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Location of Guest Molecules in Inclusion Compounds of Deoxycholic Acid by Means of van der Waals Energy Calculations

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Abstract

The crystal structures of the inclusion compounds of deoxycholic acid with phenanthrene and (*E*)-*p*-dimethylaminoazobenzene (hereafter abbreviated to DCAPHE and DCADAB respectively) have been investigated by means of van der Waals energy calculations in order to locate the guest molecules and to establish if more than one arrangement is allowed, since the standard X-ray methods were unsuccessful. Two possible packings have been found for DCAPHE and only one for DCADAB. The main interactions stabilizing the crystal packings have been identified, and discussed on the basis of measurements of the

enthalpy change due to the releasing of the guest molecule from the canals of the crystals. Strong host–guest interactions between the π charge cloud of the guest molecule and the C(18) methyl group or the H(5) atom of deoxycholic acid characterize these types of inclusion compounds.

Introduction

A major problem in solving the crystal structure of an inclusion compound is the location of the guest molecules, which, generally, contribute much less than the host molecules to the Fourier transform of the crystal. This occurs mainly for the following reasons:

(1) Often, the size of the cavity is greater than that needed to accommodate the guest molecules, which, therefore, can occupy more than one definite position or can be statistically disordered, especially in the absence of specific host-guest interactions.

(2) The thermal motion of the guest molecules is generally high.

(3) The contribution of the guest molecules to the diffraction power of the crystal is usually low.

There are, therefore, many examples in which it was impossible to locate the guest molecules at all or with a sufficient degree of accuracy by means of the standard X-ray methods, such as the Fourier difference synthesis. In these cases it could be useful to resort to potential-energy calculations, performed by fixing the known positions of the host molecules and by allowing the guest molecules to move in the empty space as a function of their rotational and translational degrees of freedom. In our laboratory this method has been successfully applied to some inclusion compounds of $3\alpha,12\alpha$ -dihydroxy- 5β -cholan-24-oic acid (deoxycholic acid, DCA, see Fig. 1) (Candeloro De Sanctis, Coiro, Giglio, Pagliuca, Pavel & Quagliata, 1978; Candeloro De Sanctis, Giglio, Petri & Quagliata, 1979; Coiro, D'Andrea & Giglio, 1980; D'Andrea, Fedeli, Giglio,

Mazza & Pavel, 1981). DCA forms orthorhombic, tetragonal and hexagonal crystalline phases, termed choleic acids, occluding molecules of various kinds (Herndon, 1967). Some crystal structures of choleic acids, which are inclusion compounds of channel type and present a well-defined host-guest stoichiometric ratio, have been solved (Giglio, 1981, and references quoted therein). The orthorhombic phases, which have been found so far to crystallize in space group $P2_12_12_1$, show the best clathrating ability. The structural unit of these phases is the bilayer, which extends into the bc plane and is mainly stabilized by an efficient network of hydrogen bonds. The crystal packing is characterized by an assembly of antiparallel bilayers, related to each other by 2_1 axes, which leave empty spaces of channel shape, running along the c axis, covered by apolar groups. The shape of the canals is flexible and depends on the size of the occluded molecule. Different shapes can be obtained by varying the a value and by shifting the bilayer along b (Fig. 2). Potential-energy calculations have been accomplished in the space group $P2_12_12_1$ as a function of these parameters, treating the bilayer as a rigid group and neglecting the contribution of the guest molecules (Candeloro De Sanctis & Giglio, 1979). It has been found that each observed crystal structure, according to its a -axis length, corresponds to one of the three deepest minima of the van der Waals energy, which have been indicated as A , B and B' . Three representative crystal packings (a), (b) and (c), corresponding to A , B and B' respectively, are shown in Fig. 2.

The orthorhombic crystal structures of the phenanthrene (PHE) and (E)- p -dimethylaminoazobenzene (DAB) choleic acids (DCAPHE and DCADAB) solved in our laboratory (Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1972; Coiro, Giglio, Mazza, Pavel & Pochetti, 1982), caused some difficulty in locating

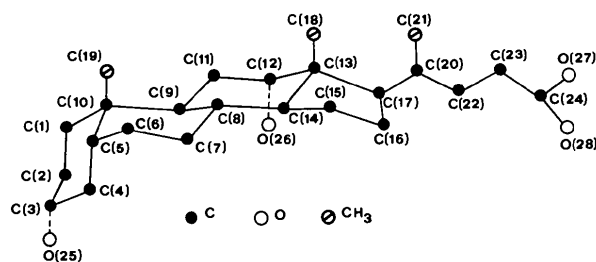


Fig. 1. Atomic numbering of DCA.

