Me(C13)···H(C16-α): the inner bond angles of atoms C(15), C(16), C(17) and C(18) [116·6 (3), 117·5 (3), 112·0 (3) and 115·0 (2)°] and the endocyclic torsion angles of the C(16)—C(17) and C(17)—C(18) bonds [−42·9 (3) and 5·9 (3)°] deviate widely from the respective normal values. Ring *E*, in contrast, closely approximates a regular boat form.

The conformations of the *D* and *E* rings of (3) are boat–boat as in triterpenes having a similar *D–E* ring skeleton, *e.g.* epifriedelinol (Laing, Burke-Laing, Bartho & Weeks, 1977), and not chair–chair as found in campanulin (Mo, 1977). Because of the conformational dependency of the ^{13}C chemical shifts (Dalling & Grant, 1972), the ^{13}C NMR spectral data of (2) and (3) indicate that their *D–E* ring conformations in $CHCl_3$ solution are different from one another, and, assuming that the conformation of (3) in the crystalline state is retained in solution, the *D–E* ring of (2) probably takes, not the boat–boat form, but another one, such as the chair–chair form in solution.

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Photochromic and Thermochromic Compounds. I. Structures of (*E*) and (*Z*) Isomers of 2-Isopropylidene-3-[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]succinic Anhydride, $C_{20}H_{18}O_3S$, and the Photoproduct 7,7a-Dihydro-4,7,7,7a-tetramethyl-2-phenylbenzo[*b*]thiophene-5,6-dicarboxylic Anhydride (*P*), $C_{20}H_{18}O_3S$

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Abstract. $M_r = 338{\cdot}42$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, room temperature. (*Z*): monoclinic, $P2_1$, $a = 14{\cdot}449\ (7)$, $b = 7{\cdot}619\ (4)$, $c = 8{\cdot}014\ (4)$ Å, $\beta = 94{\cdot}83\ (2)°$, $U = 879{\cdot}10$ Å^3, $Z = 2$, $D_x = 1{\cdot}278$ g cm^{-3}, $\mu = 1{\cdot}88$ cm^{-1}, $F(000) = 356$, $R = 0{\cdot}063$, 1156 reflections. (*E*): monoclinic, $P2_1$, $a = 14{\cdot}295\ (7)$, $b = 7{\cdot}620\ (4)$, $c = 8{\cdot}317\ (4)$ Å, $\beta = 104{\cdot}21\ (2)°$, $U = 878{\cdot}23$ Å^3, $Z = 2$, $D_x = 1{\cdot}279$ g cm^{-3}, $\mu = 1{\cdot}89$ cm^{-1}, $F(000) = 356$, $R = 0{\cdot}048$, 1500 reflections. (*P*): monoclinic, $P2_1/n$, $a = 16{\cdot}604\ (8)$, $b = 7{\cdot}490\ (4)$, $c = 14{\cdot}113\ (7)$ Å, $\beta = 106{\cdot}59\ (2)°$, $U = 1682{\cdot}08$ Å^3, $Z = 4$, $D_x = 1{\cdot}336$ g cm^{-3}, $\mu = 1{\cdot}97$cm^{-1}, $F(000) = 712$, $R = 0{\cdot}073$, 1810 reflections. The (*E*) and (*Z*) isomers crystallize in the monoclinic chiral space group $P2_1$. The pale-violet (*E*) isomer undergoes reversible photochemical reaction to yield (*P*) which crystallizes in the monoclinic achiral space group $P2_1/n$.

Introduction. Among the many classes of photochromic compounds the fulgides, first discovered and studied by Stobbe & Eckert (1905) and Stobbe (1911), are important for their relative stability. Although the first compounds of the fulgide system showed reversible photochemical properties they were unstable during repeated irradiation. Reinvestigation of the properties of some of those compounds (Heller & Szewczyk, 1974; Darcy, Hart & Heller, 1978) showed that thermal H shifts are involved in the process after the cyclization takes place, and therefore the reversibility of the process is halted during repeated irradiation. Efforts were made to improve the properties of the fulgide system in order to obtain thermally stable photochemically fatigue-resistant photochromic compounds (Darcy, Heller, Strydom & Whitall 1981; Heller & Oliver, 1981; Heller & Langan, 1981).

