

Topochemical Studies. XIV.* Structures of 3,3'-Dibromotruxinic Acid Water–Acetic Acid (0·5/0·25) Solvate and 3,3'-Dichlorotruxinic Acid Water–Acetic Acid (0·5/0·25) Solvate

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Abstract. 3,4-Bis(3-bromophenyl)-1,2-cyclobutanedicarboxylic acid water–acetic acid (0·5/0·25) solvate (1), $C_{18}H_{14}Br_2O_4 \cdot 0\cdot5H_2O \cdot 0\cdot25C_2H_4O_2$, $M_r = 478\cdot12$, triclinic, $P\bar{1}$, $a = 8\cdot670$ (1), $b = 14\cdot253$ (1), $c = 8\cdot1895$ (8) Å, $\alpha = 104\cdot567$ (8), $\beta = 102\cdot545$ (8), $\gamma = 79\cdot379$ (9)°, $V = 947\cdot0$ (2) Å³, $Z = 2$, $D_m = 1\cdot68$, $D_x = 1\cdot677$ Mg m⁻³, $\mu = 5\cdot70$ mm⁻¹, $F(000) = 474$, final $R = 0\cdot071$ for 2819 non-zero reflections. 3,4-Bis(3-chlorophenyl)-1,2-cyclobutanedicarboxylic acid water–acetic acid (0·5/0·25) solvate (2), $C_{18}H_{14}Cl_2O_4 \cdot 0\cdot5H_2O \cdot 0\cdot25C_2H_4O_2$, $M_r = 389\cdot12$, triclinic, $P\bar{1}$, $a = 8\cdot634$ (1), $b = 14\cdot228$ (2), $c = 8\cdot001$ (1) Å, $\alpha = 103\cdot49$ (1), $\beta = 102\cdot91$ (1), $\gamma = 79\cdot43$ (1)°, $V = 922\cdot6$ (2) Å³, $Z = 2$, $D_m = 1\cdot39$, $D_x = 1\cdot401$ Mg m⁻³, $\mu = 3\cdot44$ mm⁻¹, $F(000) = 402$, final $R = 0\cdot057$ for 2643 non-zero reflections. $T = 295$ K, $Cu K\alpha$, $\lambda = 1\cdot54178$ Å. The present compounds are the photodimers of 3-bromo- and 3-chlorocinnamic acids. The crystals of (1) and (2) are isomorphous with each other. These two dimers have β -truxinic acid type structures as expected from the crystal structures of the monomers. The solvent molecules in these crystals are disordered around $\bar{1}$.

Introduction. In the preceding work, the crystal structures of 3-bromocinnamic acid (3) and 3-chlorocinnamic acid (4) have been clarified (Kanao, Kashino & Haisa, 1990). In the present paper we report the structures of the photodimers [(1), bromo compound, and (2), chloro compound] formed topochemically from (3) and (4). This is the first illustration of β -truxinic acid type of structures of photodimers of cinnamic acid derivatives (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964).

Experimental. The photodimers were prepared by exposing crystals of (3) and (4) to sunlight for two weeks, and isolated by extracting (3) and (4) with benzene [the method used by Cohen, Schmidt &

Sonntag (1964)]. Crystals of (1) and (2) were grown by vapour diffusion of water into solutions of acetic acid. Analysis for (1) found: C 46·76, H 3·04%; calculated for $C_{18\cdot5}H_{16}Br_2O_5$: C 46·47, H 3·37%; for (2), found: C 56·84, H 4·08%; calculated for $C_{18\cdot5}H_{16}Cl_2O_5$: C 57·09, H 4·14%.