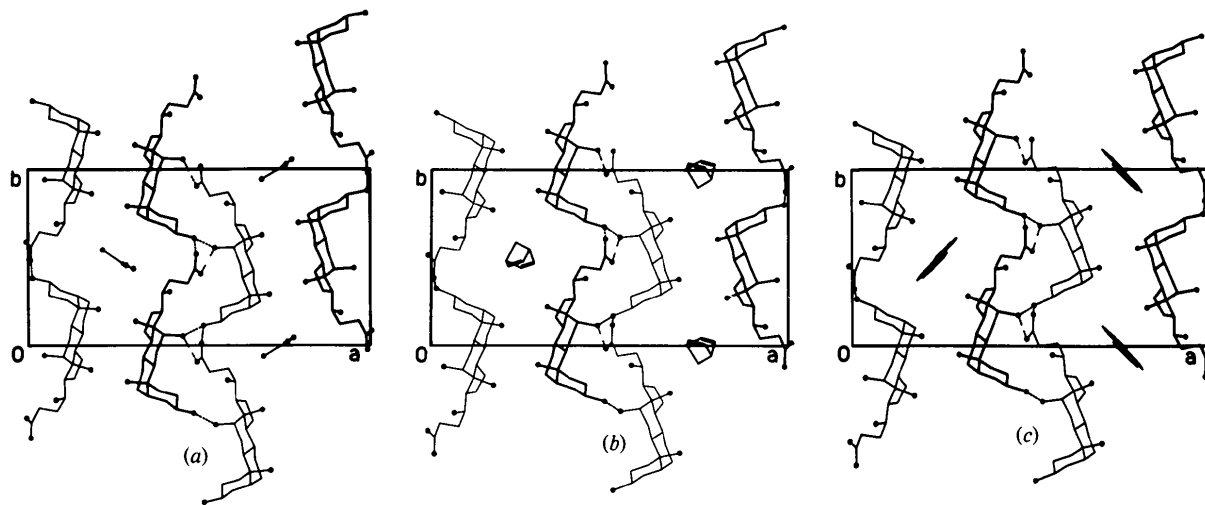


Fig. 2. Three typical crystal packings of DCA with (a) acetone, (b) norbornadiene and (c) phenanthrene, viewed along c .

the guest molecules which are present in the 3:1 and 4:1 DCA/guest stoichiometric ratio respectively. The unit-cell constants are: $a = 26.81$ (4), $b = 13.60$ (2), $c = 21.66$ (3) Å for DCAPHE and $a = 25.676$ (8), $b = 13.731$ (3), $c = 7.160$ (2) Å for DCADAB. The PHE molecules (~9 Å long) satisfy the screw axis along c (21.66 Å), while the DAB molecules do not since they are arranged with their longest axes approximately parallel to c and each one occupies two cells.

When the guest molecule is longer than ~7.2 Å (translation period along c of the DCA molecules) and does not contain heavy atoms its contribution to the structure factors is generally negligible except for the $hk0$ reflections, all the atoms lying near the special position ($a/4$, $b/2$). Thus, the agreement index is insensitive to the translation along c and, hence, the z coordinates are ill-conditioned. In the case of DCAPHE the presence of very weak layers with $l \neq 3n$, probably due mainly to the contribution of PHE, would have allowed a better location of the hydrocarbon molecule. However, the poor quality of the intensity data, recorded from a very small crystal by means of the Weissenberg technique and visually estimated, together with the omission of the few very weak reflections with $l \neq 3n$ in the refinement of the crystal structure have prompted us to resort to potential-energy calculations in order to establish whether the arrangement of the guest molecule determined from crystallographic data is acceptable and other arrangements are possible. For DCADAB the same method has been used with the aim of locating the guest molecule, not found by means of the standard X-ray methods.

