SINCLAIR, V. C., ROBERTSON, J. M. & MATHIESON, A. McL. (1950). Acta Cryst. 3, 251–256.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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

TROTTER, J. (1963). Acta Cryst. 16, 605–608.

VERMA, H. K. L. (1969). Indian J. Chem. 7, 346–350.

Optical Induction in Chiral Crystals.
III.* The Crystal and Molecular Structures of the Mixed Crystal of
1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene and 1-(2,6-Dichlorophenyl)-4-(2-thienyl)-*trans,trans*-1,3-butadiene

BY ZIPPORA SHAKKED†

Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel

Abstract

The mixed melt of the title compounds ($C_{16}H_{12}Cl_2 \cdot C_{14}H_{10}Cl_2S$, 2·5:1) crystallizes in space group $P2_12_12_1$ with $a = 9.3303$ (4), $b = 4.0360$ (2), $c = 35.2286$ (6) Å, $Z = 4$. The structure is isomorphous with the pure crystal of the host, $C_{16}H_{12}Cl_2$, and was refined to $R = 0.04$. The absolute configuration of the molecule was determined by anomalous scattering. The thienyl group of the guest shows conformational disorder between the *syn* and *anti* orientations. The correlation between the conformation of the monomer molecules and their mixed dimer formed *via* photoreaction is discussed on the basis of experimental evidence and theoretical calculations.

Introduction

The solid-state photoreactivity of substituted 1,4-diphenylbutadiene molecules stacked along a short (*ca* 4 Å) axis has been discussed in terms of the ground- and excited-state conformations (Rabinovich & Shakked, 1975). The molecular conformation is believed to control the exclusive photodimerization at the double bond adjacent to the unsubstituted phenyl ring and the formation of an optically active hetero-dimer in a mixed crystal of 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (I) with its thiophene analogue (II). Warshel & Shakked (1975) have simulated the process of excimer formation in the photodimerization of these flexible conjugated molecules in the crystal by means of theoretical

methods showing that the crystal forces induce asymmetry in the process of relaxation of an excited monomer into the excimer state thus leading to a preferred direction of excimer formation and subsequent dimerization. The verification of the predicted favorable path of photoreaction may be achieved experimentally by determining the absolute configuration of the starting monomers in the mixed crystal and that of the enantiomorphic heterodimer obtained in excess.

The present work deals with the determination of the absolute configuration of the monomer molecules in the mixed crystal of (I) and (II).

Experimental

A crystal (0·2 × 0·2 × 0·3 mm) was cut from a large crystal grown from the mixed melt of (I) and (II) in approximate molar ratio of 85:15. The crystal was mounted with |010| along the φ axis of an Enraf–Nonius CAD-3 three-circle diffractometer controlled by an IBM 1800 computer. Cell dimensions were determined from high-order reflections measured with Cu $K\alpha$ radiation. Crystal data are listed in Table 1.

Intensities ($\theta < 65°$, one octant of the reciprocal sphere, 1420 reflections measured twice) were collected at room temperature with graphite-monochromated Cu $K\alpha$ radiation. They were measured by an $\omega/2\theta$ scan followed by a background 2θ scan with an ω offset of 0·8° from the reflecting position. The range scanned for each reflection was 1·4° in 2θ plus the calculated α_1–α_2 separation, in steps of 0·01° with counting time of 0·5 and 0·2 s per step for intensity and background respectively. The intensities of four standard reflections

---

Table 1. *Crystal data*

Mixed crystal of 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene and 1-(2,6-dichlorophenyl)-4-(2-thienyl)-*trans,trans*-1,3-butadiene.

$C_{16}H_{12}Cl_2$ (I) and $C_{14}H_{14}Cl_2S$ (II) m.p. 373 K

|	
Orthorhombic, $P2_12_12_1$	$D_x = 1.38$ Mg m^{-3} for $Z = 4$
$a = 9.3303$ (4) Å	$D_m = 1.37$
$b = 4.0360$ (2)	μ(Cu $K\alpha$) = 4.57 mm^{-1}
$c = 35.2286$ (6)	

Fig. 1. Numbering of atoms.

were monitored every 25 reflections. No significant reduction was observed.

