

X-ray Structure of (+)-*trans-threo-trans*-3,3'-Bi-1,2,3,9,10,10a-hexahydro-3-phenanthrol

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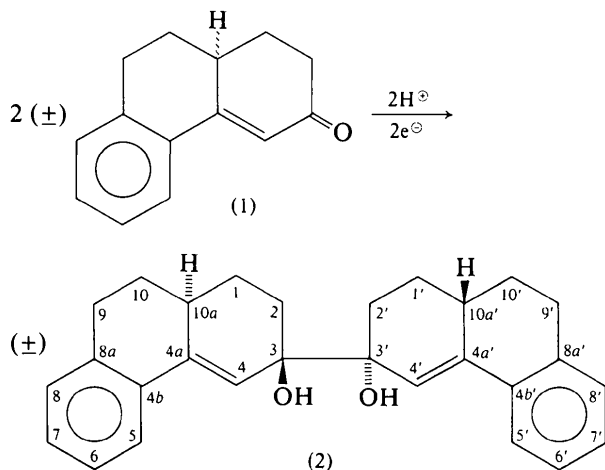
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(Received 1 August 1978; accepted 11 October 1978)

Abstract

Crystals of the dimeric diol (+)C₂₈H₃₀O₂ are orthorhombic, space group *P*2₁2₁2₁, with *a* = 9.679 (8), *b* = 10.182 (9), *c* = 21.861 (7) Å, *Z* = 4. The structure was refined to *R* = 0.033 for 2022 observed reflections. The molecular configuration is *trans-threo-trans*.

Touboul & Dana (1975) have shown that electrolytic reduction in a neutral medium of the racemic ethylenic ketone (1) conjugated with an aromatic ring, leads to only one dimeric diol (2), instead of a mixture of the six expected diastereoisomers. The reaction is highly enantioselective: two ketones having the same absolute configuration are bound together. It is also stereoselective: only one of the three possible stereoisomeric diols was obtained. Unfortunately, the usual physico-chemical methods did not provide the relative configuration of this diol so crystals were studied by X-rays. The sample corresponds to the (+) optically active isomer, [α]_D²² = +436.5° (pyridine) obtained by reduction of the dextrorotatory ketone. Single crystals were obtained by crystallization from acetone.



0567-7408/79/020420-06\$01.00

Experimental

Under the microscope, the crystals appear as small colourless parallelepipeds, which extinguish along the length (*b* axis) of the determinant face (001).

The unit-cell dimensions and space group were initially determined from oscillation and Weissenberg photographs. The conditions limiting possible reflections are: *h*00, *h* = 2*n*; 0*k*0, *k* = 2*n*; 00*l*, *l* = 2*n*. The lattice constants were refined by least squares from 2*θ* values (2*θ* > 54°) of 14 reflections manually set on a diffractometer with Cu *K*_α radiation (λ = 1.5418 Å). Crystal data are given in Table 1.

The crystal used for data collection was 0.30 × 0.20 × 0.55 mm. The intensities of 2200 reflections of the same octant were collected at 295 K on a Nonius CAD-3 three-circle automatic diffractometer in a *θ*/2*θ* scan mode, up to *θ* = 66.8°, at a rate of 10° min⁻¹. The scan width was 1.00 + 0.35 tan *θ*, to take into account *K*_{α1}–*K*_{α2} dispersion. Background was measured in fixed positions before and after the scan. Two standard reflections were monitored every 40 reflections and remained constant within ±1.5%. 178 reflections with *I* < 2σ(*I*) were considered unobserved and excluded. Standard deviations were calculated from σ(*I*) = {*I* + *I*₁ + *I*₂ + [0.02(*I* – *I*₁ – *I*₂)]²}^{1/2}, where *I*₁ and *I*₂ are the backgrounds and *I* the peak count. The intensities were corrected for Lorentz–polarization effects but not for absorption. The structure was solved by the multi-solution method (Germain & Woolfson, 1968) with *MULTAN* (Germain, Main & Woolfson, 1971). The *E*

Table 1. Crystal data

Formula (C ₁₄ H ₁₄ OH) ₂
<i>M_r</i> = 398
Space group <i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> = 9.679 (8), <i>b</i> = 10.182 (9), <i>c</i> = 21.861 (7) Å
<i>V</i> = 2154.4 Å ³
<i>Z</i> = 4
λ = 1.5418 Å
<i>F</i> (000) = 856

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map computed from the most probable starting set of phases based upon 500 reflections with $E > 1.2$ gave the positions of all the non-hydrogen atoms. Full-matrix least-squares refinement led to $R = 0.11$ ($R = \sum |F_o| - |F_c| / \sum |F_o|$) which fell to 0.085 when anisotropic thermal parameters were introduced. At this stage a difference synthesis showed all the H atoms in their expected positions. Their isotropic temperature factors were those of the atoms to which they were bound and were not refined.

