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2,2,4,5-Tetraphenyl-2*H*-1,3-thiazine

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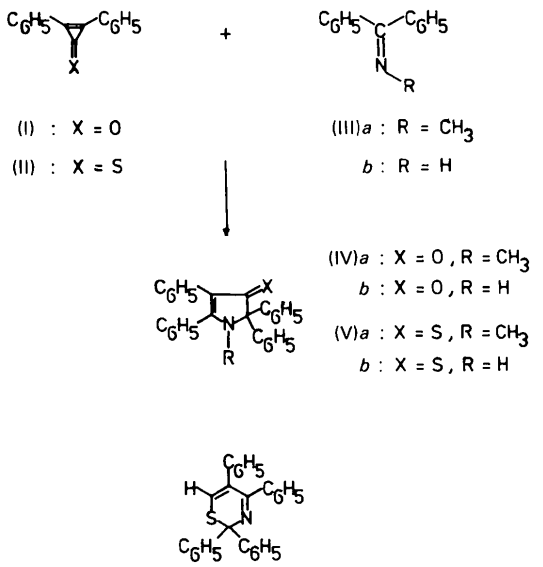
Abstract. $C_{28}H_{21}NS$, M_r = 403·55, orthorhombic, *Pbca*, a = 19·565 (3), b = 11·467 (2), c = 19·410 (3) Å, U = 4354·7 Å^3, Z = 8, D_c = 1·230 Mg m^{-3}, $F(000)$ = 1686; Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 0·125 mm^{-1}. The structure was refined to R = 0·051 for 3709 unique X-ray diffractometer data to characterize the molecule.

Introduction. 2,3-Diphenylcyclopropenone (I) and 2,3-diphenylcyclopropenethione (II) react with *N*-methyldiphenylmethanimine (III*a*) in a (2 + 3) cycloaddition of the azomethine link to the cyclopropenone bond C(1)–C(3) giving rise to the Δ^2-4-pyrrolinone (IV*a*) and its thio analogue (V*a*) (Gallasch, 1978). (III*b*), however, reacting with (I) analogously as above to give (IV*b*) yields with 2,3-diphenylcyclopropenethione a colorless 1:1 adduct which obviously does not have the expected structure (V*b*). From spectroscopic data and chemical reactions (hydrolysis, oxidation, reduction) it was not possible to make a definitive structural assignment. This X-ray analysis shows that the compound from (II) and (III*b*) is 2,2,4,5-tetraphenyl-2*H*-1,3-thiazine (VI).



(VI)

Data were collected from a crystal 1·20 × 0·87 × 0·30 mm. Cell parameters were determined by least squares from the diffractometer angles of 15 reflexions ($9 < \theta < 15°$) measured with a Hilger & Watts Y290 automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The intensities of 3839 reflexions ($I > 3\sigma$) with $2 \leq \theta \leq 30°$ were measured by the $\omega/2\theta$ scan technique, with a scan width $\Delta 2\theta = (1·34 + 0·34 \tan \theta)°$ from background to background and a scan speed of 0·02° s^{-1} in 2θ. Backgrounds were measured at either end of the scan range for 8 s. Three standard reflexions were measured every fifty reflexions and showed only random deviations from their mean intensities. Lp but no absorption corrections were applied, and after averaging of the equivalent reflexions the data set contained 3709 independent reflexions for the structure analysis. The structure was solved by the heavy-atom method and refined by blocked-full-matrix least squares with all atoms anisotropic except for H, for which a common isotropic temperature factor refined to 0·074 (4) Å^2. H atoms were placed in calculated positions (C–H = 1·08 Å, ∠HCH = 109·5° in CH_2 and CH_3 groups, C–C–H angles equal) and allowed to ride on the C atoms to which they were attached. Complex neutral-atom scattering factors were taken

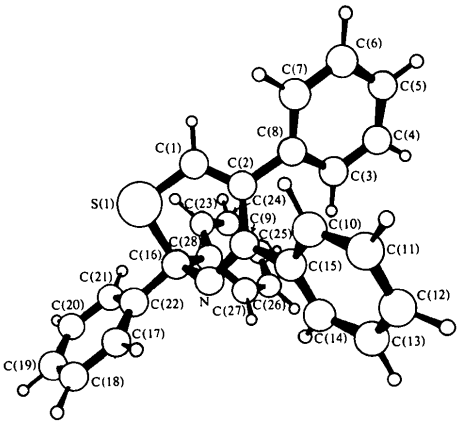


Fig. 1. A molecule of $C_{28}H_{21}NS$ showing the atom numbering.

