Table 4. *Geometry of* (C)—H···O *interactions* (Å, °)

	C—H	H···O	C···O	C—H···O
(I)				
C(2*T*)—H(2*T*)···O(4^{i})	0.99 (2)	2.61 (2)	3.503 (2)	151 (2)
C(6*T*)—H(6*T*)···O(6^{ii})	0.99 (2)	2.42 (2)	3.401 (2)	174 (2)
(II)				
C(6)—H(6)···O(3^{iii})	0.94 (2)	2.53 (2)	3.399 (2)	153 (2)
(III)				
C(6)—H(6)···O(3^{iv})	1.00 (2)	2.46 (2)	3.382 (2)	153 (1)

Symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $1-x, 1-y, 2-z$; (iv) $x, y+1, z-1$.

Stezowski, 1978; Aravamudhan, Haeberlen, Irngartinger & Krieger, 1979; Born & Heywang, 1990). An interesting feature of the anhydride $O\overset{1}{=}C\overset{2}{-}O\overset{3}{-}C\overset{4}{=}O$ grouping is seen here: if bond 1 is longer than bond 4, then bond 2 is shorter than bond 3. This condition has been attributed to differences in the crystal-packing environments of the two carbonyl groups as seen in a low-temperature study of the PMDA–anthracene (1/1) complex (Robertson & Stezowski, 1978), and as is seen also in the low-temperature structures of PMDA and NTDA.

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The Monoclinic Phase of the 2/1 Inclusion Compound Between Deoxycholic Acid and *o*-Xylene

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Abstract. (3α,5β,12α)-3,12-Dihydroxycholan-24-oic acid–*o*-xylene (2/1), $2C_{24}H_{40}O_4.C_8H_{10}$, $M_r = 891.328$, monoclinic, $P2_1$, $a = 7.238\,(7)$, $b = 26.171\,(12)$, $c = 13.510\,(9)$ Å, $\beta = 90.91\,(9)°$, $V = 2559\,(3)$ Å^3, $Z = 2$, $D_m = 1.16$, $D_x = 1.157$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.54178$ Å, $\mu = 5.15$ cm^{-1}, $F(000) = 980$, $T = 293$ K, $R = 0.123$ ($wR = 0.153$) for 2662 observed reflections and 518 refined parameters. The crystals of the title compound belong to the monoclinic system. However, the presence of pseudo-twofold screw axes among the host molecules makes the structure of the bilayer, as well as the spatial relationships between them, similar to that of all so far known orthorhombic crystals. The guest molecules fill the space in

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the channels almost completely, occupy well defined positions and interact with the surrounding host molecules at distances close to the sum of van der Waals radii.

Introduction. 3α,12α-Dihydroxy-5β-cholan-24-oic acid (deoxycholic acid, DCA), when crystallized in the orthorhombic system forms hydrophobic channels located between two-dimensional bilayers where it is able to include a great variety of small or medium size molecules. DCA inclusion compounds have been studied in order to use the channels as sites for stereospecific polymerizations or photochemical reactions.

For many years, our studies have been devoted to photochemical reactivity in inclusion compounds of the host–guest type (Guarino, 1984). Recently, the reaction processes studied were the isomerization of specific guests inside the cavities of DCA: the valence isomerization of norbornadienes (Guarino, Possagno & Bassanelli, 1987*a*), the *cis*/*trans* isomerization of stilbenes (Guarino, Possagno & Bassanelli, 1987*b*) and the position isomerization of xylenes (Guarino, Possagno & Bassanelli, 1988). In all these reaction processes the strict correlation between the isomerization yields and the photophysics of the host and of the guest moieties has been observed, as well as the influence of the symmetry of the sites where the reactions occur (Guarino, 1986, 1987).

For the specific case of xylenes included in DCA, the main difference with respect to the same reaction occurring when irradiating xylenes in *n*-hexane solution, is the elimination of by-products. The isomerization yields were found to be strongly dependent on both photophysical and symmetry factors.

In order to elucidate the host–guest interactions that allow the position-isomerization process, the X-ray analysis was undertaken to determine the structure of these DCA–xylene complexes. We now report on the crystal and molecular structure of the DCA–*o*-xylene complex.

