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# Inclusion compounds of cholic acid with mixed guests

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# Inclusion compounds of cholic acid with mixed guests

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**Cholic acid is shown to form inclusion compounds with different guest molecules, of diverse chemical nature, in the same crystal. The single crystal structures of the inclusion compounds 2CA·1,2-dichlorobenzene·acetone and 2CA·*i*-propyl acetate·methyl acetate are elucidated and the guests shown to alternate in an ordered fashion in the channel of the characteristic tubulate clathrate structures.**

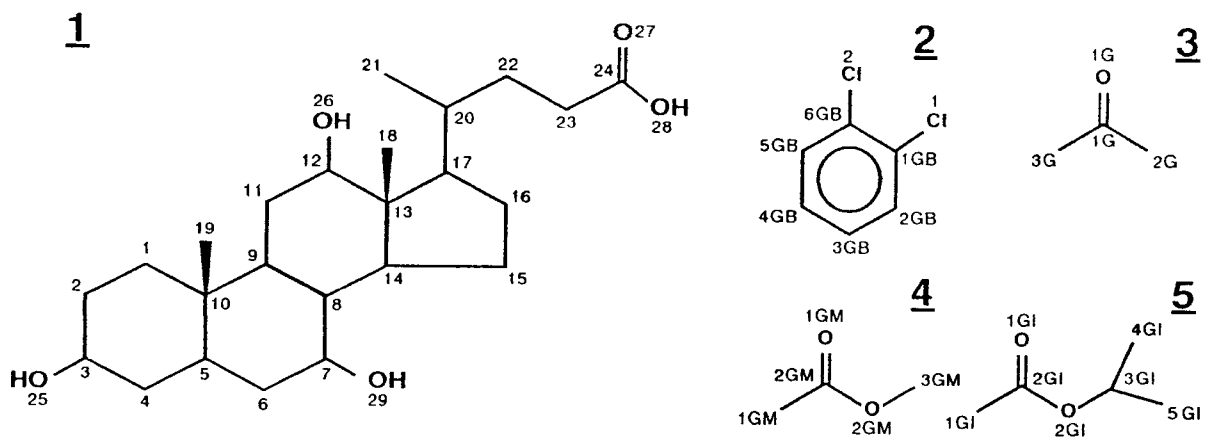


## INTRODUCTION

The steroid bile acid 3α,7α,12α-trihydroxy-5β-cholan-24-oic acid or cholic acid (CA) has been shown to form inclusion compounds with a number of different types of guest molecules. The structures of these compounds may be divided into groups according to the packing motifs and type of hydrogen-bonding displayed. The hydrates[1,2] and inclusion compounds with aliphatic alcohol guests[3,4] form extensively hydrogen bonded structures in which both host and guest participate in hydrogen-bonding.

Most CA inclusion compounds exist as tubulate clathrates in which the curved steroid host molecules are hydrogen bonded in a head-to-tail fashion resulting in the formation of puckered bilayers. The hydrophilic α-faces of the host molecules are largely buried in the interior of the bilayers which are associated with each other by weak van der Waals interactions between the hydrophobic β-faces of neighbouring bilayers. Guest molecules pack into channels which remain between the puckered bilayers and effectively form infinitely propagating, spiralling columns throughout the crystal. Guests included in such fashion include aliphatic esters[5] and ketones[6], lactones[7], aromatic hydrocarbons[8] and substituted aromatic molecules.[9,10] A few structures exist which, although they exhibit this bilayer packing motif, are stabilised by hydrogen bonding between host and guest and show H:G ratios other than 1:1.[11]

We have in the past reported the novel compound formed by CA with acetone and 3 water molecules[12] and here we describe the crystal structures and thermal decomposition of CA with mixed guest pairs: methyl acetate/*i*-propyl acetate (CAMI) and acetone/1,2-dichloro-benzene (CAAD). While other authors have




**Scheme 1**

dealt with the phenomenon of cholic acid inclusion crystals containing a mixture of enantiomers,[7] this is the first report of a mixture of guest molecules contained in a single crystal in an ordered array.

## EXPERIMENTAL

Single crystals of the inclusion compound CAMI were grown by slow cooling from a solution of CA in 50:50 (mole percent) dry methyl acetate and *i*-propyl acetate while those of CAAD crystallised from a solution of CA and 1,2-dichlorobenzene in excess acetone. In each case the crystals were transparent, colourless needles which were cut to provide single crystals suitable for x-ray diffractometry and mounted in Lindemann capillary tubes to prevent desorption of the guests during data collection.

Preliminary cell parameters were obtained photographically and intensity data were collected on an Enraf-Nonius CAD4 diffractometer at 294 K using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.7107 Å) and the $\omega - 2\theta$ scan mode. During data collection three reference reflections were monitored periodically to check crystal stability. The data were corrected for Lorentz-polarisation effects. Refined unit cell parameters were obtained by least squares analysis of 24 reflections measured on the diffractometer in the range $16 < \theta < 17°$. Crystal data and other experimental details are given in Table 1.

