

Dimers lie on planes almost parallel to (100) and their packing is regulated by normal van der Waals contacts.

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Structure of [1,4]Benzothiazino[3,2-*i*]phenothiazine, C₁₈H₁₀N₂S₂

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Abstract. $M_r = 318.2$, monoclinic, $P2_1/c$, $a = 10.472$ (2), $b = 5.430$ (3), $c = 12.356$ (10) Å, $\beta = 107.6$ (1)°, $V = 669.7$ (8) Å³, $Z = 2$, $D_x = 1.56$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54178$ Å, $\mu = 33.99$ cm⁻¹, $F(000) = 328$, $T = 293$ K, final $R = 0.071$ for 669 reflections. The molecule has C_i symmetry and is quasiplanar. The central benzene ring of the molecule has a quinonoid structure with unequal C–C bond lengths. The molecules are arranged in the unit cell in alternately parallel layers, with the planes of neighbouring layers almost perpendicular.

Introduction. Triphenodithiazine ([1,4]benzothiazino[3,2-*i*]phenothiazine), TPDT, was obtained by reaction of *N,N'*-diphenyl-1,4-phenylenediamine and sulphur (Garbarczyk & Żuk, 1979). In comparison with the analogous phenothiazine, TPDT in the solid phase has exceptional properties, such as paramagnetism detected by EPR, relatively high melting point (594 K) and low solubility in organic solvents. The X-ray structure determination of this compound was undertaken as part of our studies to explain the above properties and particularly to explain the role of TPDT in the polymorphic transition of isotactic polypropylene (Garbarczyk & Paukszta, 1981).

Experimental. Gold-violet thin plate-shaped crystals obtained by sublimation, because crystallization from various solvents did not yield samples suitable for X-ray analysis. Space group and preliminary cell parameters determined on basis of rotation and Weissenberg photographs and refined by least squares from 14 reflections (with $13 < 2\theta < 27^\circ$) measured on a Syntex $P2_1$ diffractometer. Intensities of reflections collected up to $2\theta = 114^\circ$, θ – 2θ scan technique,

graphite-monochromatized $Cu K\alpha$ radiation. Crystal $0.01 \times 0.10 \times 0.70$ mm. 887 independent reflections, 669 having $I > 1.96\sigma(I)$ used in structure analysis. h – $11 \rightarrow 10$, k 0–5, l 0–13. One standard reflection (112) measured every 50 measurements, rechecked at end of experiment, no significant change in intensity. No absorption correction. Background and integrated intensity for each reflection evaluated by profile analysis procedure (Lehmann & Larsen, 1974), by means of *PRARA* program (Jaskólski, 1979). Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on F with *SHELX76* (Sheldrick, 1976). Positional and anisotropic thermal parameters of C, N, and S atoms refined in four cycles up to $R = 0.082$. Positions of H atoms attached to C(3A), C(4A), C(5A) and C(6A) determined on basis of geometric calculations. Difference Fourier synthesis revealed hydrogen bonded to C(3B), simultaneously indicating absence of H atom in vicinity of nitrogen atom. All H atoms allowed to contribute to structure factor calculations, $U_{iso} = 0.048$ Å² for H's of C(A) atoms and $U_{iso} = 0.053$ Å² for H(C3B), with parameters fixed. Final $R(F)$ for observed data and 104 parameters = 0.071 ($wR = 0.071$), $w = 1$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Largest peak in final difference map 0.4 e Å⁻³, largest hole -0.4 e Å⁻³, $S = 1.44$; final $\Delta/\sigma = 0.02$.^{*} Atomic coordinates and thermal

^{*} Lists of structure factors, anisotropic thermal parameters coordinates of H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42073 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters are given in Table 1. Molecular geometry calculations were performed with *GEOME* (Jaskólski, 1981).

Discussion. The experimental bond lengths and valence angles with their e.s.d.'s are shown in Table 2, Fig. 1 show the atomic numbering.

The average value of the C—C bonds in the *R1* benzene ring [1.392 (5) Å] agrees with the distance [1.395 (3) Å] normally accepted for aromatic rings. Unexpectedly it was found that the C—C bonds and the valence angles in the *R3* ring are unequal [Δ/σ for C(1*B*)—C(3*B*) and C(2*B*)—C(3*B*) is 8·1] and the two N—C distances are also significantly different ($\Delta/\sigma = 7\cdot9$). Bond lengths of C(2*A*)—N [1.403 (9) and C(2*B*)—N [1.302 (3) Å], compared with theoretical values (Burke-Laing & Laing, 1976), show a tendency towards single and the double bonds respectively. This observation led to the conclusion that the investigated compound is not a secondary amine but possesses a quinonoid structure. However, it should be emphasized that the presence of the hydrogen atom at nitrogen was detected by means of IR spectroscopy in triphenodithiazine crystallized from tetrahydrofuran solution (Garbarczyk & Żuk, 1979). The conversion of the amine group into a quinonoid system probably takes place during sublimation. The C—S bonds are shorter than those in phenothiazine (McDowell, 1976) and also in 1,4-bis(phenylthio)benzene, PTB (Andretti, Garbarczyk & Królikowska, 1981). However, the C—S—C angle is larger than in phenothiazine [100·9 (3)°], but is similar to those found for PTB [105·4 (2)°] and for diphenyl sulphide [103·7 (13)°] (Rozsondai, Moore, Gregory & Hargittai, 1977).