Experimental. Suitable crystals of the DCA–*o*-xylene complex were grown at room temperature by slow evaporation of a methanol solution of DCA and *o*-xylene; they were small, needle-like and colourless. Preliminary measurements of the unit-cell dimensions and observations of the diffraction symmetry and systematic absences by photographic methods allowed the assignment of the $P2_1$ space group to the crystals. The unit-cell parameters were determined by a least-squares fitting of the setting angles of 35 selected reflections within the 2θ range 30–45°, using a Syntex $P2_1$ diffractometer. Diffraction data were collected with a crystal of dimensions 0.35 × 0.18 × 0.17 mm, in θ–2θ scanning mode to a maximum 2θ value of 114°, using Cu $K\alpha$ radiation and graphite monochromator. Three standard reflections were monitored every 97 reflections and showed only random fluctuations of their intensities. A total of 4902 reflections were measured for $3 \leq 2\theta \leq 114°$ with $-7 \leq h \leq 1$, $0 \leq k \leq 28$, $-14 \leq l \leq 14$; a final data set consisted of 2662 unique reflections having $I > 3.0\sigma(I)$, which were considered observed and used for the crystal-structure elucidation. Data were corrected for Lp factors but no corrections for extinction or absorption were applied.

The crystal structures of the cholic acids so far studied can be grouped into three crystal systems: orthorhombic, tetragonal and hexagonal (Candeloro De Sanctis & Giglio, 1979). All the orthorhombic crystals belong to the $P2_12_12_1$ space group and they have two lattice vectors in common, one of ~26.5 Å (the longest) and a second of ~13.5 Å, while the third lattice vector is ~7.2 Å (in the α group) or double (~14.2 Å in the β group), or triple (21.7 Å) (Giglio, 1984). In the unit cells with ~7.2 Å lattice vector, the host–guest ratio may vary in a wide range (from 1/1 to 8/1) and many guest molecules have disordered positions or fractional occupancy; while in the unit cells with ~14.2 and ~21.7 Å lattice vectors, the host–guest ratio is generally 2/1 and 3/1 respectively. In both α and β groups, the structures of the bilayers are very similar but the relative positions of adjacent bilayers are different by a relative shift of ~3.6 Å along the third lattice vector.

The DCA–*o*-xylene complex surprisingly belongs to the space group $P2_1$ with the twofold screw axis parallel to the longest lattice vector and cell parameters very close to those of the α group ($\beta \simeq 90°$). These observations suggest that the crystal structure does not differ too much from those of the α group, the screw symmetries around a and c vectors being disregarded and only the screw symmetry along the longest axis b being retained.

In the unit cell it is possible to accommodate four DCA and two guest molecules with no space-group symmetry violation, invoking either disordered positions or fractional occupancy of the guest molecules. The assumption of a 2/1 ratio between host and guest was based on the density measurement (D_m = 1.16 g cm^{-3}, measured by flotation) and on measurements of xylene abundance in gas chromatographic spectra of quantitatively eluted solutions of DCA–*o*-xylene crystals.

The structure was solved by the minimum residual method using only the 544 innermost reflections of the reciprocal sphere, $(\sin\theta/\lambda)_{\max} = 0.3$ Å^{-1}, and searching for the best translation and rotation of two DCA rigid molecules. The starting model for the structure solution was obtained from the crystal structure of DCA–*p*-diiodobenzene (Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1972), selecting two DCA molecules which are not related by the twofold screw axis parallel to the longest lattice vector, and applying a proper shift to the coordinates to put the origin along the twofold screw monoclinic axis; the best agreement factor was $R = 0.32$. Subsequently, the same method was used to find the position of the guest molecule in the channel; the best agreement factor was $R = 0.30$.

