PEROUTKA, S. J., GREENBERG, D. A., U'PRICHARD, D. C. & SNYDER, S. H. (1978). *Mol. Pharmacol.* **14**, 403–412.

SHELDRICK, G. M. (1975). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

STOLL, A. & HOFMANN, A. (1965). *The Alkaloids*, Vol. 8, edited by R. H. F. MANSKE, pp. 725–783. New York: Academic Press.

TITTLER, M., WEINREICH, P. & SEEMAN, P. (1977). *Proc. Natl Acad. Sci. USA*, **74**, 3750–3753.

U'PRICHARD, D. C., GREENBERG, D. A. & SNYDER, S. H. (1977). *Mol. Pharmacol.* **13**, 454–473.

WILLIAMS, L. T. & LEFKOWITZ, R. J. (1976). *Science*, **192**, 791–793.

WILLIAMS, L. T., MULLIKIN, D. & LEFKOWITZ, R. J. (1976). *J. Biol. Chem.* **251**, 6915–6923.

The Crystal Structure and the Absolute Configuration of a Chiral Vitamin B₆ Analogue, (−)-14-Hydroxy-2,8-dithia[9](2,5)-pyridinophane-15-methanol

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Abstract

The absolute configuration of the title compound, $C_{13}H_{19}NO_2S_2$, was determined through the anomalous-dispersion effect of the sulfur atoms. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 15.642$ (4), $b = 16.360$ (3) and $c = 10.953$ (2) Å, $Z = 8$. There are two independent molecules in the asymmetric unit. Both of them have the planar chirality of the S configuration. The two molecules are connected by an O···N hydrogen bond to make a linear molecular chain.

Introduction

In the course of the study directed towards enzyme models, a series of chiral vitamin B₆ analogues has been prepared and used as a catalyst for the non-enzymatic duplication of the stereospecific reactions catalyzed with vitamin B₆-dependent enzymes (Kuzuhara, Iwata & Emoto, 1977; Kuzuhara, Komatsu & Emoto, 1978). All of these B₆ analogues are 'ansa compounds' with restricted rotations and hence have planar chirality. Correlation of the stereochemistry among enantiomers of each analogue has been established by mutual chemical conversion.

This paper deals with the results of the X-ray analysis of one such analogue, (−)-14-hydroxy-2,8-dithia[9](2,5)-pyridinophane-15-methanol (1), which clarifies the absolute configuration of all of these B₆ analogues.
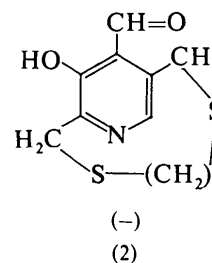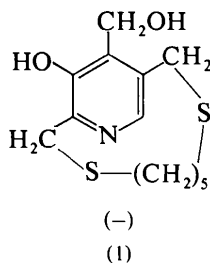
Experimental and structure determination

Compound (1) was first obtained as a by-product in the reductive amination of (2) (Kuzuhara, Komatsu & Emoto, 1978). For the experiment in this paper, however, (1) was prepared by reduction of (2) with sodium borohydride in methanol and purified by ion-exchange chromatography, using Dowex 50 (H form) and aqueous ammonia as eluant. The sample for X-ray analysis was recrystallized from methanol. Colorless needle-shaped crystals were obtained. The crystal data are shown in Table 1. X-ray diffraction data were collected on a Rigaku four-circle automatic diffractometer. The intensity data for the structure determination were taken with graphite-monochromatized Mo $K\alpha$ radiation. The size of the crystal was $0.2 \times 0.3 \times 0.8$ mm. At this stage the anomalous-dispersion effect was ignored, and the intensities were measured within the first octant up to $2\theta = 45°$. The usual Lorentz and polarization corrections were applied and 1813 independent reflections with $|F| > 3\sigma(F)$ were obtained.