Experimental details for (1) and (2) are listed in Table 1. For both crystals the densities were determined by the flotation method [aqueous $ZnCl_2$ for (1) and aqueous KCl for (2)]. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (Ni-filtered $Cu K\alpha$, 40 kV, 200 mA); ω - 2θ scan method [scan speed 6° min⁻¹ in ω ; scan range (1·2 + 0·15tan θ)° in ω], background was measured for 4 s on either side of the peak; three standard reflectins were recorded every 97 reflections. Lorentz and polarization corrections, no absorption correction. Non-zero reflections were used in the structure analyses. The positions of the halogen atoms were determined by the Patterson minimum function method. The non-H atoms of the dimer molecules were located from Fourier maps phased with the halogen atoms, and refined by block-diagonal least squares. All H atoms of the dimer molecules were located from difference Fourier maps, which showed the solvent molecules disordered around $\bar{1}$: the peaks were assigned to non-H atoms of acetic acid and O atoms of two water molecules. Their occupancy factors were assumed to be 0·25 in accordance with the composition of the unit-cell contents. The structures were finally refined by restrained-constrained full-matrix least squares with anisotropic thermal parameters for non-H atoms of the dimer and isotropic ones for the other atoms. The bond lengths and angles in the acetic acid were fixed to usual values, and the hydrogen-bond lengths O(2')...O(2A) and O(1W)...O(2W) were fixed to 2·60 and 2·76 Å, respectively. The H atoms of the solvent molecules were not included in the refinement. $\sum w(|F_o| - |F_c|)^2$ was minimized with $w = 1\cdot0/\sigma(F_o)^2$. In (2), isotropic thermal parameters of non-H atoms of acetic acid were fixed to 14·6 Å². Rather high $\Delta\rho$ values in the final difference Fourier maps were observed around the Br and Cl atoms.

* Part XIII: Kanao, Kashino & Haisa (1990).

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Table 1. *Experimental details*

	(1)	(2)
M.p. (K)	426–427	419–420
Size of specimen (mm)	0.08 × 0.18 × 0.05	0.23 × 0.30 × 0.18
Range of 2θ (20 reflections) for lattice parameters (°)	39–46	20–40
Systematic absences	No condition	No condition
2θ _{max} (°)	125	120
Range of h	–9 to 9	–9 to 9
k	–16 to 16	0 to 15
l	0 to 9	–8 to 8
Fluctuation of standard reflections (%)	1.6	0.6
No. of unique reflections	3018	2733
No. of non-zero reflections	2819	2643
No. of reflections with F _o > σ F _o	2677	2609
R _{int}	0.024 for 202 hkl reflections	0.007 for 127 h0l reflections
No. of parameters	298	292
R/wR	0.071/0.060	0.057/0.072
S	2.16	0.77
(Δ/σ) _{max} for non-H/H	0.46/0.90	0.19/0.99
Δρ _{max} /Δρ _{min} (e Å ⁻³)	0.8/–0.7	0.44/–0.61

Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs: *HBL5-V* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979), *CRLS* (Takusagawa, 1982), and *ORTEP* (Johnson, 1971). Computations were carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Discussion. The final atomic parameters are listed in Table 2.* The thermal ellipsoids of the molecules with atomic numbering are shown in Fig. 1. Bond lengths, bond angles and selected torsion angles are listed in Table 3. A stereoview of the crystal structure of (1) is shown in Fig. 2.

The crystals of (1) and (2) are isomorphous. The molecular structures of (1) and (2) are of the β-truxinic acid type as expected from their topochemical formation. Their molecular conformations are similar to each other as shown in Table 3. The conformation of C(7)–C(8) with respect to C(2)–C(1) and that of C(7')–C(8') with respect to C(2')–C(1') in (1) (χ₁ and χ₂ respectively, in Table 3) are in accord with the *cis* conformation of the corresponding part of the monomer (3). The conformations in (2) are different from the *trans* conformation of the monomer (4). This fact indicates that in (2) the rotation of the phenyl rings around the C(1)–C(7) and C(1')–C(7') bonds occurs after the topochemical formation. MM2 calculations (Allinger & Yuh, 1985), taking the molecular-mechanics parameters

