

## 7,11b-Dihydro-11b-isopropyl-2-methoxy-3,4-diphenyl-2H,6H-[1,3]thiazino[2,3-a]isoquinoline

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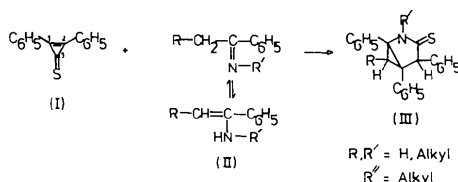
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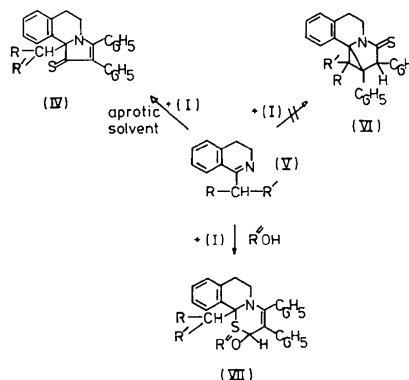
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**Abstract.**  $C_{28}H_{29}NOS$ ,  $M_r = 427.61$ , triclinic,  $a = 10.404$  (2),  $b = 12.876$  (2),  $c = 8.986$  (2) Å,  $\alpha = 98.08$  (5),  $\beta = 79.90$  (5),  $\gamma = 85.59$  (5)°,  $U = 1167.0$  Å<sup>3</sup>;  $Z = 2$ ,  $D_c = 1.216$  Mg m<sup>-3</sup>;  $F(000) = 456$ ; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.12$  mm<sup>-1</sup>. Space group  $P\bar{1}$ . Final  $R = 0.036$  for 3453 unique X-ray diffractometer data. The molecular structure was confirmed.

**Introduction.** 1,2-Diphenylcyclopropenethione (I) reacts with acyclic imines (II) *via* the tautomeric enamine form to give bicyclic thioamides (III) (Eicher & Weber, 1974). This mode of reaction [(3 + 3)-cycloaddition of the enamine unit N=C=C to C(1)–C(3) of (I)] was previously observed by Eicher & Böhm (1974). The reaction of (I) with the cyclic imine (V) does not follow this route, which should have led to thioamide systems (VI). Instead, in aprotic solvents a (2 + 3)-cycloaddition of the azomethine link C=N to C(1)–C(3) of (I) occurs, leading to the red  $\Delta^2$ -pyrroline-4-thiones (IV) (Krause, 1978). In alcoholic solvents, however, the sole product is colourless and has an elemental analysis which indicates the incorporation of one molecule of alcohol in addition to the 1:1 composition. From spectroscopic data and chemical reactions (hydrolysis, oxidation, reduction) it was not possible to make definitive structural assignments. Thus an X-ray analysis was performed of the compound (VII) arising from (I) and 1-isopropyl-3,4-dihydroisoquinoline (V,  $R = R' = \text{CH}_3$ ) in methanol, since it showed the most suitable crystallographic properties in the series of products synthesized.



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Data were collected with a crystal  $0.35 \times 0.27 \times 0.48$  mm. Cell parameters were determined by a least-squares procedure from the diffractometer angles of 23 reflexions measured with a Hilger & Watts Y290 automatic four-circle diffractometer, graphite-monochromated Mo  $K\alpha$  radiation and a scintillation counter. The intensities of 10 717 reflexions ( $I > 3\sigma$ ) with  $2 \leq \theta \leq 26.3^\circ$  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  $0.02^\circ \text{ s}^{-1}$  in  $2\theta$ . Backgrounds were measured at either end of the scan range for 7 s. Five standards were measured every fifty reflexions, and showed only random deviations from their mean intensities.  $L_p$  but not absorption corrections were applied, and after averaging the equivalent reflexions the data set contained 3453 independent reflexions.