Refinement by least-squares calculations of atomic coordinates and isotropic temperature factors of the DCA molecules and rigid-body parameters of *o*-xylene converged to $R = 0.21$, using all the observed reflections. During the final refinement, H atoms (all but those of hydroxyls and methyls) were placed in calculated positions (C—H = 1.05 Å); they were considered rigidly connected to the carrier atoms and assigned the same isotropic temperature factor. Full-matrix refinement (based on F values) of positional and anisotropic thermal parameters of DCA atoms and of the *o*-xylene molecule, considered as a rigid model but with individual isotropic temperature factors, gave the best agreement factors $R = 0.123$, $wR = 0.153$. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F) + 0.03634F^2]$. $(\Delta/\sigma)_{\max} < 0.35$; $(\Delta\rho)_{\max} = 0.6$, $(\Delta\rho)_{\min} = -0.4$ e Å^{-3}. The final atomic coordinates are given in Table 1,* selected torsion angles are reported in Table 2, and geometrical parameters of the hydrogen bonds and relevant van der Waals contacts are listed in Table 3.

The packages *SHELXTL-Plus* (Sheldrick, 1990) and *SHELX76* (Sheldrick, 1976) on a DEC MicroVAX II, and the package *SIR-CAOS* (Camalli, Capitani, Cascarano, Cerrini, Giacovazzo & Spagna, 1986) on a Data General Eclipse MV 8000 II, were used for the calculations. Atomic scattering factors and absorption coefficients were from *SHELX76*.

Discussion. The final agreement indices R and wR are rather high and the results do not allow a detailed characterization and comparison of the molecular geometry, but they can support the discussion of the general aspect of the structure.