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53173 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	$B_{eq} = \frac{1}{3} \sum \beta_{ii} / a_i^2$			$B_{eq}(\text{Å}^2)$
	x	y	z	
3,3'-Dibromotruxinic acid, $\frac{1}{2}\text{H}_2\text{O} \cdot \frac{1}{4}\text{CH}_3\text{COOH}$ (1)				
Br	0.8246 (1)	0.26989 (8)	0.0123 (1)	6.68 (5)
Br'	0.2252 (1)	0.14384 (7)	–0.2118 (1)	6.37 (5)
O(1)	0.5685 (6)	0.5131 (3)	0.8323 (5)	4.4 (2)
O(2)	0.4252 (6)	0.4001 (3)	0.8373 (5)	4.3 (2)
C(1)	0.7003 (6)	0.2327 (4)	0.4491 (7)	2.3 (2)
C(2)	0.7031 (6)	0.2654 (4)	0.3048 (7)	2.6 (2)
C(3)	0.8214 (7)	0.2245 (4)	0.2096 (7)	2.9 (2)
C(4)	0.9399 (7)	0.1509 (5)	0.2537 (8)	3.3 (3)
C(5)	0.9353 (7)	0.1195 (4)	0.3971 (9)	3.5 (3)
C(6)	0.8158 (7)	0.1588 (4)	0.4935 (8)	3.3 (3)
C(7)	0.5710 (6)	0.2742 (4)	0.5569 (6)	2.4 (2)
C(8)	0.5188 (6)	0.3874 (3)	0.5809 (6)	2.5 (2)
C(9)	0.5038 (6)	0.4389 (4)	0.7619 (7)	2.7 (2)
O(1')	0.1964 (5)	0.5130 (3)	0.5557 (7)	4.3 (2)
O(2')	0.0884 (5)	0.3766 (4)	0.451 (1)	6.7 (4)
C(1')	0.3627 (6)	0.1774 (4)	0.3122 (7)	2.4 (2)
C(2')	0.3171 (6)	0.1952 (4)	0.1495 (7)	2.9 (2)
C(3')	0.2918 (7)	0.1177 (5)	0.0102 (7)	3.4 (3)
C(4')	0.3098 (8)	0.0229 (5)	0.0305 (9)	4.1 (3)
C(5')	0.3562 (8)	0.0058 (5)	0.191 (1)	4.2 (3)
C(6')	0.3819 (8)	0.0824 (4)	0.3323 (8)	3.5 (3)
C(7')	0.3949 (6)	0.2578 (4)	0.4686 (7)	2.5 (2)
C(8')	0.3598 (6)	0.3660 (4)	0.4572 (7)	2.3 (2)
C(9')	0.2040 (6)	0.4246 (4)	0.4921 (8)	3.3 (3)
O(1A)	0.049 (3)	0.589 (2)	0.188 (3)	6.9 (6)
O(2A)	0.036 (5)	0.433 (3)	0.163 (5)	11 (1)
C(1A)	0.032 (5)	0.506 (3)	0.099 (5)	7.4 (9)
C(2A)	0.013 (6)	0.484 (4)	–0.095 (6)	8 (1)
O(W1)	0.106 (7)	0.389 (4)	–0.082 (8)	17 (2)
O(W2)	–0.043 (3)	0.563 (2)	0.084 (3)	6.7 (5)
3,3'-Dichlorotruxinic acid, $\frac{1}{2}\text{H}_2\text{O} \cdot \frac{1}{4}\text{CH}_3\text{COOH}$ (2)				
Cl	0.8227 (1)	0.2673 (1)	0.0145 (1)	7.15 (6)
Cl'	0.2308 (2)	0.1410 (1)	–0.2086 (1)	7.51 (6)
O(1)	0.5692 (3)	0.5109 (2)	0.8304 (3)	4.8 (1)
O(2)	0.4276 (3)	0.3978 (2)	0.8402 (3)	4.9 (1)
C(1)	0.7008 (3)	0.2318 (2)	0.4465 (3)	3.0 (1)
C(2)	0.7025 (3)	0.2652 (2)	0.2969 (4)	3.4 (1)
C(3)	0.8213 (3)	0.2246 (2)	0.2004 (4)	3.8 (1)
C(4)	0.9404 (3)	0.1525 (2)	0.2493 (4)	4.2 (1)
C(5)	0.9383 (4)	0.1188 (2)	0.3969 (5)	4.6 (1)
C(6)	0.8212 (3)	0.1583 (2)	0.4939 (6)	4.2 (1)
C(7)	0.5733 (3)	0.2726 (2)	0.5546 (3)	3.1 (1)
C(8)	0.5203 (3)	0.3858 (2)	0.5773 (3)	3.1 (1)
C(9)	0.5067 (3)	0.4370 (2)	0.7612 (4)	3.3 (1)
O(1')	0.1961 (2)	0.5103 (1)	0.5547 (4)	4.9 (1)
O(2')	0.0840 (3)	0.3755 (2)	0.4409 (5)	7.1 (2)
C(1')	0.3631 (3)	0.1769 (2)	0.3092 (3)	3.1 (1)
C(2')	0.3178 (3)	0.1943 (2)	0.1417 (4)	3.8 (1)
C(3')	0.2914 (4)	0.1164 (3)	0.0013 (4)	4.5 (1)
C(4')	0.3102 (4)	0.0226 (2)	0.0240 (5)	5.0 (2)
C(5')	0.3543 (4)	0.0059 (2)	0.1920 (5)	5.1 (2)
C(6')	0.3794 (4)	0.0817 (2)	0.3316 (4)	4.2 (1)
C(7')	0.3951 (3)	0.2569 (2)	0.4669 (3)	3.1 (1)
C(8')	0.3597 (3)	0.3647 (2)	0.4506 (3)	3.1 (1)
C(9')	0.2049 (3)	0.4234 (2)	0.4858 (4)	3.9 (1)
O(1A)	0.040 (3)	0.596 (2)	0.190 (4)	14.6
O(2A)	0.028 (3)	0.438 (2)	0.151 (4)	14.6
C(1A)	0.037 (5)	0.514 (3)	0.093 (5)	14.6
C(2A)	0.068 (5)	0.495 (3)	–0.093 (5)	14.6
O(1W)	0.140 (5)	0.382 (3)	–0.035 (5)	21 (1)
O(2W)	–0.033 (2)	0.561 (1)	0.076 (2)	9.3 (4)

