

Fig. 1. A molecule of C₂₈H₂₉NOS (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.

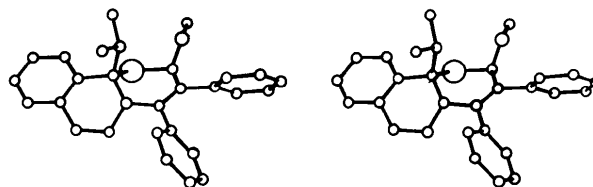


Fig. 2. Stereoscopic view of the molecule.

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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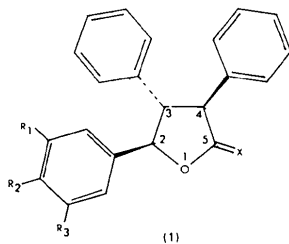
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Abstract. C₂₂H₁₈Br₂O₂, orthorhombic, *Pbca*, *a* = 13.670 (4), *b* = 21.126 (5), *c* = 13.000 (5) Å with eight molecules per unit cell. The structure was solved by heavy-atom methods, and refined by an anisotropic blocked full-matrix least-squares procedure to an *R* of 0.045 for 2098 reflections measured with Mo *K*_α 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).



(a) $R_1 = R_2 = R_3 = \text{H}; X = \text{O}$
 (b) $R_1 = R_2 = \text{Br}; R_3 = \text{OH}; X = 2\text{H}$

Most of the reported tetrahydrofuran structures, except for the gas-phase studies made by Engerholm, Luntz, Gwinn & Harris (1969), have involved chelation of the tetrahydrofuran O atom with a metal ion (Brauer & Stucky, 1970, 1972; Krause, Marx & Schödl, 1970; Muller, Krause & Schmiedeknecht, 1972). There is a structural similarity between (1b) and the one other non-chelated tetrahydrofuran derivative which has been reported (3,3,4,4-tetrahydrofuran-2-ol) (Mighell & Jacobson, 1964) but significant differences exist with chelated structures.

A cube-shaped sample of (1b) measuring $0.3 \times 0.3 \times 0.3$ mm was cut from a larger prismatic crystal bound by the faces (100), ($\bar{1}00$), (010), (010), (00 $\bar{1}$) and (001). The space group was found to be *Pbca* from the extinctions observed on precession and Weissenberg photographs: ($0kl$, $k = 2n + 1$ absent, $h0l$, $l = 2n + 1$ absent, $hk0$, $h = 2n + 1$ absent). Ten centered reflections were used to determine the best least-squares orientation matrix and cell parameters. The calculated density based on eight molecules per unit cell was 1.67 Mg m^{-3} while that measured by flotation was 1.63 Mg m^{-3} .

Integrated θ - 2θ scans with monochromatic $\text{Mo K}\alpha$ radiation were used to collect data to a 2θ value of 50° on a Syntex $P2_1$ diffractometer. Three standard reflections (008, 800, 0,14,0) were monitored every 50 reflections. A scan rate of 2° min^{-1} was used, with background measured at each end of the scan for a total time equal to the scan time. Of the 3354 reflections measured, 2098 with $I > 2\sigma$ were treated as observed. No corrections were made for the Br anomalous scattering or for absorption.

The data were processed on a PDP-10 computer using the XRAY programs of Stewart, Kruger, Ammon, Dickinson & Hall (1972). The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for Br, those for H were from Stewart, Davidson & Simpson (1965). C and N scattering factors were those calculated from numerical Hartree-Fock wave functions (Cromer & Mann, 1968). One Br was located in a three-dimensional Patterson map. A Fourier map phased on this atom revealed the other Br atom, both O atoms and 18 of the 22 C atoms. Another structure factor-Fourier cycle