Table 1. Crystal data

Formula $C_{13}H_{19}NO_2S_2$
$M_r = 285.4$
Space group $P2_12_12_1$
$a = 15.642\ (4), b = 16.360\ (3), c = 10.953\ (2)$ Å
$U = 2803\ (1)$ Å^3
$Z = 8, D_c = 1.357$ Mg m^{-3}
m.p. 435–445 K
$[\alpha]_D^{19°C} = -215°$ (c, 0.369, ethanol)

Table 2. Atomic parameters

Positional parameters are multiplied by 10^4 for C, N, O, S atoms, and 10^3 for H atoms. The temperature factors (Å^2) B_{eq} (equivalent) and B are given in the last column. The numbering scheme of atoms is shown in Fig. 3.

	x	y	z	B_{eq} or B
S(2)A	−1531 (1)	2922 (1)	2788 (2)	5.6
S(8)A	2603 (1)	2713 (1)	2037 (1)	4.4
O(14)A	−472 (3)	2448 (3)	−368 (4)	5.2
O(16)A	899 (2)	2163 (3)	−1677 (3)	4.9
N(12)A	−1 (3)	4105 (3)	1688 (4)	4.1
C(1)A	−1357 (4)	3421 (4)	1301 (6)	4.9
C(3)A	−938 (4)	1961 (4)	2666 (6)	5.0
C(4)A	−414 (4)	1777 (4)	3775 (6)	5.5
C(5)A	366 (4)	2317 (4)	3963 (6)	5.4
C(6)A	1075 (4)	2168 (4)	2067 (6)	5.4
C(7)A	1836 (4)	2762 (4)	3287 (5)	4.9
C(9)A	2279 (3)	3583 (3)	1065 (5)	3.8
C(10)A	1323 (3)	3591 (3)	888 (5)	3.4
C(11)A	844 (3)	4121 (3)	1597 (5)	3.7
C(13)A	−415 (3)	3528 (4)	1052 (5)	4.1
C(14)A	4 (3)	3000 (3)	235 (5)	4.0
C(15)A	894 (3)	3031 (3)	144 (5)	3.3
C(16)A	1386 (4)	2446 (3)	−659 (5)	3.8
S(2)B	2066 (1)	4478 (1)	7907 (2)	4.6
S(8)B	−2065 (1)	4891 (1)	6870 (2)	6.0
O(14)B	1092 (3)	5045 (3)	4775 (4)	5.3
O(16)B	−249 (3)	5332 (2)	3349 (4)	5.1
N(12)B	505 (3)	3351 (3)	6690 (4)	3.9
C(1)B	1882 (3)	3987 (4)	6414 (5)	4.5
C(3)B	1265 (4)	5283 (3)	7962 (5)	4.4
C(4)B	411 (4)	5031 (4)	8537 (5)	4.4
C(5)B	−295 (4)	5650 (4)	8291 (5)	4.7
C(6)B	−1147 (4)	5451 (4)	8887 (6)	5.7
C(7)B	−1602 (4)	4700 (4)	8397 (6)	5.8
C(9)B	−1733 (4)	3999 (4)	5996 (6)	5.3
C(10)B	−780 (3)	3947 (3)	5887 (5)	3.7
C(11)B	−348 (3)	3362 (3)	6563 (5)	3.8
C(13)B	957 (3)	3929 (3)	6130 (5)	3.7
C(14)B	571 (4)	4493 (3)	5339 (5)	3.9
C(15)B	−318 (3)	4510 (3)	5212 (5)	3.4
C(16)B	−741 (4)	5150 (4)	4418 (6)	5.0
H(1)A	−169 (3)	400 (3)	147 (4)	4.4 (1.2)
H(1')A	−162 (3)	309 (3)	68 (4)	4.2 (1.2)
H(3)A	−132 (3)	153 (3)	247 (5)	5.2 (1.3)
H(3')A	−56 (3)	199 (3)	191 (5)	5.5 (1.3)
H(4)A	−7 (3)	114 (3)	371 (5)	5.4 (1.4)
H(4')A	−78 (4)	169 (4)	447 (5)	8.1 (1.8)
H(5)A	81 (4)	224 (5)	474 (7)	12.7 (1.4)
H(5')A	16 (3)	298 (3)	382 (5)	5.7 (1.9)
H(6)A	129 (4)	157 (4)	320 (6)	9.2 (1.4)
H(6')A	80 (3)	216 (3)	217 (5)	6.2 (1.4)
H(7)A	160 (3)	340 (3)	339 (5)	5.7 (1.2)

