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Inclusion Compounds of α-Truxillic Acid. X-Ray Crystal Structures of the Coordinatoclathrates with Methanol (1 : 2) and Dimethylacetamide (1 : 2)

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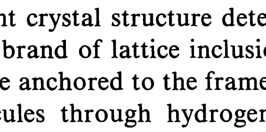
The crystal structures of the inclusion compounds of the 2*c*,4*t*-diphenylcyclobutane-1*r*,3*t*-dicarboxylic acid (α-truxillic acid) host (**1**) with methanol [MeOH] (1 : 2) and with dimethylacetamide [DMA] (1 : 2) have been determined by single crystal X-ray diffraction. The substantial difference between the effects of the protic (MeOH) and aprotic (DMA) guests on the molecular packing is discussed. Crystal data: **1**·2MeOH: monoclinic ($P2_1/n$), a=12.528(4), b=5.589(1), c=13.715(4) Å, β=101.16(4)°, Z=2, R=0.064 for 1300 reflections; **1**·2DMA: monoclinic ($P2_1/c$), a=6.151(1), b=26.586(2), c=7.938(1) Å, β=105.32(6)°, Z=2, R=0.056 for 1488 observations. In both clathrates, half of the rigid α-truxillic acid molecule occupies the asymmetric unit together with one guest molecule. The hydrogen bonds between the trans-positioned functional groups of the host acid and the guest molecules in **1**·2MeOH give rise to infinite layers parallel with the crystallographic *ac* diagonal. In contrast, the only one-way hydrogen bond from host to guest in **1**·2DMA leads to discrete 1 : 2 host–guest aggregates. In this latter case, the hosts and guests are stacked separately, along the *c* axis direction.

Elucidation of new models for molecular recognition is a recent challenge for organic chemistry.[1)] In this regard, inclusion compounds in general and lattice inclusions in particular will remain in good standing for a while. Recent crystal structure determinations have revealed a new brand of lattice inclusions in which the guest entities are anchored to the framework formed by the host molecules through hydrogen bonds.[2)] This feature is such an eminent characteristic of the crystals that the term coordinatoclathrate has been coined for them.[2,3)] Hosts that display this behavior are mainly based on rigid and symmetric dicarboxylic acids.[4)] In the compounds studied earlier,[2,4—10)] the number of bridging carbon atoms between the -COOH functions is even, and the two -COOH groups are oriented more or less at right angles to one another.[2)] Here we report on the structures of two solid coordinatoclathrates of α-truxillic acid (2*c*,4*t*-diphenylcyclobutane-1*r*,3*t*-dicarboxylic acid, **1**), which has an odd number (3) of carbon atoms between two symmetry-related -COOH functions with diametrically opposite orientations. (The synthesis and the inclusion properties of this host have been published elsewhere.[9,10)]). The methanol (MeOH) and dimethylacetamide (DMA) guests possess protic and aprotic character, respectively.



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Experimental

Sample Preparation. The α-truxillic acid host was prepared as previously described.[9)] Crystals of the inclusion compounds were obtained by dissolution of the host in the respective guest solvent, followed by slow solvent evaporation.

X-Ray Data Collection and Processing. The single crystals selected for X-ray measurement were sealed in glass capillaries. The intensitites were collected on a STOE/AED2 diffractometer at room temperature with graphite monochromatized Cu $K\alpha$ radiation (λ=1.5418 Å), using the 2θ–ω scan mode within the range $3<2\theta<140°$. The unit cell parameters were refined against θ values of 30 and 50 reflections for **1**·2MeOH and **1**·2DMA, respectively, within the range $27<2\theta<44°$.

The net intensities were corrected for Lorentz and polarization effects but not for absorption. Crystal data and selected experimental details are summarized in Table 1.

Structure Analysis and Refinement. Reasonable starting models of the structures were derived by direct methods, using MULTAN[11)] for **1**·2MeOH and SHELXS[12)] for **1**·2DMA. Only structure factors with $F>6\sigma(F)$ were included in the subsequent full-matrix least-squares refinements [SHELX[13)]]. The positions of the non-hydrogen atoms were refined together with their anisotropic thermal parameters, whereas isotropic temperature factors were refined for the hydrogen atoms.