Table 1. Positional parameters ($\times 10^4$ for C, O, Br, $\times 10^3$ for H)

	x	y	z
O(1)	776 (3)	3123 (2)	3283 (4)
C(2)	1743 (5)	3249 (5)	2884 (5)
C(3)	1704 (5)	3914 (3)	2411 (5)
C(4)	618 (5)	3939 (4)	2065 (6)
C(5)	132 (6)	3623 (4)	2976 (7)
C(1')	2473 (5)	3146 (3)	3748 (5)
C(2')	2281 (5)	3391 (3)	4726 (6)
C(3')	2914 (5)	3254 (3)	5536 (5)
C(4')	3774 (5)	2925 (3)	5405 (5)
C(5')	3969 (5)	2717 (3)	4402 (5)
C(6')	3333 (5)	2830 (3)	3600 (5)
Br(3')	2538 (1)	3542 (0)	6868 (1)
O(4')	4350 (4)	2805 (2)	6230 (4)
Br(5')	5149 (0)	2265 (0)	4157 (1)
C(1'')	2414 (5)	4063 (2)	1559 (5)
C(2'')	2947 (5)	4623 (0)	1597 (6)
C(3'')	3567 (6)	4797 (3)	779 (7)
C(4'')	3672 (7)	4398 (4)	-54 (8)
C(5'')	3152 (7)	3826 (6)	-88 (7)
C(6'')	2526 (5)	3664 (4)	695 (6)
C(1''')	169 (5)	4567 (4)	1775 (6)
C(2''')	459 (5)	5132 (4)	2210 (6)
C(3''')	-21 (6)	5690 (4)	1949 (7)
C(4''')	-796 (7)	5682 (5)	1288 (7)
C(5''')	-1073 (6)	5125 (5)	826 (6)
C(6''')	-601 (6)	4569 (4)	1093 (6)
H(2)	186 (4)	289 (2)	245 (4)
H(3)	180 (4)	419 (2)	293 (4)
H(4)	53 (5)	372 (3)	138 (3)
H(5A)	-49 (6)	346 (4)	281 (6)
H(5B)	1 (5)	387 (4)	348 (6)
H(2')	170 (6)	360 (3)	481 (6)
H(4')	479 (4)	242 (3)	590 (4)
H(6')	337 (6)	261 (4)	303 (7)
H(2'')	291 (4)	494 (3)	216 (5)
H(3'')	394 (6)	519 (4)	94 (6)
H(4'')	418 (9)	456 (6)	-73 (9)
H(5'')	329 (9)	357 (5)	-66 (10)
H(6'')	213 (6)	334 (4)	60 (7)
H(2''')	98 (6)	514 (4)	270 (8)
H(3''')	24 (5)	604 (3)	227 (6)
H(4''')	-102 (6)	601 (4)	118 (6)
H(5''')	-163 (5)	511 (3)	40 (6)
H(6''')	76 (4)	420 (3)	73 (5)

completed the structure. Isotropic refinement of the nonhydrogen atom positions resulted in an R_1 factor [$R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$] of 0.11 which was further reduced by blocked-diagonal (three-atom blocks) anisotropic refinement to 0.059. The function minimized was R_2 [$R_2 = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$].

All H positions, except that on the hydroxyl group, were calculated assuming a C-H bond distance of 1 Å and tetrahedral or trigonal angle. The H attached to the hydroxyl group was located in a difference map and included in the final refinement cycle. Weighted* aniso-

* $1/w = \sigma^2 + 0.0025F_o^2$.

tropic refinement of the non-hydrogen positions and isotropic refinement of the H positions reduced R_1 to 0.045 and R_2 to 0.059. The final positional parameters are given in Table 1.* Bond distances are given in Fig. 1.

Discussion. The bond distances and angles in the tetrahydrofuran ring of (1b) are quite similar to those of 3,3,4,4-tetrahydroxytetrahydrofuran (2) (Mighell & Jacobson, 1964) (see Fig. 2). The molecular parameters are substantially different from those of tetrahydrofuran chelated to metal ions (Krausse, Marx & Schödl, 1970). The five-membered ring is also puckered with C(3) and C(4) 0.502 (7) and 0.183 (7) Å, respec-

* Lists of structure factors, thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34154 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