In the two DCA molecules, bond distances and valence angles compare well with one another and fall within the expected ranges (Allen, Kennard, Watson, Brammer & Orpen, 1987). The mean values are 1.52 (4), 1.41 (4) and 1.18 (2) Å for C—C, C—O and C═O bonds, respectively; 112 (3) and 104 (3)° are the mean values of C—C—C valence angles in the polycyclic skeletons and side chains, and the five-membered rings, respectively.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
DCA molecule (I)				
C(1)	0.193 (2)	0.1176	0.3809 (8)	5.1 (3)
C(2)	0.255 (1)	0.0636 (4)	0.4089 (7)	4.7 (3)
C(3)	0.404 (2)	0.0642 (4)	0.4790 (8)	5.5 (3)
C(4)	0.570 (2)	0.0956 (5)	0.4406 (8)	5.1 (3)
C(5)	0.513 (1)	0.1487 (4)	0.4080 (7)	4.3 (3)
C(6)	0.681 (2)	0.1766 (5)	0.3671 (8)	5.6 (3)
C(7)	0.736 (1)	0.1579 (4)	0.2652 (7)	4.5 (3)
C(8)	0.578 (1)	0.1583 (4)	0.1917 (7)	4.6 (3)
C(9)	0.410 (1)	0.1282 (4)	0.2329 (7)	3.7 (2)
C(10)	0.354 (1)	0.1498 (4)	0.3346 (7)	4.1 (2)
C(11)	0.258 (1)	0.1233 (4)	0.1562 (7)	4.6 (3)
C(12)	0.323 (2)	0.0977 (4)	0.0609 (8)	4.7 (3)
C(13)	0.487 (1)	0.1297 (4)	0.0186 (6)	3.9 (2)
C(14)	0.634 (1)	0.1333 (4)	0.0957 (7)	4.1 (2)
C(15)	0.801 (2)	0.1551 (5)	0.0418 (7)	5.6 (3)
C(16)	0.780 (2)	0.1332 (6)	−0.0642 (9)	5.9 (3)
C(17)	0.595 (1)	0.1042 (4)	−0.0701 (7)	4.2 (3)
C(18)	0.414 (2)	0.1820 (4)	−0.0165 (8)	5.2 (3)
C(19)	0.276 (2)	0.2041 (4)	0.3234 (8)	5.5 (3)
C(20)	0.517 (2)	0.1066 (4)	−0.1736 (7)	4.8 (3)
C(21)	0.327 (2)	0.0807 (5)	−0.1873 (8)	5.5 (3)
C(22)	0.655 (2)	0.0842 (5)	−0.2494 (8)	5.4 (3)
C(23)	0.704 (2)	0.0304 (5)	−0.2325 (9)	6.9 (4)
C(24)	0.834 (2)	0.0105 (5)	−0.3135 (8)	6.0 (4)
O(25)	0.455 (1)	0.0165 (4)	0.5062 (7)	7.1 (3)
O(26)	0.381 (1)	0.0463 (3)	0.0768 (5)	4.9 (2)
O(27)	0.786 (1)	0.0075 (6)	−0.3987 (7)	9.3 (4)
O(28)	0.986 (1)	−0.0057 (4)	−0.2843 (5)	5.8 (2)
DCA molecule (II)				
C(1)	0.396 (1)	−0.1170 (5)	0.8830 (7)	5.2 (3)
C(2)	0.333 (1)	−0.0643 (4)	0.9142 (8)	4.7 (3)
C(3)	0.172 (2)	−0.0664 (5)	0.9853 (8)	5.2 (3)
C(4)	0.020 (1)	−0.0963 (4)	0.9416 (7)	4.3 (3)
C(5)	0.071 (1)	−0.1513 (5)	0.9080 (7)	4.6 (3)
C(6)	−0.083 (2)	−0.1804 (4)	0.8659 (7)	5.1 (3)
C(7)	−0.147 (2)	−0.1602 (5)	0.7633 (8)	5.4 (3)
C(8)	0.013 (2)	−0.1593 (4)	0.6933 (7)	5.0 (3)
C(9)	0.171 (1)	−0.1287 (4)	0.7371 (6)	3.8 (2)
C(10)	0.244 (1)	−0.1483 (4)	0.8377 (7)	4.5 (3)
C(11)	0.330 (1)	−0.1212 (4)	0.6605 (7)	4.5 (3)
C(12)	0.260 (1)	−0.0987 (4)	0.5637 (6)	4.1 (3)
C(13)	0.106 (1)	−0.1286 (4)	0.5186 (7)	4.4 (3)
C(14)	−0.052 (2)	−0.1356 (4)	0.5959 (7)	4.7 (3)
C(15)	−0.211 (1)	−0.1565 (5)	0.5395 (9)	5.6 (3)
C(16)	−0.198 (2)	−0.1326 (5)	0.4379 (8)	5.8 (3)
C(17)	−0.015 (1)	−0.1066 (4)	0.4324 (6)	4.1 (2)
C(18)	0.180 (2)	−0.1817 (4)	0.4884 (7)	5.0 (3)
C(19)	0.318 (2)	−0.2039 (5)	0.8294 (9)	5.8 (3)
C(20)	0.064 (1)	−0.1064 (4)	0.3258 (7)	4.6 (3)
C(21)	0.257 (2)	−0.0811 (5)	0.3195 (8)	5.7 (3)
C(22)	−0.064 (2)	−0.0839 (5)	0.2521 (8)	5.4 (3)
C(23)	−0.122 (2)	−0.0294 (5)	0.2664 (9)	6.3 (4)
C(24)	−0.244 (2)	−0.0121 (5)	0.1853 (8)	6.0 (4)
O(25)	0.119 (1)	−0.0153 (3)	1.0084 (6)	6.7 (3)
O(26)	0.2001 (9)	−0.0472 (3)	0.5808 (5)	4.6 (2)
O(27)	−0.209 (2)	−0.0101 (6)	0.1016 (6)	10.1 (4)
O(28)	−0.411 (1)	0.0053 (4)	0.2132 (5)	6.2 (2)
o-Xylene				
C(25)	0.496 (1)	0.2660 (4)	0.7231 (8)	16 (1)
C(26)	0.364 (1)	0.2807 (4)	0.7907 (8)	11.6 (6)
C(27)	0.188 (1)	0.2600 (4)	0.7858 (8)	10.3 (5)
C(28)	0.144 (1)	0.2244 (4)	0.7132 (8)	11.5 (6)
C(29)	0.276 (1)	0.2096 (4)	0.6458 (8)	15.1 (9)
C(30)	0.451 (1)	0.2305 (4)	0.6506 (8)	14.3 (8)
C(31)	0.046 (1)	0.2760 (4)	0.8588 (8)	13.5 (8)
C(32)	0.412 (1)	0.3192 (4)	0.8690 (8)	14.8 (8)