Table 2 (cont.)

	x	y	z	B_{eq} or B
H(7')A	213 (3)	269 (3)	395 (4)	4.2 (1.6)
H(9)A	248 (4)	410 (3)	144 (5)	6.8 (1.4)
H(9')A	263 (3)	347 (3)	26 (5)	5.4 (1.1)
H(11)A	111 (3)	457 (3)	191 (4)	3.5 (1.0)
H(16)A	193 (3)	275 (3)	−97 (4)	3.3 (1.5)
H(16')A	158 (3)	196 (3)	−12 (5)	6.2 (1.6)
H(O14)A	−23 (4)	222 (4)	−70 (5)	7.0 (1.1)
H(O16)A	61 (4)	221 (4)	−151 (6)	8.3 (1.2)
H(1)B	214 (3)	349 (3)	657 (4)	3.7 (1.0)
H(1')B	223 (3)	435 (3)	591 (4)	3.9 (1.7)
H(3)B	118 (3)	546 (3)	718 (4)	3.6 (1.3)
H(3')B	150 (4)	589 (4)	833 (6)	7.9 (1.4)
H(4)B	20 (3)	444 (3)	824 (5)	4.8 (1.3)
H(4')B	51 (3)	497 (3)	926 (5)	5.6 (1.3)
H(5)B	−45 (3)	567 (3)	732 (5)	5.3 (1.5)
H(5')B	−8 (3)	627 (3)	845 (5)	4.5 (1.7)
H(6)B	−105 (3)	533 (3)	973 (5)	6.1 (1.4)
H(6')B	−158 (4)	610 (4)	877 (6)	7.6 (1.7)
H(7)B	−119 (3)	406 (3)	838 (5)	5.6 (1.1)
H(7')B	−210 (4)	445 (4)	899 (6)	7.5 (1.4)
H(9)B	−208 (3)	404 (3)	528 (4)	4.0 (1.3)
H(9')B	−191 (3)	354 (3)	633 (5)	5.5 (1.6)
H(11)B	−66 (3)	288 (3)	699 (5)	5.8 (1.8)
H(16)B	−87 (4)	574 (4)	493 (5)	6.7 (2.2)
H(16')B	−133 (4)	494 (4)	418 (5)	7.7 (1.8)
H(O14)B	90 (4)	533 (4)	439 (6)	9.0 (2.3)
H(O16)B	5 (4)	536 (4)	326 (6)	11.0 (2.0)

The structure was solved by *MULTAN* (Main, Woolfson & Germain, 1971), and was refined by the block-diagonal least-squares method. Unit weight was given to all reflections. Hydrogen atom positions were derived from the difference Fourier syntheses, and included in the refinement with isotropic temperature factors. The final R was 3.8%. Atomic parameters are given in Table 2.*

The determination of the absolute configuration

The absolute configuration was determined with Cu $K\alpha$ data. The size of the crystal was $0.1 \times 0.1 \times 0.4$ mm. The linear absorption coefficient was 3.29 mm^{-1}. The anomalous-dispersion terms for Cu $K\alpha$ were taken from *International Tables for X-ray Crystallography* (1974) and were $f'_S = 0.319$, $f''_S = 0.557$, $f'_O = 0.047$ and $f''_O = 0.032$. In this space group the signs of the indices for the Bijvoet pair are divided into two groups, viz $F(+)$ for $(+++, --+, -+-, +--)$, and $F(-)$ for $(---, ++-, +-+, -++)$. The quantity

