Naphthalene Tetrachlorides and Related Compounds. Part 11.[1] trans-1,1,3,4-Tetrachlorotetralin-2-one, its Hydrate, and Related Compounds

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X-Ray crystallographic analysis of 1,1,3,4-tetrachlorotetralin-2,2-diol has shown that this compound is the trans-isomer, which can be reversibly dehydrated to give trans-1,1,3,4-tetrachlorotetralin-2-one of previously unknown configuration, produced nearly quantitatively by chlorination of 2-naphthol in acetic acid. The ^{1}H and ^{13}C spectra of these compounds are reported; most of the angular-dependent coupling constants accord with expectations, the value of $^{3}J(^{13}C-1, ^{1}H-3)$ being low, probably because the coupling path includes a carbonyl carbon atom. The rather high value of $^{3}J(H-3, H-4)$ is discussed. The properties of some related ketodichlorides and ketotetrachlorides are reported.

The chlorination of 2-naphthol in acetic acid with successively increasing amounts of chlorine follows the pathway shown in sequence (1).[2-4] The di- and poly-halogenated compounds are of synthetic interest because of their potential use in preparing 3-, 4-, and 6-substituted derivatives of 2-naphthol. Thus (4) undergoes elimination on being heated in acetic acid to give 1,1,3-trichloro-1,2-dihydronaphthalen-2-one (5), which on reduction with sodium hydrogensulphite in acetic acid gives 1,3-dichloro-2-naphthol [(6), sequence (2)]. Treatment of (3) with hydrogen chloride in acetic acid gives 1,4-dichloro-2-naphthol, apparently according to sequence (3), whereas with HBr in acetic acid, it is reported to give 1-chloro-6-bromo-2-naphthol [sequence (4)].[3]

Despite the long history of these reactions, neither the mechanism of formation nor the stereochemistry of the tetrachlorotetralinone (4) has been established. In the present work, ^{1}H and ^{13}C n.m.r. spectroscopy have been used in conjunction with X-ray crystallography to establish the configuration of this compound.

Experimental

Most of the materials and methods have been described in earlier Parts.[1,5,6] Except where otherwise mentioned, u.v. spectra were determined in hexane by using a Unicam SP 800, and i.r. spectra as mulls in Nujol by using a Unicam SP 200 instrument. Some ^{1}H n.m.r. spectra were determined by Dr. M. D. Johnson (University College London), whom we thank. For later ^{1}H spectra, a Varian T60, and for ^{13}C n.m.r. spectra, a JEOL FX-60 instrument was used. Some illustrative spectral information is included in Supplementary Publication No. SUP 23486 (43 pp).†

2-Naphthol, m.p. 121—123 °C, was commercial material used without further purification, and on chlorination with chlorine (1 mol. equiv.) in acetic acid gave 1-chloro-2-naphthol (2), m.p. 70—71 °C (lit.,[2] 70—71 °C). Earlier procedures[2,3] for preparation of 1,1-dichloro-1,2-dihydronaphthalen-2-one were not satisfactory in our hands, so the following modification was used. 2-Naphthol (4.8 g) was dissolved by being heated with anhydrous acetic acid (20 cm³) and the mixture was shaken and cooled to give a paste of needles of 2-naphthol

in acetic acid. The calculated amount (4.7 g) of chlorine in acetic acid (70 cm³) was added dropwise to the above mixture, which was cooled and stirred vigorously. A light yellow solution was finally produced, from which the solvent was removed as rapidly as possible under reduced pressure at room temperature. The residue was dissolved in benzene–light petroleum (b.p. 100—120 °C) (2:1 v/v) and the solvent was again removed under reduced pressure. This was repeated until most of the acetic acid had been removed and the resulting syrup crystallized. The solid was pressed between clay plates to remove any remaining syrup, and was eluted through a short column of silica gel by using warm (35—40 °C) light petroleum (b.p. 100—120 °C) as eluant. The eluted material was concentrated under reduced pressure, admission of moisture being avoided. 1,1-Dichloro-1,2-dihydronaphthalen-2-one (3) crystallized as nearly colourless plates, m.p. 52—54 °C (lit.,[3] 54 °C). Yields averaged 65%. This compound decomposes on being stored at room temperature, but is reasonably stable at 0 °C, $\lambda_{max.}$ (C_6H_{14}) 241 ($\log_{10} \varepsilon$ 4.40) and 325 nm (3.86), $\nu_{max.}$ (Nujol) 1 676s, 1 621m, 1 567m, 1 302, 1 279, 1 245, 1 236, 1 215, 1 199s, 1 159, 1 129m, 1 108, 990, 982, 972, 932s, 916, 882, 843m, 807s, 794m, 757s, 726w, 695s, and 652 s cm⁻¹, δ(CDCl₃) 6.3 (H-3, $J_{3,4}$ 10 Hz), 7.45 (H-4, $J_{3,4}$ 10 Hz), 7.25—7.65 (assumed 3 H, m, H-5, -6, -7), and 7.9—8.15 (1 H, m, H-8). On being reduced (NaHSO₃), it gave 1-chloro-2-naphthol (2), m.p. 70—71 °C. On being suspended in HOAc saturated with hydrogen chloride, the solid slowly disappeared, and after several days crystalline material separated as plates from the brown solution. The solid was filtered off and recrystallized from light petroleum (b.p. 100—120 °C) to give 1,4-dichloro-2-naphthol, m.p. 120—121 °C (lit.,[2] 123—124 °C). Treatment of this with the calculated amount of chlorine in chloroform gave 1,1,4-trichloro-1,2-dihydronaphthalen-2-one, m.p. 85—87° (lit.,[2] 86—87 °C). Further addition of chlorine to this has been recorded by Zincke as giving 1,1,3,4,4-pentachloro-1,2-dihydronaphthalen-2-one, but in our hands this was unstable, undergoing rapid elimination to give a mixture including 1,1,3,4-tetrachloro-1,2-dihydronaphthalene-2-one, which was better prepared from 1,3,4-trichloro-2-naphthol and chlorine, and had m.p. 87—89 °C (lit.,[2] 96—97 °C); $\lambda_{max.}$ 249 ($\log_{10} \varepsilon$ 4.36) and 337 nm (3.84); $\nu_{max.}$ 1 704s, 1 585, 1 546, 1 309, 1 289, 1 256m, 1 215s, 1 168, 1 129, 1 057, 998m, 960, 945m, 898, 881, 832, 811m, 767s, 726, and 678s cm⁻¹.

