Tetrahedron: Asymmetry Vol 3, No. 12, pp. 1555-1562, 1992
Printed in Great Britain

0957-4166/92 $5.00+.00
Pergamon Press Ltd

The Unusual Structure of the Crystalline Inclusion Compound between (11S,12S)-(-)-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid and Acetic Acid

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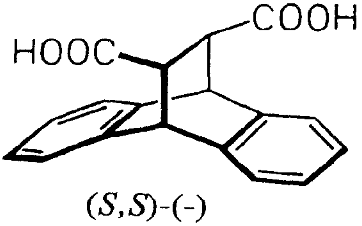
(*Received in UK* 18 *September* 1992; *accepted* 20 *October* 1992)

Abstract: The optically resolved host compound (*S*,*S*)-(-)-**1** yields a 1:1 crystalline inclusion complex with acetic acid, the structure of which was determined by X-ray diffraction and compared with the racemic analogue. Crystal data: (-)-**1** • MeCOOH, $a = b = 17.562(2)$, $c = 11.945(2)$ Å, tetragonal ($P4_3$ or $P4_1$), $Z = 8$, $R = 0.042$ for 1897 observations with $I/\sigma(I) > 2$. The clathrate type crystal consists of unusual asymmetric host-guest associates in which the isolated H-bonded guest dimers are encircled by helical chains of the H-bonded host molecules.

Crystalline enantiomorphous supramolecular structures[1] consisting of organic components are of current interest[2] with regard to optical resolutions[3], asymmetric topochemical reactions[4] and NLO materials[5]. In this context, knowledge of the building principles of enantiomorphous crystals is important[1]. It is therefore reasonable to compare racemic and enantiomorphous crystal lattices composed of different stereochemical species[6] of the same organic molecules.

We have demonstrated recently by chemical and crystallographic means that dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid **1** is an efficient clathrate host[7-9]. In the racemic form, **1** yields a channel inclusion with acetic acid[10,11]. The channels are created by the packing of H-bonded zig-zag chains of host molecules. These channels contain the acetic acid guest molecules as dimers, *i.e.* as a clathrate inclusion in a coordination assisted host lattice[9,12]. We were interested to learn whether the compound **1** in optically resolved form behaves analogously or, if not, to find out the differences. Hence we synthesized the optically resolved (-)-**1**[13,14] (previously established as 11*S*,12*S* configuration), prepared a corresponding inclusion compound with acetic acid and studied its crystal structure by X-ray diffraction.



(*S*,*S*)-(-)

1

Experimental

Synthesis. - The racemic 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1**) was synthesized by Diels-Alder reaction of anthracene with fumaric acid[14,17]. Optically resolved (-)-**1** was obtained via diastereomeric salt formation with brucine to yield 23% optically pure compound [m.p. 220 °C, $[\alpha]_D^{20}$ -15.3 ° (c = 2 in dioxane)][13]. The inclusion compound of (-)-**1** with acetic acid (1:1) was prepared by recrystallization of (-)-**1** from acetic acid (m.p. >120 °C, dec.; Found: C, 67.51; H, 5.03% cald. for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12%).

Structure Determination. - A colourless, irregularly shaped single crystal of the title compound ($C_{18}H_{14}O_4 \cdot C_2H_4O_2$, M_w = 708.72) with the approximate dimensions 0.50x0.55x0.38 mm, sealed in epoxy glue, was used for X-ray diffraction study. The unit cell is tetragonal with $a = b = 17.562(2)$ and $c = 11.945(2)$ Å, $V_c = 3684.1(9)$ Å^3 and $Z = 8$ [$D_{c,X\text{-ray}} = 1.2777(3)$ g cm^{-3}, $F(000) = 1488$]. In the refinement of the unit cell parameters 2θ values of 38 carefully centered reflections with $16° < 2\theta < 24°$ were used. Intensities of 5615 reflections were collected at room temperature on a STOE/AED2 diffractometer (ω-2θ scan), using graphite-monochromatized MoKα radiation (λ = 0.71069 Å, θ_{max} = 60°). Five standard reflections, measured approximately every 90 minutes, showed a decrease in intensity of about 2%. Data reduction included corrections for background, Lorentz and polarization effects. The rather low absorption effects (μ = 0.88 cm^{-1}) were, however, ignored.