$$d = |\Delta F_c|/\sigma(F_o)$$

Table 3. *Structure factors*

(a) Examples of the observed structure factors for reflections with significant anomalous-dispersion effects

h k l	+ + +	+ − −	− + −	− − +	− − −	− + +	+ − −	+ + −
1 2 2	35·6	35·5	35·5	34·5	27·9	28·6	28·7	27·8
2 1 5	12·6	12·8	11·9	11·4	9·5	9·6	8·8	9·0
2 7 1	28·2	27·7	28·2	27·9	23·7	23·8	23·2	23·8
4 4 2	18·7	18·9	18·5	18·2	21·0	21·5	21·7	22·6
8 2 2	44·6	45·0	44·1	43·5	39·8	39·6	39·8	39·3
12 3 5	10·5	11·1	11·1	10·2	12·9	13·2	11·7	12·6

(b) Comparison of the observed and calculated structure factors for reflections with significant anomalous-dispersion effects

h k l	mean $|F_o(+)|$	mean $|F_o(-)|$	$|F_c(+)|$	$|F_c(-)|$	ΔF_o	ΔF_c
1 2 2	35·3 (3)	28·3 (2)	38·0	30·8	7·0	7·2
2 1 5	12·2 (3)	9·2 (2)	12·6	9·4	3·0	3·2
2 7 1	28·2 (1)	23·6 (1)	28·9	24·7	4·6	4·2
4 4 2	18·6 (1)	21·5 (1)	19·6	21·9	−2·9	−2·3
8 2 2	44·3 (3)	39·6 (1)	46·0	40·7	4·7	5·3
12 3 5	10·7 (2)	12·6 (3)	10·4	12·5	−1·9	−2·1

(c) Examples of the observed structure factors for reflections with non-significant anomalous-dispersion effects

h k l	+ + +	+ − −	− + −	− − +	− − −	− + +	+ − −	+ + −
1 3 4	39·9	39·0	39·4	39·6	39·0	39·5	39·7	39·6
1 11 2	29·9	29·4	29·4	29·7	29·8	29·7	29·8	30·0
2 4 8	32·1	32·5	31·2	30·4	32·3	31·2	31·4	31·9

(d) Comparison of the observed and calculated structure factors for reflections with non-significant anomalous-dispersion effects

h k l	mean $|F_o(+)|$	mean $|F_o(-)|$	$|F_c(+)|$	$|F_c(-)|$	ΔF_o	ΔF_c
1 3 4	39·5 (2)	39·5 (2)	40·2	40·0	0·	0·2
1 11 2	29·6 (1)	29·8 (1)	28·5	28·6	−0·2	−0·1
2 4 8	31·6 (5)	31·7 (3)	31·4	31·3	−0·1	0·1

(Furusaki, Shirahama & Matsumoto, 1973) was calculated for each pair, where $\sigma(F_o)$ is the standard deviation for the Mo observation, properly scaled, and $\Delta F_c = |F_c(+)| - |F_c(-)|$ for the Cu radiation. Fifty indices with $d > 3$ were selected for the determination of the absolute configuration. As a contrast group, 40 indices with $\Delta F_c < 0.3$ were also selected. For each index, the diffraction intensities were measured for all eight combinations of plus and minus signs. The absorption effect was corrected by the method of North, Phillips & Mathews (1968). Some typical results are shown in Table 3. For the first 50 reflections, the signs of ΔF_c are the same as those calculated from the atomic parameters in Table 2 without exception. The R factor for the difference between the Bijvoet pairs:

$$R_b = \frac{2 \sum |\Delta F_o|}{|F_o(+)| + |F_o(-)|} = 15\%.$$

This value is more than ten times larger than the R factor for the observed and calculated values:

$$R = \frac{2 \sum ||F_o| - |F_c||}{|F_o(+)| + |F_o(-)|} = 1.2\%.$$

In the second group, ΔF_o is approximately zero as shown in Table 3(c, d), which ensures that these data are not biased by any systematic error. Thus it can be concluded without doubt that the parameters in Table 2 represent the correct absolute configuration.