### Structure Solution and Refinement

Both inclusion compound structures were solved by direct methods using the program SHELX-86[13] and refined by full-matrix least-squares refinement using the program SHELX-76[14], refining on $F$ with the weighting schemes $w = [\sigma^2(F) + gF_o^2]^{-1}$ (values of g detailed in Table 1) chosen to ensure constant distribution of $<w(|F_o| - |F_c|)^2>$ with respect to sin $\theta$ and $(F_o/F_{max})^{1/2}$. The co-ordinates of one carbon atom of one host molecule were fixed in each case to define the origin. All non-hydrogen atoms of the host molecules of CAAD were refined anisotropically while those of CAMI were subjected to isotropic refinement with the exception of the host oxygen and side chain atoms. Methyne, methylene and methyl hydrogen atoms were placed in geometrically generated positions and refined with positional parameters riding on the host atom and each type tied to a common temperature factor which was allowed to refine. Peaks due to hydroxyl group hydrogen atoms could not be discerned in electron density difference maps and were omitted from the final models. Guest atoms were readily located in electron density difference maps and refined isotropically with some simple bond length restraints to ensure that sensible molecular geometry was retained.

**Table 1** Crystal data, experimental and refinement parameters.

| | *CAMI* | *CAAD* |
|---|---|---|
| **Crystal data** | | |
| Molecular formula | $2C_{24}H_{40}O_5 \cdot C_3H_6O_2 \cdot C_5H_{10}O_2$ | $2C_{24}H_{40}O_5 \cdot C_3H_6O \cdot C_6H_4Cl_2$ |
| Molecular weight ($gmol^{-1}$) | 993.370 | 1022.24 |
| Space group | *P*1 | *P*1 |
| *a*(Å) | 12.289(2) | 12.474(3) |
| *b*(Å) | 8.238(4) | 8.252(2) |
| *c*(Å) | 14.246(3) | 14.214(8) |
| α(°) | 90.39(3) | 91.09(3) |
| β(°) | 105.83(1) | 106.31(3) |
| γ(°) | 94.97(2) | 94.43(2) |
| *V*(Å$^3$) | 1381.6(8) | 1398.8(10) |
| Z | 1 | 1 |
| $D_c(gcm^{-3})$ | 1.194 | 1.119 |
| μ(MoKα) ($cm^{-1}$) | 0.48 | 1.34 |
| F(000) | 544 | 514 |
| **Data collection** | | |
| Crystal dimensions (mm) | 0.3 × 0.35 × .25 | 0.5 × 0.5 × 0.5 |
| Range *h*, *k*, *l* | ±9, ±14, 17 | ±14, ±9, 17 |
| Total exposure time (h) | 40 | 42.7 |
| Intensity Variation (%) | −17.8 | 6 |
| No. of reflections collected | 5076 | 2810 |
| No. of Reflections $I_{rel} > 2\sigma I_{rel}$ | 3226 | 2324 |
| **Final refinement** | | |
| No. of reflections (independent) | 3224 | 2183 |
| No. of parameters | 325 | 310 |
| *R* indices: | | |
| *R* | 0.067 | 0.094 |
| *wR* | 0.072 | 0.098 |
| g | 0.0075 | 0.007 |
| S | 0.749 | 1.00 |
| Δρmax ($eA^{-3}$) | 0.31 | 0.25 |
| Δρmin ($eA^{-3}$) | −0.31 | −0.30 |

Final fractional coordinates are presented in Tables 2 and 3 and all data has been deposited at the Cambridge Crystallographic Data Centre.

### Thermal Analysis

Differential Scanning Calorimetry (DSC) and Thermal Gravimetry (TG) were performed on a Perkin Elmer PC7 system. Crystals of the inclusion compounds were removed from mother liquor, blotted dry and lightly crushed before analysis. Sample masses in the range 1–5 mg were analysed in the temperature range 30–230°C at a heating rate of 20°C.$min^{-1}$ with dry nitrogen purge gas at a flow rate of 40 $cm^3.min^{-1}$.

$^1$H-nmr spectroscopy was performed on a Varian VXR-200 spectrometer in $d_6$-DMSO.

