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# The 2 : 1 : 1 Canal Complex Between Deoxycholic Acid, Dimethyl Sulphoxide and Water

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**Abstract.** $C_{24}H_{40}O_4.0\cdot5C_2H_6OS.0\cdot5H_2O$, hexagonal, $P6_5$, $a = 15\cdot117$ (3), $c = 18\cdot695$ (3) Å, $Z = 6$, $D_m = 1\cdot189$, $D_c = 1\cdot189$ Mg m$^{-3}$, Mo $K\alpha$ radiation, $\mu$(Mo $K\alpha$) = 0·125 mm$^{-1}$. $R = 0\cdot11$ and $R_w = 0\cdot16$ for 969 observed data with intensity greater than $3\sigma(I)$. The dimethyl sulphoxide and water molecules alternate in canals parallel to $c$. The dimethyl sulphoxide molecules were located with the aid of potential-energy calculations. The deoxycholic acid host molecules form helices around the $6_5$ axes and give rise to hydrogen bonding with guest molecules.

**Introduction.** The crystal structure of the hexagonal 3:2:1 canal complex between 3$\alpha$,12$\alpha$-dihydroxy-5$\beta$-cholan-24-oic acid (deoxycholic acid, DCA), ethanol (ETH) and water (W) has already been solved (Candeloro De Sanctis, Coiro, Giglio, Pagliuca, Pavel & Quagliata, 1978). The crystals of this inclusion compound (DCAETH) are hexagonal, space group $P6_5$, with unit-cell dimensions $a = 15\cdot115$ and $c = 18\cdot676$ Å and $D_m = D_c = 1\cdot16$ Mg m$^{-3}$. The host molecules are arranged in spirals around the $6_5$ axes and allow the accommodation of the guest molecules inside the helices according to the repeating sequence –ETH–ETH–W–, which was found to be realizable by potential-energy calculations. These calculations indicated also that the ETH molecules have their methyl groups and, probably, their methylene groups in non-equivalent crystallographic positions.

The title compound (hereafter DCADMS) is isomorphous with DCAETH. Crystals were grown by slow evaporation from dimethyl sulphoxide (DMS) solutions. A pyramidal specimen, cut from one larger crystal and with a maximum dimension of 0·45 mm, was chosen to collect intensities up to $2\theta = 55°$ with the $\omega/2\theta$ scanning mode, using a Hilger & Watts Y290/FA228 four-circle diffractometer. No absorption correction was applied. The experimental density of the cyclohexane–carbon tetrachloride mixture in which some DCADMS crystals were suspended, measured by means of a DMA 02C densimeter, is in agreement with the 2 : 1 : 1 ratio.

The structure was solved by assuming the same atomic coordinates for DCA as observed in DCAETH. A difference synthesis showed the two highest peaks to be located within the canals very near to those of the O atom and of the methylene C atom of ETH in DCAETH, so they were attributed to the O and S atoms of DMS. Unfortunately we were unable to locate the methyl groups of DMS after a least-squares refinement, including the O and S atoms, followed by another difference synthesis. Thus it was decided to resort to van der Waals energy calculations with the atomic coordinates so far obtained. The H atoms of DCA were generated with the same rules applied for DCAETH. The coefficients of the potentials concerning H, C, O, S atoms and the methyl groups have previously been reported (Pavel, Quagliata & Scarcelli, 1976). The geometry adopted for DMS, derived from the data listed by Iball, Morgan & Wilson (1968), was S–O = 1·47, S–C = 1·81 Å, O–S–C = 107 and C–S–C = 98°. W molecules were not included since at that time their occurrence in DCADMS was not suspected. The calculations were accomplished as a function of $\varphi$, the clockwise rotation angle looking along the O–S bond with an angular increment of 5°. $\varphi = 0°$ corresponds to the atomic coordinates $x = 0\cdot235$, $y = 0\cdot058$, $z = 0\cdot146$ and $x = 0\cdot033$, $y = 0\cdot002$, $z = 0\cdot146$ for the two methyl carbons. The results clearly point out that two DMS molecules, related by a translation of $c/6$ and a rotation of $\pi/3$, cause a strong steric hindrance

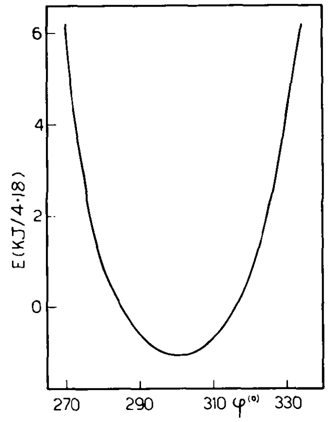

Fig. 1. Van der Waals energy *vs* $\varphi$. The interactions between one DMS and the three nearest DCA molecules have been considered.

