

Exploring Clathrate Formation with an Optically Resolved Host. X-Ray Crystal Structure of the Inclusion Compound between (11*S*,12*S*)-(–)-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid and *n*-Hexane (2 : 1)

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(Received: 25 November, 1996; in final form: 14 March, 1997)

Abstract. The crystal structure of the inclusion compound formed between (11*S*,12*S*)-(–)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid, (**1**), and *n*-hexane (2 : 1) has been studied by X-ray diffraction. It crystallizes in the tetragonal space group $P4_1$ and represents a less common type of inclusion compound, which has helical and chiral structural elements. Helical chains, formed by hydrogen-bonded host molecules, wind around the 2_1 screw axes and encircle the guest molecules. Crystal data: $a = b = 17.478(1)$; $c = 12.021(1)$ Å, $Z = 4$ host–guest 2 : 1 units, $R = 0.043$, $R_w = 0.061$ for 2225 observations with $I > 3\sigma(I)$. The general shape and conformational flexibility of **1** with respect to the requirements of inclusion formation and crystal packing are discussed.

Key words: X-ray structure analysis, inclusion compound, supramolecular helical channel formation, optically resolved dicarboxylic acid host, *n*-hexane guest, hydrogen bonding.

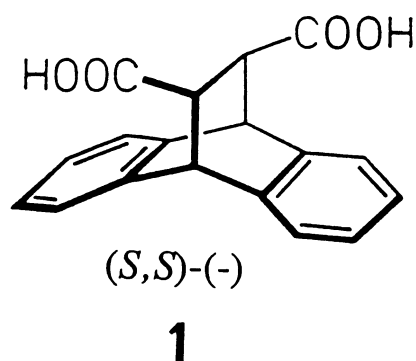
Supplementary Data relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire U.K., as Supplementary Publication No. SUP 82223 (21 pages).

1. Introduction

Chiral compounds separated into enantiomers are very useful [1], for example in optical separation processes [2, 3] and nonlinear optics [4] as well as in crystal engineering [5] and supramolecular host–guest assemblage [6]. In this context, a comparison of enantiomorphous and racemic crystal structures formed by the same organic molecule but composed of different stereochemical species is of particular interest in order to learn their specific building principles and, should the

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Scheme 1.

occasion arise, their varying inclusion behaviour [7, 8]. We have recently demonstrated that dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid **1**, a versatile clathrate host [9, 10], in its racemic form yields a 1 : 1 (host : guest) inclusion compound with acetic acid. It has monoclinic $P2_1/n$ symmetry, and the guest dimers reside in tunnels between zig-zag chains of H-bonded host molecules [11, 12]. On the other hand, in the analogous (1 : 1) inclusion compound of optically pure (*S,S*)-(-)-**1** [13], hosts are linked so as to form chiral supramolecular units which twine around the guest entities in a helical fashion. This latter crystal exhibits tetragonal $P4_1$ symmetry with eight formula units (i.e. eight hosts and eight guests) per cell, a rather uncommon combination for crystals in general [14], and for molecular crystals in particular [15]. A search in the April 1996 version of the Cambridge Structural Database (CSD) [16] yielded 112 organic structures with the space group symmetries $P4_1/P4_3$, but only eight of them (7%) crystallize with two molecules/formulas per asymmetric unit. This stimulated us to synthesize more compounds of slightly different types, e.g. deviating from the above 1 : 1 stoichiometric ratio. The present work reports the X-ray crystal structure of the supramolecular inclusion complex formed between (*S,S*)-(-)-**1** and *n*-hexane (2 : 1), including a comparison with the previously mentioned structure [13].

2. Experimental

2.1. HOST SYNTHESIS AND PREPARATION OF THE CRYSTALLINE INCLUSION COMPOUND

Racemic 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1**) was obtained by a Diels–Alder reaction of anthracene with fumaric acid [17]. Optical resolution of **1** was performed via diastereomeric salt formation with brucine to yield (-)-**1** [18], henceforth called **1**. The absolute configuration of **1** (11*S*, 12*S*) has been established by kinetic resolution and spectroscopic studies [19]. The crystalline inclusion compound **1**·*n*-hexane (2 : 1) was prepared by dissolving **1** in

n-hexane, followed by subsequent crystallization from the slowly cooled solution. The host : guest stoichiometric ratio was determined by ¹H-NMR integration.