Application of direct methods (SHELXS)[18] in the space group $P4_3$ yielded preliminary models for the two host molecules in the crystallographic asymmetric unit. The non-hydrogen atoms of the two guest acids as well as all hydrogens of the host molecules and the two carboxyl H atoms of the guests were located from subsequent difference electron density ($\Delta\rho$) calculations. The positions of the carbon-bonded hydrogens of the guests were, however, assumed to be in geometrically idealized positions with C-H = 1.08 Å, recalculated after each cycle of the refinement. Full-matrix least-squares techniques (SHELX)[19] have been used for the refinement of the structure. The non-hydrogen atom positions were refined together with their anisotropic vibrational parameters. The H positions from $\Delta\rho$ maps were held riding on their parent atoms, and together with the calculated ones had only three common vibrational parameters refined. The methyl groups of the guests were treated as rigid. Accordingly, refinement of 477 variables against 1897 reflections with $I/\sigma(I)>2$ converged to $R = 0.042$ and $wR = 0.053$. The wR_{tot} value, calculated for the final structural model using all 4465 unique non-zero reflections, was 0.064. The maximum/minimum peak heights in the final $\Delta\rho$ map were 0.089/-0.095 e Å^{-3}. Weights of the structure factors were assumed as $w = 2.2623/[\sigma^2(F)+0.00060F^2]$[19]. The atomic scattering factors for the non-hydrogen atoms were taken from Cromer and Mann[20], and those of the hydrogens from Stewart, Davidson and Simpson[21]. The correction factors for anomalous dispersion for the non-hydrogen atoms were taken from Cromer and Liberman[22].

The crystals contain the title compound in optically pure form. Systematic absences in the diffraction pattern were consistent with two enantiomerically related space groups, $P4_1$ and $P4_3$. The structure was solved and refined in space group $P4_3$. Nevertheless, the last refinement was carried out twice: once in space group $P4_3$ (see above) and again in space group $P4_1$ for a structural model having the opposite absolute configuration. These two calculations yielded identical crystallographic R values. Consequently, the absolute configurations of the chiral centres, *i.e.* the true space group, could not be determined in the X-ray diffraction study, because the crystal contained only 'light' atoms which do not yield observable anomalous dispersion effects with common radiations. However, the absolute configurations of (-)-**1** have been established by kinetic resolution and spectroscopic studies to be *S,S* for the chiral centres at C(11) and C(12)[15] (*cf.* Figure 1).

Final atomic coordinates of the non-hydrogen atoms from the refinement in space group $P4_3$ are listed in Table 1. Additional material available from the Cambridge Crystallographic Data Centre comprises intramolecular bond distances and angles involving the non-hydrogen atoms (Tables 3 and 4), fractional atomic coordinates and isotropic displacement parameters of the hydrogen atoms (Table 5), and covalent bond distances and bond angles involving the hydrogen atoms (Tables 6 and 7). Lists of anisotropic displacement parameters of the non-hydrogen atoms as well as the observed and calculated structure factors are available directly from the authors (I. C.).

Results and Discussion

The synthesis of the host molecule (-)-**1** was achieved as described in the literature[13,14,17]. A crystalline inclusion compound between (*S,S*)-(-)-**1** and acetic acid with stoichiometric ratio 1:1 was

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters[a] (Å^2) of the non-hydrogen atoms, with esd's in parentheses.