The intensities were corrected for absorption, Lorentz and polarization effects taking into account the beam polarization introduced by the graphite monochromator (Miyake, Togawa & Hosoya, 1964). The weighting scheme and assignment of unobserved reflections have been described (Rabinovich & Shakked, 1977).

Structure determination and refinement

Since the mixed crystal is isomorphous with the pure crystal of (I) it is reasonable to assume that the dichlorophenylbutadiene moieties of (I) and (II) are similarly positioned, and the main difference between the structures of the pure and mixed crystals is introduced by the partial replacement of a phenyl by a thienyl group. In order to locate the atomic positions of the thiophene, we have calculated a difference electron density map from the known structure of (I) and the observed structure factors of the mixed crystal. The coefficients (ΔF) used in the Fourier synthesis were: $\Delta F = F_o(\text{mix.}) - 0.85 F_c(\text{I})$.

The calculated structure factors $[F_c(\text{I})]$ based on the parameters of (I) in the pure crystal were given a weight of 0.85 [which equals the approximate fraction of (I) in the mixed melt] in order to obtain the electron density contribution of the guest molecule (II). The phases were derived from the parameters of (I). The difference map showed two relatively high peaks (2.5 and 2.0 e Å^{-3}) corresponding to S atoms in the vicinity of the *ortho* positions of the phenyl ring [C(5) and C(3), Fig. 1]. The existence of two peaks indicates that the thienyl group adopts two conformations (II*a*, II*b*).
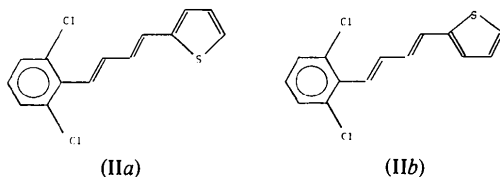
(II*a*)   (II*b*)

The approximate ratio of the three molecules (I), (II*a*), (II*b*), may be calculated from the heights of the peaks in a similar way to that suggested by Kitaigorodskii & Myasnikova (1972). The difference
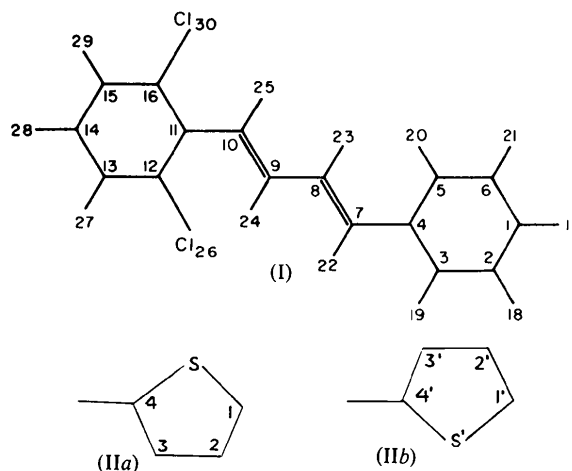
electron density at the *ortho* positions of the phenyl ring is composed of the electron density contributions of (I), (II*a*), and (II*b*) as follows:

$$X_1 Z_C + X_{IIa} Z_S + X_{IIb} Z_C - 0.85 Z_C = 2.5 \quad (1)$$

$$X_1 Z_C + X_{IIb} Z_S + X_{IIa} Z_C - 0.85 Z_C = 2.0 \quad (2)$$

$$X_1 + X_{IIa} + X_{IIb} = 1 \quad (3)$$

where X_1, X_{IIa} and X_{IIb} are weights of (I), (II*a*) and (II*b*) respectively. Z_S (= 16) and Z_C (= 6) are the corresponding atomic numbers of S and C. The first three terms in (1) and (2) represent the electron contribution of the observed structure whereas the last term represents the calculated contribution of 85% of (I).

Solution of the three equations gives: $X_1 = 0.73$, $X_{IIa} = 0.16$, $X_{IIb} = 0.11$.