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT

Intensity data were collected at ambient temperature (298 ± 1 K) with a STOE/AED2 diffractometer, using graphite-monochromated $\text{CuK}\alpha$ radiation. The crystal used for data collection was colourless, transparent and irregularly shaped. Lattice constants were determined by least-squares fitting of the setting angles of 69 carefully centered reflections in the range $47.7^\circ < 2\theta < 60.3^\circ$. Background, crystal decay, Lorentz and polarization corrections were applied, but no allowance was made for the small effects of absorption (Table I).

The diffraction pattern had $4/m$ symmetry, and the systematic absences were consistent with the enantiomorphous pair of space groups $P4_1$ and $P4_3$. The structure was solved using the MULTAN80 [20] software package. The symmetry of $P4_1$ proved to be consistent with the absolute configuration $11S, 12S$, whereas that of $P4_3$ yielded host molecules with $11R, 12R$ configuration. Since the structure contains only ‘light’ atoms, producing very moderate anomalous dispersion effects (Table I), the absolute configuration of the host molecule could not be further tested in the present X-ray diffraction study. Nevertheless, the $P4_1$ space group symmetry, which is consistent with the previously deduced assignment ($11S, 12S$) of absolute configuration (cf. above), was used in the subsequent calculations.

The crystallographic asymmetric unit contains two host molecules and one guest, the latter one exhibiting rather high mobility. The initial structural model was completed and refined by difference electron density ($\Delta\rho$) calculations and least-squares (LS) calculations based on $|F|$, using the software package SHELX76 [21]. The complete structure model had to be refined using the ‘blocked full-matrix LS’ technique [21] with two blocks of variables, due to the limitation of the program ($N_{\text{var}} < 400$). The non-hydrogen atoms of the host molecules were treated anisotropically. Isotropic displacement parameters (IDPs) were refined for the hydrogen atoms of the carboxyl groups, which were located from $\Delta\rho$ maps and were held riding on their carrier atoms during the subsequent calculations. All other hydrogen positions of both host molecules were calculated assuming ideal geometry with $\text{C—H} = 1.00 \text{ \AA}$, and four group IDPs were refined for them: one for the aromatic and one for the aliphatic hydrogens of each host (Table VII, Supplementary material). The carbon backbone of the flexible and loosely bonded *n*-hexane guest was refined with a common IDP and with distance constraints ($\text{C—C} = 1.52 \text{ \AA}$, [22]), in order to yield acceptable geometry. The hydrogen atoms of the guest molecule were introduced in the final structure model at calculated positions, and were held riding on their carrier carbon atoms with ideal geometry ($\text{C—H} = 1.00 \text{ \AA}$) and fixed IDP ($\text{IDP}_{\text{H}} \approx 1.1 \text{ IDP}_{\text{C}}$). It was noted that the intense low-angle reflections had $|F_o|$ systematically smaller than $|F_c|$, indicating that they might be affected by secondary extinction. Therefore, the final refinement

Table I. Crystal data, experimental parameters and selected details of the refinement calculations for 1-*n*-hexane (2 : 1).