The H atoms in **1**·2MeOH, except for the methyl hydrogens of the guest, were located from a difference electron density map, and their positions were kept riding on their 'mother' atoms during the subsequent refinements. The methanol $-CH_3$ group was refined as a rigid group with free rotation

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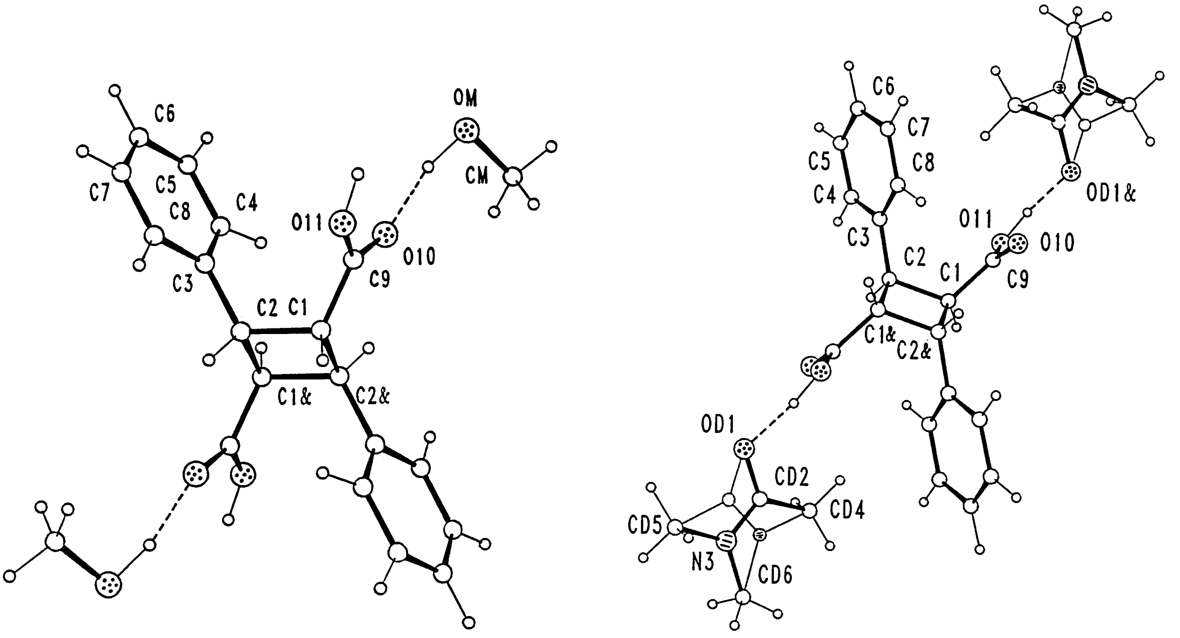
Table 1. Crystal Data and Some Selected Experimental Details (esd's, where given, are in parentheses)

Compound	1·2MeOH	1·2DMA
Formula unit	$C_{18}H_{16}O_4 \cdot 2CH_4O$	$C_{18}H_{16}O_4 \cdot 2C_4H_9ON$
Formula weight	360.41	470.56
Crystal size/mm	0.4×0.5×0.5	0.6×0.3×0.2
Unit cell dimensions		
a/Å	12.528(4)	6.151(1)
b/Å	5.589(1)	26.586(2)
c/Å	13.715(4)	7.937(1)
β/°	101.16(4)	105.32(6)
V_c/Å^3	942.2(5)	1251.8(5)
Space group	$P2_1/n$	$P2_1/c$
Z	2	2
D_c/Mg m^{-3}	1.270	1.248
$F(000)$	384	504
$\mu_{CuK\alpha}$/cm^{-1}	7.34	6.87
N of reflections measured	1724	2266
N_{obs} (unique, non-zero)	1450	1952
N_{ref} [with $I/\sigma(I)>3$]	1300	1488
$N_{variables}$	131	175
$R\ (=\sum\lvert\Delta F\rvert/\lvert\sum F_o\rvert)$	0.064	0.056
$R_w\ (=[\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2]^{1/2})$	0.094	0.072
$R_{w,tot}$	0.113	0.083
Weighting: g in SHELX[a)]	0.0003	0.00008
Highest residual electron density/e Å^{-3}	0.20	0.16

a) Weights of the structure factors in SHELX[13)] are estimated as $w=\text{const.}/(\sigma^2(F)+g\cdot F^2)$.

around the O–C bond.