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† For details of Supplementary Publications see Notice to Authors No. 7 in J. Chem. Soc., Perkin Trans. 2, 1981, Index Issue.
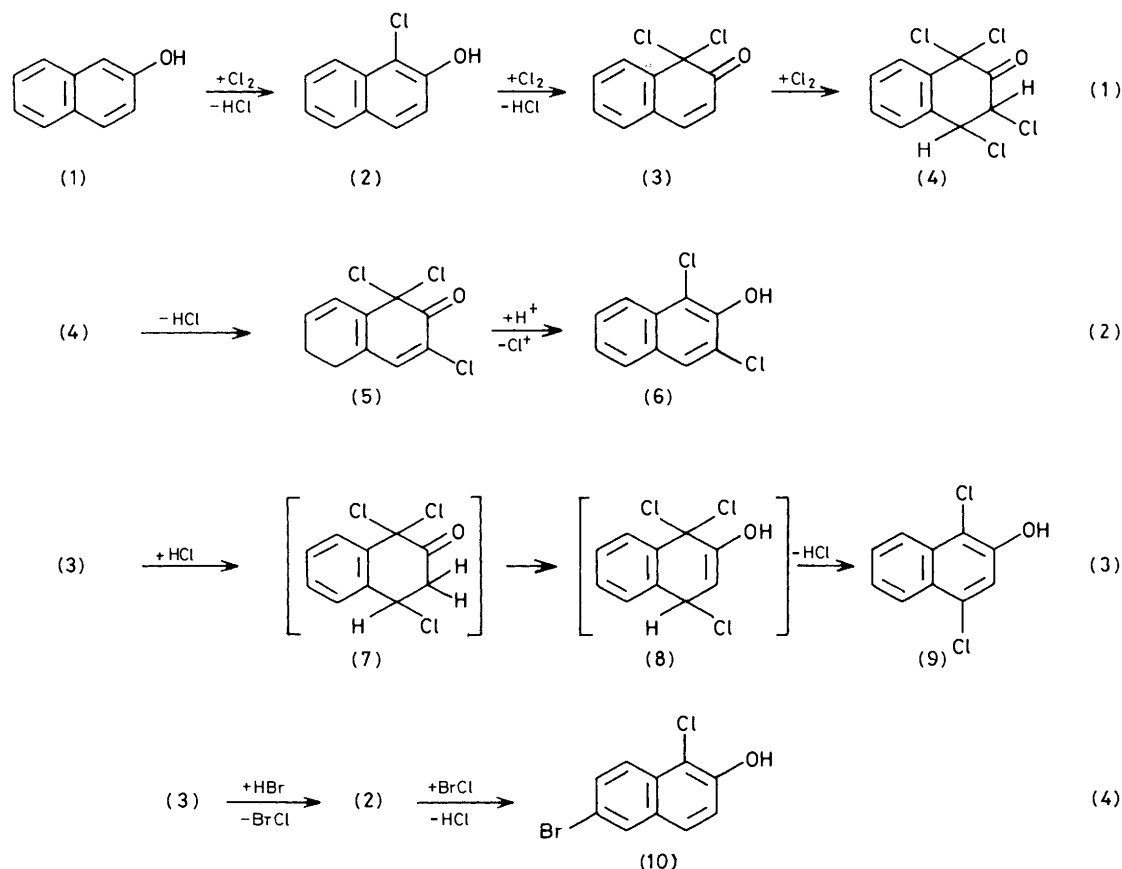
Reaction of 2-naphthol (5 g) with excess of chlorine in acetic acid (50 cm³) gave the 1,1,3,4-tetrachlorotetralin-2-one (4) which could be isolated by pouring the reaction mixture into water and recrystallizing the recovered precipitate from light petroleum (b.p. 60—80 °C), m.p. 100—102 °C (lit.,[2] 102—103 °C), λ_{max} 198 (log$_{10}$ ε 4.51), 220sh (4.00), and 315 nm (1.86). For this detailed spectrum, which is reproduced in SUP 23486, we are indebted to Dr. E. A. Johnson (Medical Research Council Laboratories, Mill Hill). Its i.r. spectrum had maxima at 1 751s, 1 348, 1 306, 1 239, 1 220m, 1 201, 1 188, 1 163, 1 153s, 1 115, 1 029m, 923m, 904, 882, 847s, 803, 786, 781, 760s, 745m, 722s, and 686 cm⁻¹. Its ¹H n.m.r. spectrum (CDCl₃) had signals at δ 4.89 (1 H, d, H-3, $J_{3,4}$ 4.8 Hz), 5.33 (1 H, d, H-4, $J_{3,4}$ 4.8 Hz), 7.35—7.85 (3 H, m, ArH), and 8.05—8.30 (m, 1 H, ArH, probably H-8). Within the experimental error of ¹H n.m.r. spectroscopy, it is formed quantitatively under the stated conditions, since no extraneous signals could be seen in the spectrum of the product obtained by evaporation of all the solvent, hydrogen chloride, and excess of chlorine from the reaction mixture. Hydrogen chloride as catalyst is necessary, however, for the final stage of addition to the intermediate ketodichloride (3). Attempted preparation of the tetrachlorotetralin-2-one by carrying out the chlorination in acetic acid containing water (10%) and sodium acetate (excess) gave only a mixture containing ≯6% of (4), up to 6% of other tetralinones (probably keto-acetoxytrichlorides), ca. 40% ketodichloride (3), and other acetoxy-containing material.