<i>Crystal data:</i>	
Formula	2C ₁₈ H ₁₄ O ₄ ·C ₆ H ₁₄
Formula weight	674.8
F(000)	1432
Crystal system	Tetragonal
Space group	<i>P</i> 4 ₁ (No 76)
<i>a</i> /Å	17.478(1)
<i>b</i> /Å	17.478(1)
<i>c</i> /Å	12.021(1)
<i>V</i> /Å ³	3672.2(4)
<i>Z</i>	4
<i>D_c</i> /g cm ⁻³	1.2205(2)
<i>μ</i> /cm ⁻¹	6.79
Approximate crystal size/mm	0.42 × 0.46 × 0.45
<i>Intensity measurements:</i>	
Radiation/ <i>λ</i>	CuK _α /1.54183 Å
Temperature/ <i>K</i>	298 ± 1
Scan type	<i>ω</i> - 2 <i>θ</i>
Range of 2 <i>θ</i> /deg	5–140
Range of <i>hkl</i>	0/21 0/19 0/14
No. of collected reflections	3403 unique, 3183 non-zero
No. of standard reflections	4
Time interval/min	90
Intensity instability	<1%
<i>Structure refinement:</i>	
No. of reflections included	2225 with <i>I</i> > 3 <i>σ</i> (<i>I</i>)
No. of refined parameters ^a	425(223/224)
Linear agreement factor	
$R = \Sigma \Delta F /\Sigma F_o $	0.043
Weighted agreement factor	
$wR = [\Sigma w \Delta F ^2/\Sigma w F_o ^2]^{1/2}$	0.061
Soof (Goodness of Fit)	1.00
Weighting: $w = k/[\sigma^2(F) + g \cdot F ^2]$ with <i>g</i>	0.0020
Weighted agreement factor for all 3183	
unique non-zero reflections <i>wR</i> _{tot}	0.068
Final $\Delta\rho_{\max}/\Delta\rho_{\min}/e^- \text{ \AA}^{-3}$	0.18/–0.15
Mean esds of the host C—C/C—O distances/Å	0.006/0.005
Mean esd of the host bond angles/deg ^b	0.4
Mean esd of the guest C—C distances/Å ^c	0.03
Mean esd of the guest C—C—C angles/deg ^c	2

^a ‘Blocked full-matrix’ refinement has been performed at the final stage (see text).

^b Involving the non-H atoms only.

^c The *n*-hexane guest was subjected to constrained refinement (cf. the text).

Table II. Selected torsion angles (deg) for the two crystallographically independent host molecules in **1**·*n*-hexane (2 : 1). The esds are in parentheses.

Sequence of the atoms	Angle	
	Unprimed molecule	Primed molecule
C(13)—C(10)—C(11)—C(16)	115.7(4)	99.9(4)
C(9)—C(10)—C(11)—C(12)	0.5(4)	−8.1(4)
C(11)—C(10)—C(13)—O(14)	5.4(6)	24.7(6)
C(11)—C(10)—C(13)—O(15)	−174.1(4)	−155.4(4)
C(10)—C(11)—C(16)—O(17)	9.5(6)	139.0(4)
C(10)—C(11)—C(16)—O(18)	−170.8(3)	−43.8(5)

calculation included also an empirical isotropic extinction correction as $F' = F(1 - 0.001x \cdot F^2 / \sin \theta)$ [21] with the extinction parameter, x , having the refined value of 0.0106(9). Further crystal data and selected experimental details are given in Table I.

3. Results and Discussion

3.1. MOLECULAR STRUCTURES

The perspective view of the asymmetric unit of **1**·*n*-hexane (2 : 1) with the crystallographic numbering scheme is shown in Figure 1. There are two chemically identical host molecules in the asymmetric unit, exhibiting slightly different conformations (Table II). Optimal rotational superposition of the primed molecule on the unprimed one was done by application of the program ROTERA [23] (Figure 2). In the superimposed molecules, the average distance between chemically identical atoms within the rigid dihydroethanoanthracene moiety is 0.033 Å, while pairs of atoms in the carboxyl groups, such as O(17)/O(17') and O(18)/O(18') are as far as 1.895 Å and 2.127 Å apart, respectively. The occurrence of host molecule **1** with two somewhat different conformations in the crystal may be attributed to the requirements of the crystal packing (cf. below). The final atomic coordinates with equivalent isotropic displacement parameters for the non-hydrogen atoms are given in Table III.

3.2. PACKING RELATION

Figure 3 shows the molecular packing of the inclusion compound **1**·*n*-hexane (2 : 1), whereas Figure 4 illustrates the organization of the host framework only. The crystal structure of **1**·*n*-hexane (2 : 1) combines the topology of the channel cavitate with the properties of helicity and chirality relating to a less commonly observed type of inclusion compound classified as ‘tubulatoclathrate’ [24].