Contrary to phenothiazine, which is folded along the N...S line (McDowell, 1976), the molecule of triphenodithiazine is nearly planar. The maximum displacement from the mean plane through all the non-H atoms is 0.07 (1) Å [atom C(6*A*)].* The sulphur and nitrogen atoms are out of the plane of the *R1* benzene ring by only -0.082 (2) and +0.032 (2) Å, respectively.

In the unit cell, molecules of TPDT are situated at centres of symmetry and are arranged in layers (Fig. 2). In the [001] direction, alternate planes of the molecules are parallel. Planes of molecules in a given layer are, however, nearly perpendicular to those in a neighbouring layer.

Intermolecular distances indicate that only van der Waals interactions take place between molecules in the unit cell.

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* See deposition footnote.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters (Å²)*

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
C(1 <i>A</i>)	0.7285 (7)	-0.020 (1)	0.4678 (6)	0.032 (2)
C(2 <i>A</i>)	0.7788 (7)	-0.030 (1)	0.3741 (6)	0.036 (3)
C(3 <i>A</i>)	0.7271 (7)	-0.209 (2)	0.2905 (6)	0.041 (3)
C(4 <i>A</i>)	0.6292 (8)	-0.371 (2)	0.2992 (6)	0.045 (3)
C(5 <i>A</i>)	0.5790 (8)	-0.355 (2)	0.3904 (7)	0.042 (3)
C(6 <i>A</i>)	0.6278 (7)	-0.180 (2)	0.4738 (6)	0.038 (3)
N	0.8769 (6)	0.128 (1)	0.3567 (5)	0.036 (2)
S	0.7908 (2)	0.1867 (4)	0.5794 (2)	0.0422 (7)
C(1 <i>B</i>)	0.9054 (6)	0.361 (1)	0.5347 (6)	0.031 (2)
C(2 <i>B</i>)	0.9311 (6)	0.304 (1)	0.4272 (6)	0.029 (2)
C(3 <i>B</i>)	0.9713 (7)	0.547 (2)	0.6012 (6)	0.038 (3)

Table 2. *Bond distances (Å) and angles (°)*

C(1 <i>A</i>)—S	1.744 (7)	C(2 <i>B</i>)—C(3 <i>B</i>)	1.430 (11)
C(1 <i>B</i>)—S	1.745 (7)	C(2 <i>A</i>)—N	1.403 (9)
C(1 <i>A</i>)—C(2 <i>A</i>)	1.411 (9)	C(2 <i>B</i>)—N	1.302 (9)
C(1 <i>B</i>)—C(2 <i>B</i>)	1.465 (9)	C(3 <i>A</i>)—C(4 <i>A</i>)	1.382 (11)
C(1 <i>A</i>)—C(6 <i>A</i>)	1.387 (10)	C(4 <i>A</i>)—C(5 <i>A</i>)	1.383 (11)
C(1 <i>B</i>)—C(3' <i>B</i>)	1.350 (12)	C(5 <i>A</i>)—C(6 <i>A</i>)	1.379 (11)
C(2 <i>A</i>)—C(3 <i>A</i>)	1.400 (11)		
C(1 <i>A</i>)—C(2 <i>A</i>)—C(3 <i>A</i>)	118.3 (7)	S—C(1 <i>B</i>)—C(2 <i>B</i>)	120.3 (6)
C(2 <i>A</i>)—C(3 <i>A</i>)—C(4 <i>A</i>)	121.1 (6)	C(1 <i>B</i>)—C(2 <i>B</i>)—N	126.8 (6)
C(3 <i>A</i>)—C(4 <i>A</i>)—C(5 <i>A</i>)	119.7 (7)	C(2 <i>B</i>)—N—C(2 <i>A</i>)	122.5 (6)
C(4 <i>A</i>)—C(5 <i>A</i>)—C(6 <i>A</i>)	120.5 (7)	N—C(2 <i>A</i>)—C(1 <i>A</i>)	125.1 (6)
C(5 <i>A</i>)—C(6 <i>A</i>)—C(1 <i>A</i>)	120.5 (6)	S—C(1 <i>B</i>)—C(3' <i>B</i>)	119.1 (5)
C(6 <i>A</i>)—C(1 <i>A</i>)—C(2 <i>A</i>)	119.9 (6)	C(2 <i>B</i>)—C(1 <i>B</i>)—C(3' <i>B</i>)	120.6 (6)
C(6 <i>A</i>)—C(1 <i>A</i>)—S	118.0 (5)	C(1 <i>B</i>)—C(2 <i>B</i>)—C(3 <i>B</i>)	116.3 (6)
C(2 <i>A</i>)—C(1 <i>A</i>)—S	122.0 (6)	C(2 <i>B</i>)—C(3 <i>B</i>)—C(1' <i>B</i>)	123.1 (6)
C(1 <i>A</i>)—S—C(1 <i>B</i>)	103.1 (3)	N—C(2 <i>B</i>)—C(3 <i>B</i>)	116.8 (6)