## RESULTS AND DISCUSSION

The ratios and chemical identities of the included guests were inferred from weight loss % on TG analysis and the occurrence of peaks due to both types of guest in

**Table 2** Fractional atomic coordinates ($\times 10^4$) for CAMI

| *Atom* | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| C(1A) | −1957( 9) | 3838(13) | 971( 8) |
| C(2A) | −1421( 9) | 3890(12) | 130( 7) |
| C(3A) | −1555( 9) | 2217(13) | −346( 8) |
| O(25A) | −973( 8) | 2309(10) | −1112( 6) |
| C(4A) | −1043( 9) | 1010(13) | 400( 8) |
| C(5A) | −1527( 9) | 964(12) | 1268( 8) |
| C(6A) | −996( 9) | −312(13) | 2007( 8) |
| C(7A) | 192( 9) | 206(12) | 2618( 7) |
| O(29A) | 1013( 8) | 239(10) | 2062( 6) |
| C(8A) | 281( 8) | 1905(12) | 3098( 7) |
| C(9A) | −212( 8) | 3188(11) | 2352( 7) |
| C(10A) | −1472( 9) | 2653(12) | 1760( 7) |
| C(19A) | −2271( 9) | 2585(15) | 2449( 8) |
| C(11A) | −71( 9) | 4878(12) | 2854( 8) |
| C(12A) | 1145( 9) | 5430(12) | 3438( 7) |
| O(26A) | 1820( 8) | 5677(10) | 2761( 6) |
| C(13A) | 1617( 8) | 4143(11) | 4200( 7) |
| C(18A) | 963( 9) | 4093(13) | 4977( 8) |
| C(14A) | 1506( 8) | 2525(12) | 3650( 7) |
| C(15A) | 2172( 9) | 1441(12) | 4408( 8) |
| C(16A) | 3177(10) | 2585(13) | 4973( 8) |
| C(17A) | 2931( 8) | 4346(12) | 4702( 7) |
| C(20A) | 3387( 9) | 5529(12) | 5574( 7) |
| C(21A) | 3103(10) | 7289(13) | 5349( 8) |
| C(22A) | 4690( 9) | 5529(14) | 5953( 8) |
| C(23A) | 5167( 9) | 6139(14) | 7027( 8) |
| C(24A) | 6417( 9) | 6231(13) | 7386( 7) |
| O(27A) | 6980( 8) | 7440(11) | 7767( 7) |
| O(28A) | 6862( 8) | 4871(11) | 7251( 7) |
| C(1B) | 12157( 9) | 9170(13) | 9176( 8) |
| C(2B) | 11524( 9) | 9097(13) | 9955( 8) |
| C(3B) | 11566( 9) | 7451(13) | 10404( 8) |
| O(25B) | 10906( 8) | 7371(10) | 11088( 6) |
| C(4B) | 11120( 9) | 6135(12) | 9614( 7) |
| C(5B) | 11680( 9) | 6177(13) | 8805( 8) |
| C(6B) | 11188( 9) | 4847(13) | 8021( 8) |
| C(7B) | 10037( 9) | 5116(12) | 7336( 8) |
| O(29B) | 9139( 7) | 4921(10) | 7813( 6) |
| C(8B) | 10036( 9) | 6815(12) | 6921( 7) |
| C(9B) | 10484( 8) | 8147(12) | 7727( 7) |
| C(10B) | 11716( 9) | 7871(13) | 8346( 8) |
| C(19B) | 12546( 9) | 7997(15) | 7719( 8) |
| C(11B) | 10343( 9) | 9851(12) | 7329( 8) |
| C(12B) | 9144( 9) | 10093(12) | 6697( 7) |
| O(26B) | 8374( 8) | 10113(10) | 7301( 6) |
| C(13B) | 8746( 9) | 8807(12) | 5865( 8) |
| C(18B) | 9470( 9) | 9131(14) | 5137( 8) |
| C(14B) | 8857( 8) | 7118(12) | 6310( 7) |
| C(15B) | 8265(10) | 5951(13) | 5454( 8) |
| C(16B) | 7297( 9) | 6879(12) | 4846( 8) |
| C(17B) | 7468( -) | 8611( -) | 5291( -) |
| C(20B) | 6953( 9) | 9872(12) | 4547( 7) |
| C(21B) | 7210(11) | 11609(13) | 4924( 9) |
| C(22B) | 5681( 9) | 9418(12) | 4152( 8) |
| C(23B) | 5092( 9) | 10275(13) | 3249( 8) |
| C(24B) | 3844( 9) | 9748(13) | 2916( 8) |
| O(27B) | 3446( 8) | 8431(11) | 3031( 7) |
| O(28B) | 3235( 8) | 10915(11) | 2487( 7) |
| C(1GI) | 6030(20) | 7282(28) | −113(18) |
| O(1GI) | 5378(24) | 8465(37) | 1073(22) |
| C(2GI) | 5506(22) | 7137(37) | 629(22) |
| C(3GI) | 4495(18) | 5590(26) | 1599(17) |
| O(2GI) | 5056(12) | 5831(18) | 842(10) |
| C(4GI) | 3580(25) | 4243(35) | 1244(22) |
| C(5GI) | 5220(25) | 5307(36) | 2460(23) |
| O(2GM) | 5304(18) | 1340(27) | 8884(14) |
| C(1GM) | 3938(16) | 2473(26) | 7763(15) |
| C(2GM) | 4986(23) | 1694(33) | 8052(18) |
| O(1GM) | 5454(16) | 970(24) | 7395(13) |
| C(3GM) | 4634(26) | 2338(39) | 9423(24) |