van der Waals energy calculations

Semi-empirical atom-atom potentials in the generalized form:

$$V(r) = a \exp(-br)/r^d - cr^{-6}$$

have been used to describe intermolecular interactions, and their coefficients were previously reported (Pavel, Quagliata & Scarcelli, 1976, and references therein). The methyl group was treated as one atom. The DCA molecules were kept fixed as found in the refinement of the crystal structures, whereas the guest molecule was moved as a rigid body by varying three Eulerian angles, ψ_1 , ψ_2 and ψ_3 , and three translations along a , b and c , t_x , t_y and t_z . The guest molecule was rotated counter-clockwise in a right-handed orthogonal coordinate system $OXYZ$ with the OX , OY and OZ semi-axes coinciding respectively with the crystallographic ones Oa , Ob and Oc . A cut-off distance of 7 Å was assumed. Angular and translational increments from 10 to 2° and from 0.4 to 0.1 Å were applied. The geometry of the PHE molecule was obtained by a neutron diffrac-

tion study (Kay, Okaya & Cox, 1971). The DAB molecule was considered planar and its geometry, reported in the paper on the crystal structure of

Table 1. Atomic coordinates (Å) of the PHE model in the starting position ($\psi_1 = \psi_2 = \psi_3 = 0^\circ$; $t_x = t_y = t_z = 0$ Å)

The H atoms have the same numbering as the C atom to which they are bonded.

	x	y	z
C(1)	6.4197	6.7272	3.1007
C(2)	7.3714	7.7168	3.3692
C(3)	8.0275	8.3500	2.3267
C(4)	7.7679	8.0183	1.0012
C(5)	7.2173	7.1551	-1.7732
C(6)	6.9038	6.7244	-3.0700
C(7)	5.9516	5.7198	-3.2880
C(8)	5.2915	5.1710	-2.2067
C(9)	4.8867	4.9874	0.2246
C(10)	5.1719	5.3667	1.4910
C(11)	6.1548	6.3674	1.7516
C(12)	6.8408	7.0059	0.6862
C(13)	6.5642	6.5941	-0.6862
C(14)	5.5840	5.6035	-0.9075
H(1)	5.8880	6.2091	3.9112
H(2)	7.5840	8.0153	4.3454
H(3)	8.7433	9.1664	2.5118
H(4)	8.2803	8.5400	0.2274
H(5)	8.0082	7.8989	-1.6845
H(6)	7.4387	7.1707	-3.9234
H(7)	5.7625	5.4381	-4.2976
H(8)	4.5521	4.3602	-2.3410
H(9)	4.1842	4.2544	-0.0059
H(10)	4.6773	4.8771	2.2916

Table 2. Atomic coordinates (Å) of the DAB model in the starting position ($\psi_1 = \psi_2 = \psi_3 = 0^\circ$; $t_x = t_y = t_z = 0$ Å)

The H atoms have the same numbering as the C atom to which they are bonded.

	x	y	z
C(1)	6.9854	6.8655	1.6822
C(2)	8.2347	6.8655	2.2915
C(3)	8.3317	6.8655	3.6781
C(4)	7.1793	6.8655	4.4554
C(5)	5.9300	6.8655	3.8461
C(6)	5.8330	6.8655	2.4595
C(7)	5.8526	6.8655	-1.6822
C(8)	4.6033	6.8655	-2.2915
C(9)	4.5063	6.8655	-3.6781
C(10)	5.6587	6.8655	-4.4554
C(11)	6.9080	6.8655	-3.8461
C(12)	7.0050	6.8655	-2.4594
C(13)	8.5751	6.8655	6.4749
C(14)	6.0782	6.8655	6.6495
N(15)	6.9854	6.8655	0.2522
N(16)	5.8526	6.8655	-0.2522
N(17)	7.2742	6.8655	5.8121
H(2)	9.1301	6.8655	1.6876
H(3)	9.3024	6.8655	4.1516
H(5)	5.0346	6.8655	4.4500
H(6)	4.8623	6.8655	1.9860
H(8)	3.7079	6.8655	-1.6876
H(9)	3.5356	6.8655	-4.1516
H(10)	5.5833	6.8655	-5.5327
H(11)	7.8034	6.8655	-4.4500
H(12)	7.9757	6.8655	-1.9860

DCADAB (Coiro, Giglio, Mazza, Pavel & Pochetti, 1982), was derived from the bond distances and angles observed in some crystal structures of molecules containing the azobenzene moiety (Brown, 1966*a,b*; Hope & Victor, 1969; Hanson, 1973; Kurosaki, Kashino & Haisa, 1976). The H atoms of DCA, except those of hydroxyl, carboxyl and methyl groups, have been generated by setting C–H at 1.08 Å and $\angle\text{H–C–C}$ at 109.5°. The H atoms linked to the tertiary C atoms make two H–C–C bond angles of 109.5°, the third being dependent on the C–C–C bond angles. The axes of rotation pass through the point *P* half-way between C(12) and C(13) for PHE and N(15) and N(16) for DAB. The atomic coordinates of the PHE and DAB models, corresponding to $\psi_1 = \psi_2 = \psi_3 = 0^\circ$ and $t_x = t_y = t_z = 0$ Å, are reported in Tables 1 and 2 respectively.