Thus the occupancy factors of (I), (II*a*), and (II*b*) in the specimen crystal are approximately 0.73, 0.16 and 0.11 respectively. The ratio (73:27) of (I) to (II) in the analyzed crystal is different from the initial composition (85:15) of (I) and (II) used in the preparation of the solid solution, which indicates that the composition of the large mixed crystal is not uniform.

The initial positions of the C atoms of the two thiophene rings were determined from geometrical considerations. The structure was refined by a least-squares procedure with three block diagonals to avoid correlation between closely positioned atoms. The first block included the parameters of the common moiety of the three molecules [C(7) to Cl(30) with the H atoms attached to them] with occupancy factor of 1.0, together with the phenyl ring [C(1) to C(6) and the related H atoms] which was given an occupancy factor of 0.73. The second block included the parameters of the thienyl ring of (II*a*) with occupancy factor of 0.16 and the third block included the thienyl ring of (II*b*)

with occupancy of 0·11. The atoms of the first block were refined anisotropically for Cl and C atoms and isotropically for H atoms. The S atoms of the two blocks were refined anisotropically whereas the C atoms of the thiophenes were refined isotropically. The H atoms attached to these C atoms were inserted in chemically reasonable positions and were not refined. At this stage $R = \sum |kF_o - |F_c||/\sum kF_o = 0·050$, $r = \sum w(k^2 F_o^2 - |F_c|^2)^2/\sum wk^4 F_o^4 = 0·015$.

The number of refined parameters and the number of observations included in the last cycle were 261 and 1388 respectively. Next, two possible enantiomorphic structures (related by the inversion operation) were refined with anomalous-dispersion corrections for Cl and S. For the two structures $R = 0·055, 0·045$; $r = 0·018, 0·012$.

Use of Hamilton's R test (Hamilton, 1965) indicates that this difference is highly significant and the choice of handedness implied by the parameters of Table 2 with a right-handed coordinate system is correct.

To obtain a better estimate of the occupancy factors and to allow for the possibility of a non-overlap of the identical molecular moieties of (I), (IIa) and (IIb), the structure was refined further in the following way. The three molecules were refined in three separate block diagonals, starting from the parameters of the correct enantiomorphic structure. The atoms of (I) were refined anisotropically for C and Cl and isotropically for H. The atoms of (IIa) and (IIb) were refined anisotropically for S and Cl and isotropically for C whereas the H atoms were kept fixed. Several models differing in the occupancy factors of the three molecules were tested by the refinement procedure. The scan of the occupancy factors was carried out in steps of 0·01, ranging from 0·70 to 0·75 for (I), keeping the sum of the three occupancy values equal to 1·0. The following occupancy values, 0·72, 0·17 and 0·11 for (I), (IIa) and (IIb) respectively, yielded the lowest agreement factors and the most reasonable bond lengths and thermal parameters. For this model $R = 0·042$, $r = 0·011$. The number of refined parameters (s) and the number of reflections (n) included in the last cycle of refinement were 377 and 1388 respectively. The use of Hamilton's test for comparing this model $(R = 0·042, s = 377)$ with the previous model $(R = 0·045, s = 261)$ indicates that the decrease in the R factor is significant.

The calculated residual electron density based on this structure shows no anomalous features. Scattering factors and anomalous-dispersion parameters were taken from *International Tables for X-ray Crystallography* (1974).*