The weighting scheme was chosen so that the averages wF^2 were constant for different ranges of F_o . Full-matrix least-squares anisotropic refinement of all non-hydrogen and isotropic of H atoms led to a final R of 0.033. $R_w = [(\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.042$. The standard deviation of unit weight, $S = [(\sum w|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, was 1.011, for $m = 2022$ reflections and $n = 360$ parameters. The completeness of the refinement is given by the ratios of the averaged and maximum parameter shifts to the related e.s.d. in the final cycle: for the non-hydrogen atoms 0.002 and 0.011 [C(7)] respectively.

All calculations were performed on an IBM 70-168 computer with local versions of the following programs: *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinement; *GEST* (De Rango, Tsoucaris, Zelter & Baudour, 1964) for Fourier synthesis; *NRC* programs (Ahmed, Hall, Pippy & Huber, 1966) for geometrical calculations. Scattering factors were those of Cromer & Waber (1965) for C and O and of Stewart, Davidson & Simpson (1965) for H.

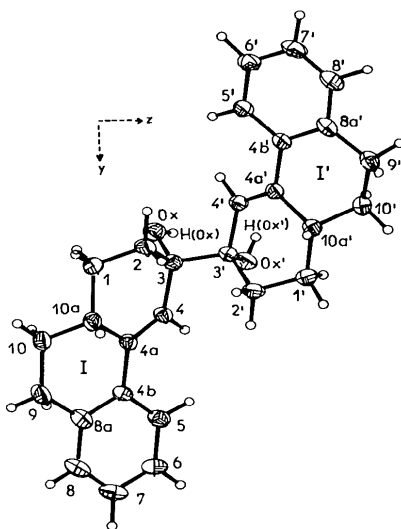


Fig. 1. yoz projection with thermal vibration ellipsoids scaled to 35% probability for the non-hydrogen atoms. The molecule was rotated by -40° around y .

Description of the structure

Fig. 1 is a projection of the molecule (*ORTEP*, Johnson, 1965) and shows the configuration with the OH and OH' groups *trans* with respect to H(10a) and H(10a'). The molecule has the *trans-threo-trans* configuration.

Atomic parameters for non-hydrogen and H atoms are listed in Tables 2 and 3,* where the results for the two halves I and I' of the molecule are separated. From Table 4 it appears that, within the limits of error, the bond lengths are equal for both halves of the molecule. The double bond corresponds to C(4)–C(4a). Aromatic bond lengths have a mean value of 1.396 for I and 1.391 Å for I'. Aliphatic bond lengths for the remaining part of the molecule have a mean value of 1.52 Å [except for C(4a)–C(4b) shortened to 1.491 Å]. Table 5 shows significant differences ($2^\circ > 10\sigma$) between the angles of I and I' around C(4), C(4a) and C(10a). Torsion angles (Table 6) also show significant

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34006 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-hydrogen atoms with e.s.d.'s in parentheses