The ¹H n.m.r. spectrum of the tetrachlorotetralin-2-one was examined in two solvents and at different temperatures. Small but significant variations in the coupling constant, ³$J_{H-3,H-4}$, were noted, as is shown in Table 1.

Solutions of the tetrachlorotetralin-2-one (4), particularly in hydroxylic solvents, gradually decomposed by loss of hydrogen

Table 1. Solvent- and temperature-dependence of the vicinal coupling constant (³$J_{H-3, H-4}$) in the ¹H n.m.r. spectrum of 1,1,3,4-tetrachlorotetralin-2-one

Solvent	$T/°C$	³$J_{H-3, H-4}$/Hz
CDCl₃	57	5.0
	40	5.0
	11	4.8
	−18	4.7
	−63	4.4
(CD₃)₂CO	50	4.5
	24	4.5
	−55	4.1
	−68	4.0

chloride. When a solution in acetic acid was heated (5 min) and poured into water, the precipitated oil slowly solidified. It was filtered off and recrystallized [light petroleum (b.p. 80—100 °C)] to give yellow needles of 1,1,3-trichloro-1,2-dihydronaphthalen-2-one (5), m.p. 93—95 °C (lit.,[2] 95—96 °C), λ_{max} 248 (log$_{10}$ ε 4.37) and 340 nm (3.86), ν_{max} 1 692s, 1 608m, 1 594, 1 564m, 1 345m, 1 308, 1 276, 1 254, 1 233s, 1 215m, 1 200, 1 157m, 1 117, 970s, 956, 926s, 874, 835s, 818s, 761s, 730, 691m, and 670s cm⁻¹. This on treatment with excess of NaHSO₃ in hot acetic acid gave 1,3-dichloro-2-naphthol, m.p. 78—79 °C (lit.,[2] 80—81 °C).

Further chlorination of (5) in acetic acid gave 1,1,3,3,4-pentachlorotetralin-2-one, m.p. 114—116 °C (lit.,[2] 116—117 °C), λ_{max} 243sh nm (log$_{10}$ ε 3.57); ν_{max} 1 761s, 1 337, 1 304, 1 265, 1 231s, 1 206m, 1 126m, 930s, 923, 882m, 861s, 826s, 787, 765, 749s, 720s, 693s, and 671s cm⁻¹, δ 5.59 (1 H, s, H-4) and 7.35—7.85 and 8.00—8.25 (4 H, m, ArH).

Reduction of this ketone and elimination of HCl (NaHSO₃,

Table 2. [13]C N.m.r. frequencies and coupling constants obtained from the spectra of *trans*-1,1,3,4-tetrachlorotetralin-2-one in CDCl₃ at *ca.* 30 °C

			Multiplicity				Derived coupling constants				
Position of signal [a]	Assignment	Single resonance [b]	LPSF Downfield aromatic [c]	LPSF Upfield aromatic [c]	LPSF Upfield alicyclic (H-3)	LPSF Downfield alicyclic (H-4)	$^1J_{C-H}$/Hz	^2J/Hz	^3J/Hz (H-3)	^3J/Hz (H-8)	^3J/Hz (H-4)
57.434	C-3	d; d	d; d	d; d	d; d	d; s	164.5	4.9			
58.018	C-4	d; m	d; m	d; d	d; m	d; m	160.6	4.4 [d]			
78.080	C-1	s; dd	s; d	s; dd	s; d	d; br d			2.9 [e]	4.9 [e]	
128.596	C-5 or -6 or -7 or -8	d; m	d; m	d; m	d; m	d; m	*ca.* 163				
128.923	C-9 or -10	s; m	s; m	s; m	s; m	s; m	—				
129.864	C-5 or -6 or -7 or -8	d; m	d; m	d; m	d; m	d; m	*ca.* 165				
130.705	C-5 or -6 or -7 or -8	d; m	d; m	d; m	d; m	d; m	*ca.* 165				
131.001	C-5 or -6 or -7 or -8	d; m	d; m	d; m	d; m	d; m	*ca.* 165				
136.518	C-9 or -10	s; m	s; m	s; m	s; m	s; m					
187.751	C-2	s; dd	s; dd	s; dd	s; d	s; d			4.6 [f]		6.6 [f]

[a] p.p.m. Downfield from Me₄Si. [b] Main multiplicity given first. [c] Aromatic signals much simplified but couplings not completely removed. [d] $^3J_{H-5, C-4}$ is not resolved. [e] LPSF Decoupling on aromatic hydrogen cuts out the larger coupling, whereas decoupling on alicyclic H cuts out the smaller coupling. [f] Both couplings are reduced by LPSF decoupling on alicyclic H; the larger is $^3J_{H-4 C-2}$.

warm HOAc) gave 1,3,4-trichloro-2-naphthol, m.p. 160—161 °C (lit.,[2] 162 °C), which on monochlorination gave 1,1,3,4-tetrachloro-1,2-dihydronaphthalen-2-one (see above), and on treatment with excess of chlorine in chloroform in diffuse daylight gave slowly 1,1,3,3,4,4-hexachlorotetralin-2-one, m.p. 128—129 °C (lit.,[2] 129 °C), $v_{max.}$ 1 763s, 1 224s, 1 197m, 1 130m, 1 120, 1 068, 1 048, 951, 928m, 890m, 871, 853s, 805m, 796m, 750s, 699s, and 683s cm⁻¹.