Results and discussion

DCAPHE

The atomic coordinates of Table 1 were obtained adjusting the model assumed from the neutron diffraction study to the best overlap with that found in the X-ray crystal structure of DCAPHE, by using a 'molecules best fitting' program (Gavuzzo, Pagliuca, Pavel & Quagliata, 1972). The calculation has been applied only to the C atoms and $\sum w(\Delta d)^2$ is equal to 0.09 Å², where $w = 1$ and Δd is the distance between corresponding atoms in the two models.

DCAPHE populates the *B* minimum of the choleic acids' *a* group which is the deepest for *a* values greater than ~26 Å (Candeloro De Sanctis & Giglio, 1979). This minimum is characterized by guest molecules sandwiched between DCA C(13)–C(17) *D* rings and side chains, constituting the longest edges of the canal rectangular cross-section about 5.0 × 7.1 Å wide.

The van der Waals energy, computed in all the parametric space taking into account PHE–DCA and PHE–PHE interactions, presents three minima, M_1 , M_2 and M_3 , characterized by the parameters listed in Table 3, where the energy values are given only for a qualitative comparison. However, inspection of the closest M_1 , M_2 and M_3 intermolecular contacts, reported in Table 4, shows that M_3 can be discarded owing to some short C...H and H...H distances, 2.5 and 2.1 Å long, which do not recur in M_1 and M_2 . This situation is also reflected in the M_3 energy value of Table 3, higher than those of M_1 and M_2 which are nearly equal. Thus, the energy search points out two permissible PHE arrangements. The first one (M_1) is very close to that proposed from the X-ray analysis; the second one (M_2) gives rise to a PHE least-squares molecular plane nearly coinciding with that found for M_1 , both being approximately parallel to the *c* axis. The

corresponding PHE molecules are related by an approximate mirror plane (see Fig. 3).

The PHE molecule in M_1 is anchored to two C(18) methyl groups belonging to the $(x, 1 + y, z)$ and $(\frac{1}{2} - x,$

Table 3. Eulerian angles (°), translations (Å) and energy values (kJ) corresponding to the van der Waals energy minima of the phenanthrene molecule

Minimum	ψ_1	ψ_2	ψ_3	t_x	t_y	t_z	<i>E</i>
M_1	−4	2	−2	0.3	0.3	0.2	−113.8
M_2	42	38	−47	0.4	0.2	6.0	−115.1
M_3	−171	−11	−13	−0.5	−0.5	5.4	−105.9

Table 4. The most relevant intermolecular contacts (Å) of the energy minima found for DCAPHE

The first atom in the DCA–PHE interactions belongs to DCA. The H atoms have the same numbering as the C atom to which they are bonded.