The relatively high symmetry of a molecular crystal ($P4_1$) and/or $Z' > 1$ ($Z' = Z/n$, where Z is the number of molecules in the unit cell and n is the order

Table III. Fractional atomic coordinates and equivalent isotropic^a/isotropic,^b $U_{\text{eq}}/U_{\text{iso}}$, (\AA^2), displacement parameters for the non-hydrogen atoms in the **1**-*n*-hexane (2 : 1) compound, with esds in parentheses.

Atom	x/a	y/b	z/c	$U_{\text{eq}}/U_{\text{iso}}$
C(1a)	0.5329(3)	0.3732(2)	0.7274(4)	0.052(1)
C(1)	0.5219(3)	0.4413(3)	0.6704(4)	0.065(2)
C(2)	0.5847(4)	0.4835(3)	0.6364(5)	0.080(2)
C(3)	0.6570(4)	0.4585(3)	0.6600(5)	0.081(2)
C(4)	0.6696(3)	0.3908(3)	0.7168(4)	0.068(2)
C(4a)	0.6070(2)	0.3488(2)	0.7511(3)	0.050(1)
C(5a)	0.5593(2)	0.2771(2)	0.9119(3)	0.050(1)
C(5)	0.5805(3)	0.2593(3)	1.0194(4)	0.066(2)
C(6)	0.5278(4)	0.2684(3)	1.1059(5)	0.083(2)
C(7)	0.4559(4)	0.2930(3)	1.0831(5)	0.081(2)
C(8)	0.4333(3)	0.3108(3)	0.9743(4)	0.066(2)
C(8a)	0.4854(2)	0.3028(2)	0.8875(4)	0.050(1)
C(9)	0.4715(2)	0.3188(2)	0.7670(4)	0.049(1)
C(10)	0.4866(2)	0.2424(2)	0.7031(4)	0.046(1)
C(11)	0.5695(2)	0.2138(2)	0.7277(3)	0.046(1)
C(12)	0.6092(2)	0.2715(2)	0.8096(4)	0.052(1)
C(13)	0.4278(2)	0.1837(2)	0.7301(4)	0.051(1)
O(14)	0.4422(2)	0.1224(2)	0.7747(4)	0.083(1)
O(15)	0.3584(2)	0.2018(2)	0.7020(4)	0.075(1)
C(16)	0.6159(2)	0.2082(2)	0.6222(4)	0.051(1)
O(17)	0.5965(2)	0.2320(2)	0.5332	0.074(1)
O(18)	0.6827(2)	0.1737(2)	0.6375(3)	0.072(1)
C(1a')	0.8040(2)	0.1193(2)	0.0663(3)	0.045(1)
C(1')	0.7834(2)	0.1422(3)	-0.0395(4)	0.054(1)
C(2')	0.7932(3)	0.0912(3)	-0.1272(4)	0.068(2)
C(3')	0.8243(3)	0.0209(3)	-0.1115(4)	0.072(2)
C(4')	0.8443(3)	-0.0033(3)	-0.0036(4)	0.060(2)
C(4a')	0.8342(2)	0.0466(2)	0.0848(3)	0.047(1)
C(5a')	0.9038(2)	0.0946(2)	0.2451(4)	0.048(1)
C(5')	0.9744(2)	0.0858(3)	0.2961(4)	0.058(2)
C(6')	1.0130(3)	0.1513(3)	0.3336(4)	0.069(2)
C(7')	0.9823(3)	0.2221(3)	0.3205(4)	0.068(2)
C(8')	0.9106(3)	0.2317(3)	0.2692(4)	0.060(2)
C(8a')	0.8724(2)	0.1667(2)	0.2298(3)	0.048(1)
C(9')	0.7958(2)	0.1660(2)	0.1722(3)	0.048(1)
C(10')	0.7393(2)	0.1182(2)	0.2457(3)	0.046(1)
C(11')	0.7775(2)	0.0400(2)	0.2725(4)	0.046(1)
C(12')	0.8522(2)	0.0308(2)	0.2048(3)	0.046(1)
C(13')	0.7167(2)	0.1598(2)	0.3501(4)	0.052(1)