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Table 1. *Positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	*y*	*z*
S(1)	1251 (0)	1852 (0)	1390 (0)
C(1)	1018 (1)	2590 (2)	2129 (1)
H(1)	950 (1)	3524 (2)	2108 (1)
C(2)	917 (1)	2033 (2)	2731 (1)
C(3)	1241 (1)	2431 (2)	3941 (1)
H(3)	1571 (1)	1677 (2)	3923 (1)
C(4)	1218 (1)	3116 (2)	4530 (1)
H(4)	1530 (1)	2892 (2)	4970 (1)
C(5)	800 (1)	4078 (2)	4557 (1)
H(5)	786 (1)	4611 (2)	5016 (1)
C(6)	395 (1)	4365 (2)	3996 (1)
H(6)	63 (1)	5117 (2)	4019 (1)
C(7)	415 (1)	3688 (2)	3405 (1)
H(7)	102 (1)	3917 (2)	2968 (1)
C(8)	839 (1)	2714 (2)	3372 (1)
C(9)	866 (1)	753 (2)	2730 (1)
C(10)	−206 (1)	668 (2)	3434 (1)
H(10)	−388 (1)	1442 (2)	3176 (1)
C(11)	−600 (1)	138 (3)	3942 (2)
H(11)	−1093 (1)	500 (3)	4072 (2)
C(12)	−370 (2)	−836 (3)	4280 (1)
H(12)	−676 (2)	−1224 (3)	4682 (1)
C(13)	244 (2)	−1314 (3)	4107 (1)
H(13)	421 (2)	−2089 (3)	4368 (1)
C(14)	645 (1)	−804 (2)	3592 (1)
H(14)	1129 (1)	−1191 (2)	3453 (1)
C(15)	425 (1)	190 (2)	3261 (1)
N(1)	1141 (1)	66 (1)	2280 (1)
C(16)	1646 (1)	588 (2)	1813 (1)
C(17)	1387 (1)	−1158 (2)	1055 (1)
H(17)	956 (1)	−1356 (2)	1382 (1)
C(18)	1516 (1)	−1846 (2)	479 (1)
H(18)	1183 (1)	−2570 (2)	361 (1)
C(19)	2065 (2)	−1611 (3)	60 (1)
H(19)	2173 (2)	−2160 (3)	−380 (1)
C(20)	2477 (1)	−671 (3)	204 (1)
H(20)	2899 (1)	461 (3)	−132 (1)
C(21)	2349 (1)	9 (3)	781 (1)
H(21)	2681 (1)	735 (3)	897 (1)
C(22)	1802 (1)	−231 (2)	1211 (1)
C(23)	2679 (1)	1875 (2)	2111 (1)
H(23)	2525 (1)	2492 (2)	1721 (1)
C(24)	3262 (1)	2081 (2)	2498 (1)
H(24)	3557 (1)	2863 (2)	2410 (1)
C(25)	3468 (1)	1299 (2)	2995 (1)
H(25)	3923 (1)	1463 (2)	3295 (1)
C(26)	3087 (1)	300 (2)	3106 (1)
H(26)	3243 (1)	−320 (2)	3495 (1)
C(27)	2507 (1)	97 (2)	2722 (1)
H(27)	2215 (1)	−688 (2)	2809 (1)
C(28)	2294 (1)	887 (2)	2223 (1)

Table 2. *Bond lengths* (Å)