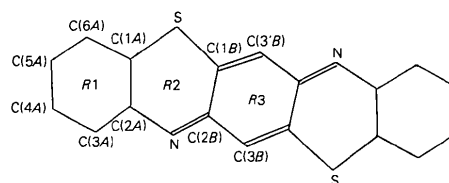


Fig. 1. Atomic numbering.

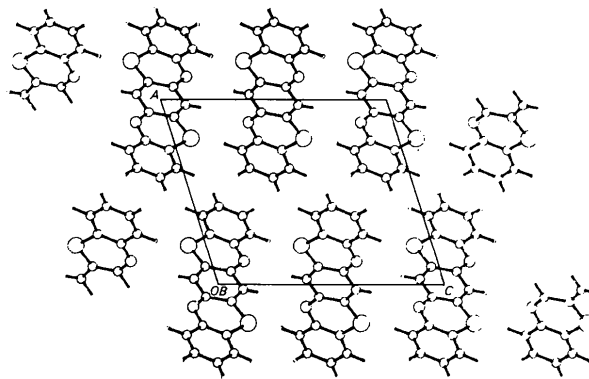


Fig. 2. The arrangement of triphenodithiazine molecules in the unit cell projected down *b*. The large circles are S atoms.

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Structure of (*Z*)-3-Ethoxycarbonyl-4-phenyl-3-pentenoic acid, C₁₄H₁₆O₄*

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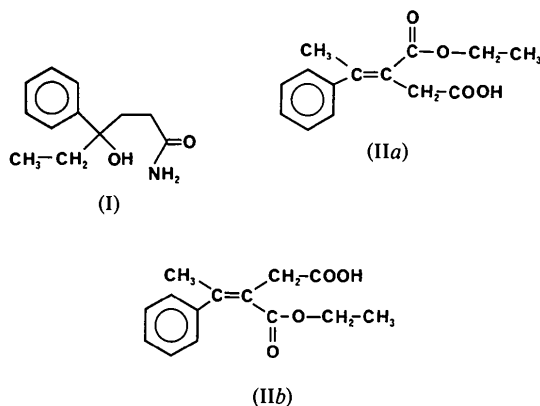
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Abstract. $M_r = 248.3$, orthorhombic, *Pbcn*, $a = 35.934$ (5), $b = 7.502$ (2), $c = 10.056$ (2) Å, $V = 2711$ (2) Å³, $Z = 8$, $D_x = 1.22$ Mg m⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.697$ mm⁻¹, $F(000) = 1056$, $T = 293$ K, final $R = 0.050$ for 1600 observed reflections. The X-ray study confirms that in the solid state the structure of the *Z* isomer is similar to that inferred on the basis of chemical and spectroscopic evidence. In the crystal the title compound has a non-planar conformation and forms centrosymmetric hydrogen-bonded dimers, O...O distance 2.690 (3) Å, O—H...O angle 171 (2)°. There is no conjugation between the phenyl ring and the C(3) double bond.

Introduction. As a part of our studies regarding the total synthesis of compounds with anticonvulsant activity, we became interested in designing a synthetic entry into the γ -hydroxy, γ -phenyl caproamide (Carvajal, Russek, Tapia & Massieu, 1964; Pérez de la Mora & Tapia, 1973; Joseph-Nathan, Massieu, Carvajal & Tapia, 1978), molecule (I). Careful analysis of the structural features characteristic of this anticonvulsant molecule suggests the utilization of (II) as a versatile intermediate for this synthesis. The (*E* and *Z*) geometric isomers of (II) were obtained from the condensation of acetophenone with diethyl succinate at alkaline pH

(Stobbe, 1899). Both isomers (IIa, IIb) were characterized on the basis of chemical and spectroscopic methods (García, 1983).



It was of interest to study the crystallographic structure of the *Z* isomer (IIb) in order to ascertain its conformation and to obtain further information concerning its molecular geometry.

Experimental. Cubic shaped crystal 0.36 × 0.36 × 0.38 mm, Nicolet R3 four-circle diffractometer, graphite-monochromated $\text{Cu } K\alpha$, lattice parameters from 15 machine-centred reflections with $4.9 < 2\theta < 26.2^\circ$; 2079 reflections with $3 < 2\theta < 115^\circ$ for an

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