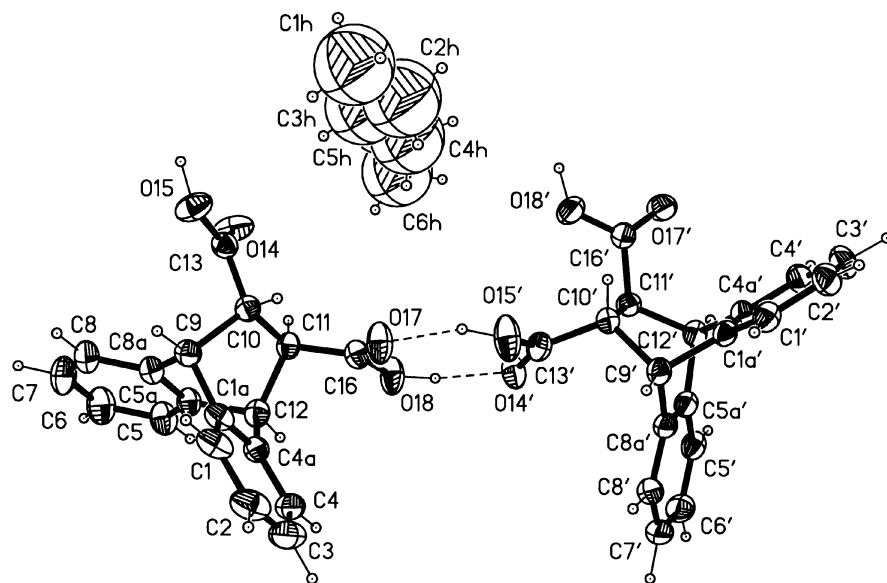


Figure 1. Perspective view of the asymmetric unit of the compound **1**·*n*-hexane (2 : 1) with the crystallographic numbering scheme. Hydrogen bonds are indicated by dashed lines. The displacement ellipsoids for the non-hydrogen atoms are drawn at 50% probability level, whereas the H atoms are shown as spheres of arbitrary radii.

Table III. Continued.

Atom	x/a	y/b	z/c	U_{eq}/U_{iso}
O(14')	0.7460(2)	0.1505(2)	0.4399(3)	0.065(1)
O(15')	0.6602(2)	0.2091(2)	0.3349(3)	0.085(1)
C(16')	0.7216(2)	-0.0246(2)	0.2594(4)	0.052(1)
O(17')	0.7377(2)	-0.0855(2)	0.2174(4)	0.070(1)
O(18')	0.6544(2)	-0.0094(2)	0.3026(4)	0.079(1)
C(1h)	0.301(1)	0.155(1)	0.313(2)	0.40(1)
C(2h)	0.377(1)	0.112(2)	0.319(2)	0.40(1)
C(3h)	0.384(1)	0.076(2)	0.433(2)	0.40(1)
C(4h)	0.462(1)	0.039(2)	0.444(2)	0.40(1)
C(5h)	0.458(1)	0.027(1)	0.526(3)	0.40(1)
C(6h)	0.534(2)	-0.033(1)	0.586(2)	0.40(1)

$$^a U_{eq} = 1/3 \sum_i \sum_j a_i^* a_j^* U_{ij} a_i a_j.$$

^b The non-hydrogen atoms of the *n*-hexane guest were refined isotropically.

of the group [25]), constitutes evidence for structure-determining intermolecular interactions [14]. In the case of **1**·*n*-hexane (2 : 1) with $Z' = 2$ for the host molecules only, the interaction between the host carboxyl groups is expected to play a decisive