Atom	x/a	y/b	z/c	U_{eq}[a]
C(1a)	1.3692(3)	0.4683(4)	0.1278	0.047(2)
C(1)	1.4370(4)	0.4795(5)	0.1860(7)	0.063(3)
C(2)	1.4776(4)	0.4156(5)	0.2186(8)	0.073(3)
C(3)	1.4531(5)	0.3435(5)	0.1928(8)	0.075(3)
C(4)	1.3856(4)	0.3333(4)	0.1349(8)	0.059(3)
C(4a)	1.3444(4)	0.3948(4)	0.1020(7)	0.049(2)
C(5a)	1.2747(3)	0.4444(4)	-0.0586(7)	0.051(2)
C(5)	1.2587(4)	0.4248(5)	-0.1696(7)	0.066(3)
C(6)	1.2710(5)	0.4748(5)	-0.2538(8)	0.082(3)
C(7)	1.2971(5)	0.5462(6)	-0.2327(8)	0.084(4)
C(8)	1.3130(4)	0.5691(4)	-0.1219(8)	0.064(3)
C(8a)	1.3017(3)	0.5178(4)	-0.0356(7)	0.051(2)
C(9)	1.3164(3)	0.5307(3)	0.0887(7)	0.045(2)
C(10)	1.2390(3)	0 5158(3)	0.1500(7)	0.045(2)
C(11)	1.2105(3)	0.4341(3)	0.1259(7)	0.044(2)
C(12)	1.2686(4)	0.3941(3)	0.0435(7)	0.049(2)
C(13)	1.1817(4)	0.5756(4)	0.1212(7)	0.053(2)
O(14)	1.1231(3)	0.5622(3)	0.0705(7)	0.085(2)
O(15)	1.1982(3)	0.6436(3)	0.1545(7)	0.048(2)
C(16)	1.2038(3)	0.3875(4)	0.2317(7)	0.079(2)
O(17)	1.2301(3)	0.4064(3)	0.3200(6)	0.048(2)
O(18)	1.1686(3)	0.3229(3)	0.2167(6)	0.070(2)
C(1a')	0.9045(4)	0.9032(3)	0.1079(6)	0.046(2)
C(1')	0.9126(4)	0.9741(3)	0.0567(7)	0.057(3)
C(2')	0.8486(5)	1 0120(4)	0.0217(7)	0.063(3)
C(3')	0.7775(5)	0.9798(4)	0.0336(7)	0.067(3)
C(4')	0.7691(4)	0.9085(4)	0.0851(7)	0.058(2)
C(4a')	0.8333(4)	0.8718(3)	0.1237(7)	0.044(2)
C(5a')	0.8809(4)	0.8039(3)	0.2884(7)	0.046(2)
C(5')	0.8592(4)	0.7827(3)	0.3960(8)	0.054(2)
C(6')	0.9101(5)	0.7936(4)	0.4834(7)	0.066(3)
C(7')	0.9803(5)	0.8247(4)	0.4660(8)	0.067(3)
C(8')	1.0033(4)	0.8451(4)	0.3580(7)	0.046(2)
C(8a')	0.9535(4)	0.8343(3)	0.2710(7)	0.044(2)
C(9')	0.9690(3)	0.8527(3)	0.1491(7)	0.044(2)
C(10')	0.9598(3)	0.7779(3)	0.0796(7)	0 041(2)
C(11')	0.8834(3)	0.7388(3)	0.1083(7)	0.046(2)
C(12')	0.8349(3)	0.7951(3)	0.1815(7)	0.046(2)
C(13')	1.0239(4)	0.7233(4)	0.0922(7)	0.049(2)
O(14')	1.0847(3)	0.7385(2)	0.1372(7)	0.067(2)
O(15')	1.0104(3)	0.6582(3)	0.0433(7)	0.071(2)
C(16')	0.8414(4)	0.7138(4)	0.0042(7)	0.051(2)
O(17')	0.8492(3)	0.7441(3)	-0.0858(6)	0.062(2)
O(18')	0.7971(3)	0.6560(3)	0.0204(6)	0.084(2)
C(1A)	0.8773(8)	0.3556(11)	-0.0184(16)	0.17(1)
O(1A)	0.9416(9)	0.3424(7)	-0.0273(19)	0.31(1)
O(2A)	0.8552(5)	0.4208(6)	-0.0412(11)	0.19(1)
C(2A)	0.8297(9)	0.3078(9)	0.0599(15)	0.19(1)
C(1'A)	1.0067(11)	0.4794(12)	-0.1960(18)	0.18(1)
O(1'A)	0.9436(7)	0.5052(6)	-0.1677(13)	0.19(1)
O(2'A)	1.0257(9)	0.4173(8)	-0.1718(17)	0.30(1)
C(2'A)	1.0545(9)	0.5273(11)	-0.2694(22)	0.28(2)

[a] $U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j a^*_i a^*_j U_{ij} a_i a_j$

readily obtained. In this respect, racemic 1[9,10] and optically resolved (*S*,*S*)-(-)-**1** behave similarly. Nevertheless, the crystal structure of the present inclusion compound is different from that of the racemic analogue[9,10].