Zincke and Kegel[2] reported that the tetrachlorotetralin-2-one (4) can be obtained by recrystallization from aqueous acetic acid as a hydrate ($C_{10}H_6Cl_4O,H_2O$), m.p. 90—91 °C. We found that the anhydrous form, m.p. 100—102 °C, is more easy to prepare. Attempted recrystallization of (4) at 0° from moist chloroform, however, gave crystals from which at least two forms could be sorted by hand. One of these forms was sufficiently stable for collection and analysis of the X-ray diffraction pattern. It was the trihydrate of (4) ($C_{10}H_6Cl_4O,3H_2O$), with one molecule of water covalently bound by addition to the carbonyl group. Slightly moist material had m.p. 65—69 °C. Its ¹H n.m.r. spectrum was determined in CDCl₃ by using a sample obtained by recrystallization from aqueous acetic acid, and shows that the organic species present in solution is *trans*-1,1,3,4-tetrachlorotetralin-2,2-diol (11), δ 3.75 (1 H, s, OH), 4.20 (1 H, s, OH), 5.05 and 5.48 (1 H, each d, H-3, -4, $J_{3,4}$ 10 Hz), 7.3—7.8 (3 H, m, ArH), and 7.85—8.05 (1 H, m, ArH, probably H-8). We assume that under these conditions the two extra molecules of water present in the crystal have dissociated. The large value of the $^3J_{H,H}$ coupling constant establishes that the conformation of the hydrate is as shown in (11), with 3- and 4-H atoms respectively axial and pseudoaxial. The molecule, like that of (4), is chiral, and all our results refer to racemic mixtures including the enantiomorphs.

The hydrate undergoes dehydration on being kept at room temperature under vacuum with P₂O₅ in a separate vessel to act as drying agent. The product is the expected tetralinone (4), which evidently has the structure and conformation (12), and is hydrated very slowly in wet CHCl₃ as shown by the ¹H n.m.r. spectrum examined over the course of several days. Relatively rapid hydration occurs in wet acetic acid, though this reaction is slow on the ¹H n.m.r. time-scale, since the

(11) ⇌ (12)   (−H₂O / +H₂O)
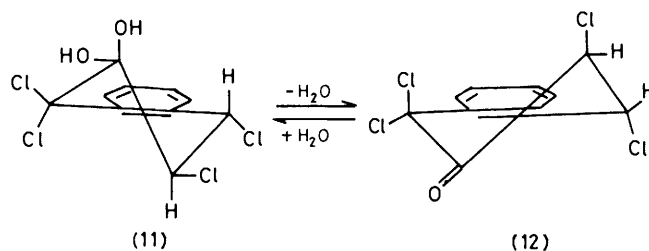
signals of the two compounds are quite distinct in solutions containing mixtures. When the mixture was allowed to stand in CH₃CO₂D containing D₂O, slow decomposition occurred; after 7 days, no alicyclic signals remained, and the product was mainly 1,1,3-trichloro-2-dihydronaphthalene (5). Both before and after partial decomposition of the mixture of 1,1,3,4-tetrachlorotetralin-2-one and its hydrate in this solvent, the alicyclic signals characteristic of the former compound were still a clear doublet of doublets, so neither the 3- nor the 4-H was involved in the formation of the hydrate.

[13]C *N.m.r. Spectra.*—Details of the [13]C n.m.r. spectra of the tetrachlorotetralin-2-one (12) and of its hydrate are given in SUP 23486. For the former compound in CDCl₃, the signals in the single-resonance spectra have been analysed by low-power single-frequency decoupling at the frequencies corresponding with the various resonances in the ¹H spectrum. They determine the assignments and values of the various coupling constants to be as shown in Table 2.

The hydrate (11) was only slightly soluble in deuteriochloroform, and the spectrum in this solvent included signals of (12), present as an impurity or formed by partial dissociation. A better spectrum was obtained in a mixture of CD₃CO₂D (90%) and D₂O (10%), when only slight decomposition occurred during accumulation of the single-resonance spectrum. For reference, Me₃C·CD₂CD₂·CO₂Na was used; values given below have been corrected to Me₄Si as reference by deduction of 3.0 p.p.m., which is the mean difference in positions of the signals identified both in this solvent and in CDCl₃. Individual signals differed, however, by up to 1.5

Table 3. Dihydrate of *trans*-1,1,3,4-tetrachlorotetralin-2,2-diol

(i) Crystal properties

$C_{10}H_{12}O_4Cl_4$	$M = 338.0$
Orthorhombic	$a = 7.102\ 1(4)$ Å
Space group *Pcab*	$b = 12.655\ 9(6)$ Å
$Z = 8$	$c = 30.876\ 4(22)$ Å
Cu-K_α radiation	$U = 2\ 775.3$ Å^3
μ(Cu-K_α) = 77.8 cm^{-1}	

(ii) Experimental conditions for data collection

Crystal size (mm)	crystal 1, 0.30 × 0.34 × 0.06
	crystal 2, 0.52 × 0.40 × 0.07
$\theta_{min.}, \theta_{max.}$	crystal 1, 1, 50°;
	crystal 2, 50, 67°.
Scan mode	ω–2θ
Scan-width parameters	A,B in width = $A + B\tan\theta$: 1.7, 1.2
Total unique data	2 880
Observed data $[I > 3\sigma(I)]$	1 583

Table 4. Bond distances (Å) with standard deviations in parentheses

Cl(1)-C(1)	1.782(5)	C(3)-C(4)	1.535(7)
Cl(2)-C(1)	1.801(5)	C(4)-C(10)	1.512(7)
Cl(3)-C(3)	1.795(5)	C(5)-C(10)	1.396(8)
Cl(4)-C(4)	1.808(5)	C(5)-C(6)	1.376(10)
O(1)-C(2)	1.394(6)	C(6)-C(7)	1.384(10)
O(2)-C(2)	1.390(6)	C(7)-C(8)	1.398(9)
C(1)-C(2)	1.558(7)	C(8)-C(9)	1.393(8)
C(1)-C(9)	1.528(7)	C(9)-C(10)	1.380(7)
C(2)-C(3)	1.525(7)		
O(1)-HO(1)	0.82(7)	C(3)-H(3)	1.03(6)
O(2)-HO(2)	0.90(7)	C(4)-H(4)	1.05(6)
O(3)-H(1)O(3)	0.94(7)	C(5)-H(5)	0.94(7)
O(3)-H(2)O(3)	0.87(7)	C(6)-H(6)	0.96(7)
O(4)-H(1)O(4)	0.86(7)	C(7)-H(7)	0.97(7)
O(4)-H(2)O(4)	0.67(8)	C(8)-H(8)	1.00(7)

Atoms O(3), H(1)O(3), H(2)O(3), and O(4), H(1)O(4), H(2)O(4) refer to the water molecules of crystallization.