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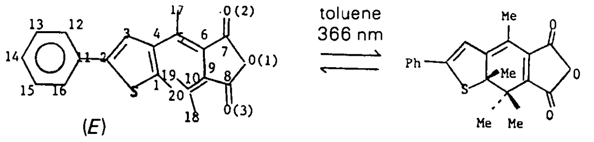
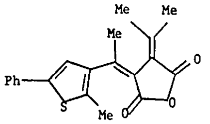
The title compound (Heller, 1984, private communication) was found to have the qualities stated above and may be used as a convenient chemical actinometer. In a study of the possible existence of compounds which show photochromic properties in the solid state in general and may undergo reversible colour change in single crystals in particular, the crystal structure of the title compounds have been elucidated by X-ray diffraction methods.



(E) (P)



(Z)

Experimental. Intensities from single crystals of deep-red (*P*) compound, pale-violet (*E*) isomer and pale-yellow (*Z*) isomer. Philips PW 1100 four-circle computer-controlled diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Densities not measured. No absorption corrections. Three standard reflections (for each compound) every 120 min: intensity variation lower than ±2%. Crystallographic data and details of intensity measurements are given in Table 1.

Structures solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Least-squares refinement (according to *F*) by means of *SHELX* (Sheldrick, 1976), using anisotropic parameters for non-hydrogen atoms, isotropic for H atoms. As the intensity data of the (*Z*) isomer were poor the refinement of the H atoms was carried out applying geometrical constraints. Scattering factors for S, O, and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Final agreement factors and weighting schemes are given in Table 1.

Discussion. Final positional parameters are listed in Tables 2, 3 and 4.* Bond lengths and angles are compared in Tables 5 and 6. The C—H distances (not given in the tables) are as follows: 0·84–1·10 Å in (*P*); 0·85–1·15 Å in (*E*); 0·82–1·10 Å in (*Z*). Stereoscopic drawings of the packing of the various molecules are given in Figs. 1–3.

Table 1. *Crystallographic and experimental details*

	(*P*)	(*E*)	(*Z*)
Crystal shape	Prism	Prism	Prism
Crystal size (mm)	0·4 × 0·4 × 0·3	0·3 × 0·3 × 0·2	0·2 × 0·1 × 0·1
Reflections for measuring lattice parameters	24	25	25
$\Delta\omega$(°)	1·3	1·3	1·0
Scan time (s)	26·0	26·0	40·0
Background time (s)*	20·0	20·0	20·0
θ_{max} (°)	23·0	24·0	22·0
Reflections measured	1810	1500	1156
Significant $[F_o > 1\cdot5\sigma(F_o)]$	1458	1324	1134†
Weighting coefficients (*k*; *g*)‡	1·0610: 0·0063	0·9128: 0·0010	0·3704: 0·0018
R_w	0·078	0·048	0·059
R	0·073	0·048	0·063
$(\Delta/\sigma)_{max}$	0·7	0·5	0·8
$\Delta\rho_{max}$ (e Å^{-3})	0·5	0·2	0·2
$\Delta\rho_{min}$ (e Å^{-3})	–0·3	–0·3	–0·2

* Total background counting time.
† Significant reflections used as $F_o > 0\cdot0$.
‡ $w = k[\sigma^2(F_o) + gF_o^2]$.

Table 2. (*P*): *positional parameters* (×10⁴) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\,\text{trace}\,\tilde{\mathbf{U}}.$$

	x	*y*	*z*	U_{eq}(Å^2)
S(1)	1937 (1)	2004 (2)	1316 (1)	52 (1)
O(1)	1347 (3)	1345 (7)	−3362 (3)	76 (3)
O(2)	22 (4)	2366 (9)	−3694 (3)	85 (3)
O(3)	2627 (3)	273 (8)	−2548 (3)	91 (4)
C(1)	1693 (3)	2462 (7)	−26 (4)	41 (3)
C(2)	887 (4)	2419 (7)	1300 (4)	39 (3)
C(3)	361 (3)	2627 (7)	383 (4)	41 (3)
C(4)	741 (3)	2437 (7)	−408 (4)	36 (3)
C(5)	334 (4)	2363 (8)	−1379 (4)	46 (3)
C(6)	882 (4)	1933 (8)	−1994 (4)	46 (3)
C(7)	651 (5)	1963 (10)	−3098 (5)	65 (4)
C(8)	1985 (4)	922 (10)	−2503 (4)	67 (4)
C(9)	1681 (4)	1414 (7)	−1649 (4)	50 (3)
C(10)	2122 (3)	1101 (7)	−565 (4)	44 (3)
C(11)	656 (4)	2452 (8)	2233 (4)	42 (3)
C(12)	1209 (4)	1941 (9)	3128 (4)	58 (3)
C(13)	960 (4)	1927 (12)	3991 (5)	71 (4)
C(14)	172 (4)	2489 (11)	3974 (4)	68 (4)
C(15)	−386 (4)	3008 (11)	3094 (5)	66 (4)
C(16)	−135 (4)	3012 (10)	2233 (4)	56 (3)
C(17)	−594 (4)	2526 (11)	−1818 (5)	54 (3)
C(18)	3076 (4)	1398 (12)	−309 (5)	65 (4)
C(19)	1935 (5)	−816 (8)	−342 (5)	57 (4)
C(20)	1979 (4)	4402 (9)	−118 (5)	55 (4)