The structure was solved by multisolution  $\sum_2$  sign expansion. A starting set of three origin-fixing and 16 multisolution reflexions, selected by hand on the basis of a convergence map, was employed to generate signs for the 260 reflexions with  $E > 1.40$ . The best  $E$  map revealed 30 of the 31 unique atoms. The structure was refined by a blocked full-matrix least-squares method

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

	x	y	z
S(1)	1739 (0)	699 (0)	4794 (1)
C(1)	1928 (2)	2025 (1)	5808 (2)
C(2)	2830 (2)	1812 (1)	6926 (2)
C(3)	4025 (2)	1186 (2)	6386 (2)
H(3)	4263 (2)	814 (2)	5203 (2)
C(4)	4910 (2)	1035 (2)	7341 (3)
H(4)	5831 (2)	552 (3)	6903 (3)
C(5)	4608 (2)	1503 (2)	8856 (3)
H(5)	5302 (2)	1403 (2)	9601 (3)
C(6)	3415 (2)	2098 (2)	9417 (2)
H(6)	3179 (2)	2456 (2)	606 (2)
C(7)	2515 (2)	2245 (1)	8471 (2)
C(8)	1154 (2)	2772 (2)	9132 (2)
H(8)	867 (2)	2634 (2)	296 (2)
H(8)	1132 (2)	3610 (2)	9114 (2)
C(9)	226 (2)	2309 (2)	8168 (2)
H(9)	-761 (2)	2674 (2)	8623 (2)
H(9)	257 (2)	1470 (2)	8179 (2)
N(1)	630 (1)	2506 (1)	6594 (2)
C(10)	-374 (2)	2584 (1)	5737 (2)
C(11)	-1274 (2)	4365 (2)	7192 (3)
H(11)	-282 (2)	4578 (2)	7098 (3)
C(12)	-2319 (3)	5085 (2)	7980 (3)
H(12)	-2134 (3)	5859 (2)	8480 (3)
C(13)	-3579 (3)	4823 (2)	8126 (3)
H(13)	-4386 (3)	5384 (2)	8745 (3)
C(14)	-3812 (2)	3834 (2)	7475 (3)
H(14)	-4805 (2)	3622 (2)	7588 (3)
C(15)	-2781 (2)	3113 (2)	6681 (3)
H(15)	-2974 (2)	2342 (2)	6178 (3)
C(16)	-1502 (2)	3375 (1)	6527 (2)
C(17)	-343 (2)	2040 (1)	4334 (2)
C(18)	-1365 (2)	3318 (1)	2926 (2)
H(18)	-797 (2)	3910 (1)	3386 (2)
C(19)	-2181 (2)	3566 (2)	1930 (3)
H(19)	-2233 (2)	4344 (2)	1613 (3)
C(20)	-2924 (2)	2827 (2)	1344 (2)
H(20)	-3559 (2)	3022 (2)	570 (2)
C(21)	-2848 (2)	1834 (2)	1757 (3)
H(21)	-3435 (2)	1252 (2)	1313 (3)
C(22)	-2028 (2)	1578 (2)	2734 (2)
H(22)	-1970 (2)	795 (2)	3034 (2)
C(23)	-1273 (2)	2323 (1)	3336 (2)
C(24)	612 (2)	1093 (1)	3612 (2)
H(24)	57 (2)	422 (1)	3479 (2)
O(1)	1254 (1)	1262 (1)	2145 (1)
C(25)	1720 (2)	304 (2)	1140 (3)
H(25)	2190 (2)	513 (2)	69 (3)
H(25)	868 (2)	-95 (2)	970 (3)
H(25)	2400 (2)	-213 (2)	1549 (3)
C(26)	2517 (2)	2781 (1)	4705 (2)
H(26)	1803 (2)	2881 (1)	3984 (2)
C(27)	3793 (2)	2345 (2)	3605 (2)
H(27)	3690 (2)	1591 (2)	2963 (2)
H(27)	4581 (2)	2258 (2)	4231 (2)
H(27)	4012 (2)	2903 (2)	2828 (2)
C(28)	2700 (2)	3831 (2)	5626 (3)
H(28)	1798 (2)	4158 (2)	6396 (3)
H(28)	2989 (2)	4374 (2)	4845 (3)
H(28)	3462 (2)	3704 (2)	6277 (3)

with all atoms anisotropic except for H, for which a common isotropic temperature factor refined to 0.061 (3) Å<sup>2</sup>. H atoms were placed in geometrically

Table 2. *Bond lengths* (Å)