**Table 3** Fractional atomic coordinates ($\times 10^4$) for CAAD

| *Atom* | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| C(1A) | 2127( 9) | −2351(13) | −838( 8) |
| C(2A) | 1515( 9) | −2403(12) | −53( 7) |
| C(3A) | 1568( 9) | −4083(13) | 380( 7) |
| O(25A) | 926( 7) | −4112( 9) | 1106( 5) |
| C(4A) | 1089( 9) | −5394(11) | −389( 8) |
| C(5A) | 1649( 9) | −5329(13) | −1208( 8) |
| C(6A) | 1128( 8) | −6713(12) | −2018( 8) |
| C(7A) | −13(10) | −6382(12) | −2679( 8) |
| O(29A) | −876( −) | −6566( −) | −2198( −) |
| C(8A) | −21( 9) | −4696(12) | −3085( 8) |
| C(9A) | 435( 8) | −3398(11) | −2286( 7) |
| C(10A) | 1648( 9) | −3644(12) | −1674( 8) |
| C(19A) | 2492(10) | −3535(19) | −2323( 9) |
| C(11A) | 291( 9) | −1643(12) | −2690( 7) |
| C(12A) | −879( 8) | −1421(11) | −3296( 7) |
| O(26A) | −1603( 6) | −1368( 8) | −2688( 5) |
| C(13A) | −1276( 8) | −2665(11) | −4148( 8) |
| C(18A) | −590(10) | −2396(14) | −4889( 8) |
| C(14A) | −1185( 8) | −4398(11) | −3722( 7) |
| C(15A) | −1764( 9) | −5533(12) | −4569( 7) |
| C(16A) | −2742( 9) | −4616(12) | −5167( 8) |
| C(17A) | −2556( 8) | −2879(10) | −4695( 7) |
| C(20A) | −3079( 9) | −1627(12) | −5474( 8) |
| C(21A) | −2859(12) | 140(13) | −5056(11) |
| C(22A) | −4347( 9) | −2032(12) | −5836( 8) |
| C(23A) | −4975( 9) | −1135(14) | −6670( 9) |
| C(24A) | −6172(10) | −1731(13) | −7021( 9) |
| O(27A) | −6575( 7) | −3066( 9) | −6932( 7) |
| O(28A) | −6829( 6) | −609( 9) | −7488( 6) |
| C(1B) | −11925(10) | 2406(15) | −9041( 9) |
| C(2B) | −11379( 9) | 2440(13) | −9858( 8) |
| C(3B) | −11492( 9) | 810(13) | −10345( 8) |
| O(25B) | −10927( 7) | 840( 8) | −11107( 5) |
| C(4B) | −11023( 9) | −417(12) | −9611( 8) |
| C(5B) | −11519( 9) | −467(11) | −8736( 8) |
| C(6B) | −11005(10) | −1735(13) | −8004( 8) |
| C(7B) | −9808( 9) | −1246(13) | −7353( 8) |
| O(29B) | −9006( 6) | −1280( 8) | −7923( 5) |
| C(8B) | −9702( 9) | 482(12) | −6885( 7) |
| C(9B) | −10223( 8) | 1731(11) | −7641( 7) |
| C(10B) | −11445( 8) | 1205(13) | −8243( 7) |
| C(19B) | −12257( 9) | 1182(16) | −7564( 9) |
| C(11B) | −10044( 9) | 3414(13) | −7135( 8) |
| C(12B) | −8868( 9) | 3955(12) | −6531( 7) |
| O(26B) | −8184( 6) | 4191( 8) | −7222( 5) |
| C(13B) | −8361( 8) | 2726(11) | −5762( 7) |
| C(18B) | −9033( 9) | 2702(14) | −4997( 7) |
| C(14B) | −8530( 8) | 1041(10) | −6337( 7) |
| C(15B) | −7880(10) | −29(13) | −5571( 8) |
| C(16B) | −6865(10) | 1063(13) | −4995(10) |
| C(17B) | −7104( 9) | 2842(12) | −5284( 7) |
| C(20B) | −6601( 8) | 4063(12) | −4405( 7) |
| C(21B) | −6891(10) | 5822(12) | −4639( 9) |
| C(22B) | −5334( 9) | 4020(15) | −4032( 8) |
| C(23B) | −4844(10) | 4583(16) | −2978( 8) |
| C(24B) | −3582( 8) | 4761(13) | −2623( 7) |
| O(27B) | −3028( 7) | 5946(10) | −2250( 6) |
| O(28B) | −3129( 6) | 3402( 9) | −2779( 6) |
| O(1G) | 4054(16) | 566(24) | −2193(15) |
| C(1G) | 5284(23) | −946(33) | −1048(21) |
| C(3G) | 5505(17) | −458(25) | −2748(16) |
| C(2G) | 4959(16) | −179(23) | −2032(15) |
| Cl(1) | 6301( 8) | 6175(11) | 1698( 8) |
| Cl(2) | 5759( 7) | 4691(11) | −403( 7) |
| C(1GB) | 5271(12) | −5328(16) | 1315(11) |
| C(2GB) | 4718(12) | −5935(16) | 1978(11) |
| C(3GB) | 3926(12) | −7276(16) | 1703(11) |
| C(4GB) | 3690(12) | −8008(16) | 768(11) |
| C(5GB) | 4243(12) | −7400(16) | 105(11) |
| C(6GB) | 5033(12) | −6060(16) | 378(11) |