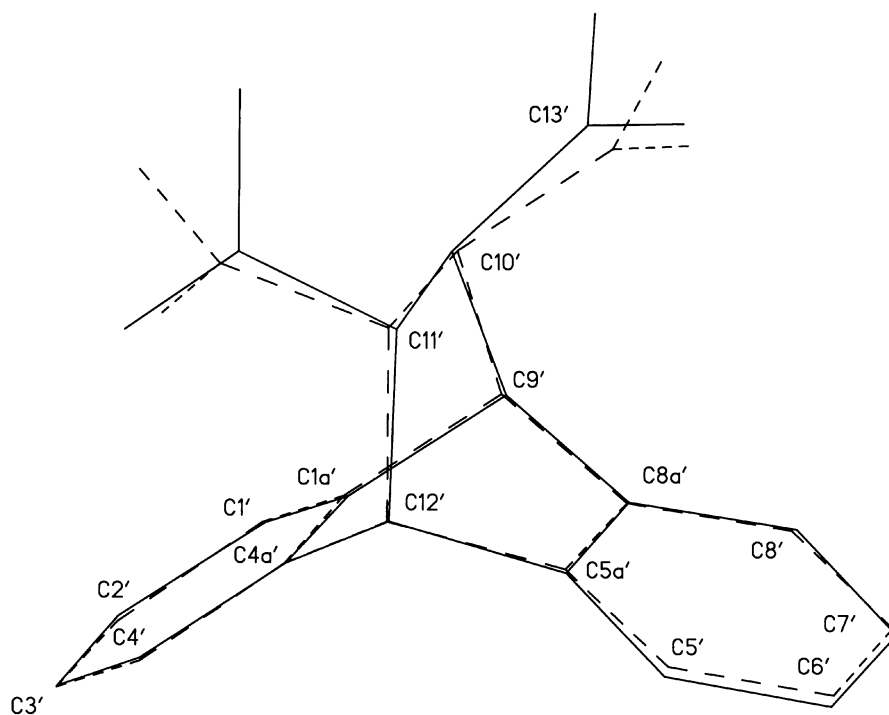


Figure 2. Model fitting plot of the unprimed and primed conformers of host **1**.

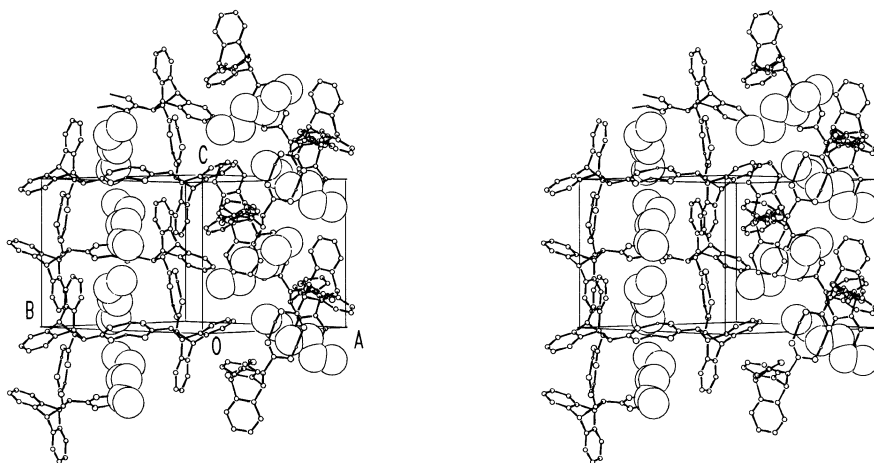


Figure 3. Stereo packing diagram of the inclusion compound **1**·*n*-hexane (2:1). The host molecules are shown in ball-and-stick style. The guest molecules are drawn as space filling models. The hydrogen atoms, except those taking part in hydrogen bonds, are omitted for clarity.