Discussion of the structure

There are two independent molecules in the unit cell. Both of them have the same planar chirality as shown in the stereoscopic drawings (Fig. 1). Viewed down along the normal of the pyridine plane (Fig. 2a), the *ansa* chain is under the plane. The pilot atom is S(2), and the torsion angle about N(12)–C(13)–C(1)–S(2) is about −75°, indicating that the planar chirality of (1) is S. Furthermore, this means that the other related levorotatory B$_6$ analogues (Kuzuhara, Iwata & Emoto, 1977; Kuzuhara, Komatsu & Emoto, 1978) also have the S configuration.

Since the stereospecificity of the non-enzymatic model reactions catalyzed with these B$_6$ analogues is essentially ascribable to the spatial relationship between
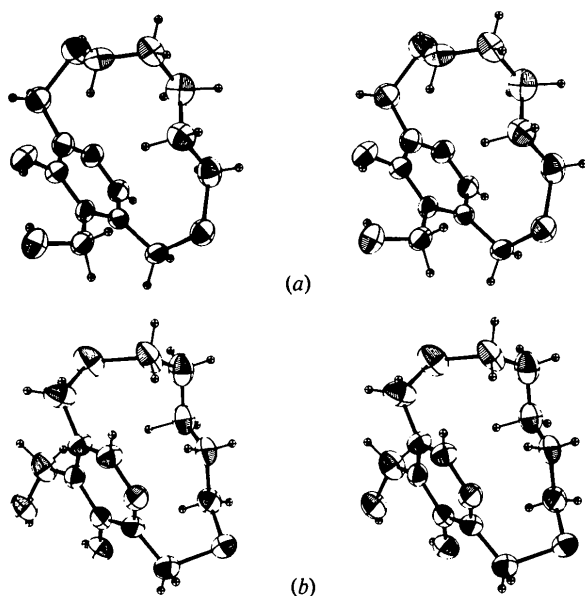
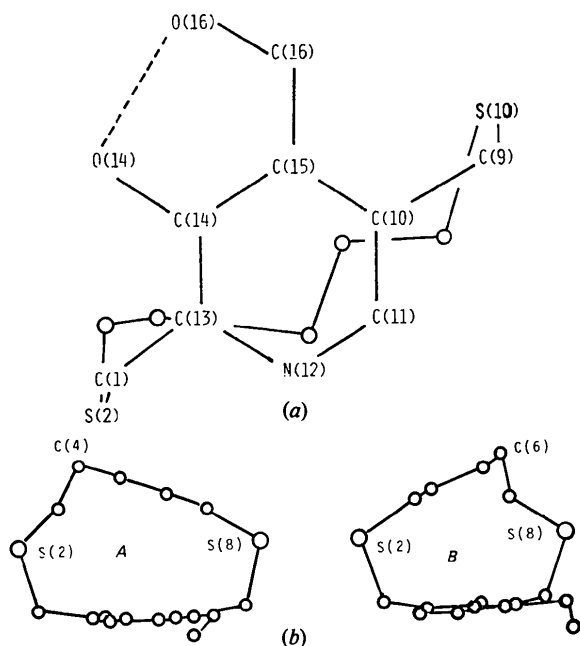Fig. 1. Stereoscopic drawings. (a) Molecule A. (b) Molecule B.

Fig. 2. Schematic view of the molecules. (a) View down along the normal of the pyridine plane. (b) View parallel to the pyridine plane.