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between them, even if their $\varphi$ values are different. Moreover $\varphi$ can only vary within the range 290–310° as far as the DMS–DCA interactions are concerned (see Fig. 1). However a sequence ... DMS–$V$–DMS–$V$ ..., where $V$ represents a vacancy, gives rise to an unsatisfactory density value as compared with the measured one. At this stage gas-chromatographic measurements allowed us to establish the presence of W molecules. The ratio DCA:DMS:W was 2:0·9:1·2, thus supporting the ordered sequence –DMS–W– (see Figs. 2 and 3).

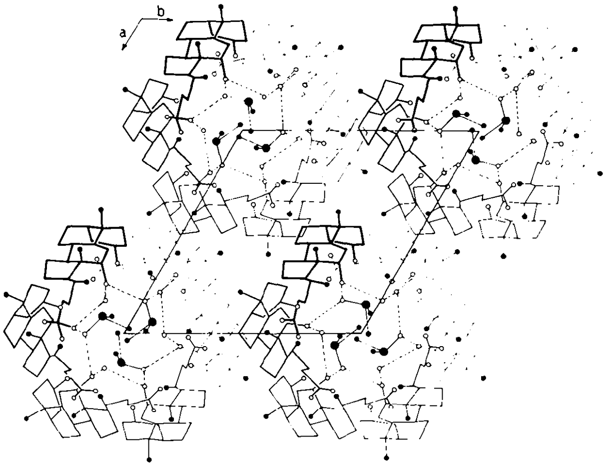

Fig. 2. A view of the DCADMS crystal packing along $c$. The broken lines indicate hydrogen bonds among DCA and DMS or W molecules. Small and large black circles represent methyl groups and S atoms respectively; open circles refer to O atoms.

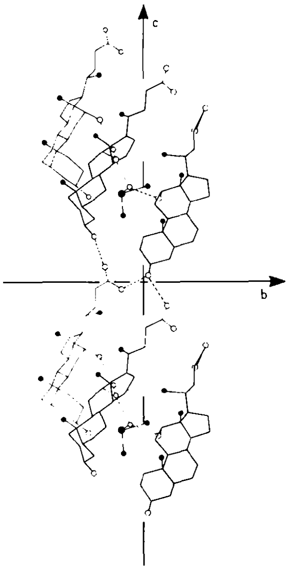

Fig. 3. Part of DCADMS packing viewed along the normal to the $bc$ plane. The symbols have the same meaning as in Fig. 2.

New energy calculations, performed introducing the W molecules, confirmed the experimental results and the correctness of the model. The O atoms of the W and DMS molecules occupied crystallographic equivalent positions with respect to the $6_5$ axis.

This model ($\varphi$ = 300°) was refined by a block-diagonal least-squares method with isotropic temperature factors, using the programs of Domenicano, Spagna & Vaciago (1969). The H atoms were generated and included in the last cycles with a $B$ of 5 Å$^2$. Scattering factors for C, O and S were taken from Cromer & Mann (1968) and for H from Hanson, Herman, Lea & Skillman (1964). The atomic parameters of the O and S atoms converge, while those of the C(29) and C(30) methyl C atoms do not. Thus the atomic parameters of DMS were kept fixed according to the assumed geometry in the last cycles and are reported in Table 1 together with the final values of DCA.* $R$ and $R_w$ are 0·11 and 0·16 respectively. The

Table 1. *Atom coordinates* (×10$^3$) *and isotropic temperature factors* (Å$^2$)