Table 5. Bond angles (°) with standard deviations in parentheses

Cl(1)-C(1)-Cl(2)	107.6(3)	C(2)-C(3)-C(4)	110.9(4)
Cl(1)-C(1)-C(2)	108.0(3)	Cl(4)-C(4)-C(3)	106.9(4)
Cl(1)-C(1)-C(9)	111.4(4)	Cl(4)-C(4)-C(10)	110.8(4)
Cl(2)-C(1)-C(2)	109.9(3)	C(3)-C(4)-C(10)	113.0(4)
Cl(2)-C(1)-C(9)	108.8(4)	C(6)-C(5)-C(10)	121.1(6)
C(2)-C(1)-C(9)	112.1(4)	C(5)-C(6)-C(7)	120.0(6)
O(1)-C(2)-O(2)	112.8(4)	C(6)-C(7)-C(8)	119.4(6)
O(1)-C(2)-C(1)	110.2(4)	C(7)-C(8)-C(9)	120.1(6)
O(1)-C(2)-C(3)	107.0(4)	C(1)-C(9)-C(8)	119.5(5)
O(2)-C(2)-C(1)	106.9(4)	C(1)-C(9)-C(10)	120.3(5)
O(2)-C(2)-C(3)	112.8(4)	C(8)-C(9)-C(10)	120.2(5)
C(1)-C(2)-C(3)	106.9(4)	C(4)-C(10)-C(5)	117.9(5)
Cl(3)-C(3)-C(2)	109.5(3)	C(4)-C(10)-C(9)	122.9(5)
Cl(3)-C(3)-C(4)	108.5(3)	C(5)-C(10)-C(9)	119.1(5)
Cl(3)-C(3)-H(3)	104(4)	C(7)-C(6)-H(6)	119(4)
C(2)-C(3)-H(3)	109(4)	C(6)-C(7)-H(7)	126(4)
C(4)-C(3)-H(3)	114(4)	C(8)-C(7)-H(7)	114(4)
Cl(4)-C(4)-H(4)	108(4)	C(7)-C(8)-H(8)	114(4)
C(3)-C(4)-H(4)	109(4)	C(9)-C(8)-H(8)	126(4)
C(10)-C(4)-H(4)	109(4)	C(2)-O(1)-HO(1)	115(5)
C(6)-C(5)-H(5)	120(4)	C(2)-O(2)-HO(2)	115(4)
C(10)-C(5)-H(5)	118(4)	H(1)O(3)-O(3)-H(2)O(3)	113(6)
C(5)-C(6)-H(6)	121(4)	H(1)O(4)-O(4)-H(2)O(4)	101(8)

Atoms O(3), H(1)O(3), H(2)O(3) and O(4), H(1)O(4), H(2)O(4) refer to the water molecules of crystallization.
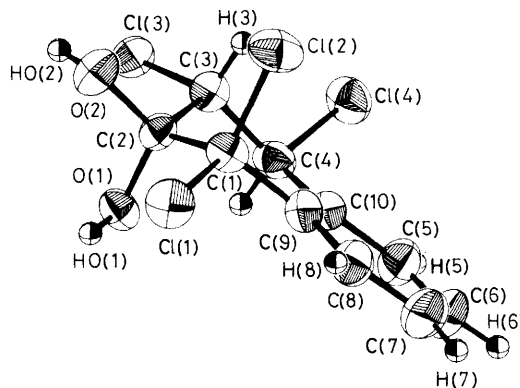

Figure 1. View of the organic part of the dihydrate of *trans*-1,1,3,4-tetrachlorotetralin-2,2-diol. The atoms have been drawn at their 50% probability levels, except for hydrogen atoms which have been drawn artificially small

p.p.m. in the amount by which they shifted with solvent, and it is likely that the extent of association with extra molecules of water varied with the solvent. Signals occurred at the following values of δ: 62.5 (C-4, d, ^1J 160 Hz, minor couplings m, ^2J with H-3, ^3J with H-5); 66.9 (C-3, d, ^1J 158 Hz, minor couplings d, $^2J_{C-3,H-4}$ 7.6 Hz); 91.6 (C-1 or -2, minor coupling d, probably $^3J_{H-8,C-1}$ 4.4 Hz); 95.7 (C-2 or -1, s, minor coupling d, J 2.0 Hz); 127.9, 128.9, 129.2, 130.0 (C-5—C-8, each d, minor couplings each m); 131.3 (probably C-8a, s, minor couplings dd, ^3J with H-5, ^3J with H-7); 136.9 p.p.m. (probably C-4a, s, minor couplings m). In this solvent $^3J_{H,3,H-4}$ was 9.5 Hz.

X-Ray Data Collection and Structure Solution.—Two plate-like crystals of 1,1,3,4-tetrachlorotetralin-2,2-diol which displayed faces of the forms $\{0\ \bar{1}\ 1\}$, $\{1\ 1\ 0\}$, $\{\bar{1}\ 1\ 0\}$, $\{0\ 0\ 1\}$ and $\{0\ 0\ \bar{1}\}$ were used in the data collection.