The guest in the 1·2DMA structure shows positional disorder. The difference electron density map, calculated for the structural model containing C, O, and N atoms, remained blurred in the region of the guest molecule. It was, however, possible to construct a proper model of the disorder with the aid of molecular modelling [CHEM-X 86[14)]]. This model consists of two orientations of the DMA molecule, partly overlapping each other (cf. Fig. 1b). Accordingly, the refinement was extended to two additional peaks representing the alternative positions for C(D2) and N(3) atoms, and two sets of hydrogens for the C(D4), C(D5), and C(D6) methyl carbons



(a) (b)

Fig. 1. Perspective views of the formula units of (a) 1·2MeOH and (b) 1·2DMA, with atoms labeled as in the text. Solid and dashed lines represent covalent and hydrogen bonds, respectively; O atoms are dotted, N atoms are hatched. In the structure of 1·2DMA, the guest shows rotational disorder: it assumes two orientations partly overlapping each other.

were included in the structure factor calculations. The hydrogens of the host molecule, except for three H atoms, were assumed to be at geometrically predictable positions. H(1) and H(2) of the *c*-butane ring (Fig. 1b) and the carboxylic H(11) atom were located by difference electron density calculation and were kept riding on their 'mother' atoms. The refinement of the alternative C(D2a)/C(D2b) and N(3a)/N(3b) disorder sites yielded site occupancies of 0.47/0.53, respectively.

Some strong low-θ reflections (26 for **1**·2MeOH and 30 for **1**·2DMA), with considerably higher F_c than F_o, probably due to extinction effects, were excluded from the last refinements, where the final residual indices (R and R_w in Table 1) were reached.

Results and Discussion

Figure 1 shows perspective views of the formula units of the present two inclusion compounds of α-truxillic acid (**1**). The final atomic positional parameters are given in Table 2. Hydrogen bond geometries are listed in Table 3. The helical chain of hydrogen bonds in **1**·2MeOH is illustrated in Fig. 2, whereas the crystal packings are depicted in Figs. 3 and 4.[15]

Molecular Structures. In the two inclusion compounds the geometry of α-truxillic acid (**1**), possessing C_i molecular symmetry, is similar within experimental error (Fig. 1). The cyclobutane ring is planar with somewhat strained bond lenghts and bond angles: C(1)–C(2)=1.581(3) and 1.571(4), C(1)–C(2)$^{\&}$=1.551(1) and 1.539(4) Å, $\angle$C(1)–C(2)–C(1)$^{\&}$=89.4(2) and 89.8(2), $\angle$C(2)–C(1)–C(2)$^{\&}$=90.6(2) and 90.7(2)° in **1**·2MeOH and **1**·2DMA, respectively (&=1−*x*, 1−*y*, 1−*z* for **1**·2MeOH and −*x*, 1−*y*, 1−*z* for **1**·2DMA). The C(2)–C(1)–C(9)–C(11) torsion angles[16] [84.2(3) and 82.5(3)°] indicate similar orientations of the carboxyl functions. Even the rotational angles of the phenyl rings about the C(2)–C(3) bond differ by only 14°. The dihedral angles between the least-squares (LS) planes[17] of the cyclobutane and the phenyl rings are 76.9(1) and 82.8(1)°, whereas the COO(H) groups are inclined through 66.8(2) and 63.9(2)° away from the attached phenyl substituents in **1**·2MeOH and **1**·2DMA, respectively.

Two distinct models (termed hereinafter *A* and *B*) can be used to describe the disorder of the DMA with respect to the rotation axis through the oxygen and one of the *N*-methyl carbon [C(D6)] atoms. Thus, the C(4D)/C(5D) atomic pair occupies alternatively the same positions with about 50% probability, whereas C(D2) and N(3) have two disorder sites (Fig. 1b). The