Table 2. *Fractional coordinates with e.s.d.'s in parentheses*

	$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^5)$
C(1)	−2196 (5)	−3466 (15)	8945 (13)
C(2)	−982 (5)	−5195 (15)	7774 (12)
C(3)	−810 (5)	−6054 (13)	4009 (12)
C(4)	−1842 (4)	−5113 (12)	1325 (11)
C(5)	−3037 (5)	−3407 (14)	2616 (13)
C(6)	−3227 (5)	−2634 (16)	6322 (13)
C(7)	−1589 (5)	−6107 (13)	−2585 (12)
C(8)	−2283 (5)	−5023 (13)	−5682 (11)
C(9)	−1976 (5)	−6316 (13)	−9438 (12)
C(10)	−2622 (5)	−5290 (15)	−12604 (12)
C(11)	−2416 (5)	−6658 (14)	−16424 (11)
C(12)	−1102 (5)	−7688 (15)	−17957 (12)
C(13)	−968 (7)	−9044 (17)	−21527 (14)
C(14)	−2175 (7)	−9415 (17)	−23787 (14)
C(15)	−3477 (7)	−8356 (20)	−22476 (13)
C(16)	−3598 (5)	−7031 (16)	−18877 (12)
Cl(26)	492 (1)	−7115 (5)	−15487 (4)
Cl(30)	−5287 (1)	−5804 (5)	−17387 (4)

	$x (\times 10^3)$	$y (\times 10^3)$	$z (\times 10^4)$
H(17)	−239 (5)	−319 (15)	1182 (14)
H(18)	−34 (6)	−572 (15)	975 (16)
H(19)	−21 (5)	−726 (15)	341 (14)
H(20)	−372 (5)	−282 (13)	70 (11)
H(21)	−398 (6)	−144 (17)	710 (15)
H(22)	−84 (5)	−773 (15)	−300 (13)
H(23)	−303 (5)	−326 (14)	−548 (12)
H(24)	−124 (5)	−816 (15)	−945 (13)
H(25)	−323 (5)	−343 (15)	−1233 (14)
H(27)	−9 (7)	−976 (20)	−2248 (17)
H(28)	−212 (6)	−1035 (16)	−2627 (17)
H(29)	−438 (6)	−827 (18)	−2401 (17)

The thienyl ring parameters of (IIa) and (IIb)

	$x (\times 10^4)$	$y (\times 10^4)$	$z (\times 10^5)$
S	−3271 (5)	−2990 (14)	2643 (12)
S'	−831 (9)	−5858 (26)	4952 (21)

	$x (\times 10^3)$	$y (\times 10^3)$	$z (\times 10^4)$
C(1)	−296 (2)	−259 (5)	694 (5)
C(2)	−170 (2)	−409 (5)	821 (4)
C(3)	−86 (2)	−577 (5)	503 (5)
C(4)	−182 (2)	−510 (5)	140 (5)
C(1')	−153 (4)	−515 (9)	842 (8)
C(2')	−276 (3)	−322 (8)	748 (7)
C(3')	−308 (3)	−276 (8)	270 (8)
C(4')	−180 (3)	−512 (7)	146 (7)

Results

The numbering of the atoms of (I) and the thiophene ring of (II) are shown in Fig. 1. The final fractional coordinates of (I) and the parameters of the thiophene atoms of (IIa) and (IIb) are listed in Table 2. The other parameters of (IIa) and (IIb) are not given since they are equal (within the corresponding e.s.d.'s) to that of (I). The absolute configuration of the analyzed crystal is opposite to that of the pure crystal (Rabinovich & Shakked, 1975). The bond lengths, bond angles and
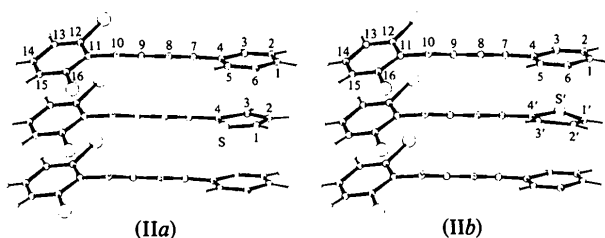
Fig. 2. A guest molecule (IIa) or (IIb) with its nearest host molecules (I) along b shown edge-on along the butadiene plane.

torsion angles of (I) are given in Table 3. The shortest S · · · C contacts between guest and host molecules along the 4 Å axis are given in Table 4. Fig. 2 shows each conformation of the guest [(IIa) and (IIb)] interleaved between the two nearest neighbors of the host (I) along the short axis, viewed edge-on along the butadiene plane.