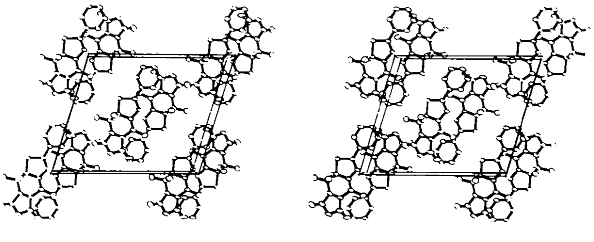


Fig. 1. Packing of molecules of (*P*) in the unit cell.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39193 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. (*E*): *positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\,\mathrm{trace}\,\tilde{\mathbf{U}}.$

	x	y	z	U_{eq}(Å^2)
S(1)	1581 (1)	1764	3113 (2)	533 (7)
O(1)	4699 (3)	−1381 (9)	−1133 (7)	995 (39)
O(2)	3471 (4)	−1062 (9)	−3335 (6)	1041 (41)
O(3)	5668 (3)	−1690 (12)	1399 (8)	1242 (52)
C(1)	2353 (4)	1281 (7)	1895 (6)	435 (29)
C(2)	641 (4)	565 (8)	1909 (6)	467 (29)
C(3)	925 (4)	−147 (8)	606 (7)	470 (30)
C(4)	1902 (3)	240 (7)	596 (5)	392 (26)
C(5)	2338 (4)	−362 (8)	−754 (6)	485 (31)
C(6)	3213 (4)	−1108 (8)	−510 (7)	572 (34)
C(7)	3733 (5)	−1176 (10)	−1872 (9)	779 (46)
C(8)	4868 (4)	−1580 (12)	580 (10)	854 (54)
C(9)	3919 (4)	−1679 (8)	1006 (7)	556 (34)
C(10)	3805 (4)	−2455 (9)	2379 (7)	562 (34)
C(11)	−283 (4)	415 (8)	2363 (7)	527 (32)
C(12)	−1102 (4)	−174 (9)	1222 (8)	642 (39)
C(13)	−1980 (5)	−293 (11)	1690 (11)	801 (50)
C(14)	−2039 (5)	140 (11)	3256 (10)	784 (48)
C(15)	−1232 (6)	710 (13)	4384 (10)	904 (54)
C(16)	−360 (5)	876 (11)	3936 (8)	714 (44)
C(17)	1720 (6)	14 (14)	−2448 (8)	712 (53)
C(18)	4630 (6)	−3021 (17)	3793 (11)	890 (67)
C(19)	2833 (5)	−2900 (10)	2672 (8)	626 (42)
C(20)	3360 (5)	1998 (13)	2329 (11)	648 (45)

Table 4. (*Z*): *positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\,\mathrm{trace}\,\tilde{\mathbf{U}}.$