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic[a] or Isotropic Temperture Factors of the Non-Hydrogen Atoms and of the Hydrogens, Involved in the Hydrogen Bonds, in Compounds **1**·2MeOH and **1**·2DMA, Respectively (esd's, where given, are in parentheses)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]/U (Å^2)
1·2MeOH				
C(1)	0.9995(2)	0.3401(5)	0.5468(2)	0.040(1)
C(2)	0.9431(2)	0.4133(4)	0.4377(2)	0.041(1)
C(3)	0.8208(2)	0.4079(4)	0.4108(2)	0.043(1)
C(4)	0.7564(2)	0.5765(5)	0.4458(2)	0.054(1)
C(5)	0.6433(2)	0.5671(6)	0.4193(3)	0.063(1)
C(6)	0.5940(2)	0.3840(6)	0.3590(3)	0.064(1)
C(7)	0.6562(3)	0.2150(6)	0.3249(2)	0.061(1)
C(8)	0.7691(2)	0.2253(5)	0.3503(2)	0.053(1)
C(9)	0.9230(2)	0.2831(5)	0.6144(2)	0.044(1)
O(10)	0.8934(2)	0.4242(4)	0.6704(2)	0.063(1)
O(11)	0.8884(2)	0.0586(4)	0.6049(2)	0.057(1)
O(M)	0.7874(2)	0.4872(5)	0.8252(2)	0.085(1)
C(M)	0.8704(3)	0.6231(9)	0.8801(3)	0.097(2)
H(11)	0.8325	0.0237	0.6409	0.08(1)
H(OM)	0.8193	0.4605	0.7562	0.17(2)
1·2DMA				
C(1)	−0.0974(4)	0.5346(1)	0.4663(4)	0.049(1)
C(2)	0.0393(4)	0.5092(1)	0.6408(4)	0.049(1)
C(3)	0.2353(4)	0.5370(1)	0.7597(4)	0.048(1)
C(4)	0.2359(5)	0.5474(1)	0.9309(4)	0.054(1)
C(5)	0.4193(5)	0.5710(1)	1.0435(4)	0.064(1)
C(6)	0.6024(5)	0.5851(1)	0.9840(4)	0.064(2)
C(7)	0.6030(5)	0.5760(1)	0.8129(4)	0.060(1)
C(8)	0.4210(5)	0.5516(1)	0.7016(4)	0.054(1)
C(9)	−0.0249(5)	0.5863(1)	0.4273(4)	0.053(1)
O(10)	0.0977(4)	0.5951(1)	0.3354(3)	0.070(1)
O(11)	−0.1096(4)	0.6216(1)	0.5089(3)	0.077(1)
O(D1)	0.0038(5)	0.2847(1)	0.5230(4)	0.104(2)
C(D2a)	−0.2032(23)	0.2731(5)	0.4417(14)	0.077(5)
C(D2b)	−0.1143(15)	0.2470(4)	0.4747(11)	0.070(3)
N(3a)	−0.2456(17)	0.2238(4)	0.4242(11)	0.078(4)
N(3b)	−0.3314(14)	0.2551(4)	0.3959(10)	0.078(3)
C(D4)	−0.4044(7)	0.3079(2)	0.3653(6)	0.111(2)
C(D5)	−0.0479(7)	0.1911(2)	0.5003(7)	0.101(2)
C(D6)	−0.4787(7)	0.2097(2)	0.3259(7)	0.128(3)
H(11)	−0.0301	0.6541	0.4883	0.086(4)

a) $U_{ij}=1/3\sum_i\sum_j U_{ij}\alpha_i^*\alpha_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Bond Lengths and Bond Angles in Possible Hydrogen Bonds in Compounds **1**·2MeOH and **1**·2DMA (esd's, where given,[a] are in parentheses)

Atoms involved	Symmetry	Distances/Å			Angle/°
		O···O	O–H	H···O	∡O–H···O
1·2MeOH					
O(11)–H(11)···O(M)	1.5−*x*, −0.5+*y*, 1.5−*z*	2.596(3)	0.95	1.67	164
O(M)–H(OM)···O(10)	*x*, *y*, *z*,	2.737(3)	1.11	1.65	167
1·2DMA					
O(11)–H(11)···O(D1)	−*x*, 1−*y*, 1−*z*	2.605(3)	1.03	1.64	154

a) The position of the hydrogens involved in hydrogen bonds are taken from difference electron density maps and are not refined.

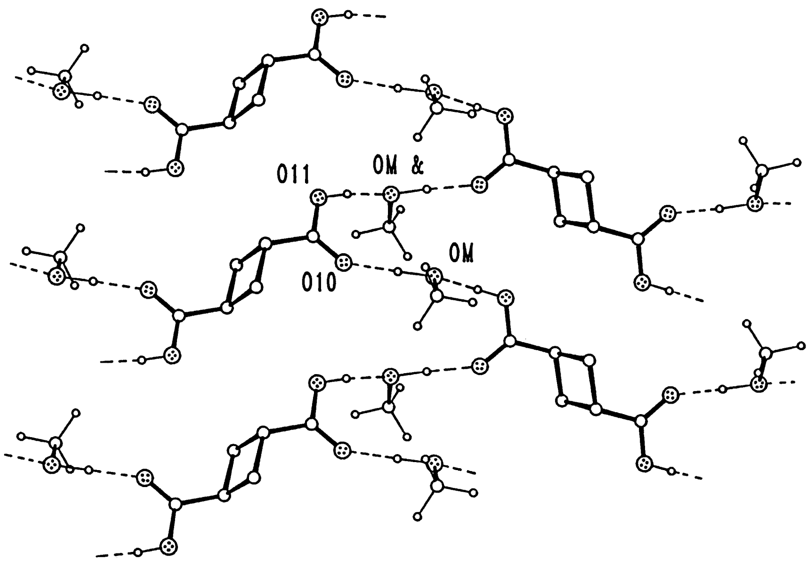


Fig. 2. Diagram of the hydrogen bond network in the crystal structure of **1**·2MeOH. The phenyl substituents and the hydrogens of the host, except H(11), which is involved in H-bonding, are omitted for clarity. Solid and dashed lines represent covalent and hydrogen bonds, respectively.