for Cl from Bowen, Reddy, Patterson & Allinger (1988), show that the rotational barrier between the *cis* and *trans* conformations of (2) is fairly low, $1.3 \times 10^4 \text{ J mol}^{-1}$.

Because of short intramolecular contacts, C(1)⋯C(1') [3.070 (8) Å for (1) and 3.053 (4) Å for (2)] and C(9)⋯C(9') [3.025 (9) Å for (1) and 3.017 (4) Å for (2)], the exocyclic bond angles around C(7') and C(8') are widened. Twisting of the cyclobutane rings as seen from χ₇ and χ₈ is larger than

Table 3. Bond lengths (Å), angles (°) and selected torsion angles (°) with *e.s.d.*'s in parentheses

	3,3'-Dibromotruxinic acid (1) (<i>X</i> = Br)	3,3'-Dichlorotruxinic acid (2) (<i>X</i> = Cl)
<i>X</i> —C(3)	1.893 (6)	1.736 (3)
O(1)—C(9)	1.240 (8)	1.227 (4)
O(2)—C(9)	1.282 (8)	1.294 (4)
C(1)—C(2)	1.381 (8)	1.391 (4)
C(1)—C(6)	1.375 (9)	1.389 (4)
C(1)—C(7)	1.520 (7)	1.501 (4)
C(2)—C(3)	1.378 (8)	1.382 (4)
C(3)—C(4)	1.385 (9)	1.372 (4)
C(4)—C(5)	1.368 (10)	1.379 (6)
C(5)—C(6)	1.389 (10)	1.371 (5)
C(7)—C(8)	1.567 (7)	1.571 (4)
C(8)—C(9)	1.501 (8)	1.502 (4)
C(7)—C(7')	1.573 (8)	1.575 (4)
C(8)—C(8')	1.553 (7)	1.557 (4)
<i>X'</i> —C(3')	1.893 (7)	1.741 (4)
O(1')—C(9')	1.232 (9)	1.227 (4)
O(2')—C(9')	1.255 (11)	1.289 (5)
C(1')—C(2')	1.379 (8)	1.377 (4)
C(1')—C(6')	1.380 (9)	1.385 (4)
C(1')—C(7')	1.502 (8)	1.501 (4)
C(2')—C(3')	1.384 (9)	1.393 (5)
C(3')—C(4')	1.379 (11)	1.364 (6)
C(4')—C(5')	1.358 (11)	1.377 (6)
C(5')—C(6')	1.387 (11)	1.369 (5)
C(7')—C(8')	1.539 (8)	1.538 (4)
C(8')—C(9')	1.495 (9)	1.487 (4)
C(2)—C(1)—C(6)	118.8 (5)	117.9 (3)
C(2)—C(1)—C(7)	121.9 (5)	121.8 (3)
C(6)—C(1)—C(7)	119.3 (5)	120.2 (3)
C(1)—C(2)—C(3)	119.8 (5)	119.7 (3)
<i>X</i> —C(3)—C(2)	119.5 (5)	119.3 (2)
<i>X</i> —C(3)—C(4)	118.3 (5)	118.9 (3)
C(2)—C(3)—C(4)	122.2 (6)	121.8 (3)
C(3)—C(4)—C(5)	117.2 (6)	118.6 (4)
C(4)—C(5)—C(6)	121.5 (7)	120.3 (4)
C(1)—C(6)—C(5)	120.5 (6)	121.6 (3)
C(1)—C(7)—C(8)	114.8 (4)	115.2 (3)
C(7)—C(8)—C(9)	113.8 (4)	114.3 (3)