S(1)—C(1)	1.861 (2)	C(12)—C(13)	1.367 (4)
S(1)—C(24)	1.805 (2)	C(13)—C(14)	1.383 (4)
C(1)—C(2)	1.528 (3)	C(14)—C(15)	1.384 (3)
C(1)—C(26)	1.567 (3)	C(15)—C(16)	1.386 (3)
C(1)—N(1)	1.456 (2)	C(10)—C(17)	1.347 (2)
C(2)—C(3)	1.399 (2)	C(17)—C(23)	1.488 (3)
C(3)—C(4)	1.385 (3)	C(23)—C(18)	1.383 (3)
C(4)—C(5)	1.380 (3)	C(18)—C(19)	1.388 (3)
C(5)—C(6)	1.381 (3)	C(19)—C(20)	1.376 (3)
C(6)—C(7)	1.391 (3)	C(20)—C(21)	1.381 (3)
C(7)—C(2)	1.393 (2)	C(21)—C(22)	1.381 (3)
C(7)—C(8)	1.504 (3)	C(22)—C(23)	1.396 (3)
C(8)—C(9)	1.508 (3)	C(17)—C(24)	1.504 (2)
C(9)—N(1)	1.467 (2)	C(24)—O(1)	1.423 (2)
N(1)—C(10)	1.408 (2)	O(1)—C(25)	1.419 (2)
C(10)—C(16)	1.496 (2)	C(26)—C(27)	1.524 (2)
C(16)—C(11)	1.386 (3)	C(26)—C(28)	1.526 (3)
C(11)—C(12)	1.390 (3)		

Table 3. *Bond angles* (°)

C(24)—S(1)—C(1)	98.8 (1)	C(16)—C(11)—C(12)	120.2 (2)
S(1)—C(1)—N(1)	107.8 (1)	C(11)—C(12)—C(13)	120.7 (2)
S(1)—C(1)—C(2)	104.9 (1)	C(12)—C(13)—C(14)	119.5 (2)
S(1)—C(1)—C(26)	113.3 (1)	C(13)—C(14)—C(15)	120.4 (2)
N(1)—C(1)—C(2)	112.1 (1)	C(14)—C(15)—C(16)	120.4 (2)
N(1)—C(1)—C(26)	107.8 (1)	C(15)—C(16)—C(11)	118.9 (2)
C(2)—C(1)—C(26)	111.0 (1)	C(15)—C(16)—C(10)	120.8 (2)
C(1)—C(2)—C(3)	119.5 (2)	C(10)—C(16)—C(11)	120.2 (2)
C(1)—C(2)—C(7)	122.0 (1)	C(10)—C(17)—C(23)	122.7 (1)
C(3)—C(2)—C(7)	118.5 (2)	C(10)—C(17)—C(24)	124.2 (2)
C(2)—C(3)—C(4)	121.2 (2)	C(23)—C(17)—C(24)	112.9 (1)
C(3)—C(4)—C(5)	119.6 (2)	C(23)—C(18)—C(19)	120.7 (2)
C(4)—C(5)—C(6)	119.9 (2)	C(18)—C(19)—C(20)	120.6 (2)
C(5)—C(6)—C(7)	120.9 (2)	C(19)—C(20)—C(21)	119.1 (2)
C(6)—C(7)—C(2)	119.8 (2)	C(20)—C(21)—C(22)	120.7 (2)
C(6)—C(7)—C(8)	120.4 (2)	C(21)—C(22)—C(23)	120.6 (2)
C(2)—C(7)—C(8)	119.5 (2)	C(22)—C(23)—C(18)	118.3 (2)
C(7)—C(8)—C(9)	108.2 (2)	C(22)—C(23)—C(17)	120.9 (2)
C(8)—C(9)—N(1)	108.9 (2)	C(17)—C(23)—C(18)	120.7 (2)
C(9)—N(1)—C(1)	115.8 (1)	C(17)—C(24)—S(1)	114.7 (1)
C(1)—N(1)—C(10)	118.5 (1)	C(17)—C(24)—O(1)	109.0 (1)
C(10)—N(1)—C(9)	116.1 (1)	S(1)—C(24)—O(1)	113.1 (1)
N(1)—C(10)—C(16)	112.9 (1)	C(24)—O(1)—C(25)	112.4 (1)
N(1)—C(10)—C(17)	125.1 (1)	C(1)—C(26)—C(27)	115.8 (2)
C(16)—C(10)—C(17)	122.0 (2)	C(1)—C(26)—C(28)	110.1 (1)
		C(27)—C(26)—C(28)	109.7 (2)

calculated positions (C—H 1.08 Å, H—C—H 109.5° in CH<sub>2</sub> and CH<sub>3</sub> groups, C—C—H angles equal) and allowed to ride on the C atoms to which they are attached; the methyl groups were refined as rigid groups. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974); the weighting scheme was  $w = 1/[\sigma^2(F) + 0.005|F_o|^2]$ . Refinement converged to  $R = 0.036$  with  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.044$ .\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34244 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