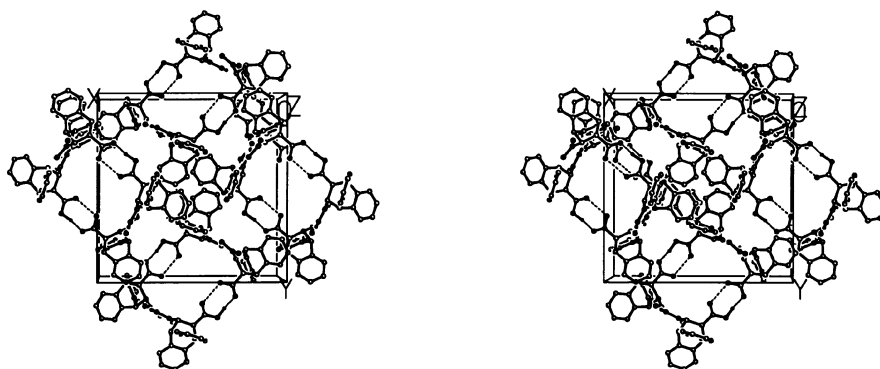


Figure 4. Stereo diagram of the packing arrangement of the host framework in the **1**·*n*-hexane (2 : 1) compound, viewed along the [001] direction. The hydrogen atoms are omitted for clarity.

role in the crystal packing [5, 26]. One may expect infinite chains, in which the hosts are linked *via* hydrogen bonded carboxyl pairs, since such chains have been observed in related compounds, for example in selected cocrystals of the racemic 9,10-dihydro-9,10-ethano-anthracene-11,12-dicarboxylic acid (i.e. those without coordinative host–guest interactions) [11, 12, 27], and in the guest-free crystal of this racemic host as well [9, 27]. In general, infinite hydrogen-bonded chains of enantiomerically pure dicarboxylic acids may be created using either purely translational or two-fold screw axis symmetry [28]. Pure translation of host **1** might give rise to unfavourable proximity of the bulky dihydroanthracene moieties of neighbouring molecules, whereas these moieties are brought apart by 2_1 symmetry. At the same time, although the synplanar $C_{\text{bridge}}-C_{\text{bridge}}-C=O$ arrangement [where $C_{\text{bridge}}-C_{\text{bridge}}$ represents the C(10)—C(11) bond] is conformationally favourable for the carboxylic groups [29], formation of the cyclic hydrogen bond linkage between hosts related by 2_1 symmetry leads also to energetically less favourable carboxyl orientations [cf. the anticlinal arrangement of the C(16')=O(17') group relative to the C(10')—C(11') bond], thus developing strain in the molecules. The presence of two host molecules in the asymmetric unit with somewhat different conformations of the carboxyl groups probably abates the strain in the structure as a whole. Furthermore, in the absence of stronger interaction between the 2_1 helices, the crystalline architecture is directed by the requirement of dense packing. The infinite helices pack most effectively when extending parallel with each other so as to yield the tetragonal ($P4_1$) space group for this compound, thus supporting the view that molecular crystals with high-symmetry space groups occur more likely in the case of salts and solvate inclusions [14].

Another notable feature of this structure is the alignment of the guest molecules in the host framework. The host molecules are interlinked by hydrogen bonds, which either run along the *c* axis or are extended nearly perpendicular to it (Table IV). The latter H-bonds give rise to repeatedly appearing narrowings inside

Table IV. Distances (Å) and angles (deg) in interhost hydrogen bonds in **1**·*n*-hexane (2 : 1). The esds, where given,^a are in parentheses.

Atoms involved	Symmetry	Distances			Angle
		O···O	O—H	H···O	<O—H···O
O(18)—H(18)···O(14')	<i>x, y, z</i>	2.651(5)	0.93	1.74	169
O(15')—H(15')···O(17)	<i>x, y, z</i>	2.661(4)	0.94	1.77	158
O(15)—H(15)···O(17')	$-x + 1, -y, z + 0.5$	2.642(4)	0.99	1.65	179
O(18')—H(18')···O(14)	$-x + 1, -y, z - 0.5$	2.620(5)	1.05	1.66	151

^a The positions of the H(O) atoms were derived from $\Delta\rho$ maps and were not refined (cf. text).