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| C(1) | 517 (1) | 260 (1) | 191 (1) | 5·0 (4) |
| C(2) | 425 (1) | 194 (1) | 140 (1) | 5·0 (4) |
| C(3) | 438 (1) | 261 (1) | 76 (1) | 5·4 (4) |
| C(4) | 437 (1) | 356 (1) | 99 (1) | 4·1 (3) |
| C(5) | 526 (1) | 418 (1) | 150 (1) | 3·9 (3) |
| C(6) | 528 (1) | 519 (1) | 169 (1) | 4·3 (4) |
| C(7) | 443 (1) | 502 (1) | 221 (1) | 4·3 (3) |
| C(8) | 445 (1) | 446 (1) | 288 (1) | 3·7 (3) |
| C(9) | 437 (1) | 342 (1) | 266 (1) | 2·9 (3) |
| C(10) | 526 (1) | 359 (1) | 214 (1) | 4·8 (4) |
| C(11) | 423 (1) | 275 (1) | 332 (1) | 5·1 (4) |
| C(12) | 346 (1) | 265 (2) | 388 (1) | 4·9 (4) |
| C(13) | 359 (1) | 370 (1) | 408 (1) | 2·6 (2) |
| C(14) | 358 (1) | 423 (1) | 338 (1) | 3·4 (3) |
| C(15) | 349 (1) | 514 (1) | 366 (1) | 4·8 (4) |
| C(16) | 285 (1) | 476 (1) | 435 (1) | 5·2 (4) |
| C(17) | 267 (1) | 365 (1) | 448 (1) | 2·7 (2) |
| C(18) | 457 (1) | 430 (1) | 449 (1) | 4·5 (4) |
| C(19) | 627 (1) | 417 (1) | 256 (1) | 5·3 (4) |
| C(20) | 255 (1) | 343 (1) | 528 (1) | 4·6 (3) |
| C(21) | 237 (2) | 239 (2) | 542 (1) | 8·6 (6) |
| C(22) | 158 (1) | 343 (1) | 558 (1) | 5·6 (4) |
| C(23) | 156 (2) | 344 (2) | 641 (1) | 7·0 (5) |
| C(24) | 64 (1) | 320 (1) | 673 (1) | 5·8 (4) |
| O(25) | 354 (1) | 201 (1) | 27* | 7·0 (3) |
| O(26) | 243 (1) | 199 (1) | 357 (1) | 5·3 (2) |
| O(27) | −26 (1) | 260 (1) | 636 (1) | 6·9 (3) |
| O(28) | 53 (1) | 350 (1) | 734 (1) | 7·0 (3) |
| C(29) | 119 | 34 | 111 | 11·4 |
| C(30) | 10 | −24 | 236 | 15·1 |
| O(31) | 169 | 162 | 220 | 9·7 |
| S(32) | 141 | 55 | 207 | 12·8 |

* Coordinate kept fixed during the refinement.

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33875 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

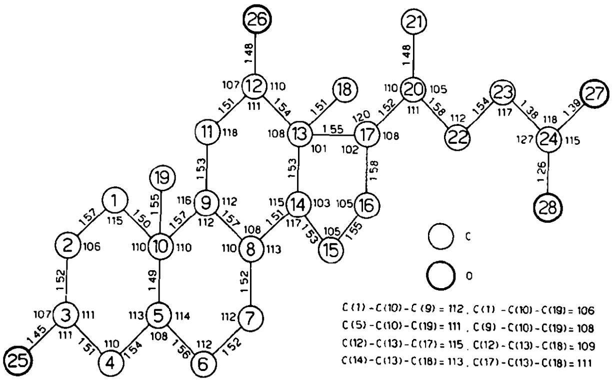

Fig. 4. Bond distances (Å) and angles (°) of DCA.

bond lengths and angles of DCA are given in Fig. 4. Their average e.s.d.'s are 0·027Å and 1·5° with maximum values of 0·037 Å and 2·1°.

**Discussion.** The low number of intensity data recorded (34% of the whole Cu $K\alpha$ sphere) have caused large standard deviations in the atomic coordinates and in the bond lengths and angles. Nevertheless, since the DCA geometry is known from the DCAETH crystal structure, the main interests of this work lie both in the determination of the DMS arrangement within the canals and in the possibility of locating the guest molecules by potential-energy calculations. The packing is equal to that of DCAETH (see Figs. 2 and 3). The O(31) coordinates probably represent an average position of the DMS and W O atoms, which were indistinguishable in the difference syntheses. The O atoms of DMS and W both form two hydrogen bonds with two O(26) atoms, the O···O distances being 2·74 and 2·77 Å, and are necessarily acceptor and donor in turn. Good van der Waals contacts exist among the DMS methyl groups. The S—C bonds of DMS nearly coincide with the two directions allowed for the C—C bond of ETH in DCAETH. Moreover the dimensions of the cavities suggest that molecules bulkier than DMS can be accommodated with difficulty without a change of the host lattice.

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# Absolute Configurations of the Stereoisomeric *N*,*N*-Dimethyl-4-methyl-4-phenyl-1,2,3,4-tetrahydro-2-naphthylamines*

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**Abstract.** $C_{19}H_{24}IN$, $M_r = 393{\cdot}3$, orthorhombic, $P2_12_12_1$ (systematic absences: $h00$, $h$ odd; $0k0$, $k$ odd; $00l$, $l$ odd), $a = 7{\cdot}569$ (3), $b = 8{\cdot}201$ (8), $c = 30{\cdot}01$ (2) Å, $Z = 4$, $D_c = D_o$ ($CCl_4/C_6H_6$) = 1·40 Mg m$^{-3}$. The structure was refined to a final $R$ of 0·038 for 1667 reflections. The absolute configuration, determined using anomalous dispersion by iodine, confirms tentative absolute configurations proposed earlier for this series of potent analgetics.

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