The two independent molecules of DCA are conformationally very similar (see Fig. 1); however, pronounced differences are observed in the D ring (Table 2) which assumes an envelope conformation [C_s-C(13)β, $\Delta C_s = 8.4°$ (Duax & Norton, 1975)] in molecule (I), and a half-chair conformation [C_2-C(13)β, $\Delta C_2 = 4.5°$] in molecule (II). The phase angle

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55700 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected torsion angles* (°)

		Molecule (I)	Molecule (II)
D rings			
C(13)—C(14)—C(15)—C(16)	φ_4	−32 (1)	−34 (1)
C(14)—C(15)—C(16)—C(17)	φ_3	5 (1)	11 (1)
C(15)—C(16)—C(17)—C(13)	φ_2	22 (1)	17 (1)
C(16)—C(17)—C(13)—C(14)	φ_1	−41 (1)	−35 (1)
C(17)—C(13)—C(14)—C(15)	φ_o	46 (1)	42 (1)
	φ_m	46.9	42.0
	Δ	20.4	6.4
Side chains			
C(13)—C(17)—C(20)—C(22)		174 (1)	−179 (1)
C(17)—C(20)—C(22)—C(23)		60 (1)	60 (1)
C(20)—C(22)—C(23)—C(24)		177 (1)	178 (1)
C(22)—C(23)—C(24)—O(27)		−64 (2)	−61 (2)

Table 3. *Geometric parameters* (Å, °) *of the hydrogen bonds and relevant van der Waals contacts* (Å) *between host and guest molecules*

An asterisk denotes an atom of DCA molecule (II).

Hydrogen bonds			
$O(27)^1\cdots O(25)$	2.71 (1)	$C(24)^1—O(27)^1\cdots O(25)$	133.5 (1)
$O(25)\cdots O(26)^*$	2.69 (1)	$O(27)^1\cdots O(25)\cdots O(26)^*$	112.0 (4)
$O(26)^*\cdots O(28)^2$	2.65 (1)	$O(25)\cdots O(26)^*\cdots O(28)^2$	114.6 (4)
		$O(26)^*\cdots O(28)^2—C(24)^2$	116.7 (7)
$O(27)^*\cdots O(25)^{*4}$	2.70 (1)	$C(24)^*—O(27)^*\cdots O(25)^4$	131 (1)
$O(25)^{*4}\cdots O(26)$	2.64 (1)	$O(27)^*\cdots O(25)^{*4}\cdots O(26)$	115.8 (4)
$O(26)\cdots O(28)^{*3}$	2.60 (1)	$O(25)^{*4}\cdots O(26)\cdots O(28)^{*3}$	115.8 (4)
		$O(26)\cdots O(28)^{*3}—C(24)^{*3}$	116.9 (4)
Host–guest van der Waals contacts			
$C(25)\cdots C(18)^1$	4.20 (2)	$C(29)\cdots C(21)^1$	4.07 (2)
$C(25)\cdots C(16)^{*5}$	4.04 (2)	$C(30)\cdots C(5)$	3.95 (1)
$C(25)\cdots C(18)^{*6}$	3.97 (2)	$C(30)\cdots C(20)^1$	4.04 (2)
$C(26)\cdots C(18)^1$	3.68 (2)	$C(30)\cdots C(15)^{*5}$	4.27 (2)
$C(26)\cdots C(16)^{*5}$	4.00 (2)	$C(30)\cdots C(16)^{*5}$	4.19 (2)
$C(26)\cdots C(22)^{*5}$	4.19 (2)	$C(30)\cdots C(18)^{*6}$	4.01 (2)
$C(27)\cdots C(18)^1$	3.72 (2)	$C(31)\cdots C(18)^1$	3.98 (2)
$C(27)\cdots C(16)^{*5}$	4.13 (2)	$C(31)\cdots C(5)^{*7}$	3.79 (1)
$C(27)\cdots C(20)^{*5}$	4.21 (2)	$C(31)\cdots C(6)^{*7}$	3.90 (1)
$C(27)\cdots C(22)^{*5}$	4.22 (2)	$C(31)\cdots C(20)^{*5}$	4.03 (2)
$C(28)\cdots C(18)^1$	4.26 (2)	$C(31)\cdots C(22)^{*5}$	3.97 (2)
$C(28)\cdots C(21)^1$	4.20 (2)	$C(32)\cdots C(18)^1$	3.91 (2)
$C(28)\cdots C(16)^{*5}$	4.28 (2)	$C(32)\cdots C(1)^{*8}$	3.97 (2)
$C(29)\cdots C(5)$	4.00 (2)	$C(32)\cdots C(22)^{*5}$	3.91 (2)
$C(29)\cdots C(20)^1$	4.02 (2)		
Guest–guest distances			
$C(25)\cdots C(31)^1$	4.37 (2)	$C(32)\cdots C(31)^1$	4.73 (2)
$C(25)\cdots C(28)^1$	4.82 (2)		