the channel. The *n*-hexane molecule is longer (*ca.* 7.4 Å) than one half of the repeating length of the host channel (6.0 Å) measured along the *c* axis. Accordingly, the *n*-hexane guest has to be aligned at an oblique angle to the *c* axis (Figure 3). Each guest extends approximately between the centers of two successive narrowings of the inner channel, forming a zig-zag arrangement. As a consequence, the translational mobility of the guest molecules along the helical axis is diminished and a three-dimensional periodicity of the guest arrangement is anchored. Moreover, this made it possible, in contrast to many tubulatoclathrates described in the literature [31], to resolve the guest electron density into individual atoms, although the space in the channel is big enough to allow considerable mobility for the guests. The packing coefficient of the **1**·*n*-hexane (2:1) complex, estimated using the program PLATON [30], is only 0.65, i.e. at the lower limit of the values (0.65–0.77) usually observed for molecular crystals [15].

4. Comparative Study, Summary and Conclusion

The host architecture in **1**·*n*-hexane (2 : 1) shows both similarities and substantial differences to those of earlier investigated tubulatoclathrates [31, 32]. The network formed by **1** is very open, similar to those of alicyclic diol hosts [31], whereas in urea/thiourea tubulands [33] a specific network of H-bonds has been observed within the walls of the tubes. The adjacent helices in **1**·*n*-hexane (2:1), on the other hand, are not fused, in contrast to the inclusion compounds formed by both alicyclic diols and urea/thiourea hosts.

In order to further characterize the guest inclusion and crystal packing modes, a search for inclusion compounds of enantiomerically pure dicarboxylic acid hosts was made on the April 1996 version of the CSD [16]. The only compound found was the closely related **1**-acetic acid (1 : 1), reported earlier by us [13]. Despite unequal host-guest stoichiometries and the very different character and shape of the guest molecules, the host frameworks in the acetic acid and *n*-hexane inclusion compounds of **1** proved to be isostructural. The acid guest in **1**-acetic acid (1 : 1) forms H-bonded dimers. It may be mentioned that formation of isolated H-bonded

dimers of acidic guests was found to occur frequently in inclusion crystals between carboxylic acids [12], though a H-bonded chain of guest acetic acid was also observed, such as in the 1 : 1 complex of deoxycholic acid and acetic acid [34]. The guest dimer in **1**·acetic acid (1 : 1), exhibiting a van der Waals surface similar to that of *n*-hexane, is aligned within the host helices in the same manner as the *n*-hexane guest in **1**·*n*-hexane (2 : 1). Although the non-hydrogen skeleton of the dimeric acetic acid (6.8 Å) is significantly longer than the aliphatic carbon chain of *n*-hexane (6.3 Å), the two crystals have about the same packing coefficient (0.65) [30], and the backbone of the acidic dimer forms practically the same oblique angle to the helical axis (54.2°) as the *n*-hexane chain (54.0°). There is only weak van der Waals interaction between host and guest in both inclusion compounds, but the *n*-hexane guest exhibits higher mobility [the refined common U_{iso} of the six C atoms is 0.402(7) Å², Table III] than the acetic acid dimer (U_{eq} averaged for all non-hydrogen atoms is 0.23 Å²) [13], thus indicating slightly more free space around the somewhat smaller *n*-hexane guest than around the acidic dimer.

In summary, the resolved semirigid dicarboxylic acid **1** is capable of forming helical chains *via* cyclic inter-host hydrogen bonds. This host framework is necessarily stabilized by inclusion of suitable guest molecules, which are incorporated in the crystal in a strictly stoichiometric host-guest ratio. The isostructurality of the acetic acid and *n*-hexane inclusion compounds of **1** indicates that guests of different character and different shape and size may be included in the helical channels formed by host **1**. However, how much the shape and size of the guest molecule can be modified without destabilizing the helical tubular host structure has not yet been investigated. The detailed structural requirements for the formation of the helical tubular system based on **1**, and the full details of their inclusion capacity, need more systematic investigations.

Acknowledgements

Financial support from the Swedish Natural Science Research Council (NFR), the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie is gratefully acknowledged. This work is part of the Graduate School Program (GRK 208/1) of the TU Bergakademie Freiberg supported by the DFG.

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