The crystal properties and the experimental conditions for data collection are summarised in Table 3. Unit cell and crystal orientation data were obtained using the SEARCH and INDEX [7] routines on an Enraf–Nonius CAD-4 diffractometer and accurate values by least-squares refinement of the setting angles of 25 reflections. Because of a systematic decrease in intensity of the standard reflections with X-ray exposure time two crystals were used in the data collection. Data were processed by a standard procedure allowing for the

intensity fall-off and absorption corrections were applied.* The structure was solved by the direct methods phasing program MULTAN [8] and refinement converged with R 0.042 (R_w 0.044). Two scale factors for the two different crystals were refined in the analysis. Positional parameters only were refined for the hydrogen atoms (B 6.0). The configuration and conformation of the molecule is shown in Figure 1 together with the numbering system used. Positional and thermal parameters together with observed and calculated structure-factors are given in SUP 23486. Intramolecular bond distances and angles are listed in Tables 4 and 5 together with

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* Most of the calculations were carried out by using a PDP11/34 computer using the Enraf-Nonius CAD4-SDP set of programs. Corrections for absorption followed the gaussian integration method. For the final stages of refinement, a local version of ORFLS by W. R. Busing, K. O. Martin, and H. A. Levy was used on a Burroughs B6700 computer. ORTEP by C. K. Johnson was used for the illustrations of crystal structure.

Table 6. Hydrogen-bonding distances (Å) and angles (°)

A–H $\cdots$ B	Bond A $\cdots$ B	Bond H $\cdots$ B	Angle A–H $\cdots$ B
O(1)–HO(1) $\cdots$ O(3)	2.739(5)[1]	1.96(7)	159(7)
O(2)–HO(2) $\cdots$ O(3)	2.756(5)[2]	1.96(7)	146(6)
O(3)–H(1)O(3) $\cdots$ O(4)	2.832(6)[3]	1.90(7)	172(6)
O(3)–H(2)O(3) $\cdots$ O(4)	2.875(6)[4]	2.01(7)	178(7)
O(4)–H(1)O(4) $\cdots$ O(2)	2.849(6)[2]	2.00(7)	169(7)
O(4)–H(2)O(4) $\cdots$ O(1)	3.061(6)[1]	2.41(8)	165(9)

	Symmetry position	Translation
1	$\bar{x}, \bar{y}, \bar{z}$	1 1 0
2	x, y, z	0 0 0
3	$\bar{x}, \bar{y}, \bar{z}$	0 1 0
4	$\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$	0 0 0

Other relevant bond angles

C(2)–O(1) $\cdots$ H(2)O(4)	127(2)	C(2)–O(2) $\cdots$ H(1)O(4)	139(2)
H(1)O(3)–O(3) $\cdots$ HO(1)	104(5)	H(1)O(4)–O(4) $\cdots$ H(1)O(3)	113(5)
H(1)O(3)–O(3) $\cdots$ HO(2)	99(5)	H(1)O(4)–O(4) $\cdots$ H(2)O(3)	119(5)
H(2)O(3)–O(3) $\cdots$ HO(1)	123(5)	H(2)O(4)–O(4) $\cdots$ H(1)O(3)	110(7)
H(2)O(3)–O(3) $\cdots$ HO(2)	110(5)	H(2)O(4)–O(4) $\cdots$ H(2)O(3)	110(7)
HO(1) $\cdots$ O(3) $\cdots$ HO(2)	105(3)	H(1)O(3) $\cdots$ O(4) $\cdots$ H(2)O(3)	103(3)

Atoms O(3), H(1)O(3), H(2)O(3) and O(4), H(1)O(4), H(2)O(4) refer to the water molecules of crystallization.

Table 7. Displacements (Å) of selected atoms from the 'plane of best fit' through atoms C(5)—C(10)

Atom	Displacement	Atom	Displacement
C(5)	0.005(6)	C(1)	−0.054(5)
C(6)	0.002(7)	C(2)	0.531(5)
C(7)	−0.008(7)	C(3)	−0.217(5)
C(8)	0.004(6)	C(4)	0.075(5)
C(9)	0.002(5)		
C(10)	−0.004(5)		

their standard deviations.* Hydrogen-bonding distances and angles are given in Table 6. Table 7 presents information relating to the 'plane of best fit' through atoms C(5)—C(10), the equation for which is $0.7496x - 0.2427y - 0.6158z - 1.1618 = 0$. Figure 2 gives a stereoview of the unit cell and shows the hydrogen-bonding network.

Discussion

Much of the preparative work reported by Zincke and Kegel[2] and Fries and Schimmelschmidt[3] on compounds obtainable by chlorination of 2-naphthol has been confirmed in the course of the present investigation. We have established that the final stage of sequence (1) is an addition catalysed by hydrogen chloride, since hydrogen chloride generated in the reaction mixture ensured quantitative reaction to give 1,1,3,4-tetra-chlorotetralin-2-one (4) $\equiv$ (12), which was formed only to an insignificant extent when the addition was attempted in the presence of excess of sodium acetate and water. Additions of halogens to $\alpha\beta$-unsaturated carbonyl compounds catalysed by hydrogen halides usually give predominantly the product of *trans*-addition,[9] for reasons not yet fully understood,[10] and it is now clear that the conversion of (3) into (4) is a highly stereoselective example of this kind.

The hydration of this tetrachlorotetralin-2-one [(12) $\longrightarrow$ (11)] is slow in wet chloroform, but is relatively fast in aqueous acetic acid. The water molecule becomes covalently bound to C-2 in the hydrate, as is evident from the n.m.r. spectra of the two compounds, as well as from the crystal structure of the

hydrate. Both in the solid and in solution, this has its two alicyclic hydrogen atoms axial and pseudoaxial respectively, with the result that the value of $^3J_{H-3,H-4}$ (10 Hz) is near to the expected maximum value, ca. 12 Hz.[11] It is not unexpected that the tetrachlorotetralin-2-one should adopt the conformation (12) reversed from that of its hydrate, i.e. with 3- and 4-Cl axial rather than equatorial. The keto-group tends to flatten the alicyclic ring, and its dipole is better accommodated with C–Cl bonds normal rather than parallel to it. A similar conformational preference is shown in 1,2-dichloro-1,2-dihydronaphthalenes.[11]

If enolization of 3-H [(12) $\longrightarrow$ (13), equation (6)], occurred, it would provide a possible mechanism allowing reversible interconversion of (11) and (12) without requiring maintenance of the stereochemistry about C-3 and -4.