Symmetry code: (1) $(x, y, z) + \mathbf{c}$; (2) $(x, y, z) - \mathbf{a} + \mathbf{c}$; (3) $(x, y, z) + \mathbf{a}$; (4) $(x, y, z) - \mathbf{c}$; (5) $(-x, \frac{1}{2} + y, -z) + \mathbf{c}$; (6) $(-x, \frac{1}{2} + y, -z) + \mathbf{a} + \mathbf{c}$; (7) $(-x, \frac{1}{2} + y, -z) + 2\mathbf{c}$; (8) $(-x, \frac{1}{2} + y, -z) + \mathbf{a} + 2\mathbf{c}$.

of pseudo-rotation Δ and the maximum possible torsion angle φ_m (Altona, Geise & Romers, 1968) are respectively 20.4 and 46.9° for molecule (I), and 6.4 and 42.0° for molecule (II).

The conformation of the side chain, described in Table 2, is one of the more energetically stable and corresponds to the folded one; C(17)—C(20)—C(22)—C(23) ≃ 60° (Giglio & Quagliata, 1975).

The half-chair type conformation of the *D* ring, joined with the folded conformation of the side chain, is a feature of all the so far known orthorhombic phases of choleic acids and of the tetragonal phase of the canal complex between DCA, ethanol and water (Coiro, D'Andrea & Giglio, 1979). The envelope type conformation of the *D* ring has been found in the hexagonal phases of canal complexes of DCA (Candeloro De Sanctis, Coiro, Giglio, Pagliuca, Pavel & Quagliata, 1978; Candeloro De Sanctis, Giglio, Petri & Quagliata, 1979).

In spite of the different space group ($P2_1$) of the present structure, the DCA bilayer and the spatial relationships between bilayers closely resemble those observed in the DCA inclusion compounds exhibiting the $P2_12_12_1$ symmetry (α group); see Fig. 2.

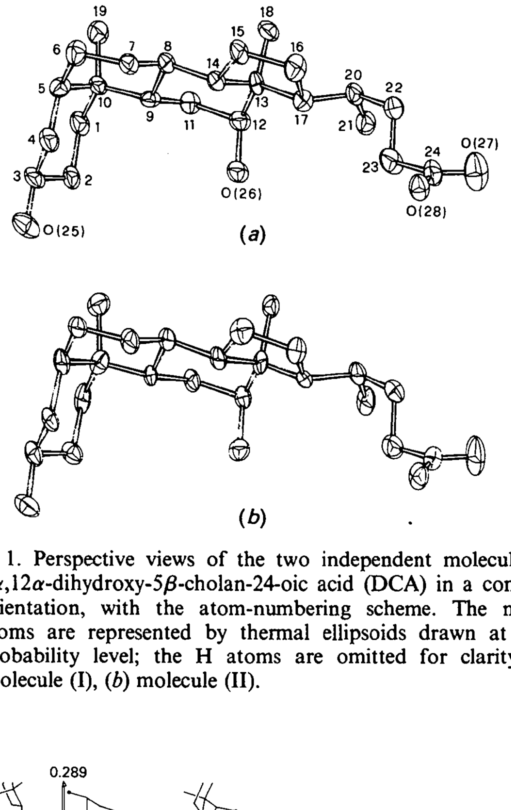

Fig. 1. Perspective views of the two independent molecules of $3\alpha,12\alpha$-dihydroxy-5β-cholan-24-oic acid (DCA) in a common orientation, with the atom-numbering scheme. The non-H atoms are represented by thermal ellipsoids drawn at 50% probability level; the H atoms are omitted for clarity. (*a*) Molecule (I), (*b*) molecule (II).