Discussion

Molecular geometry

The geometry of (I) in the mixed crystal is nearly identical to that in the pure crystal (Rabinovich & Shakked, 1975). The difference between equivalent bond lengths in the two structures is $<3\sigma$. Any discussion of the geometry of the thiophene rings is rather meaningless because of the inaccurate determination of their positional parameters resulting from their low concentration in the crystal.

The expected orientation of the thiophene ring with respect to the rest of the molecule is that where C(4)—S is nearly synplanar with the adjacent C(7)—C(8) double bond (a), since the other possible orientation where C(4)—S is antiplanar to the double bond (b) results in a close 1 · · · 6 interaction of H atoms (scheme 1).

(a)   (b)
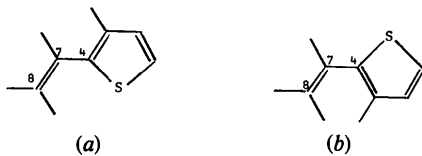
Although thienyl derivatives often exhibit conformational disorder (e.g. Visser, Heeres, Wolters & Vos, 1968; Hazel, Hazel & Pawley, 1977) form (a) has been found to be the only conformation in all 2-thienylvinyl derivatives determined so far, namely γ- and β-trans-β-2-thienylacrylic acid (Block, Filippakis & Schmidt, 1967), 1,2-di-2-thienylethylene (Ruban & Zobel, 1975) and 1,4-bis(2-thienylvinyl)benzene (Zobel, 1976). The existence of both forms in the present structure results probably from the twist about the single C(4)—C(7) bond. The twist about this bond in (I), (IIa) and (IIb) is

Table 3. Bond lengths (Å) bond angles and torsion angles (°) with their e.s.d.'s

C(1)—C(2)	1·393 (7)	C(1)—H(17)	1·03 (5)
C(2)—C(3)	1·381 (6)	C(2)—H(18)	0·94 (6)
C(3)—C(4)	1·402 (6)	C(3)—H(19)	0·77 (5)
C(4)—C(5)	1·388 (6)	C(5)—H(20)	0·96 (4)
C(5)—C(6)	1·355 (7)	C(6)—H(21)	0·89 (6)
C(6)—C(1)	1·376 (7)	C(7)—H(22)	0·97 (5)
C(4)—C(7)	1·454 (6)	C(8)—H(23)	1·00 (5)
C(7)—C(8)	1·342 (6)	C(9)—H(24)	1·01 (6)
C(8)—C(9)	1·451 (6)	C(10)—H(25)	0·95 (6)
C(9)—C(10)	1·333 (6)	C(13)—H(27)	0·94 (6)
C(10)—C(11)	1·467 (6)	C(14)—H(28)	0·95 (6)
C(11)—C(12)	1·403 (7)	C(15)—H(29)	1·00 (6)
C(12)—C(13)	1·377 (7)		
C(13)—C(14)	1·387 (9)		
C(14)—C(15)	1·368 (9)		
C(15)—C(16)	1·381 (7)		
C(16)—C(11)	1·409 (7)		
C(12)—Cl(26)	1·739 (5)		
C(16)—Cl(30)	1·733 (5)		