S(1)–C(1)	1·727 (2)	C(13)–C(14)	1·400 (4)
S(1)–C(16)	1·837 (2)	C(14)–C(15)	1·376 (3)
C(1)–C(2)	1·347 (3)	N(1)–C(16)	1·468 (2)
C(2)–C(8)	1·476 (2)	C(16)–C(22)	1·529 (3)
C(3)–C(8)	1·393 (3)	C(17)–C(22)	1·372 (3)
C(3)–C(4)	1·389 (3)	C(17)–C(18)	1·391 (3)
C(4)–C(5)	1·374 (4)	C(18)–C(19)	1·375 (4)
C(5)–C(6)	1·387 (3)	C(19)–C(20)	1·374 (4)
C(6)–C(7)	1·385 (3)	C(20)–C(21)	1·387 (4)
C(7)–C(8)	1·393 (3)	C(21)–C(22)	1·385 (3)
C(9)–C(2)	1·470 (3)	C(23)–C(24)	1·387 (3)
C(9)–C(15)	1·491 (3)	C(23)–C(28)	1·377 (3)
C(9)–N(1)	1·294 (2)	C(24)–C(25)	1·377 (4)
C(10)–C(15)	1·392 (3)	C(25)–C(26)	1·384 (3)
C(10)–C(11)	1·391 (4)	C(26)–C(27)	1·377 (3)
C(11)–C(12)	1·371 (5)	C(27)–C(28)	1·390 (3)
C(12)–C(13)	1·362 (5)	C(28)–C(16)	1·536 (3)

Table 3. *Bond angles* (°)

C(16)–S(1)–C(1)	97·3 (1)	C(14)–C(15)–C(10)	119·4 (2)
S(1)–C(1)–C(2)	121·8 (2)	C(9)–N(1)–C(16)	116·7 (2)
C(1)–C(2)–C(8)	119·7 (2)	N(1)–C(16)–S(1)	108·3 (1)
C(1)–C(2)–C(9)	118·8 (2)	N(1)–C(16)–C(28)	109·1 (1)
C(8)–C(2)–C(9)	121·5 (2)	C(22)–C(16)–C(28)	111·6 (1)
C(8)–C(3)–C(4)	120·2 (2)	N(1)–C(16)–C(22)	110·9 (1)
C(3)–C(4)–C(5)	120·3 (2)	C(22)–C(16)–S(1)	103·1 (1)
C(4)–C(5)–C(6)	120·1 (2)	S(1)–C(16)–C(28)	113·7 (1)
C(5)–C(6)–C(7)	120·0 (2)	C(22)–C(17)–C(18)	120·6 (2)
C(6)–C(7)–C(8)	120·3 (2)	C(17)–C(18)–C(19)	120·4 (2)
C(2)–C(8)–C(3)	119·0 (2)	C(18)–C(19)–C(20)	119·4 (3)
C(2)–C(8)–C(7)	121·6 (2)	C(19)–C(20)–C(21)	120·0 (3)
C(7)–C(8)–C(3)	119·1 (2)	C(20)–C(21)–C(22)	120·9 (2)
C(2)–C(9)–C(15)	118·1 (2)	C(16)–C(22)–C(17)	121·7 (2)
C(2)–C(9)–N(1)	125·5 (2)	C(16)–C(22)–C(21)	119·5 (2)
N(1)–C(9)–C(15)	116·3 (2)	C(21)–C(22)–C(17)	118·6 (2)
C(15)–C(10)–C(11)	119·4 (2)	C(28)–C(23)–C(24)	120·3 (2)
C(10)–C(11)–C(12)	120·9 (3)	C(23)–C(24)–C(25)	120·6 (2)
C(11)–C(12)–C(13)	120·0 (3)	C(24)–C(25)–C(26)	119·4 (2)
C(12)–C(13)–C(14)	120·1 (3)	C(25)–C(26)–C(27)	119·9 (2)
C(13)–C(14)–C(15)	120·3 (2)	C(26)–C(27)–C(28)	121·0 (2)
C(9)–C(15)–C(10)	120·6 (2)	C(27)–C(28)–C(23)	118·8 (2)
C(9)–C(15)–C(14)	120·0 (2)	C(16)–C(28)–C(23)	123·6 (2)
		C(16)–C(28)–C(27)	117·6 (2)

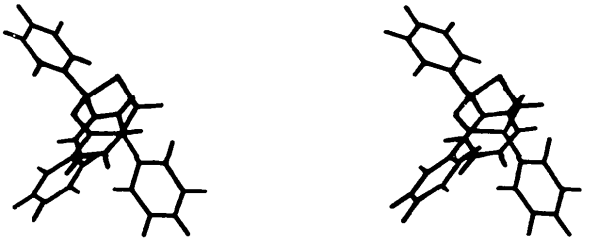

Fig. 2. Stereoscopic view of the molecule.

