3)—N(1) and C(14)—C(11)—N(2) directions are oblique with an angle of 35 (1)° between them.

#### Molecular packing

Two intermolecular hydrogen bonds are observed between the amide N and the carbonyl O (Fig. 2). The

Table 3. Bond distances and angles of analogous disulphides

Compounds	(1)	(2)	(3)	(4)
Bond type (Å)				
S—S	2.030 (5)	2.019 (5)	2.045 (3)	2.022 (2)
S—C	1.79 (1)	1.767 (10)	1.784 (8)	1.804 (5)
	1.81 (1)		1.808 (8)	1.817 (5)
N—C		1.488 (13)	1.476 (13)	1.408 (5)
			1.425 (11)	1.416 (5)
C—C	1.39 (3)	1.38 (3)	1.39 (3)	1.380 (12)
(phenyl rings)				
C—S—S	106.5 (4)	106.0 (6)	104.3 (6)	103.0 (2)
angle (°)	105.8 (4)		104.6 (6)	102.8 (2)

#### Compounds:

- (1) Diphenyl disulphide (Lee & Bryant, 1969).
- (2) Bis(*p*-nitrophenyl) disulphide (Ricci & Bernal, 1969).
- (3) Bis(*o*-nitrophenyl) disulphide (Ricci & Bernal, 1970).
- (4) Bis(*o*-chlorophenylaminocarbonylmethyl) disulphide (this work).

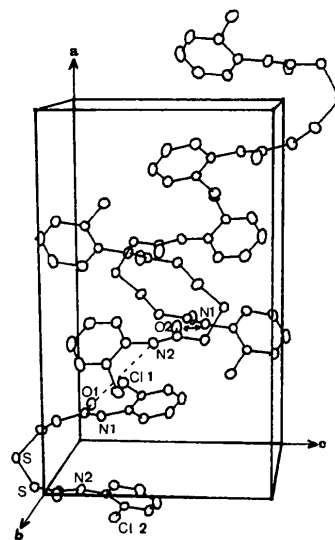


Fig. 2. View of the unit-cell contents down the *b* axis. The hydrogen bonds are indicated by broken lines.

N(1)—O(2) distance is 2.85 (2) Å, whilst the N(2)—O(1) distance is 2.88 (2) Å. In both cases the hydrogen-bond distance is less than 3.0 Å, hence these bonds play an important role in the packing of the molecules in a unit cell. The unit cell consists of four molecules with Cl(1) and Cl(2) as terminal atoms. The molecules are arranged in two pairs held by van der Waals forces of attraction and form columns along the screw axis as a result of the intermolecular hydrogen-bond system.

Thanks are due to Professor K. C. Joshi for providing all necessary laboratory facilities and to Dr G. Shrivastava for academic discussions.

#### References

- ADAMS, M. J., BLUNDELL, T. L., DODSON, E. J., DODSON, G. G., VIJAYAN, M., BAKER, E. N., HARDING, M. M., HODGKIN, D. C., RIMMER, B. & SHEAT, S. (1969). *Nature (London)*, **224**, 491–495.
- DICKERSON, R. E. & GEIS, I. (1969). *The Structure of Proteins*. New York: Harper & Row.
- FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, 64–71. Delft Univ. Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KAGAN, H. (1979). *Organic Stereochemistry*, pp. 28–29. London: Edward Arnold.
- LEE, J. D. & BRYANT, M. W. R. (1969). *Acta Cryst.* **B25**, 2094–2101.
- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MAIRE, J. C., KAPOOR, T. S., BACHLAS, B. P. & VINCENT, E. J. (1984). *Tetrahedron Lett.* In the press.
- MEYER, K. P. (1977). 7th Proc. Int. Congr. Vac. Technol. Vol. 2, pp. 1085–1088.
- RICCI, J. S. & BERNAL, I. (1969). *J. Am. Chem. Soc.* **91**, 4078–4082.
- RICCI, J. S. & BERNAL, I. (1970). *J. Chem. Soc. B*, pp. 806–811.

*Acta Cryst.* (1984). **C40**, 1934–1937

## Structure of the Twofold Addition Product Tetramethyl 6-Diethylamino-3,7a,10,11b-tetrahydro-7H-dipyridazino[4,5-*b*:4',5'-*d*]azepine-1,4,8,11-tetracarboxylate, C<sub>22</sub>H<sub>28</sub>N<sub>6</sub>O<sub>8</sub>

BY MARTIN R. BRYCE

*Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England*

ZBIGNIEW DAUTER\*

*Department of Chemistry, University of York, Heslington, York YO1 5DD, England*

THOMAS KÄMPCHEN

*Pharmazeutische Chemie Institut der Universität Marburg, Marbacher Weg 6, D-3550 Marburg/Lahn, Federal Republic of Germany*

COLIN D. REYNOLDS

*Department of Chemistry, University of York, Heslington, York YO1 5DD, England*

AND GUNTER SEITZ

*Pharmazeutische Chemie Institut der Universität Marburg, Marbacher Weg 6, D-3550 Marburg/Lahn, Federal Republic of Germany*

(Received 10 February 1984; accepted 13 July 1984)

**Abstract.**  $M_r = 504.51$ , triclinic,  $P\bar{1}$ ,  $a = 9.565$  (2),  $b = 13.699$  (3),  $c = 9.463$  (2) Å,  $\alpha = 96.95$  (2),  $\beta = 97.12$  (2),  $\gamma = 97.05$  (2)°,  $V = 1209.34$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.385$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha)$

$= 0.863$  mm<sup>-1</sup>,  $F(000) = 532$ ,  $T = 290$  (1) K,  $R = 0.072$  for 2469 observed reflections. The molecule contains a seven-membered azepine ring which adopts a distorted boat conformation such that the dihedral angle between the best planes through the two dihydropyridazino rings is 88.5° and thus reduces the crowding of the ester groups on these rings.

\* Permanent address: Department of Biochemistry, Technical University of Gdańsk, Gdańsk, Poland.