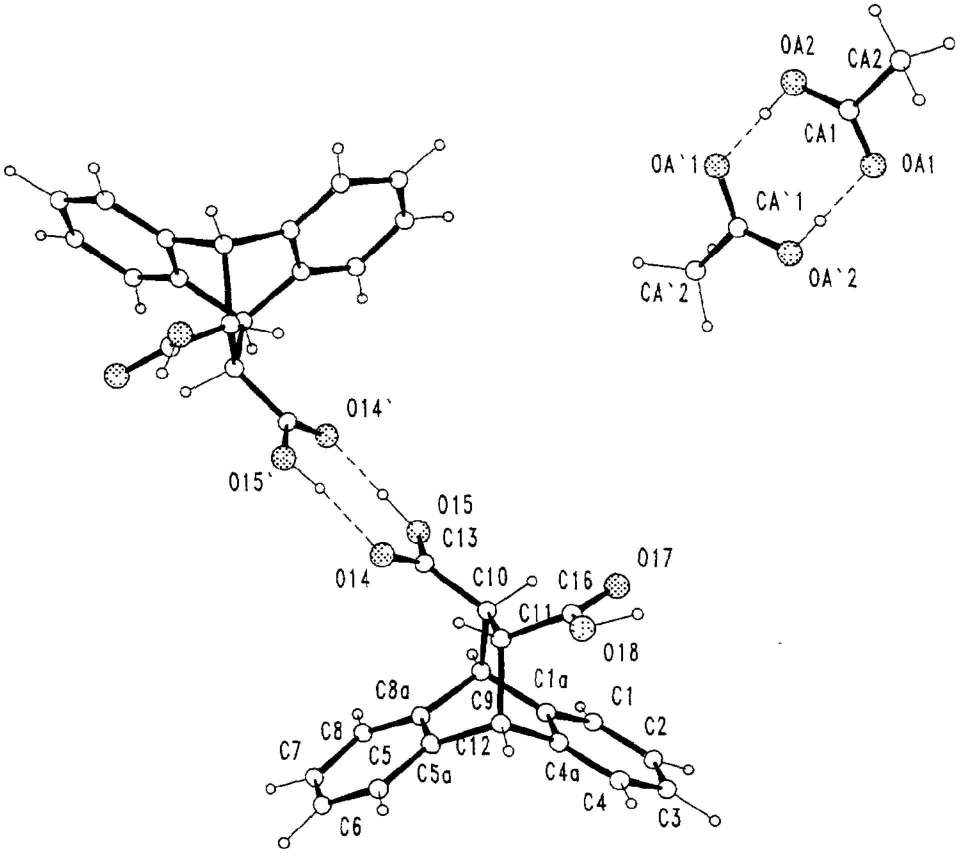


Figure 1. Perspective view of the crystallographic asymmetric unit of (11*S*,12*S*)-(-)-**1** • acetic acid (1:1) structure with the labelling of the atoms. Solid and dashed lines represent covalent and hydrogen bonds, respectively; O atoms are dotted.

*Crystal Structure Description of (S,S)-(-)-***1** *Acetic Acid (1:1) Inclusion Compound.* - A perspective view of the crystallographic asymmetric unit is shown in Figure 1. Table 2 lists the hydrogen bond geometries. The crystal packing is illustrated in Figure 2.

The conformations of the rigid roof-shaped host molecules (unprimed and primed) agree with each other within experimental error and show the expected geometry[8-9,11]. In the ethano bridge the elongated C(9)-C(10) and C(11)-C(12) bonds (*cf.* Fig. 1) have an average length of 1.570[8] Å (with root-mean-square deviation given in angular brackets), and the mean value of the C(10)-C(11) bond distance is 1.546 Å. No anomalous bond lengths or bond angles were detected. All the non-planar six-membered rings have boat conformation and the dihedral angles between the phenyl rings are 56.5(2) and 55.0(2)° in the unprimed and the primed molecules, respectively. However, the atomic displacement parameters (*cf.* Table 1) indicate considerably larger mobility for the guest molecules than for those of the hosts. This may be the reason for the somewhat larger differences (≈ 0.03-0.05 Å) between the observed and expected[23] bond distances in the acetic acid guests.