from *International Tables for X-ray Crystallography* (1974); the weighting scheme was $w = 1/[\sigma^2(F) + 0{\cdot}640|F_o|^2]$. Refinement converged to $R = 0{\cdot}051$ with a corresponding $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}064$.*

The structure was solved and refined with *SHELX* (Sheldrick, 1976). The figures were drawn with *ORTEP* (Johnson, 1965). Final positional parameters are given in Table 1.

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34446 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The molecule has been characterized and the numbering scheme is shown in Fig. 1. Bond lengths and angles involving the non-hydrogen atoms are given in Tables 2 and 3 respectively. A stereoscopic view of the molecule is shown in Fig. 2.

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β-(2-Hydroxyphenyl)ethanolamine Hydrochloride [2-Amino-1-(2-hydroxyphenyl)ethanol Hydrochloride]*

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Abstract. $C_8H_{12}NO_2^+.Cl^-$, m.p. 441–449 K (from ethyl acetate), $P2_12_12_1$, $a = 7{\cdot}363$ (2), $b = 21{\cdot}824$ (6), $c = 5{\cdot}790$ (2) Å, $Z = 4$, $D_x = 1{\cdot}354$, $D_m = 1{\cdot}356$ Mg m^{-3} (flotation: CCl_4–C_6H_6). The structure was solved by *MULTAN*. Full-matrix least-squares refinement converged to $R = 0{\cdot}057$ for the *R* configuration and to $R = 0{\cdot}056$ for the *S* configuration ($P < 0{\cdot}05$). This is consistent with spontaneous resolution of the title compound, single crystals of which provided optically active aqueous solutions. A partially occupied oxygen site O(1)′ is attributed to the oxidation of the alkyl hydroxyl group to a ketone during the data collection. The Cl^- is hydrogen bonded to $H2(N)_{554}$, $H3(N)_{555}$, and $H(O2)_{655}$ (2·37, 2·19, and 2·10 Å). Both O(1) and O(2) are internally hydrogen bonded [H1(N)···O(1), 2·41 and H(O1)···O(2) = 2·24 Å]. Intramolecular hydrogen bonding may account for the unusual pharmacological properties of this compound in which only the N–C(1)–C(2)–O(1) and the O(1)–C(2)–C(3)–C(4) and O(1)–C(2)–C(3)–C(8) torsion angles (−41, −60, +122°) differ significantly from those of other phenylethanolamines.

Introduction. It is generally believed (Iversen, 1967) that, after its release into the circulation, norepinephrine is primarily inactivated through an efficient, specific norepinephrine-uptake process located in the sympathetic nerve terminals. This uptake system has served as a target for the design and the synthesis of compounds (Rotman, Lundstrom, McNeal, Daly & Creveling, 1975) which interfere with the uptake of norepinephrine and thus produce their effects by controlling the amount of this neurotransmitter available in the circulation. A great deal of the research has focused on obtaining information related to the drug structural requirements for interaction with the adrenergic sites of uptake. Such information is necessary for the rational design of drugs that would have a high degree of pharmacological specificity.

Of the compounds tested, the phenylethylamine and phenylethanolamine analogs with hydroxyl substituents in various positions of the aromatic ring have received special attention. Most of these analogs were found (Rotman *et al.*, 1975; Katz, Heller, Jacobson, Rotman & Creveling, 1974) to produce an immediate inhibition of norepinephrine uptake, probably by competing with it for the sites of uptake. However, the *ortho*-hydroxyphenylethanolamines were a striking exception. Unexpectedly, these compounds were all found to have little or no activity as inhibitors of the uptake process (Rotman *et al.*, 1975; Katz *et al.*, 1974) thus raising the possibility that the *o*-hydroxyl group may produce this effect by altering the conformation of the flexible side chain. The *o*-hydroxyl groups are indeed favorably positioned on the phenylethanolamine molecule so that they can easily interact with either one of the functional groups (−OH, $-NH_3$) of the ethanolamine side chain and alter its conformation.

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