Fig. 3. Bond lengths (Å), angles and significant torsion angles (°). Their standard deviations are S—C (0·006), O—C (0·007), N—C (0·007), C—C (0·008 Å); C—S—C (0·3), S—C—C (0·4), O—C—C (0·5), C—N—C (0·5), N—C—C (0·5), C—C—C (0·6); C—S—C—C (0·5), S—C—C—C (0·6), S—C—C—N (0·6), C—C—C—C (0·6°). Since the geometry of the pyridoxine moiety is almost the same for molecules A and B, the averaged parameters are given in (a) and (b). (a) Bond lengths in the pyridoxine moiety. (b) Bond angles in the pyridoxine moiety. (c) Bond lengths in the ansa chain of molecule A. (d) Bond lengths and torsion angles (in parentheses) of molecule A. (e) Bond lengths in the ansa chain of molecule B. (f) Bond angles and torsion angles (in parentheses) of molecule B.

the ansa chain and the functional groups such as the formyl and the hydroxyl groups in the case of (2), the results obtained here will be of great help for analysis of the non-enzymatic reactions.

The bond lengths and angles are shown in Fig. 3. For the pyridoxine moiety, Fig. 3(a,b), the molecular dimensions are almost the same for both A and B
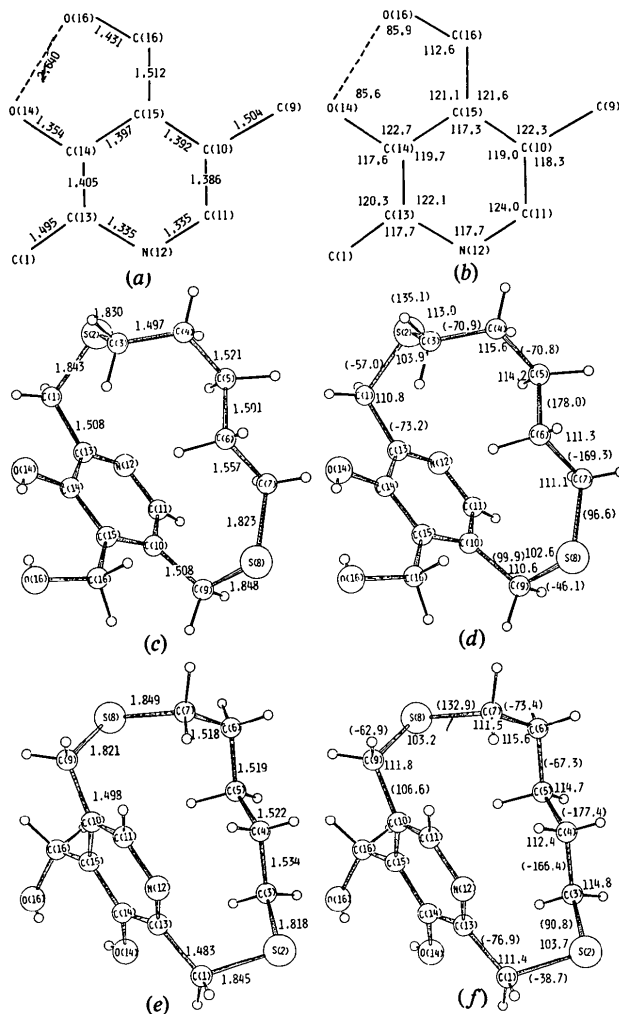
molecules. Compared with various forms of vitamin B_6 derivatives (Cole, Lachmann, Korytnyk, 1972; Fujiwara, 1973; Mangia, Nardelli, Pelizzi, Voltattorni, Orlacchio & Turano, 1975), the bond lengths are essentially the same. The C—N—C bond angle, 117·7°, is considerably smaller than the ca 124° of other compounds. This is due to the absence of an extra-annular hydrogen atom in the present structure, as suggested by Singh (1965).
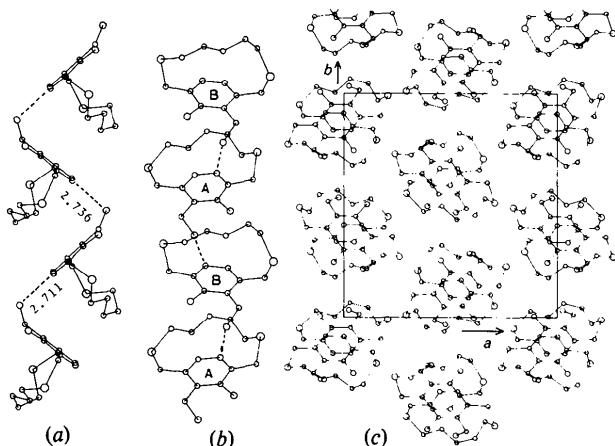
Fig. 4. The molecules in the crystal. (a) The molecular chain projected along a. (b) The molecular chain projected along b. (c) The packing of the molecule in the crystal projected along c.