**Table 4** Thermal Analysis Results

| | *CAMI* | *CAAD* |
|---|---|---|
| **TG wght loss %** | | |
| Experimental | 16.9 | 18.7 |
| Calculated[a] | 17.7 | 20.1 |
| **DSC peak onset T (°C)** | | |
| Guest loss | 103 | 80,108 |
| Melt | 202 | 205 |

[a]Assuming 2:1:1 H:$G_1$:$G_2$ stoichiometry.

$^1$H-NMR spectra of the inclusion compounds. The calculated and experimental values for weight loss % due to loss of guest are in good agreement as indicated in Table 4. Although the weight loss for CAAD appears lower than expected, analysis of $^1$H-NMR spectra indicates the presence of each guest in equal ratios and this is borne out by the high degree of order noted in the crystal structure analysis.

Molecular numbering of host and guest molecules are indicated previously and molecular geometry of the host molecules is shown in Figures 1a and b. Numbering of the host molecules follows conventional steroid notation. In each case the packing motif is that of the tubulate clathrate type structure with guest molecules packed alternately in the channels. The different size and shape

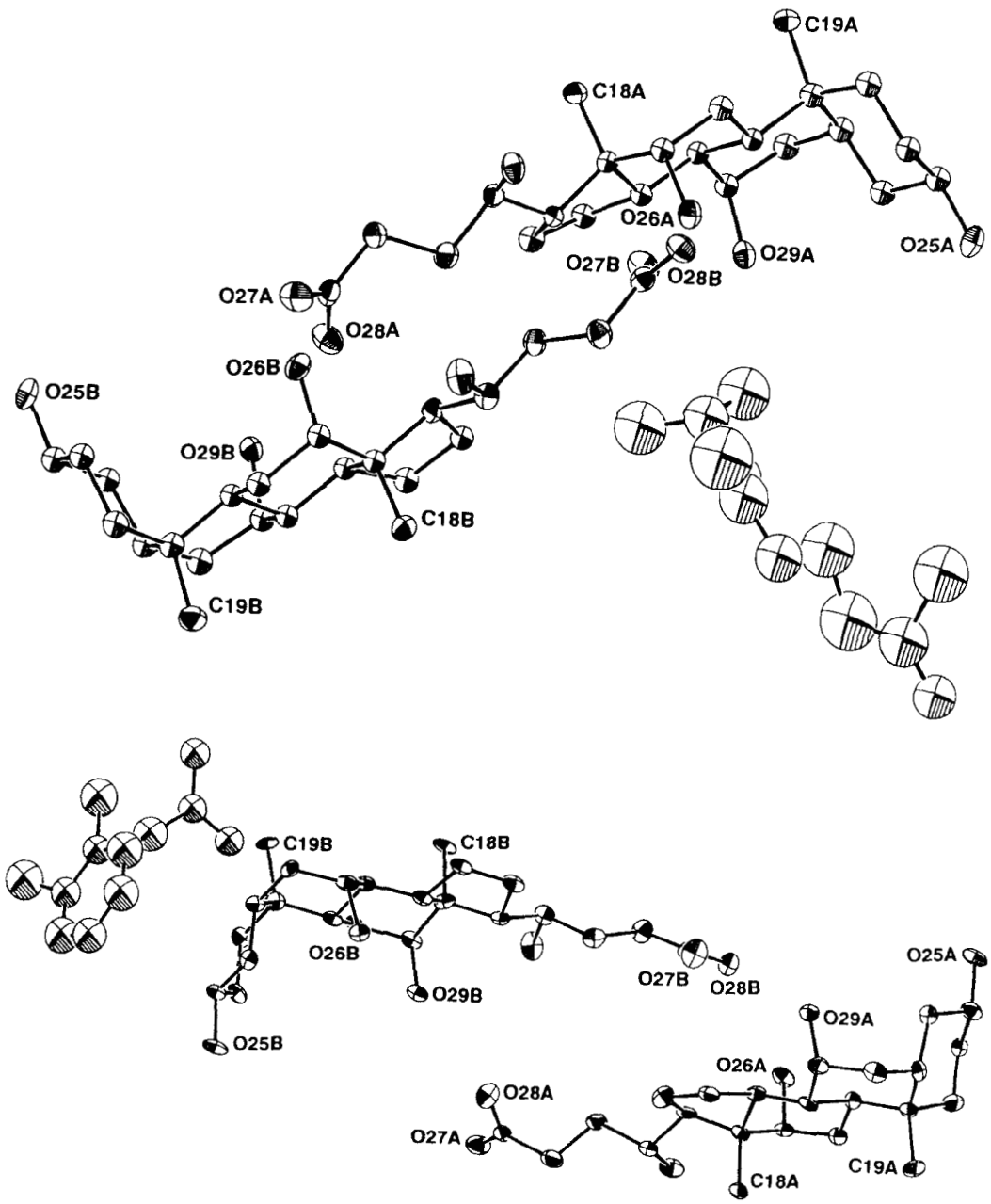



**Figure 1** Molecular diagrams showing thermal ellipsoids at 30% probability for a) CAMI and b) CAAD. Only oxygen atoms and angular methyl groups of the hosts are labelled, for complete molecular numbering refer to scheme 1.

of the guests and their ordered alternating array leads to the loss of the $2_1$ axis noted in most similar structures. The bilayers, and thus the channels, which propagate in the *b* direction are tilted from the normal to *a* and *c*. Packing diagrams are presented as Figures 2a and b and the stacking of the guest molecules in the channels is illustrated in Figure 3a and b.

The conformations of the rigid fused ring backbone of the steroid host is similar to that found in similar structures with the D-ring adopting a conformation part-way between a half chair with C(14) α and C(13) β and an envelope with C(13) β. The conformations of the side chains of the host molecules in the structure CAAD are both extended as indicated by the values for the