	x	y	z	U_{eq}(Å^2)
S(1)	3830 (2)	0	−3246 (3)	86 (1)
O(1)	956 (4)	5305 (10)	−925 (9)	95 (4)
O(2)	1805 (4)	3872 (13)	−2681 (9)	116 (5)
O(3)	276 (5)	6263 (12)	1244 (11)	126 (6)
C(1)	2993 (5)	558 (13)	−1948 (9)	73 (5)
C(2)	4636 (4)	1424 (11)	−2281 (10)	62 (4)
C(3)	4259 (5)	2262 (12)	−971 (11)	67 (5)
C(4)	3305 (4)	1775 (11)	−784 (9)	53 (4)
C(5)	2774 (4)	2387 (11)	560 (8)	55 (4)
C(6)	1914 (5)	3144 (11)	285 (9)	59 (5)
C(7)	1591 (6)	3991 (15)	−1285 (13)	82 (6)
C(8)	768 (6)	5184 (15)	723 (14)	83 (6)
C(9)	1245 (4)	3671 (11)	1476 (10)	58 (4)
C(10)	946 (5)	2763 (13)	2738 (9)	61 (4)
C(11)	5557 (6)	1532 (12)	−2873 (12)	76 (5)
C(12)	5724 (7)	871 (15)	−4455 (13)	95 (7)
C(13)	6631 (9)	919 (18)	−4950 (18)	115 (9)
C(14)	7328 (9)	1530 (18)	−3964 (25)	124 (11)
C(15)	7187 (7)	2170 (16)	−2419 (29)	109 (11)
C(16)	6298 (7)	2166 (14)	−1869 (18)	91 (8)
C(17)	3220 (7)	2143 (15)	2282 (12)	66 (6)
C(18)	237 (7)	3391 (20)	3859 (12)	95 (7)
C(19)	1251 (6)	951 (14)	3169 (10)	80 (5)
C(20)	2067 (8)	−386 (19)	−2154 (13)	102 (8)

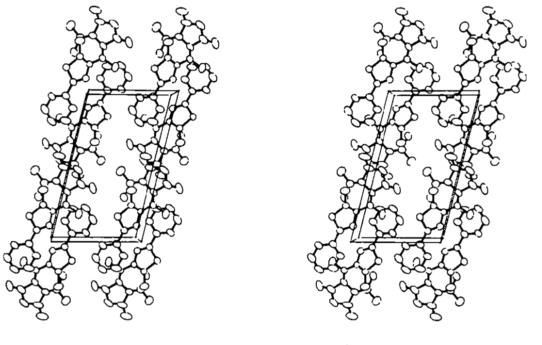

Fig. 2. Packing of molecules of (*E*) in the unit cell.

Table 5. *Comparison of bond lengths* (Å) *in* (*P*), (*E*) *and* (*Z*)

	(*P*)	(*E*)	(*Z*)
S(1)–C(1)	1·853 (5)	1·712 (5)	1·713 (8)
S(1)–C(2)	1·764 (6)	1·727 (5)	1·726 (7)
O(1)–C(7)	1·391 (9)	1·376 (7)	1·40 (1)
O(1)–C(8)	1·399 (6)	1·39 (1)	1·37 (1)
O(2)–C(7)	1·178 (8)	1·185 (8)	1·19 (1)
O(3)–C(8)	1·190 (9)	1·182 (7)	1·19 (1)
C(1)–C(14)	1·518 (7)	1·368 (6)	1·36 (1)
C(1)–C(10)	1·560 (8)		
C(1)–C(20)	1·545 (8)	1·499 (8)	1·52 (1)
C(2)–C(3)	1·348 (6)	1·359 (8)	1·38 (1)
C(2)–C(11)	1·475 (8)	1·465 (8)	1·45 (1)
C(3)–C(4)	1·437 (8)	1·430 (7)	1·448 (9)
C(4)–C(5)	1·345 (7)	1·484 (7)	1·451 (9)
C(5)–C(6)	1·461 (9)	1·343 (7)	1·370 (9)
C(5)–C(17)	1·494 (8)	1·496 (8)	1·48 (1)
C(6)–C(7)	1·496 (8)	1·50 (1)	1·46 (1)
C(6)–C(9)	1·333 (7)	1·474 (7)	1·47 (1)
C(8)–C(9)	1·479 (9)	1·486 (9)	1·45 (1)
C(9)–C(10)	1·514 (6)	1·331 (9)	1·33 (1)
C(10)–C(18)	1·537 (8)	1·509 (9)	1·50 (1)
C(10)–C(19)	1·521 (8)	1·507 (9)	1·48 (1)
C(11)–C(12)	1·387 (7)	1·388 (7)	1·40 (1)
C(11)–C(16)	1·379 (8)	1·384 (9)	1·37 (1)
C(12)–C(13)	1·393 (9)	1·41 (1)	1·40 (1)
C(13)–C(14)	1·37 (1)	1·37 (1)	1·31 (1)
C(14)–C(15)	1·376 (8)	1·37 (1)	1·36 (2)
C(15)–C(16)	1·393 (9)	1·39 (1)	1·39 (1)