The two molecules A and B are different in the shape of the ansa chain. For molecule A, the torsion angles C(4)—C(5)—C(6)—C(7), and C(5)—C(6)—C(7)—S(8) are trans, and the atoms from C(4) to S(8) make an approximately linear chain, while for molecule B, the trans conformations appear at C(3)—C(4) and C(4)—C(5), and the atoms from S(2) to C(6) make an approximately linear chain (Fig. 2b). These two conformations of the ansa chain are approximately mirror related to each other, with respect to the plane perpendicular to the pyridine plane, and may have similar conformational energies.

The hydrogen atoms attached to O(14) and O(16) are not well resolved, but judging from the O···O distances (2·622 and 2·658 Å for molecules A and B, respectively), an intramolecular hydrogen bond is assumed to exist between O(14) and O(16). The two molecules are connected by an intermolecular hydrogen bond between O(16) of molecule A and N(2) of molecule B and vice versa, thus forming a long chain of the molecules along the c axis (Fig. 4a,b).

The calculations were performed on the FACOM 230-75 computer of this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979).

References

COLE, F. E., LACHMANN, B. & KORYTNYK, W. (1972). J. Heterocycl. Chem. 9, 1129–1131.
FUJIWARA, T. (1973). Bull. Chem. Soc. Jpn, 46, 863–871.
FURUSAKI, A., SHIRAHAMA, H. & MATSUMOTO, T. (1973). Chem. Lett. pp. 1293–1294.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 149. Birmingham: Kynoch Press.
KUZUHARA, H., IWATA, M. & EMOTO, S. (1977). J. Am. Chem. Soc. 99, 4173–4175.
KUZUHARA, H., KOMATSU, T. & EMOTO, S. (1978). Tetrahedron Lett. pp. 3563–3566.
MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). MULTAN. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
MANGIA, A., NARDELLI, M., PELIZZI, G., VOLTATTORNI, C. B., ORLACCHIO, A. & TURANO, C. (1975). J. Chem. Soc. Perkin Trans. 2, pp. 60–63.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). Acta Cryst. A24, 351–359.
SAKURAI, T. & KOBAYASHI, K. (1979). Rikagaku Kenkyusho Hokoku, 55, 69–77.
SINGH, C. (1965). Acta Cryst. 19, 861–864.

Mixed-Stack Complexes of Tetrathiafulvalene. The Structures of the Charge-Transfer Complexes of TTF with Chloranil and Fluoranil

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Abstract

The structures of the 1:1 charge-transfer complexes of tetrathiafulvalene (TTF) with chloranil and fluoranil have been determined. The two materials are not isomorphous. TTF–chloranil, $C_6H_4S_4.C_6Cl_4O_2$, crystallizes in $P2_1/n$ with $a = 7·411$ (1), $b = 7·621$ (2), $c = 14·571$ (3) Å, $\beta = 99·20$ (1)°, and $Z = 2$. TTF–fluoranil, $C_6H_4S_4.C_6F_4O_2$, crystallizes in $P\bar{1}$ with $a = 7·298$ (2), $b = 7·357$ (3), $c = 7·045$ (2) Å, $\alpha = 93·07$ (1), $\beta = 102·31$ (1), $\gamma = 106·12$ (1)°, and $Z = 1$. In both structures the molecules stack in columns of