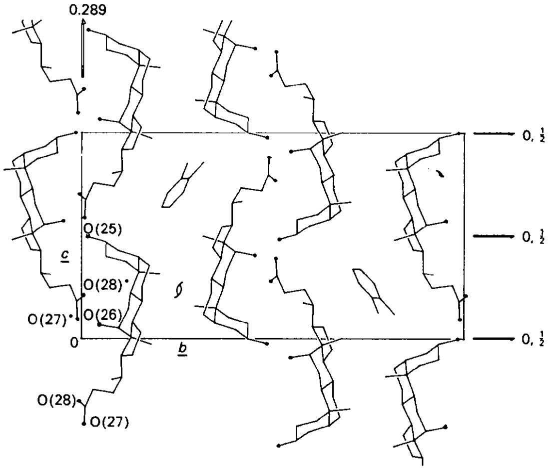

Fig. 2. Arrangement of the host and guest molecules in the crystal, projected onto the *bc* plane. The crystallographic twofold screw axes are represented with filled arrows, the pseudo-twofold screw axes with unfilled arrows.

The similarity results from the presence of pseudo-twofold screw axes parallel to both *a* and *c* lattice vectors. Infact, a rigid-body displacement connects molecules (I) and (II) that can be described (Cerrini & Pelliccioni, 1990) as resulting from a rotation of 179 (2)° about an axis oriented as the unit vector $\mathbf{u} = [0.000\,(1),\ 0.0000\,(3),\ 0.0740\,(3)]$ (coincident with *c*), located at $\mathbf{s} = [0.289\,(3),\ -0.0001\,(2),\ 0.005\,(2)]$, coupled with a translation $\mathbf{t}_u = [-0.0004\,(1),\ 0.0005\,(2),\ -0.507\,(9)]$ parallel to the rotation axis. After the best fit the two molecules superpose with a total discrepancy $S = 0.1053$ Å^2, calculated as the sum of the squared distances between matching atoms.

Correspondingly, molecule (II′), obtained from (II) by the symmetry operation $-x,\ \frac{1}{2}+y,\ 1-z$, superposes to molecule (I) with the following rigid displacement: a rotation of 180 (1)° about the unit vector $\mathbf{u} = [0.138\,(2),\ -0.0003\,(7),\ 0.001\,(7)]$ (coincident with *a*) located at $\mathbf{s} = [0.0085\,(1),\ 0.2501\,(1),\ 0.2479\,(2)]$ and followed by a translation $\mathbf{t}_u = [0.596\,(15),\ -0.0015\,(1),\ 0.0049\,(1)]$. The best superposition gives a sum of squared distances $S = 0.1068$ Å^2. The spatial relationships between the crystallographic twofold screw axis and the pseudo-twofold screw axes parallel to *a* and *c* closely mimic the three non-intersecting twofold screw axes of the $P2_12_12_1$ space group.

These findings show that the deviation from the $P2_12_12_1$ symmetry of the DCA frame in the present structure is mainly owing to a mutual misfit of the two independent molecules along the *a* axis, that results from a shift of 0.28 Å of the position of the first pseudo-symmetry and from an increase of 0.70 Å of the translation of the second one ($\mathbf{s} = [0.289,\ -0.0001,\ 0.005]$ instead of [0.25, 0, 0] for the first pseudo-screw axis, and $\mathbf{t}_u = [0.596,\ -0.0015,\ 0.0049]$ instead of [0.5, 0, 0] for the second one).

It is noteworthy that the pseudo-twofold screw axes relate only the DCA molecules and do not repeat the guest molecule which has one definite position.