Table 6. *Comparison of bond angles* (°) *in* (*P*), (*E*) *and* (*Z*)

	(*P*)	(*E*)	(*Z*)
C(1)–S(1)–C(2)	91·6 (2)	93·8 (2)	93·2 (3)
C(7)–O(1)–C(8)	109·0 (4)	111·8 (5)	109·6 (7)
S(1)–C(1)–C(4)	105·2 (3)	110·2 (3)	112·0 (5)
S(1)–C(1)–C(10)	112·4 (3)		
S(1)–C(1)–C(20)	106·1 (4)	120·0 (4)	118·5 (6)
C(4)–C(1)–C(10)	113·2 (4)		
C(4)–C(1)–C(20)	107·2 (4)	129·8 (4)	129·3 (7)
C(10)–C(1)–C(20)	112·3 (4)		
S(1)–C(2)–C(3)	113·6 (3)	109·4 (3)	109·7 (5)
S(1)–C(2)–C(11)	120·0 (4)	120·9 (4)	119·4 (6)
C(3)–C(2)–C(11)	126·4 (5)	129·7 (5)	130·8 (7)
C(2)–C(3)–C(4)	115·2 (5)	113·9 (5)	113·6 (7)
C(1)–C(4)–C(3)	111·5 (5)	112·8 (4)	111·4 (6)
C(1)–C(4)–C(5)	122·1 (4)	124·9 (4)	124·2 (6)
C(3)–C(4)–C(5)	126·3 (5)	122·2 (4)	124·2 (6)
C(4)–C(5)–C(6)	113·5 (5)	124·4 (5)	123·0 (6)
C(4)–C(5)–C(17)	125·3 (4)	113·1 (5)	115·7 (6)
C(6)–C(5)–C(17)	121·0 (5)	122·4 (5)	121·3 (6)
C(5)–C(6)–C(7)	126·7 (6)	121·1 (5)	123·1 (6)
C(5)–C(6)–C(9)	124·8 (5)	132·1 (4)	130·3 (6)
C(7)–C(6)–C(9)	108·5 (5)	105·9 (5)	105·0 (6)
O(1)–C(7)–O(2)	122·0 (6)	119·8 (6)	118·3 (9)
O(1)–C(7)–C(6)	106·7 (6)	107·2 (6)	107·8 (7)
O(2)–C(7)–C(6)	131·3 (6)	133·0 (6)	133·6 (9)
O(1)–C(8)–O(3)	121·0 (5)	119·8 (6)	118 (1)
O(1)–C(8)–C(9)	107·4 (5)	108·0 (6)	109·2 (8)
O(3)–C(8)–C(9)	131·6 (6)	132·1 (7)	133 (1)
C(6)–C(9)–C(8)	108·1 (5)	104·8 (5)	105·2 (6)
C(6)–C(9)–C(10)	123·9 (4)	131·5 (5)	128·7 (7)
C(8)–C(9)–C(10)	127·2 (5)	122·5 (6)	124·0 (7)
C(1)–C(10)–C(9)	103·6 (4)		
C(1)–C(10)–C(18)	112·0 (5)		
C(1)–C(10)–C(19)	111·5 (4)		
C(9)–C(10)–C(18)	112·6 (4)	124·0 (5)	125·0 (9)
C(9)–C(10)–C(19)	106·7 (5)	123·4 (6)	123·6 (7)
C(18)–C(10)–C(19)	110·2 (5)	112·6 (5)	111·3 (8)
C(2)–C(11)–C(12)	122·4 (5)	120·7 (4)	120·4 (8)
C(2)–C(11)–C(16)	119·7 (5)	120·7 (5)	121·3 (9)
C(12)–C(11)–C(16)	117·9 (5)	118·6 (5)	118·1 (8)
C(11)–C(12)–C(13)	120·9 (6)	119·5 (6)	119 (1)
C(12)–C(13)–C(14)	120·2 (7)	121·1 (7)	122 (1)
C(13)–C(14)–C(15)	119·9 (5)	119·5 (6)	121 (1)
C(14)–C(15)–C(16)	119·7 (6)	120·3 (7)	120 (1)
C(11)–C(16)–C(15)	121·4 (6)	120·9 (7)	121 (1)

Molecular geometry

The estimated standard deviations of bond lengths and angles in the three structures are large and it would be of no significance to account for small variations in bond lengths and bond angles; however, some comments should be made: S—C bond lengths are dramatically shorter in the thiophene ring in (*E*) and (*Z*) (1·712, 1·727, 1·713, 1·726 Å) than the bonds in the thieno ring in (*P*) which are 1·853 and 1·764 Å. These differences are ascribed to the delocalization of these bonds in a thiophene ring compared with the localized bonds in the thieno ring. The differences between the bond lengths in the thieno ring are expected since an S—C(sp^3) single bond would be longer than an S—C(sp^2) single bond.