PHE–PHE interactions

M_1	M_2	M_3			
H(2)...H(7 ^h)	2.2	H(2)...H(7 ^h)	2.2	H(2)...H(7 ^h)	2.2

DCA–PHE interactions

M_1	M_2	M_3			
H'(1 ^h)...H(3)	2.3	H'(1 ^h)...H(6)	2.2	H'(1 ^h)...C(3)	2.9
H'(1 ^h)...H(9)	2.3	H(3 ^h)...H(5)	2.4	H'(1 ^h)...H(3)	2.1
C(5 ^h)...H(4)	2.9	H(5 ^h)...H(5)	2.2	H(3 ^h)...H(3)	2.1
H(5 ^h)...H(4)	2.2	H(5 ^h)...H(9)	2.3	H(5 ^h)...H(3)	2.4
H(5 ^h)...H(10)	2.3	H'(16 ^h)...C(3)	2.9	H(5 ^h)...C(5)	2.9
C(18 ^h)...C(1)	3.7	H'(16 ^h)...C(7)	2.9	H(5 ^h)...H(5)	2.2
C(18 ^h)...C(11)	3.7	C(18 ^h)...C(3)	3.7	H(5 ^h)...C(9)	2.9
C(18 ^h)...C(14)	3.7	C(18 ^h)...C(11)	3.7	H(5 ^h)...C(10)	2.8
H(20 ^h)...C(1)	2.9	C(18 ^h)...C(12)	3.7	H(5 ^h)...H(10)	2.2
H(20 ^h)...C(10)	2.8	H(20 ^h)...C(2)	2.9	H'(16 ^h)...C(7)	2.8
H(20 ^h)...C(5)	2.7	H(20 ^h)...C(4)	2.7	C(18 ^h)...C(1)	3.7
H(20 ^h)...C(13)	2.9	H(20 ^h)...C(5)	2.9	C(18 ^h)...C(12)	3.6
H(20 ^h)...C(7)	2.8	H(20 ^h)...C(12)	2.8	H(20 ^h)...C(2)	2.8
C(22 ^h)...C(4)	3.3	H(20 ^h)...C(13)	2.9	H(20 ^h)...H(2)	2.3
H'(22 ^h)...C(3)	2.8	H(20 ^h)...C(9)	2.9	H(20 ^h)...C(5)	2.7
H'(22 ^h)...C(4)	2.8	C(21 ^h)...C(5)	3.7	H(20 ^h)...C(6)	2.8
H'(22 ^h)...C(8)	2.8	C(22 ^h)...C(9)	3.4	H(20 ^h)...C(9)	2.9
		H'(22 ^h)...C(7)	2.9	H(20 ^h)...C(10)	2.5
		H'(22 ^h)...C(10)	2.8	H(20 ^h)...C(11)	2.9

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

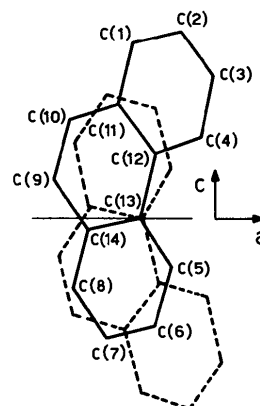


Fig. 3. Projection on the *ac* plane of the PHE molecule from M_1 (full line) and from M_2 (dashed line). The intersection of the pseudo mirror plane is indicated with a thin line.

$-y, z - \frac{1}{6}$) DCA molecules, giving rise to good carbon–methyl contacts, three of which are 3.7 Å long. The two C(18) point approximately towards the centres of the outermost rings of PHE, so that a strong interaction with the PHE π charge can be invoked. A similar situation arises in M_2 where C(18) and C(21) of the $(\frac{1}{2} - x, -y, \frac{1}{6} + z)$ asymmetric unit grasp the PHE central ring and the C(5)–C(6) bond respectively. The host–guest attractive energy is reinforced by the interactions of two other C(18), belonging to the $(x, 1 + y, z)$ and $(x, 1 + y, \frac{1}{3} + z)$ asymmetric units, with the PHE C(7)–C(8) and C(2)–C(3) outermost bonds respectively. In this case there are four carbon–methyl contacts 3.7 Å long. Other DCA atoms particularly active in forming efficient attractive interactions are H'(1), H(5), H'(16), H(20) and H'(22), which protrude towards the centre of the canal. Of these, H'(1) and H(5) belong to the shorter edge of the canal rectangular cross-section, constituted by the C(1)–C(10) *A* ring and C(6) methylenic group of DCA and approximately perpendicular to the PHE molecular plane, and act as clips of the guest molecule. All the interactions mentioned above give rise to the high stability of the DCAPHE choleic acid which is supported by vapour-pressure measurements as a function of the temperature, performed by means of the torsion-effusion method (Ferro, Imperatori & Quagliata, 1983). An enthalpy change of 128.9 kJ mol⁻¹, associated with the releasing of the guest molecule from the crystal of DCAPHE, has been derived from the pressure–temperature equation. This value is much greater than those found for the styrene and naphthalene choleic acids, 56.9 and 72.0 kJ mol⁻¹ respectively (Ferro, Quagliata, Giglio & Piacente, 1981), since for each of these hydrocarbon molecules just one C(18) is engaged.

As can be inferred from the previous description, the M_1 and M_2 minima are sharp and represent two well-defined packings. This is shown in Fig. 4 where some significant sections through the minima of the van der Waals energy are reported. In Fig. 4(a–c) some of the parameters listed in Table 3 and specified in the legend of the figures are varied, while the others are kept fixed. In Fig. 4(d–e) the energy is computed for M_1 and M_2 as a function of a counterclockwise rotation ϕ around an axis perpendicular to the PHE molecular plane, passing through *P* (Fig. 4d), and χ around an axis passing through *P*, parallel to the *ab* plane and lying in the PHE molecular plane (Fig. 4e). ϕ and χ equal to 0° correspond to the parameters of M_1 and M_2 (see Table 3).