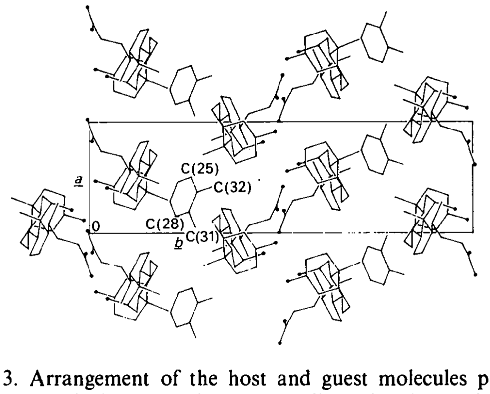

Fig. 3. Arrangement of the host and guest molecules projected onto the *ab* plane, showing the one-dimensional crystals formed by the *o*-xylene molecules, sited between the bilayers of DCA.

Repetition of DCA according to the pseudo-symmetry parallel to *c* and to the *ac* lattice vectors gives rise to the bilayer, in which molecules (I) and (II) are linked through the characteristic and efficient net of hydrogen bonds, reported in Table 3 and shown in Figs. 2 and 3. The monoclinic screw axis and the pseudo-symmetry along *a* govern the relative positions of adjacent bilayers.

The channel extends along the *a* vector around the line ($x,\ y = \frac{1}{4},\ z = \frac{3}{4}$) and has a nearly rectangular cross section with a ratio of ~1.5 between the edges (see Fig. 2). The short edge is delimited by methyl group C(19), the methylenic and methynic groups of the *A* rings; the long edge is delimited by the methyl group C(18), methylenic groups of the *D* rings and by the side chains.

In the channel, the *o*-xylene molecule lies almost perpendicularly to the *bc* plane [the interplanar angle being 73.0 (5)°] and is inclined and positioned to conform to the shape and the internal dimensions of the channel. The interatomic distances reported in Table 3 show that favourable van der Waals contacts occur between the guest and host molecules, which stabilize the crystal structure and keep the *o*-xylene molecule in a well defined position. The shortest distances (~3.7 Å) are found between the C(18) methyl of DCA and the aromatic C atoms C(26) and C(27) of *o*-xylene, substituted with methyl groups.

In the channels, the *o*-xylene molecules form one-dimensional crystals along the lines ($x,\ y \simeq \frac{1}{4},\ z \simeq \frac{3}{4}$) and ($x,\ y \simeq \frac{3}{4},\ z \simeq \frac{1}{4}$) (see Figs. 2 and 3), which are enclosed by host molecules. The guest molecules interact very weakly, the shortest distance between atoms of two contiguous molecules being 4.37 (2) Å. The existence of numerous intramolecular contacts around each atom of the guest with the surrounding hosts, across the channel, and of the feeble interactions among the guests, along the channel, shows that the *o*-xylene molecules fill almost completely the free space of the channel.

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Mesoionic Compounds. 4.* Structure of 1,4,5-Triphenyl-1,2,4-triazolium-3-thiolate

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Abstract. $C_{20}H_{15}N_3S$, $M_r = 329.43$, monoclinic, $P2_1/c$, $a = 11.745\,(4)$, $b = 7.600\,(4)$, $c = 21.929\,(6)$ Å, $\beta = 118.36\,(4)°$, $V = 1722.4\,(1.0)$ Å^3, $Z = 4$, $D_x = 1.270$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.8$ cm^{-1}, $F(000) = 688$, $T = 297$ K, $R = 0.038$ for 1372 reflections. The mesoionic compound has a nearly planar pentatomic heterocyclic ring and an exocyclic C—S$^-$ bond.

Introduction. The title compound (*B*) is a rearrangement product of 4,5-diphenyl-1,3,4-thiadiazolium-2-phenylaminide (*A*), in which the S atom of (*A*) becomes the exocyclic S atom of (*B*). Alternatively, (*B*) may be obtained directly from

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* Part 3: Cheung, Echevarria, Galembeck, Maciel, Miller, Rumjanek & Simas (1992).

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