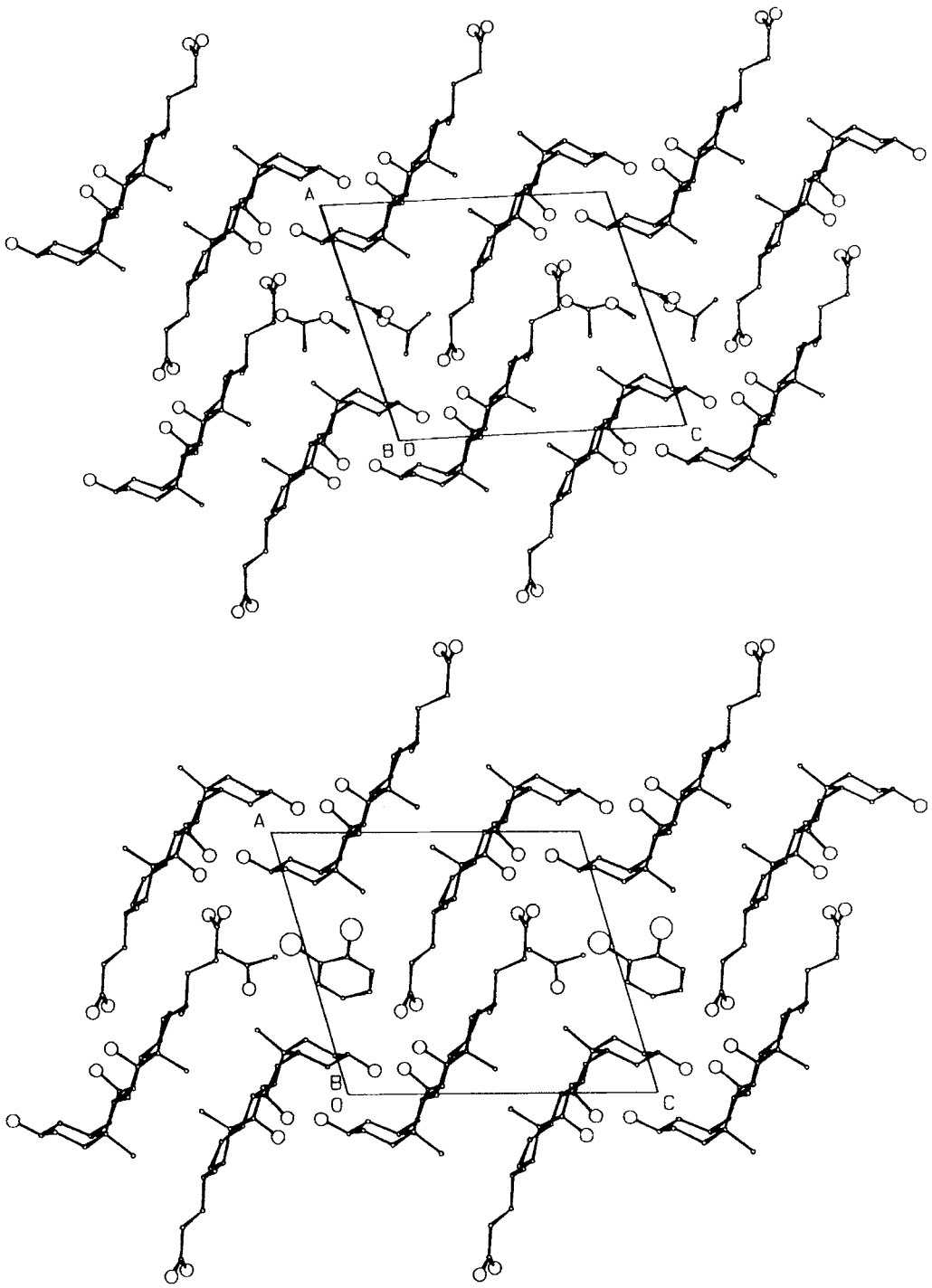



**Figure 2** Packing diagrams of a) CAMI and b) CAAD viewed as projections of the (010) plane. Oxygen and chlorine atoms are indicated as large open circles.

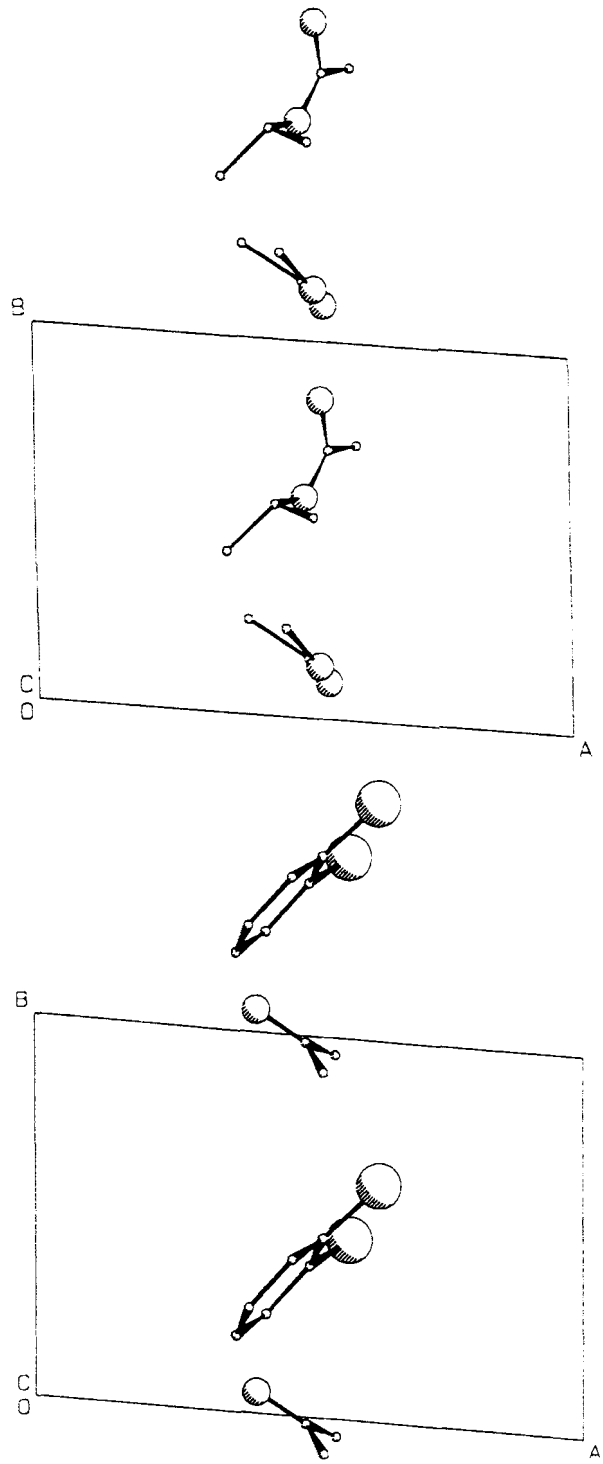



**Figure 3** Stacking of guest molecules in the channel of a) CAMI and b) CAAD. Note alternating guest types.

torsion angles $\tau_2$ and $\tau_3$ detailed in Table 5. These approach $-170°C$ which is one of the values identified as corresponding to a minimum energy conformation by Giglio and Quagliata[15]. The host-host hydrogen bonding schemes are depicted in Figure 4.