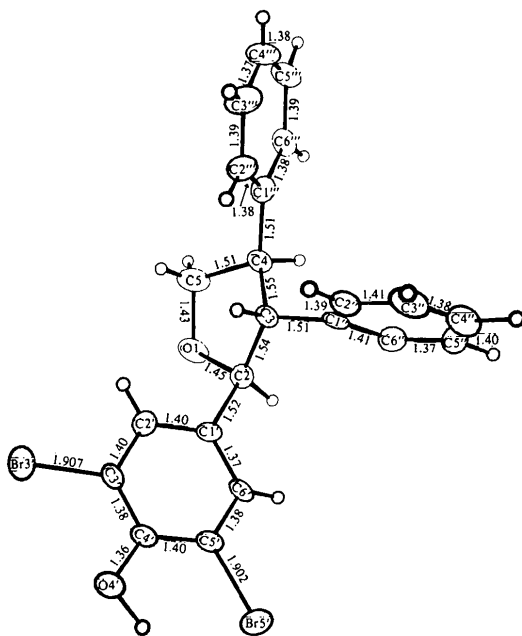


Fig. 1. ORTEP drawing and numbering scheme for 2,6-dibromo-4-[3(S),4(S)-diphenyl-2(R)-tetrahydrofuryl]phenol, with bond lengths (Å). The e.s.d. of all bond lengths is ± 0.01 Å.

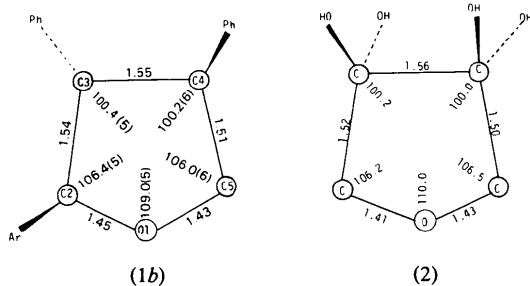


Fig. 2. A comparison of bond angles ($^{\circ}$) and distances (Å) in the tetrahydrofuran portion of compounds (1b) and (2).

Table 2. Torsional angles ($^{\circ}$) (Klyne & Prelog, 1960)

(a) THF ring (twist conformation)	
C(5)—O(1)—C(2)—C(3)	-7.1 (7)
O(1)—C(2)—C(3)—C(4)	30.3 (6)
C(2)—C(3)—C(4)—C(5)	-40.6 (7)
C(3)—C(4)—C(5)—O(1)	38.3 (7)
C(4)—C(5)—O(1)—C(2)	-20.2 (8)
(b) Aromatic ring to tetrahydrofuran ring	
C(2')—C(1')—C(2)—C(3)	74.7 (8)
C(2')—C(1')—C(2)—O(1)	-45.0 (8)
C(2'')—C(1'')—C(3)—C(4)	111.1 (7)
C(2'')—C(1'')—C(3)—C(2)	-132.3 (7)
C(6'')—C(1'')—C(4)—C(5)	87.5 (9)
C(6'')—C(1'')—C(4)—C(3)	-30.7 (10)

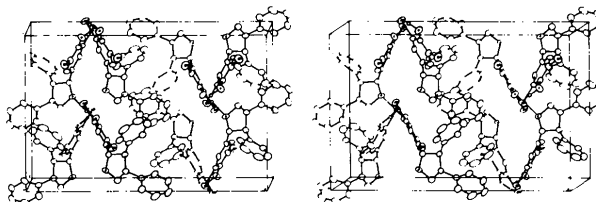


Fig. 3. Stereoview of molecular packing and hydrogen bonding in 2,6-dibromo-4-[3(S),4(S)-diphenyl-2(R)-tetrahydrofuryl]phenol.

tively, above and below the plane formed by C(2)—O(1)—C(5). The torsional angles between the aromatic rings and the tetrahydrofuran ring are given in Table 2.

There is an intramolecular hydrogen bond of 2.34 (6) Å between H(4') of the hydroxyl group and the adjacent Br(5'). The same hydroxyl group forms a hydrogen bond with a distance of 2.06 (6) Å between H(4') and the furan O(1) atom in an adjacent molecule (Fig. 3).

We wish to thank Dr N. Anand for a sample of compound (1b) and for bringing this problem to our attention. We also thank Professor R. LaLancette for the use of the Syntex P2₁ Diffractometer at Rutgers University, Newark.