	x	y	z	B (Å ²)
C(1)	3560 (3)	6510 (3)	7173 (1)	4.26
C(2)	3571 (3)	6198 (2)	7855 (1)	3.75
C(3)	2229 (2)	6667 (2)	8145 (1)	2.97
C(4)	1927 (2)	8074 (2)	7966 (1)	3.06
C(4a)	2535 (2)	8692 (2)	7500 (1)	2.79
C(4b)	2290 (2)	107 (2)	7363 (1)	2.90
C(5)	1814 (3)	977 (3)	7816 (1)	3.66
C(6)	1607 (3)	2305 (3)	7700 (1)	4.32
C(7)	1906 (3)	2800 (2)	7124 (1)	4.52
C(8)	2392 (3)	1970 (3)	6675 (1)	4.28
C(8a)	2585 (3)	618 (2)	6779 (1)	3.35
C(9)	3108 (3)	9753 (3)	6269 (1)	4.23
C(10)	2970 (3)	8301 (1)	6408 (1)	3.91
C(10a)	3482 (3)	7998 (2)	7056 (1)	3.27
C(1')	3231 (3)	7127 (2)	9862 (1)	4.12
C(2')	3079 (3)	7528 (2)	9190 (1)	4.00
C(3')	2208 (3)	6511 (2)	8856 (1)	3.07
C(4')	2632 (2)	5124 (2)	9024 (1)	2.78
C(4a')	3464 (2)	4803 (2)	9488 (1)	2.68
C(4b')	3880 (2)	3417 (2)	9606 (1)	2.87
C(5')	3664 (3)	2422 (2)	9169 (1)	3.56
C(6')	4073 (3)	1133 (2)	9270 (1)	4.19
C(7')	4730 (3)	814 (3)	9811 (2)	4.83
C(8')	4960 (3)	1771 (3)	243 (1)	4.72
C(8a')	4556 (3)	3071 (3)	149 (1)	3.63
C(9')	4868 (3)	4093 (3)	634 (1)	4.56
C(10')	3972 (3)	5303 (3)	577 (1)	3.99
C(10a')	4021 (3)	5834 (2)	9922 (1)	3.31
Ox	1138 (2)	5792 (2)	7932 (1)	3.85
Ox'	800 (2)	6733 (2)	9058 (1)	4.01

Table 3. H atom coordinates ($\times 10^3$) with e.s.d.'s in parentheses

	x	y	z
H(11)	444 (3)	613 (3)	695 (1)
H(12)	275 (3)	608 (3)	698 (3)
H(21)	444 (3)	664 (3)	808 (1)
H(22)	367 (3)	520 (3)	792 (1)
H(4)	125 (3)	850 (3)	820 (1)
H(5)	159 (3)	60 (3)	821 (1)
H(6)	122 (4)	289 (3)	803 (1)
H(7)	178 (3)	370 (3)	703 (1)
H(8)	266 (3)	237 (3)	625 (1)
H(91)	423 (3)	1 (3)	617 (1)
H(92)	296 (3)	997 (3)	588 (1)
H(101)	351 (3)	767 (3)	611 (1)
H(102)	196 (3)	806 (3)	637 (1)
H(10a)	450 (3)	833 (3)	712 (1)
H(11')	378 (4)	782 (4)	8 (1)
H(12')	226 (3)	711 (3)	7 (1)
H(21')	403 (3)	757 (3)	899 (1)
H(22')	226 (3)	838 (3)	913 (1)
H(4')	225 (3)	437 (3)	875 (1)
H(5')	331 (3)	266 (3)	879 (1)
H(6')	396 (3)	45 (3)	897 (1)
H(7')	510 (4)	-6 (3)	986 (1)
H(8')	545 (4)	160 (3)	62 (1)
H(91')	590 (3)	439 (3)	59 (1)
H(92')	481 (4)	371 (3)	105 (1)
H(101')	429 (3)	600 (3)	87 (1)
H(102')	299 (3)	509 (3)	69 (1)
H(10a')	503 (3)	606 (3)	983 (1)
H(Ox)	48 (3)	617 (3)	777 (1)
H(Ox')	29 (3)	632 (3)	880 (1)

differences (up to 11°) between the two non-planar rings of both halves, particularly with respect to C(4a)—C(10a), C(10a)—C(1), C(9)—C(8a) and C(4b)—C(4a). The torsion angles are completely different with respect to the Ox—C(3) and Ox'—C(3') bonds, the two hydroxyl groups being involved in different hydrogen bonds.

The differences between the two non-planar rings are more evident in Table 7 which gives the deviations from the respective mean planes of the C atoms for each half. Half I appears to be less flat than I'. For example, the total deviation between C(3) and C(2) from the mean plane is $0.31 + 0.57 = 0.88 \text{ \AA}$ for I and $0.18 + 0.47 = 0.65 \text{ \AA}$ for I': the total deviations between C(10a) and C(10) are respectively 0.85 \AA for I and 0.75 \AA for I'. This conclusion agrees with the observation that χ^2 is 102 020 for half I and 54 590 for I', *i.e.* about twice as large: $\chi^2 = \sum_{i=1}^N d_i^2/\sigma^2(d_i)$, where d_i is the distance to the mean plane (Ahmed, Hall, Pippy & Huber, 1966). Table 8 shows the deviations of atoms from the mean plane through all the C atoms.

The angle between the mean planes of the two halves is 43° .