C(1)—C(2)—C(3)	120·3 (4)	H(17)—C(1)—C(2)	119 (3)
C(2)—C(3)—C(4)	120·0 (4)	H(17)—C(1)—C(6)	121 (3)
C(3)—C(4)—C(5)	117·7 (4)	H(18)—C(2)—C(1)	114 (4)
C(4)—C(5)—C(6)	122·4 (4)	H(18)—C(2)—C(3)	125 (4)
C(5)—C(6)—C(1)	120·0 (5)	H(19)—C(3)—C(2)	120 (4)
C(6)—C(1)—C(2)	119·5 (4)	H(19)—C(3)—C(4)	119 (4)
C(3)—C(4)—C(7)	116·9 (4)	H(20)—C(5)—C(4)	115 (3)
C(5)—C(4)—C(7)	125·3 (4)	H(20)—C(5)—C(6)	122 (3)
C(4)—C(7)—C(8)	127·0 (4)	H(21)—C(6)—C(5)	121 (3)
C(7)—C(8)—C(9)	122·0 (4)	H(21)—C(6)—C(1)	118 (3)
C(8)—C(9)—C(10)	124·2 (5)	H(22)—C(7)—C(4)	117 (3)
C(9)—C(10)—C(11)	126·2 (5)	H(22)—C(7)—C(8)	116 (3)
C(10)—C(11)—C(12)	125·4 (4)	H(23)—C(8)—C(7)	121 (2)
C(10)—C(11)—C(16)	120·0 (4)	H(23)—C(8)—C(9)	117 (2)
C(11)—C(12)—C(13)	123·3 (5)	H(24)—C(9)—C(8)	114 (3)
C(12)—C(13)—C(14)	119·6 (5)	H(24)—C(9)—C(10)	122 (3)
C(13)—C(14)—C(15)	119·6 (5)	H(25)—C(10)—C(9)	116 (3)
C(14)—C(15)—C(16)	120·2 (5)	H(25)—C(10)—C(11)	118 (3)
C(15)—C(16)—C(11)	122·7 (5)	H(27)—C(13)—C(12)	122 (4)
C(16)—C(11)—C(12)	114·6 (4)	H(27)—C(13)—C(14)	118 (4)
C(11)—C(12)—Cl(26)	121·0 (3)	H(28)—C(14)—C(13)	121 (3)
C(13)—C(12)—Cl(26)	115·6 (4)	H(28)—C(14)—C(15)	119 (3)
C(11)—C(16)—Cl(30)	119·7 (3)	H(29)—C(15)—C(14)	125 (4)
C(15)—C(16)—Cl(30)	117·6 (4)	H(29)—C(15)—C(16)	114 (4)

C(5)—C(4)—C(7)—C(8)	14·5 (8)
C(4)—C(7)—C(8)—C(9)	−177·2 (5)
C(7)—C(8)—C(9)—C(10)	−179·0 (5)
C(8)—C(9)—C(10)—C(11)	−175·9 (5)
C(9)—C(10)—C(11)—C(12)	−39·5 (8)
C(9)—C(10)—C(11)—C(16)	140·3 (6)
C(10)—C(11)—C(12)—Cl(16)	−5·2 (8)
C(10)—C(11)—C(16)—Cl(30)	1·0 (7)

Table 4. Intermolecular S · · · C contacts (Å) between adjacent guest and host molecules along b

The second atom in each pair (belonging to I) is related to the equivalent atom in Table 2 by the corresponding translation along b.

(IIa)	(I)			(IIb)	(I)		
S · · · C(4)	0 1 0	3·47		S · · · C(6)	0 −1 0	3·57	
S · · · C(3)	0 1 0	3·65		S · · · C(1)	0 −1 0	3·61	
S · · · C(7)	0 1 0	3·68		S · · · C(5)	0 −1 0	3·77	
S · · · C(5)	0 1 0	3·88		S · · · C(2)	0 −1 0	3·90	

similar (14, 14 and 13° respectively) due to packing requirements and results from crystal forces (Rabinovich & Shakked, 1975). The partial relaxation of the 1···6 interaction in (IIb) caused by this twist decreases the energy difference between (IIa) and (IIb). Nevertheless, (IIb) is still less favorable than (IIa) as reflected by its lower population in the crystal.

The accurate determination of the distribution of different conformations of guest molecules may provide information on intra- and intermolecular forces. A similar approach concerning positional distribution rather than conformational distribution was suggested by Kitaigorodskii & Myasnikova (1972). They proposed that the study of impurity molecules distributed between equivalent positions could provide information concerning intermolecular interactions, since the distribution will not be equally probable if the interaction of each substituting molecule with the surrounding molecules is different. This approach was applied in structural and theoretical studies on mixed crystals of tolane (Samarskaya, Myasnikova & Kitaigorodskii, 1969) and stilbene (Frank, Myasnikova & Kitaigorodskii, 1971) with a small quantity of diphenylmercury. Despite the low accuracy of the structure determination it was possible to show that replacement of the host molecules (tolane or stilbene) by diphenylmercury molecules occurred preferentially in one of the two symmetry-independent layers of molecules.