The diene system in both (*E*) and (*Z*) isomers is severely skewed (Ottersen, Jelinski, Kiefer & Seff, 1974). The torsion angles C(5)—C(6)—C(9)—C(10) are 39 (1) and −48 (1)° in (*E*) and (*Z*) respectively. Pasto & Scheidt (1975) have found a torsion angle of 52·3° in a slightly more overcrowded diene system. The inner torsion angles C(7)—C(6)—C(9)—C(8) are much small [15 (0) and −18 (1)° for (*E*) and (*Z*) respectively] due to the strained succinic anhydride moiety.

Other distortions, mainly in bond angles, arise from severe steric interactions between the two methyl groups C(17) and C(19) in (*Z*). The non-bonded distances are 3·058 and 3·125 Å respectively. These steric interactions are reflected also in the opening of the bond angles C(5)—C(6)—C(9) [132·1 and 130·3° for (*E*) and (*Z*)], C(6)—C(9)—C(10) [131·5 and 128·7° for (*E*) and (*Z*)]. As a result of the distortions discussed above, particularly the opening of the angles at the diene, there is a non-bonded interaction between the methyl group C(18) and the O atom of the neighbouring carbonyl group [2·94 (1) and 3·03 (1) Å in (*E*) and (*Z*)]; to accommodate this interaction there is a twist around the double bond leading to the torsion angle C(8)—C(9)—C(10)—C(18) of 12 (1) and −17 (1)° in (*E*) and (*Z*) respectively. The out-of-plane bending coordinates (Winkler & Dunitz, 1971) are C(9) = 14·5, −18·8° and C(10) = 1·5, −2·7° in (*E*) and (*Z*) respectively. The twisting coordinates of the double bond are therefore 8·0 and −10·8°.

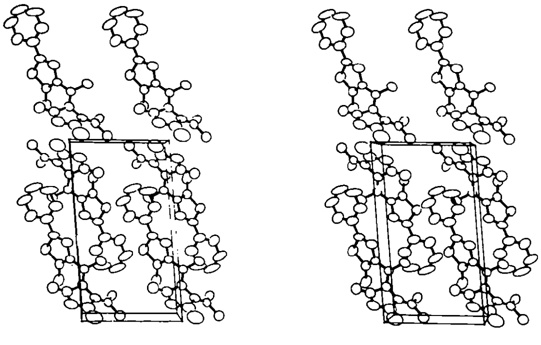

Fig. 3. Packing of molecules of (*Z*) in the unit cell.

Molecular conformation and packing

The two isomers, (*E*) and (*Z*), differ in the relative position of the ethylidene group compared with the methyl group at the isopropylidene moiety [C(17)]. In isomer (*E*) the ethylidene is *trans*, in (*Z*) it is *cis* to that methyl group. The torsion angles C(9)—C(6)—C(5)—C(17) are −176 (1) and −7 (1)° respectively.

Only the (*E*) isomer can undergo conrotatory photocyclization to give the (*P*) form. The conrotatory cyclization occurs by rotation of the two parts of the molecules of (*E*) around the C(4)—C(5) single bond. The torsion angle around this bond in the (*E*) isomer is 50 (1)° [C(1)—C(4)—C(5)—C(6)] while in the (*P*) form it is 12 (1)°. The distance between the reacting centres in (*E*), C(1)···C(10), is 3·9 (1) Å. In all three compounds the phenyl ring is not coplanar with the thiophene ring and is rotated by 11 (1), 16 (1), 17 (1)° in (*P*), (*E*) and (*Z*), respectively, to avoid close contacts between H atoms at the thiophene ring and the *ortho* position of the phenyl ring.