There is an intramolecular OH...O hydrogen bond (Fig. 2) between Ox' and Ox, with Ox'...Ox = $2.661 (3)$, H(Ox')...Ox = $2.13 (3) \text{ \AA}$ and Ox'—H(Ox')...Ox = $119 (3)^\circ$. Another short intra-

Table 4. Bond lengths (\AA) in halves I and I' of the molecule with e.s.d.'s in parentheses

	I	I'
C(1)—C(2)	1.523 (2)	1.531 (4)
C(2)—C(3)	1.522 (4)	1.522 (4)
C(3)—C(4)	1.513 (3)	1.516 (3)
C(4)—C(4a)	1.335 (3)	1.336 (3)
C(4a)—C(4b)	1.491 (3)	1.491 (3)
C(4b)—C(5)	1.407 (3)	1.409 (3)
C(5)—C(6)	1.390 (4)	1.389 (3)
C(6)—C(7)	1.385 (4)	1.380 (4)
C(7)—C(8)	1.378 (4)	1.377 (4)
C(8)—C(8a)	1.407 (4)	1.395 (3)
C(4b)—C(8a)	1.408 (3)	1.400 (4)
C(8a)—C(9)	1.508 (4)	1.515 (4)
C(9)—C(10)	1.514 (4)	1.512 (4)
C(10)—C(10a)	1.532 (4)	1.530 (3)
C(4a)—C(10a)	1.510 (3)	1.514 (3)
C(1)—C(10a)	1.538 (4)	1.529 (3)
C(3)—C(3')	1.561 (3)	
C(3)—Ox	1.458 (3)	1.450 (3)
C(1)—H(11)	1.04 (3)	1.04 (3)
C(1)—H(12)	1.02 (3)	1.02 (3)
C(2)—H(21)	1.07 (3)	1.02 (3)
C(2)—H(22)	1.03 (3)	0.96 (3)
C(4)—H(4)	0.94 (3)	1.04 (3)
C(5)—H(5)	0.96 (3)	0.94 (3)
C(6)—H(6)	1.01 (3)	0.97 (3)
C(7)—H(7)	0.95 (3)	0.97 (3)
C(8)—H(8)	1.05 (3)	0.99 (3)
C(9)—H(91)	1.00 (3)	1.05 (3)
C(9)—H(92)	1.14 (3)	0.98 (3)
C(10)—H(101)	1.01 (3)	1.00 (3)
C(10)—H(102)	1.02 (3)	1.01 (3)
C(10a)—H(10a)	1.04 (3)	1.02 (3)
Ox—H(Ox)	0.82 (3)	0.86 (3)

molecular distance is found, in half I alone, between H(Ox) and C(4), with H(Ox)...C(4) = $2.43 (3)$, Ox...C(4) = $2.447 (3) \text{ \AA}$ and Ox—H(Ox)...C(4) = $81 (2)^\circ$. All the intramolecular distances involving four adjacent atoms including one H atom range from $2.52 (3)$ to $2.78 (3) \text{ \AA}$. The short distance of 2.43 \AA might be considered as an intramolecular interaction between H(Ox) and the double bond C(4)=C(4a). Such intramolecular OH... π bonding, between donors and unsaturated linkages (multiple bond or aromatic ring), is now firmly established by infrared spectroscopy (Schuster, Zundel & Sandorfy, 1975; Joesten & Schaad, 1974; Iwamura, 1970; Tichy, 1965).

Consequently an infrared spectrum was recorded with a crystalline powder sample in Fluorolube. The curve obtained (Fig. 3) shows two absorption bands but these do not correspond to a tertiary hydroxyl group which should give one band close to 362.0 mm^{-1} in a dilute solution. Of the two OH absorption bands, the lower frequency broad band (353.0 mm^{-1}) is attributed to an OH...O intramolecular hydrogen bond. The studies of Ben Redjeb, Pascal & Perchard (1978), with solid samples and the method of Lippincott & Schroeder (1955), have shown that this

Table 5. Angles ($^{\circ}$) in halves I and I' of the molecule with *e.s.d.*'s in parentheses