Although in our case the distribution of the thienyl conformations seems to result mainly from intramolecular forces, one should also consider the interactions of the thienyl molecule with its environment since these are different for (IIa) and (IIb) as reflected by the intermolecular S···C contacts along the b axis (Table 4). For estimating intermolecular forces it is desirable to have a very dilute solid solution so that the assumption of infinitely dilute solution is valid (Kitaigorodskii & Myasnikova, 1972). However, the lower the concentration of the guest in the crystal, the less accurate is its analysis by X-ray methods. In cases where the concentration of the guest is relatively large one should consider the possibility of short-range ordered regions of the guest (Flack, 1970; Glazer, 1970).

Photoreactivity

The interactions which mainly determine the course of photodimerization are those of the excited molecule with the nearest neighbors above and below it along the 4 Å axis. Although the ground-state geometry leads to different molecular contacts between the guest molecule and the host molecules above and below it in the 4 Å stack (Fig. 2), these differences seem to be insufficient to explain the formation of a large excess of one of the two enantiomorphic heterodimers. However, these differences may be enhanced as a result of the selective

excitation of the guest, thus leading to a preferred direction of excimer formation between the guest and adjacent host molecule and their subsequent dimerization. We have predicted the favorable path of photoreaction in this crystalline system by means of theoretical calculations (Warshel & Shakked, 1975) with the pure crystal of (I) as a model for the ground-state geometry. According to the theoretical analysis the interaction of the excited molecule with its upper ground-state neighbor (0,1,0) is more probable than that with its lower ground-state neighbor (0,−1,0) along b. In order to apply these results to the real two-component system of (I) and (II) one should consider the fact that the chirality of the mixed crystal is opposite to that of the pure crystal. The molecules of Fig. 2 are related to the molecules of Fig. 3 in Warshel & Shakked (1975) by a pseudo-mirror plane parallel to the butadiene plane. Therefore, the excited guest molecule (II) in the analyzed crystal is expected to interact preferentially with the bottom ground-state host molecule (I) of Fig. 2. Since dimerization occurs at C(7)—C(8) and the adjacent C(7)—C(4) and C(8)—C(9) bonds in Fig. 2 are pointing upwards and downwards respectively, the cyclobutane obtained in excess should possess the absolute configuration denoted by (2) in scheme 2.
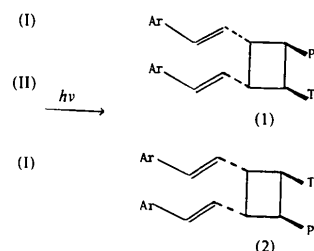
Ph = phenyl, Th = 2-thienyl, Ar = 2,6-dichlorophenyl

The experimental verification of the preferred path of photodimerization will be achieved by comparing the absolute configuration of the monomer molecules in the analyzed mixed crystal with that of the dominant enantiomorphic dimer obtained *via* photoreaction of the same specimen crystal. Such verification may provide a powerful tool for the critical examination of theoretical methods.

References

BLOCK, S., FILIPPAKIS, S. F. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. B*, pp. 233–238.

FLACK, H. D. (1970). *Phil. Trans. R. Soc. London Ser. A*, 266, 583–591.

FRANK, G. W., MYASNIKOVA, R. M. & KITAIGORODSKII, A. I. (1971). *Sov. Phys. Crystallogr.* 16, 270–274.

GLAZER, A. M. (1970). *Phil. Trans. R. Soc. London Ser. A*, 266, 593–622.

HAMILTON, W. C. (1965). *Acta Cryst.* 18, 502–510.

HAZEL, A. C., HAZEL, R. G. & PAWLEY, G. S. (1977). *Acta Cryst.* B33, 1105–1108.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KITAIGORODSKII, A. I. & MYASNIKOVA, R. M. (1972). *Sov. Phys. Crystallogr.* **16**, 1096–1100.