O(1)—C(9)—O(2)	123.4 (6)	123.1 (3)
O(1)—C(9)—C(8)	120.5 (5)	121.0 (3)
O(2)—C(9)—C(8)	116.1 (5)	115.9 (3)
C(1)—C(7)—C(7')	117.2 (4)	117.8 (3)
C(8)—C(7)—C(7')	89.1 (4)	89.0 (2)
C(7)—C(8)—C(8')	88.5 (4)	88.3 (2)
C(9)—C(8)—C(8')	115.6 (4)	115.9 (3)
C(7)—C(7)—C(1')	120.6 (5)	119.6 (3)
C(7)—C(7)—C(8')	88.8 (4)	88.8 (2)
C(8)—C(8)—C(7')	90.9 (4)	90.8 (2)
C(8)—C(8)—C(9')	121.2 (5)	120.6 (3)
C(2')—C(1')—C(6')	119.1 (6)	118.3 (3)
C(2')—C(1')—C(7')	122.2 (5)	122.5 (3)
C(6')—C(1')—C(7')	118.7 (6)	119.2 (3)
C(1')—C(2')—C(3')	119.4 (6)	119.4 (3)
<i>X'</i> —C(3')—C(2')	118.8 (5)	118.3 (3)
<i>X'</i> —C(3')—C(4')	119.7 (6)	119.6 (3)
C(2')—C(3')—C(4')	121.5 (7)	122.1 (4)
C(3')—C(4')—C(5')	118.8 (7)	118.2 (4)
C(4')—C(5')—C(6')	120.7 (7)	120.5 (4)
C(1')—C(6')—C(5')	120.6 (7)	121.6 (3)
C(1')—C(7')—C(8')	121.2 (5)	121.0 (3)
C(7')—C(8')—C(9')	119.8 (5)	119.7 (3)
O(1')—C(9')—O(2')	125.2 (7)	123.6 (3)
O(1')—C(9')—C(8')	120.1 (6)	121.6 (3)
O(2')—C(9')—C(8')	114.7 (6)	114.8 (3)
χ_1 C(2)—C(1)—C(7)—C(8)	-39.0 (7)	-39.1 (4)
χ_2 C(2)—C(1')—C(7')—C(8')	7.2 (9)	7.2 (4)
χ_3 C(1)—C(7)—C(7')—C(1')	20.8 (7)	20.5 (4)
χ_4 C(9)—C(8)—C(8')—C(9')	23.0 (7)	22.8 (4)
χ_5 C(1)—C(7)—C(8)—C(9)	-135.0 (5)	-134.7 (3)
χ_6 C(1')—C(7')—C(8')—C(9')	94.6 (7)	95.8 (3)
χ_7 C(8)—C(7)—C(7')—C(8')	12.3 (4)	13.2 (2)
χ_8 C(7)—C(8)—C(8')—C(7')	12.5 (4)	13.3 (2)

In both crystals the molecules of the photodimers are held together by O—H...O hydrogen bonds between the carboxyl groups around $\bar{1}$ at $(\frac{1}{2}, \frac{1}{2}, 0)$ [O...O 2.671 (7) Å for (1), and 2.649 (4) Å for (2)] and $\bar{1}$ at $(0, \frac{1}{2}, \frac{1}{2})$ [O...O 2.67 (1) Å for (1), and 2.657 (5) Å for (2)] to form a chain along [101]. The large anisotropic thermal parameters of the halogen atoms and the O atoms of the carboxyl groups can be explained by the existence of a cavity around $\bar{1}$ at $(0, \frac{1}{2}, 0)$. Either an acetic acid molecule or two water