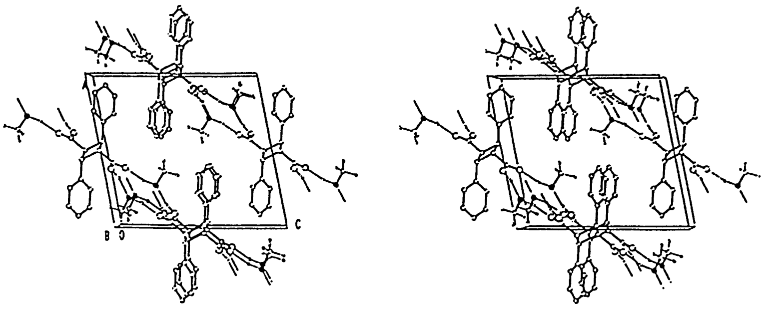


Fig. 3. Stereo packing illustration of the **1**·2MeOH crystal structure. The O atoms of the guest are in bold. The hydrogens of the host, not invloved in hydrogen bonds, are omitted for clarity.

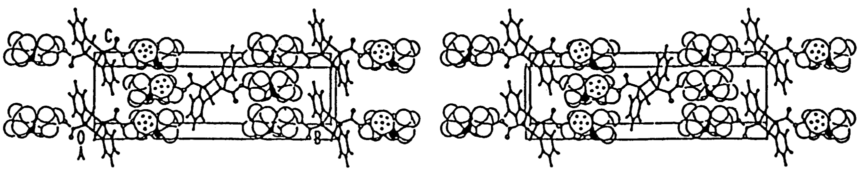


Fig. 4. Stereo packing diagram of the **1**·2DMA crystal structure. The host molecule is shown in ball-and-stick style, the guest molecule is drawn as space filling models with only one disorder site for each C(2D) and N(3). The N and O atoms of the guest are indicated by black filling and dotting, respectively.

non-hydrogen atoms of the DMA molecule are coplanar within 0.040 and 0.072 Å in *A* and *B*, respectively.

Packing Relations and Host-Guest Interactions. The protic MeOH and aprotic DMA arrange the host entities in substantially different ways (Figs. 3 and 4).

In **1**·2MeOH the hydrogen bonding between the host acid and the alcoholic guests results in infinite helices (Fig. 2), similar to those found in the alcoholic inclusions of the related 3,3-diphenyl-*cis*-cyclopropane-1,2-dicarboxylic acid.[9,10,18)] Nevertheless, due to the intramolecular hydrogen bond between the *cis*-positioned –COOH groups, the cyclopropane host behaves externally as monofunctional, forming inclusions usually with 1 : 1 stoichiometry. As a consequence, the Hbonded helices in the EtOH[18] and *t*-BuOH inclusions[9,10] of the *cis*-cyclopropanedicarboxylic acid host are endless in one dimension, and are held together by weaker Van der Waals' forces.

In contrast, the *trans*-truxillic acid (**1**) is a bifunctional host, forming inclusions usually with 1:2 host–guest stoichiometry. In its MeOH inclusion the alcoholic guests, helically arranged around the screw axes at 1/4, *y*, 1/4 and 3/4, *y*, 3/4, connect both ends of the hosts via strong OH···O bonds. The divalent host entities, located either at $a/2$ or $c/2$ are linked together by the hydrogen-bonded helices (cf. Fig. 4) into infinite layers. These two-dimensional, infinite 'supramolecules' are then held together by Van der Waals' forces between the hydrophobic phenyl rings.

In **1**·2DMA (Fig. 4) the one-way hydrogen bond interaction between host and guests gives rise to discrete host–guest aggregates. The single OH···O hydrogen bond, from the donor at each end of **1** to the carbonyl group of the DMA molecule, fixes the DMA·**1**·DMA aggregates along the *b* axis. The twofold screw axes translate these aggregates and the two apolar DMA units fit exactly between two other DMA molecules separated by the short [7.937(1)Å] *c* axis. It seems probable that the bulky, closely packed DMA molecules assume alternatively either disorder form *A* or *B* in order to avoid formation of short, (<2.4 Å) unfavorable H···H intermolecular contacts. The infinite columns of the apolar DMA guests completely isolate the host molecules. This particular mode of packing suggests possibilities for future applications in topochemical reactivity[19] and for the development of other crystalline materials properties.[20]

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