Without hydrogen atoms

	I	I'		I	I'
C(10a)—C(1)—C(2)	111.6 (2)	111.2 (2)	H(11)—C(1)—C(2)	111 (2)	108 (2)
C(1)—C(2)—C(3)	109.7 (2)	109.4 (2)	H(11)—C(1)—C(10a)	109 (2)	108 (2)
C(2)—C(3)—C(4)	110.8 (2)	112.6 (2)	H(12)—C(1)—C(2)	110 (2)	109 (2)
C(2)—C(3)—C(3')	113.8 (2)	113.2 (2)	H(12)—C(1)—C(10a)	109 (2)	114 (2)
C(4)—C(3)—C(3')	110.0 (2)	109.4 (2)	H(11)—C(1)—H(12)	107 (3)	107 (3)
C(4)—C(3)—Ox	110.9 (2)	109.0 (2)	H(21)—C(2)—C(3)	111 (2)	109 (2)
C(2)—C(3)—Ox	107.0 (2)	105.6 (2)	H(21)—C(2)—C(1)	111 (2)	110 (2)
C(3')—C(3)—Ox	104.3 (2)	107.4 (2)	H(22)—C(2)—C(3)	109 (2)	109 (2)
C(3)—C(4)—C(4a)	123.9 (2)	125.1 (2)	H(22)—C(2)—C(1)	110 (2)	114 (2)
C(4)—C(4a)—C(10a)	122.5 (2)	121.4 (2)	H(21)—C(2)—H(22)	106 (3)	106 (3)
C(4)—C(4a)—C(4b)	122.6 (2)	121.8 (2)	H(4)—C(4)—C(3)	116 (2)	117 (2)
C(10a)—C(4a)—C(4b)	114.8 (2)	116.8 (2)	H(4)—C(4)—C(4a)	121 (2)	118 (2)
C(4a)—C(4b)—C(8a)	120.5 (2)	120.5 (2)	H(5)—C(5)—C(4b)	117 (2)	119 (2)
C(4a)—C(4b)—C(5)	121.3 (2)	121.5 (2)	H(5)—C(5)—C(6)	121 (2)	119 (2)
C(8a)—C(4b)—C(5)	118.2 (2)	117.7 (2)	H(6)—C(6)—C(5)	120 (2)	123 (2)
C(4b)—C(5)—C(6)	122.0 (2)	121.9 (2)	H(6)—C(6)—C(7)	121 (2)	118 (2)
C(5)—C(6)—C(7)	119.5 (3)	119.4 (2)	H(7)—C(7)—C(6)	122 (2)	119 (2)
C(6)—C(7)—C(8)	119.6 (3)	119.7 (3)	H(7)—C(7)—C(8)	118 (2)	121 (2)
C(7)—C(8)—C(8a)	122.1 (3)	121.7 (3)	H(8)—C(8)—C(8a)	119 (2)	116 (2)
C(8)—C(8a)—C(9)	119.8 (2)	119.4 (2)	H(8)—C(8)—C(7)	119 (2)	123 (2)
C(8)—C(8a)—C(4b)	118.7 (2)	119.7 (2)	H(91)—C(9)—C(10)	110 (2)	108 (2)
C(9)—C(8a)—C(4b)	121.5 (2)	120.9 (2)	H(91)—C(9)—C(8a)	109 (2)	108 (2)
C(8a)—C(9)—C(10)	113.1 (2)	112.8 (2)	H(92)—C(9)—C(10)	110 (2)	112 (2)
C(9)—C(10)—C(10a)	110.7 (2)	110.3 (2)	H(92)—C(9)—C(8a)	109 (2)	111 (2)
C(10)—C(10a)—C(1)	111.6 (2)	111.7 (2)	H(91)—C(9)—H(92)	105 (3)	105 (3)
C(4a)—C(10a)—C(1)	112.6 (2)	111.4 (2)	H(101)—C(10)—C(10a)	109 (2)	108 (2)
C(4a)—C(10a)—C(10)	107.7 (2)	109.3 (2)	H(101)—C(10)—C(9)	111 (2)	110 (2)
			H(102)—C(10)—C(9)	108 (2)	110 (2)
			H(101)—C(10)—H(102)	108 (3)	107 (3)
			H(102)—C(10)—C(10a)	110 (2)	109 (2)
			H(10a)—C(10a)—C(4a)	110 (2)	112 (2)
			H(10a)—C(10a)—C(1)	104 (2)	106 (2)
			H(10a)—C(10a)—C(10)	111 (2)	107 (2)
			H(Ox)—Ox—C(3)	114 (2)	106 (2)