Inspection of Fig. 4(a) confirms that the translation along *c* of PHE is hindered, rather surprisingly for a planar molecule, owing to the highly specific interactions with groups like C(18). Moreover, the elliptical shape of the minima of Fig. 4(b), elongated along a direction nearly coinciding with the *ab* projection of the PHE molecular plane, indicates that the motion of PHE

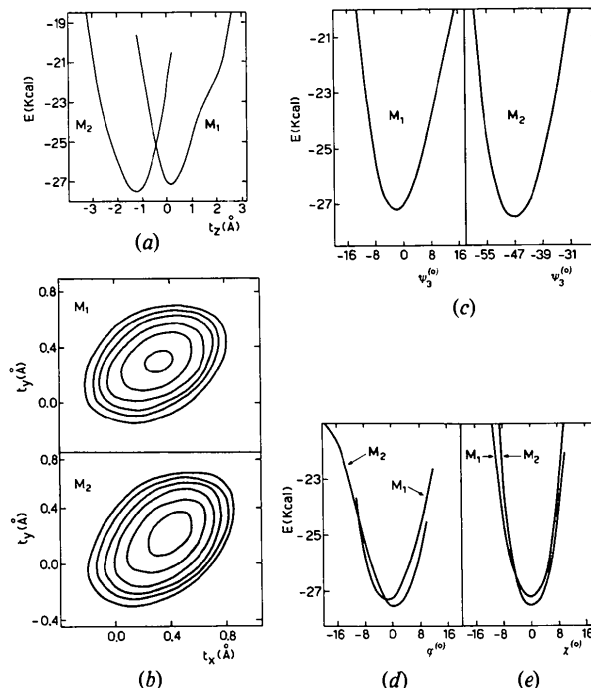


Fig. 4. van der Waals energy of the PHE molecule for M_1 and M_2 as a function of: (a) t_z , (b) t_x and t_y (contour lines are drawn at intervals of 1 kcal starting from 22 kcal), (c) ψ_3 , (d) ϕ , (e) χ (1 kcal = 4.184 kJ).

is favoured along this direction, whereas translations perpendicular to it cause a sudden increasing of the energy as expected because of the rectangular cross-section of the canal. The analysis of other relevant motions (Fig. 4c, d and e) further supports the guest molecules being almost frozen in the canals and, hence, regularly arranged. However, these calculations do not allow one to decide if both the arrangements of M_1 and M_2 or just one are present in the DCAPHE crystal, although the regular shape and the sharpness of those reflections due mainly to PHE and the lack of diffuse extra layers seem to suggest the existence of only one type of structure. This hypothesis can be reasonably accepted since a comparison of M_1 with M_2 leads one to prefer M_1 , which has probably better methyl groups– π -charge-cloud interactions, not taken into account in the evaluation of the energy.

Further more accurate crystallographic work is needed in order to clarify this intriguing aspect of the DCAPHE packing unambiguously.

DCADAB

DCADAB populates the *A* minimum of the choleic acids' α group, which is the lowest for a values less than or equal to ~26 Å (Candeloro De Sanctis & Giglio, 1979). The guest molecules are sandwiched in canals of rectangular cross-section, about 2.8 × 5.5 Å wide, with

the two longer edges occupied by rings *A* and C(6) methylenic groups and the two shorter ones by side chains as in the acetone–choleic acid crystal structure (Fig. 2*a*). A 2_1 axis parallel to *c* relates the opposite edges. This type of packing is common to the choleic acids containing acetic and palmitic acid, chloroacetone, ethyl methyl ketone, diethyl ketone and acetophenone (Craven & De Titta, 1972; Coiro, D'Andrea & Giglio, 1980; Tang, 1979; Popovitz-Biro, Chang, Tang, Shochet, Lahav & Leiserowitz, 1980), this last molecule being the only aromatic one besides DAB.