The signals of the 3- and 4-hydrogen atoms in the [1]H n.m.r. spectra are, however, unchanged when the hydration is carried out in the presence of D$_2$O, so the participation of reaction (6) in the hydration and dehydration of the tetrachlorotetralin-2-one is excluded. It seems, in fact, that loss of a proton from the 3-position results in elimination, and consequent slow decomposition [sequence (2), first stage].

U.v. and I.r. Spectra.—The u.v. spectra of the polychloro-tetralinones show gradually increasing absorption from 300—220 nm; for the tetrachlorotetralin-2-one, the detailed form of the spectrum is shown, including the low intensity $n\rightarrow\pi^*$ carbonyl transition at 315 nm (see SUP 23486). In contrast, 1,1-dichloro-1,2-dihydronaphthalen-2-one, 1,1,3-trichloro-1,2-dihydronaphthalen-2-one, and 1,1,3,4-tetrachloro-1,2-dihydronaphthalen-2-one all have relatively intense absorption maxima (log$_{10}$ ε, 3.86, 3.86, and 3.84), at the relatively long wavelength of 325 nm for the first of these compounds (as is expected for a compound with such extended conjugation) and at somewhat longer wavelength (ca. 340 nm) in the more highly substituted compounds.

The i.r. spectra likewise accord generally with expectations, and are discussed more extensively in the accompanying paper.

N.m.r. Spectra.—The [1]H n.m.r. spectra of the tetrachloro-tetralin-2-one (4), (12), and of its hydrate (11) establish the main conformations of these compounds. For the former,

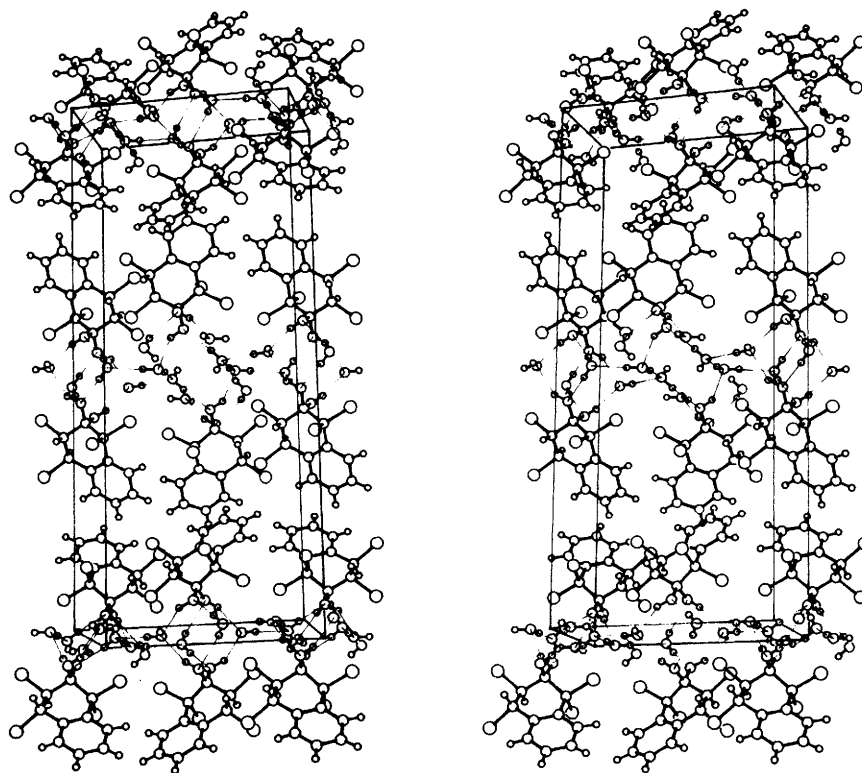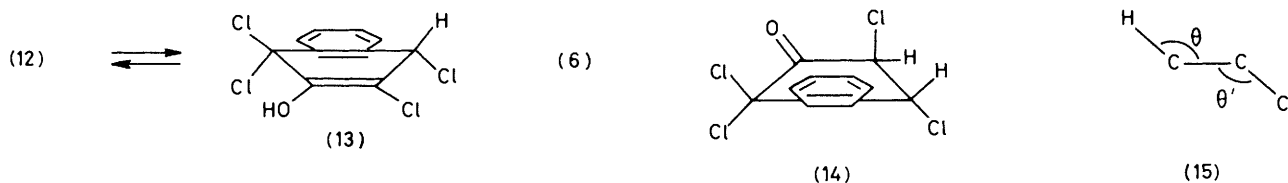* The numbering of Figure 1 is used in Tables 4—7 and in the last subsection of the Discussion section.

Figure 2. The dihydrate of *trans*-1,1,3,4-tetrachlorotetralin-2,2-diol; stereoview of the unit cell contents showing the hydrogen bonding network

however, the value of $^3J_{3-H,4-H}$ (5.0 Hz in CDCl$_3$ at 40 °C) is relatively high for a compound existing wholly in this conformation, but it varies significantly with temperature and with solvent, being significantly lower [4.0 Hz in (CD$_3$)$_2$CO at -68 °C] at the lowest temperature at which meaningful measurements could be made. It would seem that this variation implies a change in the proportions of conformational isomers present in the solution; examination of models indicates that the molecule would be expected to be quite flexible.

Assignment of signals in the ^{13}C n.m.r. spectrum of this compound can be made unambiguously. That for C-3 is distinguished from that for C-4 because in the single resonance spectrum the latter is a broad multiplet because of coupling with the aromatic protons, whereas the former is a well resolved doublet. The signal for C-1 is further downfield because of the deshielding effect of the additional chlorine substituent. The signals for the aromatic protons lie in the expected region, as does that for the carbonyl carbon atom.