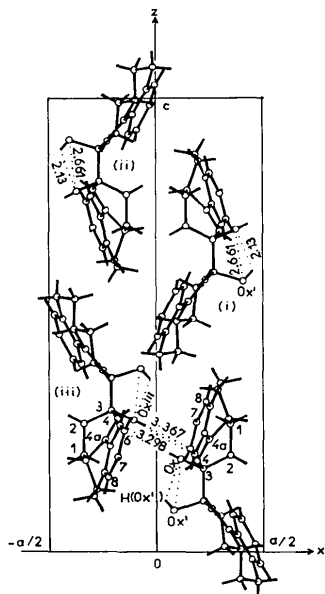
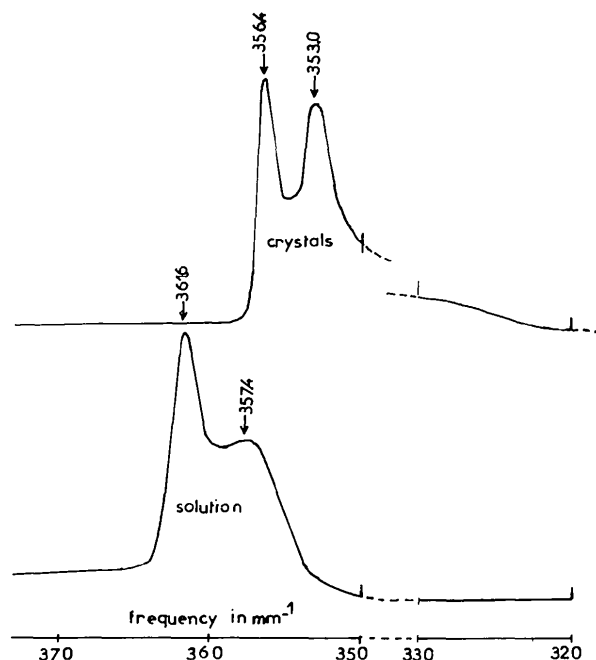
Fig. 2. $x0z$ projection, showing the intramolecular OH...O bond and the short intermolecular distances in one cell.

Fig. 3. Infrared spectra of the compound in the crystalline state (above) and in solution (below).

Table 6. Torsion angles ($^{\circ}$) in the two non-planar rings of the two halves I and I' of the molecule (σ 0.5 $^{\circ}$)

Bond	Atoms		I	I'
	In front	Behind		
C(1)–C(2)	C(10a)	C(3)	–62.4	–63.9
C(2)–C(3)	C(1)	C(4)	49.6	44.2
	C(1)	C(3')	174.4	168.5
	C(1)	Ox	–71.3	–74.1
C(3)–C(4)	C(2)	C(4a)	–16.4	–12.4
	C(3')	C(4a)	–142.7	–138.9
	Ox	C(4a)	102.3	103.9
C(4)–C(4a)	C(3)	C(10a)	–6.9	–3.1
	C(3)	C(4b)	175.5	177.3
C(4a)–C(10a)	C(4)	C(1)	–4.6	–14.9
	C(4)	C(10)	–128.1	–138.8
	C(4b)	C(1)	173.2	164.7
	C(4b)	C(10)	49.7	40.8
C(10a)–C(1)	C(4a)	C(2)	38.9	47.9
	C(10)	C(2)	160.1	170.5
C(4a)–C(4b)	C(10a)	C(8a)	–17.6	–10.4
	C(4)	C(8a)	160.2	169.2
	C(4)	C(5)	–22.4	–13.5
	C(10a)	C(5)	159.8	166.9
C(4b)–C(8a)	C(4a)	C(9)	–2.1	–0.7
	C(5)	C(9)	–179.7	–178.1
	C(8)	C(4a)	177.5	178.7
C(8a)–C(9)	C(4b)	C(10)	–12.7	–20.3
	C(8)	C(10)	167.7	160.3
C(9)–C(10)	C(8a)	C(10a)	46.2	51.3
C(10)–C(10a)	C(9)	C(4a)	–64.3	–61.4
	C(9)	C(1)	171.4	174.9
C(3)–C(3')	C(2)	C(2')	–75.1	
	C(2)	C(4')	50.3	
	C(2)	Ox'	168.6	
	C(4)	C(2')	49.8	
	C(4)	C(4')	175.2	
	C(4)	Ox'	–66.4	
	Ox	C(2')	169.0	
	Ox	C(4')	–65.6	
	Ox	Ox'	52.6	
Ox–C(3)	H(Ox)	C(4)	5.4	75.6
	H(Ox)	C(2)	126.3	–164.5
	H(Ox)	C(3')	–113.5	–42.9

Table 7. Equations of the mean planes through the carbon atoms of the two halves I and I' and deviations of the atoms (\AA) from these planes, with e.s.d.'s in parentheses