**Table 5** Torsion Angles defining the steroid side-chain conformation.

| | $\tau_2$ C(17)-C(20)-C(22)-C(23) | $\tau_3$ C(20)-C(22)-C(23)-C(24) |
|---|---|---|
| **CAMI** | | |
| **A** | −157.9(9) | −176.9(9) |
| **B** | −165.8(8) | 180.0(9) |
| **CAAD** | | |
| **A** | −171.8(9) | 174.3(10) |
| **B** | −155.5(9) | −172.5(9) |

The rising temperature thermal analysis traces of CAMI is presented as Figure 5a and that of CAAD as Figure 5b. The mixed ester guests are lost in a single guest loss event as evidenced by a single smooth weight loss on TG analysis and one sharp endotherm on DSC analysis. The 1,2-dichlorobenzene and acetone guests are lost in a single, but not smooth, step and the DSC trace indicates the existence of at least two clearly defined thermal events other than the host melt (at ca. 200°C). The first endotherm (labelled A) appears to occur as guest loss commences and observation of the crystals under heating indicates cracking of the crystals at this temperature followed at a significantly higher temperature by guest loss evidenced by the loss of translucence of the crystals. As no change in phase was detected by rising temperature continuous powder photography below the temperature of B it is possible that the endotherm A is due to mechanical failure of the crystals while B is due to guest loss and concomitant collapse to the host α structure.

These structures are remarkable as they are the first examples of cholic acid inclusion compounds containing mixed guests in a single crystal arrayed in an ordered fashion.

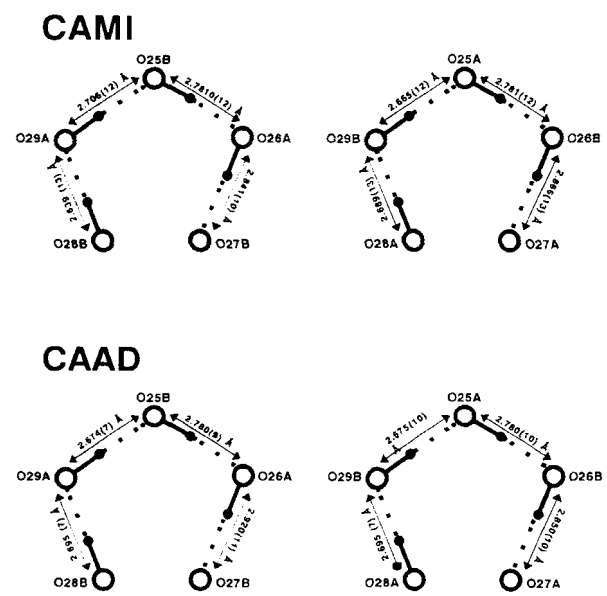



**Figure 4** Schematic representation of the hydrogen bonding schemes of CAMI and CAAD indicating donors, acceptors and O ... O distances.

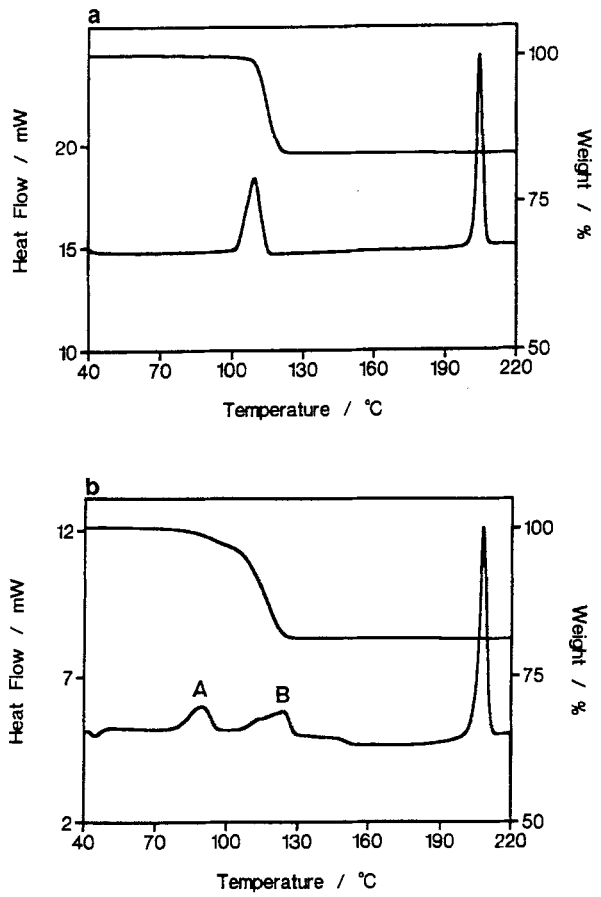



**Figure 5** TG and DSC curves of a) CAMI and b) CAAD measured at a scanning rate of 20 °C/min.



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