MIYAKE, S., TOGAWA, S. & HOSOYA, S. (1964). *Acta Cryst.* **17**, 1083–1085.

RABINOVICH, D. & SHAKKED, Z. (1975). *Acta Cryst.* **B31**, 819–825.

RABINOVICH, D. & SHAKKED, Z. (1977). *Acta Cryst.* **B33**, 809–815.

RUBAN, G. & ZOBEL, D. (1975). *Acta Cryst.* **B31**, 2632–2634.

SAMARSKAYA, V. D., MYASNIKOVA, R. M. & KITAIGORODSKII, A. I. (1969). *Sov. Phys. Crystallogr.* **13**, 525–529.

VISSER, G. J., HEERES, G. J., WOLTERS, J. & VOS, A. (1968). *Acta Cryst.* **B24**, 467–473.

WARSHEL, A. & SHAKKED, Z. (1975). *J. Am. Chem. Soc.* **97**, 5679–5684.

ZOBEL, D. (1976). *Acta Cryst.* **B32**, 2838–2841.

Crystal Structure of a Methanol Solvate of 3,3'-Diethyl-9-phenylthiacarbocyanine Iodide, a Photographic Sensitizing Dye

BY KENJI NAKAO, KAZUTO YAKENO, HIROSHI YOSHIOKA AND KAZUMI NAKATSU*

Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 622, Japan

Abstract

The crystal structure of the title compound, $(C_{27}H_{25}N_2S_2)^+I^-.xCH_3OH$, $x \simeq 0.5$, a spectral sensitizing dye in silver halide photography, has been determined by X-ray analysis. The compound crystallizes in the monoclinic space group $C2/c$, with eight formula units in a cell of dimensions: $a = 19.766$ (3), $b = 11.112$ (2), $c = 25.296$ (4) Å, and $\beta = 110.47$ (1)°. The structure was refined by block-diagonal least-squares calculations to a conventional R of 0.051 for 3301 observed [$|F_o| > 3\sigma(F)$] reflexions collected on an automatic diffractometer. The dye cation has approximate m symmetry: the methine chain assumes an extended all-*trans* form, the S atoms are *cis* about the chain, and the phenyl-ring plane is almost perpendicular to the conjugate system. In the crystals the cations are stacked in columns, the mean perpendicular separations between them being alternately 4.10 and 3.66 Å with the respective slip angle of about 90 and 25°. The columns aggregate to form a herring-bone-like pattern. The I⁻ ions occupy special positions having the site symmetries of 1 and 2. The disordered methanol molecules partially fill vacancies in the crystal structure.

Introduction

Thiacarbocyanines are useful spectral sensitizing dyes in silver halide photography. Various derivatives have been examined for practical use. A bulky *meso*-(or 9-) substituent in a thiacarbocyanine dye causes a large steric influence on its conformation, and hence on its spectral sensitization (review articles: Sturmer & Heseltine, 1977; Herz, 1977). As a part of our studies on the spectral sensitizing dyes by means of X-ray crystallography, the present study has been undertaken to elucidate the influence of a *meso*-phenyl substituent on the molecular structure and the stacking of dyes in the crystals.
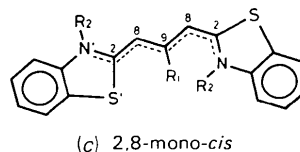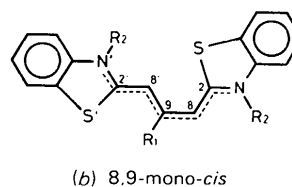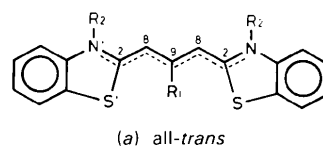

(a) all-*trans*

(b) 8,9-mono-*cis*

(c) 2,8-mono-*cis*

Fig. 1. Possible configurations of thiacarbocyanine dye. R_1: alkyl or phenyl, R_2: alkyl.

---

* To whom all correspondence should be addressed.