Planes are represented by equations of the type $lx + my + nz - p = 0$ referred to an orthogonal system of axes, which has x along a , y in the ab plane, z along c .

$$\text{Half I: } 0.9188x + 0.2296y + 0.3211z - 9.5673 = 0$$

$$\text{Half I': } 0.8908x + 0.1849y - 0.4150z + 4.7274 = 0$$

Atoms in plane	I	I'
C(1)	–0.155 (4)	0.093 (4)
C(2)	–0.572 (3)	–0.466 (4)
C(3)	0.310 (3)	0.176 (3)
C(4)	0.375 (3)	0.225 (3)
C(4a)	0.020 (3)	–0.012 (3)
C(4b)	0.001 (3)	–0.003 (3)
C(5)	–0.099 (3)	–0.026 (3)
C(6)	–0.139 (4)	–0.042 (4)
C(7)	–0.119 (4)	–0.063 (4)
C(8)	–0.044 (4)	–0.050 (3)
C(8a)	0.029 (3)	–0.029 (3)
C(9)	0.118 (4)	–0.055 (4)
C(10)	0.496 (4)	0.448 (4)
C(10a)	–0.358 (3)	–0.298 (3)

Other atoms

Ox	1.635 (2)	1.530 (2)
H(11)	–0.80 (4)	–0.29 (4)
H(12)	0.81 (4)	1.15 (4)
H(21)	–1.61 (3)	–1.53 (3)
H(22)	–0.49 (3)	–0.34 (4)
H(4)	0.77 (3)	0.48 (3)
H(5)	–0.05 (3)	–0.12 (3)
H(6)	–0.09 (4)	–0.09 (4)
H(7)	–0.06 (3)	–0.18 (4)
H(8)	–0.06 (4)	–0.15 (4)
H(91)	–0.89 (4)	–1.15 (4)
H(92)	0.75 (4)	0.39 (4)
H(101)	0.38 (3)	0.37 (4)
H(102)	1.54 (3)	1.52 (4)
H(10a)	–1.48 (3)	–1.34 (3)
H(Ox)	2.29 (3)	1.88 (3)

frequency should correspond to a value of about 53 $^{\circ}$ for the angle H(Ox')–Ox'–Ox. This is close to the experimental angle of 45 $^{\circ}$. If we consider a probable error of +3(σ) for the bond length measured in this X-ray study, it will give H(Ox')–Ox' = 0.98 \AA and Ox...H(Ox') = 2.21 \AA , and this angle would be 53 $^{\circ}$. The value of the higher-frequency narrow band (356.4 mm^{-1}) is lower than that observed in solution for the stretching mode OH... π (over 358.5 mm^{-1}); it is however known that absorption bands are shifted towards lower frequencies on passing from solution to solid (Richards & Thompson, 1947).

In order to investigate this question further another infrared spectrum was recorded with a solution of the compound in anhydrous CCl_4 . This also shows two bands at 357.4 mm^{-1} and 361.6 mm^{-1} (Fig. 3). The first frequency is attributed, for this dilute solution, to the intramolecular OH...O bond; the second band is

the normal one for a free tertiary OH group. Nevertheless, the observed 356.4 mm^{-1} value of the spectrum for the solid would suggest a strong OH... π interaction in the solid state. H(Ox) is not however symmetrically located with respect to C(4) and C(4a) as might be expected. H(Ox)–C(4a) is 3.31 (3) \AA long and furthermore the OH bond is nearly perpendicular to the C(4)–C(4a)–H(Ox) plane [Ox–H(Ox)...C(4a) = 88 (2) $^{\circ}$]. These two observations rule out the possibility of a strong intramolecular OH... π interaction (Bonchev & Cremaschi, 1974). We conclude that there is probably in the crystals an intermolecular interaction involving H(Ox).

The intermolecular distances in this structure are approximately equal to the sum of the van der Waals radii for C and O (Bondi, 1964). The shortest intermolecular distances are, however, precisely those between the OH group of the molecule in the position

Table 8. Mean plane through all the carbon atoms of the molecule: deviations of these atoms from the plane and distances of the other atoms (Å), with e.s.d.'s in parentheses