Since, after the DCA atomic coordinates were known the DAB molecule could not be located by coupling the minimum residual method with difference syntheses, an attempt was made to solve the crystal structure by means of van der Waals energy calculations, using the planar model previously mentioned (see Table 2). Other non-planar models, obtained by rotating around the N(15)–C(1) and N(16)–C(7) bonds (see Fig. 5 for atomic numbering), were checked; these, however, gave worse results. The DCA atomic coordinates used were those corresponding to an agreement index of 0.15. The global minimum is very sharp and is the only one with acceptable intermolecular contacts. Its parameters, related to the starting position of Table 2, are: $\psi_1 = 128$, $\psi_2 = 10$, $\psi_3 = 188^\circ$, $t_x = -0.2 \text{ \AA}$, $t_y = 0.0 \text{ \AA}$, $t_z = -3.7 \text{ \AA}$. The most relevant intermolecular distances are reported in Table 5. The introduction of this DAB rigid model with an occupancy factor of $\frac{1}{4}$ in the refinement allowed convergence to a final *R* factor of 0.09 by slightly moving the DAB molecule. Fig. 5 shows the situation at the beginning and at the end of the refinement. The DAB position found at the end of the refinement lies in the minimum region with an energy value rather close to the lowest one. However, some intermolecular contacts are unrealistic and therefore the position corresponding to the global minimum seems more reliable.

Fig. 6 shows some significant sections of the DAB van der Waals energy as a function of the same parameters as in Fig. 4 for PHE. The energy is computed around the minimum point with the same rules as those previously described for PHE. Inspection of Fig. 6 indicates that the DCADAB minimum is sharper than those of DCAPHE, so that DAB is much

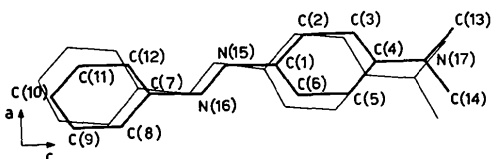


Fig. 5. Projection on the *ac* plane of the DAB molecule corresponding to the energy minimum (thick line) and at the end of the refinement (thin line).

Table 5. The most relevant intermolecular contacts (\AA) of the energy minimum found for DCADAB

The first atom in the DCA–DAB interactions belongs to DCA. The H atoms have the same numbering as the C atom to which they are bonded.

DAB–DAB interactions

C(13)···C(10 ^b)	3.7	C(14)···C(10 ^b)	3.7
C(13)···H(10 ^b)	2.8	C(14)···H(10 ^b)	2.9

DCA–DAB interactions

H'(1 ^{ll})···C(13)	3.2	C(19 ^{ll})···C(11)	3.6
C(5 ^{lll})···C(4)	3.4	C(19 ^{ll})···C(12)	3.3
H(5 ^{lll})···C(1)	2.8	C(19 ^{ll})···H(12)	3.1
H(5 ^{lll})···C(2)	2.8	C(19 ^{ll})···C(14)	3.8
H(5 ^{lll})···C(3)	2.7	C(20 ^{ll})···H(2)	2.9
H(5 ^{lll})···C(4)	2.7	C(20 ^{ll})···H(3)	2.9
H(5 ^{lll})···C(5)	2.7	C(20 ^{ll})···H(8)	2.9
H(5 ^{lll})···C(6)	2.8	C(20 ^{lll})···C(14)	3.6
H(5 ^{lv})···C(7)	2.6	H(20 ^{vl})···C(2)	2.7
H(5 ^{lv})···C(12)	2.9	H(20 ^{vl})···H(2)	2.0
H(5 ^{lv})···N(15)	2.6	H(20 ^{vl})···C(3)	2.8
H(5 ^{lv})···N(16)	2.5	H(20 ^{vl})···H(3)	2.3
C(6 ^{lll})···C(4)	3.3	H(20 ^{vl})···H(8)	2.2
C(6 ^{lll})···C(5)	3.3	H(20 ^{lv})···H(11)	2.1
C(6 ^{lll})···C(14)	3.5	H(20 ^{lll})···C(14)	2.6
H'(6 ^v)···C(10)	2.7	C(21 ^{vl})···H(2)	3.1
H'(6 ^v)···C(11)	2.9	C(21 ^{lll})···H(8)	2.8
H'(6 ^{ll})···C(13)	3.2	C(22 ^{vl})···H(3)	2.6
H'(6 ^{ll})···C(14)	2.8	C(22 ^{lv})···H(9)	2.9
H''(6 ^{ll})···N(17)	2.6	H'(22 ^{vl})···H(3)	2.4
H''(6 ^{ll})···C(5)	2.7	H''(22 ^{vl})···H(3)	2.2
H''(6 ^{ll})···C(14)	3.1	H''(22 ^{lll})···H(6)	2.4
C(19 ^{lll})···C(6)	3.5	H''(22 ^{lv})···H(9)	2.0