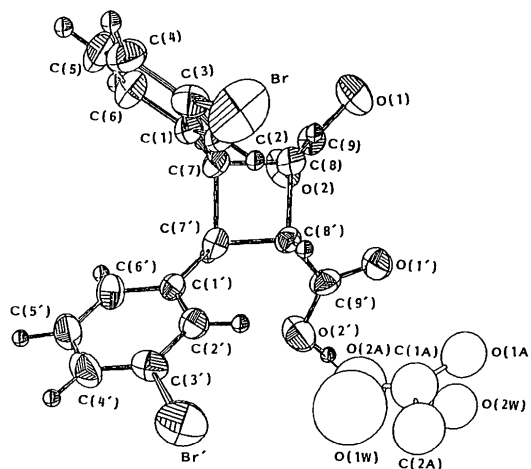


Fig. 1. The thermal ellipsoids of the molecules with atomic numbering for (1). Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms of the dimers are represented as spheres equivalent to $B = 1.0 \text{ \AA}^2$. The two water molecules or acetic acid molecule exist alternately and randomly at the positions shown in the figure. The atomic numbering for (2) is the same as that for (1).

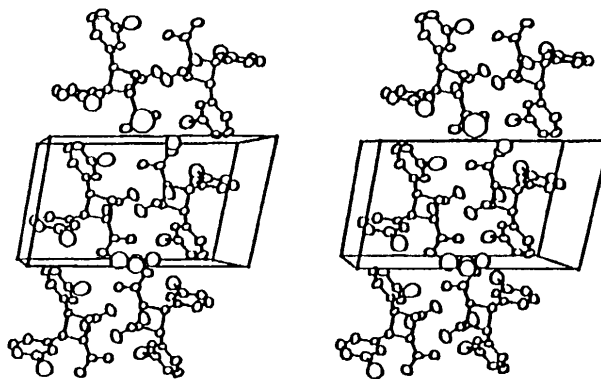


Fig. 2. A stereoview of molecular packing of (1). The *a* axis points upward, the *b* axis from left to right, and the *c* axis into the plane of the paper. The acetic acid molecule is shown at the site near $\bar{1}$ at $(0, \frac{1}{2}, 0)$ and two water molecules are shown at the site near $\bar{1}$ at $(1, \frac{1}{2}, 0)$. However, both sites are occupied by either an acetic acid molecule or two water molecules alternately and randomly with equal probability of 0.5. Furthermore, all these molecules are disordered around $\bar{1}$. The structure of (2) is isomorphous with that of (1).

that found in some cyclobutane rings having $\bar{1}$ symmetry in crystals (Kashino, Oka & Haisa, 1989; Iwamoto, Kashino & Haisa, 1989).

molecules are included in this cavity. The high anisotropic thermal parameter for β_{33} of O(2') [14.0 (6) Å² for (1); 13.9 (3) Å² for (2)] may be an indication of disordering of O(2') effected by the disorder of the solvent molecules. O(2') is linked by an O—H...O hydrogen bond to O(2A). O(1W) donates another O—H...O hydrogen bond to O(2)(x, y, 1+z). Furthermore, O(1W) is linked by an O—H...O hydrogen bond to O(2W) [O...O 3.02 (7) Å for (1), and 2.94 (4) Å for (2)]. Any one of the three H atoms [one H of O(1W) and two H of O(2W)] may participate in this hydrogen bond. However, the probability of participation of each H atom could not be determined. Such solvent inclusion as found in the present crystals has been observed in some β -truxinic acid type photodimers by UV and IR spectroscopy and differential scanning calorimetry (Nakanishi, Nakanishi, Tsuchiya & Hasegawa, 1976).

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Crystal Structure of Cholic Acid with No Guest Molecules

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Abstract. Cholic acid, C₂₄H₄₀O₅, $M_r = 408.58$, orthorhombic, $P2_12_12_1$, $a = 16.477$ (4), $b = 8.394$ (3), $c = 16.993$ (3) Å, $V = 2350.3$ (9) Å³, $Z = 4$, $D_x = 1.155$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.851$ cm⁻¹, $F(000) = 896$, $T = 295$ K, $R = 0.057$ for 1807 observed reflections. The crystal structure of

cholic acid containing no guest organic molecules has been found from recrystallization from acetone. The hydrogen-bond network is rigidly formed between four OH and one C=O groups of cholic acid molecules in the crystal structure.

Introduction. Many crystal structures have been reported for the typical steroidal bile acid deoxy-

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