Atoms in plane	I	I'
C(1)	0.338 (4)	0.166 (4)
C(2)	0.280 (3)	0.116 (4)
C(3)	-0.882 (3)	-0.937 (3)
C(4)	-0.851 (3)	-0.852 (3)
C(4a)	-0.140 (3)	-0.138 (3)
C(4b)	-0.048 (3)	-0.058 (3)
C(5)	-0.300 (3)	-0.489 (3)
C(6)	-0.200 (4)	-0.496 (4)
C(7)	0.199 (4)	0.159 (4)
C(8)	0.470 (4)	0.594 (4)
C(8a)	0.346 (3)	0.504 (3)
C(9)	0.650 (4)	1.034 (4)
C(10)	0.178 (4)	0.451 (4)
C(10a)	0.607 (3)	0.628 (3)
Other atoms		
Ox	-2.110 (2)	-2.215 (2)
H(11)	-0.52 (4)	-0.78 (4)
H(12)	1.17 (4)	0.81 (4)
H(21)	1.21 (4)	1.09 (4)
H(22)	0.17 (3)	-0.06 (4)
H(4)	-1.44 (3)	-1.40 (3)
H(5)	-0.65 (3)	-0.78 (3)
H(6)	-0.51 (4)	-0.66 (4)
H(7)	0.19 (4)	0.31 (4)
H(8)	0.82 (4)	1.06 (4)
H(91)	0.26 (4)	0.93 (4)
H(92)	1.79 (4)	2.18 (4)
H(101)	0.55 (4)	0.84 (4)
H(102)	-0.88 (4)	-0.61 (4)
H(10a)	1.74 (3)	1.68 (3)
H(Ox)	-2.83 (3)	-2.70 (3)

(x, y, z) and the phenyl atoms, particularly C(5) and C(6), of the molecule in the equivalent position (iii) [$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$]. The relevant distances are: $Ox \cdots C(5iii) = 3.298$ (3) Å [with $H(Ox) \cdots C(5iii) = 2.57$ (3) Å and $Ox-H(Ox) \cdots C(5iii) = 148^\circ$] and $Ox \cdots C(6iii) = 3.367$ (3) Å [with $H(Ox) \cdots C(6iii) = 2.54$ (3) Å and $Ox-H(Ox) \cdots C(6iii) = 180^\circ$]. The angles between $Ox-H(Ox)$ and the two C atoms of the phenyl group (iii) are large, which supports the conclusion suggested by the infrared studies that there is $OH \cdots$ phenyl intermolecular interaction. Literature searches have, to date, provided only two examples of $OH \cdots$ phenyl bonds established by X-ray crystal structure studies, both

about 3 Å in length and both intramolecular in character (Hardy & McNicol, 1976; McPhail, Sim, Frey & Ott, 1966). No examples of intermolecular $OH \cdots$ phenyl bonds, except that observed here, have been found in X-ray crystal structure studies carried out, either alone or in conjunction with infrared studies.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM 360 System. *World List of Crystallographic Computer Programs*, 2nd ed., p. 52. Utrecht: Oosthoek.
- BEN REDJEB, S., PASCAL, Y. L. & PERCHARD, J. P. (1978). *J. Chim. Phys. Phys.-Chim. Biol.* In the press.
- BONCHEV, D. & CREMASCHI, P. (1974). *Gazz. Chim. Ital.* **104**, 1195-1205.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441-451.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
- DE RANGO, C., TSOUCARIS, G., ZELVER, C. & BAUDOUR, J. L. (1964). *Bull. Soc. Sci. Bretagne*, **39**, 155-161.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368-370.
- GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **A24**, 91-96.
- HARDY, A. D. U. & MCNICOL, D. D. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 1140-1142.
- IWAMURA, H. (1970). *Tetrahedron Lett.* pp. 2227-2230.
- JOESTEN, M. D. & SCHAAD, L. J. (1974). *Hydrogen Bonding*. New York: Dekker.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- LIPPINCOTT, E. R. & SCHROEDER, R. (1955). *J. Chem. Phys.* **23**, 1099-1106.
- MCPhAIL, A. T., SIM, G. A., FREY, A. J. & OTT, H. (1966). *J. Chem. Soc. B*, pp. 377-395.
- RICHARDS, R. E. & THOMPSON, H. W. (1947). *J. Chem. Soc.* pp. 1260-1277.
- SCHUSTER, P., ZUNDEL, G. & SANDORFY, C. (1975). *The Hydrogen Bond*. Amsterdam: North-Holland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
- TICHY, M. (1965). *Advances in Organic Chemistry*, Vol. 5, pp. 157-161. New York: Wiley-Interscience.
- TOUBOUL, E. & DANA, G. (1975). *Tetrahedron*, **31**, 1925-1931.