For the aromatic carbon atoms, values of $^1J_{C,H}$ seem to be slightly greater (163—165 Hz) than those recorded for the naphthalene tetrachlorides (161—163 Hz).[1] For the alicyclic carbon atoms, the corresponding value for C-4 (160.6 Hz) is as expected, but that for C-3 (164.5 Hz) is distinctly higher than in any of the naphthalene tetrachlorides, probably because of the electronegativity of the adjacent carbonyl group. Three values of $^2J_{C,H}$ have been estimated, and these (to C-2—C-4) are all between 4 and 5 Hz. Values in the range 1.2—6.7 Hz have been recorded for the naphthalene tetrachlorides.[1]

Three values of $^3J_{H,C}$ have been determined. One of these, $^3J_{H-8,C-1}$, involves a fixed dihedral angle of 0° between the relevant bonds, and its value (4.9 Hz) is close to that obtained for several analogous couplings in the naphthalene tetrachlorides.[1] The other two should depend on the conformation adopted by the molecule, which from models would be expected to be quite flexible. The experimental value of $^3J_{H-4,C-2}$, 6.6 Hz, is near the maximum value expected for this coupling by analogy with the results for the naphthalene tetrachlorides;[1] it suggests that three-bond coupling to a carbonyl carbon atom is of similar magnitude to that found in the corresponding saturated system, and that the main conformation of the molecule has the 4-proton disposed approximately equatorially, as in structure (12) or in the half-boat form (14). The value of $^3J_{H-3,C-1}$ (2.9 Hz) is a good deal lower than would be expected if the conformation were (12) and the parameters representing the variation in coupling with dihedral angle were the same as in the naphthalene tetrachlorides. Three-bond couplings are thought, however, to depend not only on dihedral angle, but also on the bonding angles [θ and θ', in system (15)].[12,13] Tarpley and Goldstein[14] have shown that the average coupling constant between the protons of the methyl group in acetone and the carbon atom of the other methyl group is 1.5 Hz, whereas the corresponding coupling involving an intervening tetrahedral carbon is usually[15] *ca.* 4 Hz [*e.g.* 4.2 Hz, in $^1H_3C\cdot C(Et)(Cl)\cdot^{13}CH_3$]. The observed value in the present system may, therefore, represent approximately

the maximum three-bond coupling ($^3J_{H.C}$) expected through the 2-keto-group, the dihedral angle being *ca.* 170°, but the C-1$^-$C-2$^-$C-3 bond angles being *ca.* 120° instead of *ca.* 109° in the naphthalene tetrachlorides. Alternatively, or additionally, some contribution to the conformational equilibrium from the half-boat form (14) may contribute to the smallness of the coupling constant under discussion.

The value of $^3J_{H-3,H-4}$ (4—5 Hz, depending on temperature) is higher than would have been expected for a molecule existing mainly in conformation (12), even if (14) made a contribution to the conformational equilibrium. It is accepted, of course, that the expressions which we have used [1] to represent the relationship between dihedral angle and coupling constant are only approximate, and do not take account of all of the factors which can affect these couplings.[12,13] We expect to return in a subsequent paper to consider some of the issues involved in discussion of vicinal coupling constants in this series.

Detailed Geometry of the Ketone Trihydrate as determined by X-Ray Diffraction.—A view of the organic part of this molecule is given in Figure 1, and corresponds to structure (11). Bond distances and angles within the aromatic ring do not differ significantly from ideal values of 1.395 Å and 120°, respectively. The alicyclic part of the molecule has a distorted half-chair conformation with asymmetric displacements of atoms C(2) ($+0.53$ Å) and C(3) (-0.22 Å) on either side of the plane formed by atoms C(5)—C(10) (see Table 5). Such asymmetric distortions have been found in other similar tetralin derivatives.[16,17] The dihedral angle between the C(3)$^-$H(3) and C(4)$^-$H(4) bonds is 160°; if this angle is maintained in solution, the value of $^3J_{H-3,H-4}$ (10 Hz) would be expected on the usual assumptions of the Karplus [13] equation to be less than the maximum value by *ca.* 12%. Some deviations from the ideal tetrahedral angles are observed within the puckered ring; they arise, at least in part, from non-bonded intramolecular Cl $\cdots$ Cl and Cl $\cdots$ O contacts. A slight variation in C$^-$C distances is also noted within the puckered ring; C(1)$^-$C(9) is shorter than (Cl)$^-$C(2), and C(4)$^-$C(10) is correspondingly shorter than C(4)$^-$C(3). The C$^-$Cl distances are similar to those previously observed in similar molecules.[16] The value for C(1)$^-$Cl(1) of 1.782(5) Å is associated with a pseudoequatorially disposed substituent and is slightly shorter than the C$^-$Cl distances involving the two pseudoaxial chlorine atoms, *viz.* 1.801(5) and 1.808(3) Å for C(1)$^-$Cl(2) and C(4)$^-$Cl(4), respectively. The remaining equatorial chlorine has a bond length C(3)$^-$Cl(3) of 1.795(5) Å which lies closer to that for C(1)$^-$Cl(1) although it is not strictly distinguishable from the other pair at the 3σ level. Shorter bonds to equatorial chlorine substituents are, however, in accord with the results of i.r. data on chlorine-substituted cyclohexanes where a difference typically of *ca.* 50 cm^{-1} between the stretching frequencies of the two types of bond has been observed.[18] No such distinction

in C$^-$O bond length is observed for the *gem*-dihydroxy group, but these two oxygens are involved in hydrogen-bonding interactions to different extents. The atom O(2) forms hydrogen bonds to two crystallographically different water molecules at distances of 2.756 [O(2) $\cdots$ O(3)] and 2.849 Å [O(2) $\cdots$ O(4)]; oxygen O(1) is linked to O(3) and O(4) at distances of 2.739 and 3.061 Å, respectively. The chain-like arrangement is completed by two further hydrogen bonds between O(3) and O(4) (2.832, 2.875 Å) (see Table 6). This hydrogen bonding network within the crystal can be seen in Figure 2 which also shows the molecular packing.

Acknowledgements

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