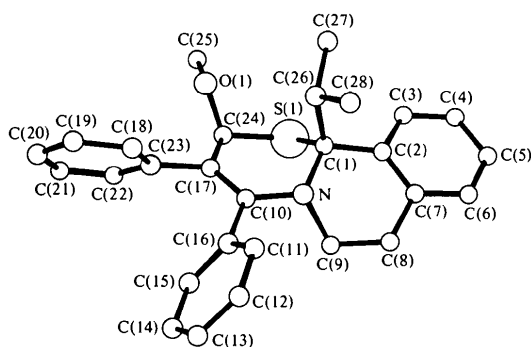


Fig. 1. A molecule of C<sub>28</sub>H<sub>29</sub>NOS (without H atoms) showing the atom numbering.

**Discussion.** The molecular structure of the title compound is shown in Fig. 1; a stereoview of the molecule is given in Fig. 2. The final atomic coordinates, bond distances and angles are given in Tables 1–3. The S(1)–C(1) distance of 1.861 Å is somewhat longer than the C–S length found in alkyl-substituted thioesters (1.820 Å). This anomaly could be interpreted in terms of the influence brought about by the aminal-thioetal functionality of the C(1) centre which could lead to weakening of the C–S bond.

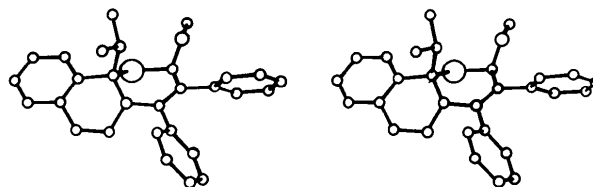


Fig. 2. Stereoscopic view of the molecule.

We thank Professor Friedo Huber for his support. The structure was solved and refined at the Twente Summer School on Crystallographic Computing with the program *SHELX* written by GMS. The figures were drawn with *PLUTO* written by Drs W. D. S. Motherwell and W. Clegg.

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## The Structure of Racemic 2,6-Dibromo-4-[3(*S*),4(*S*)-diphenyl-2(*R*)-tetrahydrofuryl]phenol

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**Abstract.** C<sub>22</sub>H<sub>18</sub>Br<sub>2</sub>O<sub>2</sub>, orthorhombic, *Pbca*, *a* = 13.670 (4), *b* = 21.126 (5), *c* = 13.000 (5) Å with eight molecules per unit cell. The structure was solved by heavy-atom methods, and refined by an anisotropic blocked full-matrix least-squares procedure to an *R* of 0.045 for 2098 reflections measured with Mo *K*<sub>α</sub> radiation. The structure analysis has established the stereochemistry of a series of triphenyltetrahydrofuran-2-ones, one of which possesses anti-fertility activity.

**Introduction.** Interest in the post-coital, non-steroidal anti-fertility activity of some triphenylfuranones and triphenyltetrahydrofurans led to the synthesis of all the possible stereoisomers (Dikshit, Munshi, Kapil, Anand,

van der Veen & Fujiwara, 1977). It was not possible to assign the stereochemistry on the basis of NMR spectra alone, although relative configurational relationships between some of the eight isomers could be deduced.

Suitable crystals of the biologically active unsubstituted triphenylfuranone, (1*a*), could not be obtained, but satisfactory prismatic single crystals of (1*b*) were formed by slow evaporation of a methanol solution. The transformation of (1*a*) to the dibromotetrahydrofuran derivative is believed to leave the chiral centers unchanged so that the relative configurations at the three asymmetric centers C(2), C(3) and C(4) determined for (1*b*) should be the same as those in (1*a*). The relationship of (1*a*) to the structure of the other triphenylfuranones and triphenyltetrahydrofurans is discussed elsewhere (Dikshit *et al.*, 1977).