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

more frozen than PHE in the canals. The strongest interactions between two adjacent DAB molecules in the same canal, related by a translation of 14.32 \AA , involve the C(10)–H(10) group and the two amino-methyl groups. Those between DCA and DAB molecules engage many DCA atoms, such as H(5), H'(6), H''(6), C(6), C(19), H(20), C(20), C(21), H'(22), H''(22) and C(22) belonging to the two *cis*-fused rings and to the side chain (see Table 5). Particularly important seem to be the interactions between two DCA H(5) atoms, related by a 2_1 axis parallel to *c*, with the C(1)–C(6) phenyl group and with the $\text{>C(7)–N(16)=N(15)–}$ fragment. The C(5)–H(5) bonds are roughly perpendicular to the DAB molecular plane and one of them points approximately towards the centre of a phenyl ring, assuming the same role as C(18) in the case of DCAPHE. Thus, it may reasonably be supposed that the two C(5)–H(5) bonds give rise to a strong polarization bonding with the π charge cloud of DAB. Thus in the case of acetophenone–choleic acid, very similar to that of DCADAB, H(5) can be abstracted on UV irradiation, yielding an addition product at C(5) (Popovitz-Biro, Chang, Tang, Shochet, Lahav & Leiserowitz, 1980).

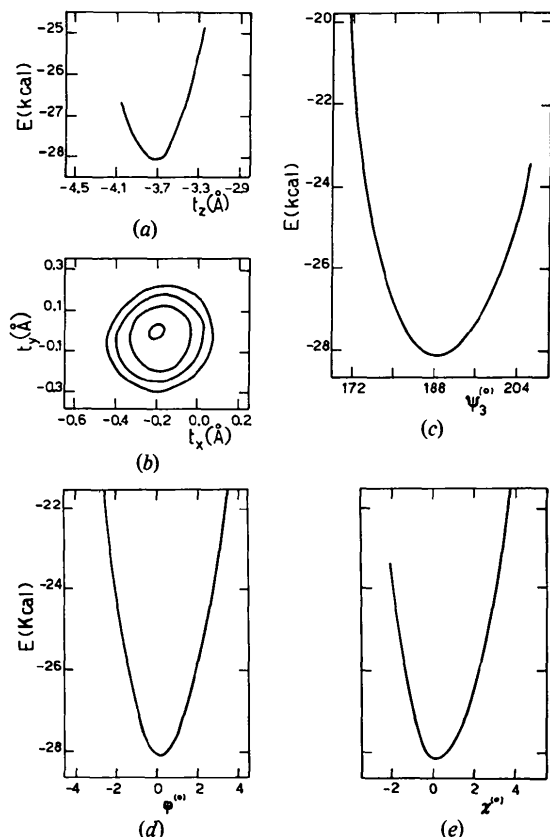


Fig. 6. van der Waals energy of the DAB molecule as a function of: (a) t_z , (b) t_x and t_y (contour lines are drawn at intervals of 2 kcal starting from 22 kcal), (c) ψ_3 , (d) ϕ , (e) χ (ϕ and χ equal to 0° correspond to the parameters of the minimum) (1 kcal \equiv 4.184 kJ).

The vapour-pressure measurements confirm the remarkable stability of DCADAB, reflected by its high melting point (479–490 K, 22–23 K higher than that of DCAPHE) and by its shorter intermolecular distances (see Table 5) as compared with those of DCAPHE (see Table 4). In fact, in the plot of $\log P$ vs $(1/T)$ the DCADAB crystals begin to vapourize at ~ 450 K, close to the melting point of DCA alone, and both DCA and DAB strongly contribute to the total vapour pressure, at variance with DCAPHE and other DCA

inclusion compounds in which the DCA contribution is negligible with respect to that of the guest component. The enthalpy change associated with the releasing of DAB (Candeloro De Sanctis, Ferro & Pavel, 1983, unpublished results) is equal to or greater than that of DCA (179.0 kJ mol $^{-1}$), much greater than that of PHE (128.9 kJ mol $^{-1}$). Thus the experimental data support the arrangement corresponding to the energy minimum and the correctness of the proposed crystal structure.

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