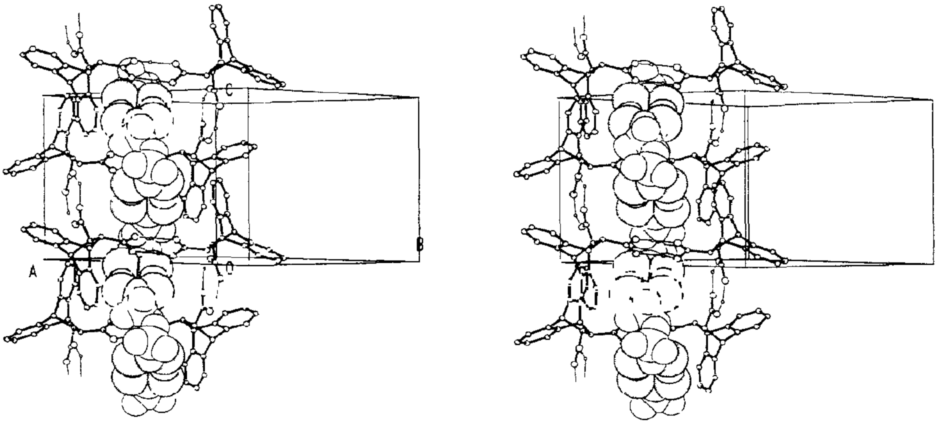


Figure 2. Stereo packing diagram of the (1:1) inclusion compound of (11*S*,12*S*)-(-)-**1** with acetic acid guest. The host molecules are shown in ball-and-stick style and the guest dimers are drawn as space filling models. The O atoms of the guests are indicated by dotting.

Strong hydrogen bonds (*cf.* Table 2) link together the host molecules, and also the guest acids, by forming cyclic pairs of carboxyl groups (*cf.* Figs. 1 and 2), a commonly occuring motif in crystals of carboxylic acids[24]. Nevertheless, in accordance with our earlier observations on related carboxylic acid inclusions[11], there is no H-bond interaction between host and guest: the small guest molecules form isolated dimers. These dimers are encircled by endless helical chains of the host acid (Fig. 2). The helices wind around the crystallographic fourfold screw (4_3 or 4_1) parallel to the *c* axis (Fig. 2). Inspection of the intermolecular contact distances indicates mainly common Van der Waals' type interactions between host and guest associates as well as between helices.

Table 2. Bond distances (Å) and angles (°) in hydrogen bond interactions between the carboxyl groups. The esd's, where given[a], are in parentheses.

Atoms involved	Symmetry	Distances			Angle
		O•••O	O-H	H•••O	<O-H•••O
O(15)-H(15)•••O(14')	*x, y, z*	2.606(6)	1.01	1.600	174
O(15')-H(15')••O(14)	*x, y, z*	2.620(7)	0.93	1.73	158
O(18)-H(18)•••O(17')	*2-x, 1-y, 0.5+z*	2.654(10)	1.05	1.64	162
O(18')-H(18')••O(17)	*2-x, 1-y, -0.5+z*	2.677(10)	0.96	1.79	152
O(2A)-H(1A)•••O(1'A)	*x, y, z*	2.62(2)	0.97	1.66	179
O(2'A)-H(1'A)••O(1A)	*x, y, z*	2.63(3)	1.02	1.61	178

[a] The H atom positions are derived from difference electron density maps and are not refined (cf. the text).

Accordingly, comparison of the acetic acid inclusions of the racemic **1**[11] and the present resolved (*S,S*)-(-)-**1** host shows similarities, but also differences. In both cases, the mono-functional guest acid forms H-bonded dimers, whereas the host diacids are linked *via* hydrogen bond interactions into infinite chains, having the guest dimers trapped in the voids of the host matrix by lattice forces only. Thus, both these structures can be described as clathrates in the common sense. Nevertheless, the crystal packings are organized differently. In the racemic analogue[11], with the ubiquitous monoclinic $P2_1/n$ symmetry, the guest dimers reside in tunnels between the zig-zag chains of the H-bonded host molecules, whereas the optically pure (*S,S*)-(-)-**1** hosts are linked so as to form chiral supramolecular units which twine around the guest entities. In this way unusual helical host-guest associates are created, which are packed with tetragonal ($P4_3$ or $P4_1$) space group symmetry, more rarely encountered with organic heteromolecular crystals.

Acknowledgements

I. C. is indebted to the Swedish Natural Science Research Council (NFR) for economic support; E. W. thanks the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for financial aid.

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