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Produit de Cyclisation: La Dihydro-5,6 (Oxo-2 propyl)-6 4H-Pyrrolo[1,2-a]thiéno[3,2-f][diazépine-1,4] One-4

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Abstract. C₁₃H₁₂N₂O₂S, $M_r = 248.18$, monoclinic, $P2_1/b$, $a = 9.285$ (3), $b = 9.330$ (3), $c = 14.316$ (8) Å, $\gamma = 94.05$ (4)°, $Z = 4$, $D_m = 1.36$, $D_x = 1.34$ Mg m⁻³, $\mu = 0.23$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. The structure was solved by direct methods and refined by least-squares methods to a final $R = 0.048$ for 1924 independent reflexions. The central seven-membered 1,4-diazepine ring deviates considerably from planarity and the planes of the two thiophene and pyrrole rings form a dihedral angle of 19.7°.

Introduction. La réaction de cyclisation en milieu alcalin du *N*-(cyano-3 thiényl-2) formyl-2 pyrrole avec l'acétone en présence de peroxyde d'hydrogène a permis d'obtenir un composé tricyclique substitué et dérivé de la pyrrolothiéndiazépine (Rault, Cugnon de Sevrécourt, Robba & Nguyen-Huy-Dung, 1979). La structure du produit de réaction, la dihydro-5,6 (oxo-2 propyl)-6 4H-pyrrolo[1,2-a]thiéno[3,2-f][diazépine-1,4] one-4, n'a pu être établie sans ambiguïté par les méthodes physico-chimiques habituelles (microanalyse élémentaire, résonance magnétique nucléaire, spectrométrie infrarouge et de masse) et une étude radio-cristallographique aux rayons X a été entreprise qui a permis de mettre en évidence la présence d'un hétérocycle à sept atomes, hypothèse retenue par les chimistes comme étant le plus probable.

Cette étude s'avère d'autant plus intéressante que le composé présente une certaine analogie structurale avec l'antramycine, antibiotique connu pour ses

Tableau 1. Paramètres atomiques ($\times 10^4$, pour H $\times 10^3$) et facteurs d'agitation thermique B_{eq} (Å²) accompagnés de leurs écarts types entre parenthèses

	x	y	z	B (Å ²)
S	-709 (2)	2458 (2)	1492 (1)	3,6 (1)
C(1)	-707 (7)	4303 (7)	1514 (5)	3,3 (1)
C(2)	503 (7)	4936 (7)	1138 (5)	3,3 (1)
C(3)	1483 (7)	3937 (7)	813 (5)	2,5 (1)
C(4)	952 (6)	2549 (7)	967 (5)	2,7 (1)
N(1)	1598 (6)	1279 (5)	761 (4)	2,9 (1)
C(5)	2540 (7)	1102 (7)	26 (5)	2,7 (1)
C(6)	2898 (7)	2323 (7)	-624 (5)	2,2 (1)
N(2)	3600 (6)	3568 (6)	-126 (4)	2,4 (1)
C(7)	2929 (7)	4410 (7)	459 (5)	2,4 (1)
O(1)	3517 (5)	5578 (5)	735 (3)	3,3 (1)
C(8)	2925 (7)	-282 (7)	58 (5)	3,3 (1)
C(9)	2194 (7)	-961 (7)	815 (5)	4,1 (1)
C(10)	1395 (7)	-14 (7)	1244 (5)	3,9 (1)
C(11)	3925 (7)	1881 (7)	-1380 (5)	3,0 (1)
C(12)	4182 (7)	2947 (7)	-2158 (5)	3,1 (1)
O(2)	3460 (4)	3956 (4)	-2251 (3)	4,1 (1)
C(13)	5352 (8)	2686 (8)	-2824 (5)	4,7 (1)
H(C1)	-149 (8)	480 (8)	181 (5)	3,6
H(C2)	67 (8)	589 (8)	107 (5)	3,3
H(C6)	199 (8)	265 (7)	-91 (5)	2,2
H(N2)	458 (8)	392 (7)	-30 (5)	2,4
H(C8)	350 (8)	-64 (8)	-37 (5)	3,3
H(C9)	230 (9)	-191 (9)	103 (6)	4,1
H(C10)	74 (9)	0 (8)	183 (6)	4,1
H(C11)	489 (9)	169 (8)	-112 (5)	3,0
H'(C11)	353 (8)	106 (8)	-165 (6)	3,0
H(C13)	546 (9)	171 (9)	-288 (7)	4,7
H'(C13)	538 (8)	326 (8)	-334 (6)	4,7
H''(C13)	620 (9)	267 (9)	-258 (6)	4,7