It was noticed that the colour of a single crystal of the pale-violet (*E*) isomer was changed upon irradiation (sunlight) and the external shape of the crystal was not damaged. Moreover, there is a remarkably close resemblance between the unit-cell dimensions of the (*E*) isomer and its irradiated product (*P*) isomer. The *a* and *b* axes of (*E*) differ by less than 0·2 Å from the *c* and *b* axes of (*P*); the *a* axis of (*P*) is twice the *c* axis of (*E*) and the *β* angle differs by *ca* 2°. These observations might suggest that there is a single-crystal (*E*) to (*P*) transformation upon irradiation. However, careful examination of the packing of molecules in the unit cells of both forms shows that such a transformation cannot take place. The unit cell in (*E*) consists of molecules of one chirality which have their longest molecular axis along the unit cell's longest axis ($a = 14 \cdot 295$ Å). Different sheets along the *b* axis are related by a twofold screw axis.

The packing arrangement in (*P*) is very similar; however, the sheets along the *b* axis are related by an inversion centre, hence the molecules are not of the same chirality. Molecular-model inspection shows that there is severe steric hindrance to a rotation around the C(4)—C(5) bond. As a result, molecules of (*E*) of a given chirality can undergo cyclization to molecules of (*P*) of the same chirality. Therefore a transformation of a single crystal of (*E*), which consists of molecules of the same chirality, to a single crystal of (*P*), which consists of a racemic mixture, cannot occur.

The conclusions are therefore that a solution of (*E*) isomer consists of a racemic mixture which undergoes spontaneous resolution upon crystallization. The (*P*) form which was obtained by irradiation of a solution of (*E*) tends to crystallize as a racemic mixture. The observed change in colour of a single crystal of (*E*) can be explained as a surface effect. Molecules at the surface may undergo cyclization to the (*P*) form resulting from the changes observed. This assumption will be further investigated.

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Structure de la Benzoyl-6 Dihydro-2,3 Benzoxazole-1,3 One-2, $C_{14}H_9NO_3$

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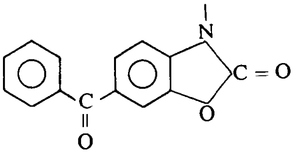
Abstract. $M_r = 239\cdot2$, monoclinic, $P2_1/c$, $a = 8\cdot853\ (3)$, $b = 14\cdot944\ (5)$, $c = 11\cdot223\ (4)$ Å, $\beta = 131\cdot1\ (3)°$, $V = 1119$ Å^3, $Z = 4$, $D_x = 1\cdot42$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0\cdot7107$ Å, $\mu = 1\cdot1$ cm^{-1}, $F(000) = 496$, $T = 298$ K, $R = 0\cdot046$, $R_w = 0\cdot056$ for 2153 observed reflexions. This molecule is an original one with analgesic properties. The bond lengths and angles are normal and the planar benzoxazolone moiety forms a dihedral angle of 54 (1)° with the benzene plane. The molecules form pairs connected by hydrogen bonds between nitrogen and the oxygen of the cyclic ketone.

Introduction. La benzoyl-6 dihydro-2,3 benzoazole-1,3 one-2 est une molécule originale obtenue par acylation directe du noyau aromatique de la dihydro-2,3 benzoxazolone-2 (Lespagnol, Lesieur & Bonte, 1973).



Les études pharmacologiques ont mis en évidence des propriétés analgésiques remarquables associées à une faible toxicité (Bonte, Lesieur, Lespagnol, Plat, Cazin & Cazin, 1974) et justifiant des essais cliniques actuellement en cours. La structure de ce produit ne s'apparentant à aucune des familles de médicaments analgésiques utilisés en thérapeutique, l'étude de sa structure cristalline a été entreprise dans le but de déterminer ses caractéristiques stériques et sa conformation spatiale.

Partie expérimentale. Monocristaux en forme de parallélépipède (~ 0,4 × 0,4 × 0,3 mm) préparés par évaporation d'une solution dans l'éthanol absolu; paramètres de maille obtenus à partir de 25 réflexions; diffractomètre 4 cercles Philips PW 1100, radiation Mo $K\bar{\alpha}$, monochromateur en graphite, 3579 réflexions telles que $2 \leq \theta \leq 30°$, $-12 \leq h \leq 0$, $0 \leq k \leq 20$, $-12 \leq l \leq 12$, dont 2153 indépendantes avec $I > 3\sigma(I)$, 3 réflexions de référence ($\bar{2}12$, $01\bar{2}$, $2\bar{3}\bar{3}$); corrections de Lorentz–polarisation, pas de corrections d'absorption; méthodes directes, *MULTAN* (Germain, Main & Woolfson, 1970), affinement par moindres carrés avec

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