

Pseudodimorphism of the *Trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid Clathrates with Acetic and Propionic Acids *

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Abstract

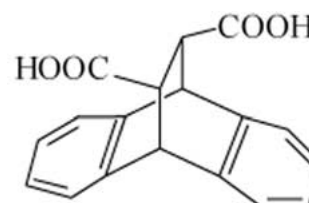
The versatile host compound *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1**) forms under ambient conditions isostructural complexes with acetic and propionic acids being true clathrates without host-guest type H-bonds. A new modification of the clathrate between **1** and acetic acid (**1a**) is obtained at sub-room temperature (5 °C) while for preparation of the new crystal form of the clathrate with propionic acid (**1b**) crystallization temperature should be increased up to 50 °C. Crystal structures of the pseudodimorphs show that homo carboxylic acid dimers existing in the conventional phases are also observed here, demonstrating the new compounds to be of same clathrate type. Crystal data: for **1a**: triclinic P-1, $a = 8.626(2)$ Å, $b = 9.073(2)$ Å, $c = 12.042(2)$ Å, $\alpha = 76.34(3)^\circ$, $\beta = 77.41(3)^\circ$, $\gamma = 84.13(3)^\circ$, $V = 892.5(4)$ Å³, $Z = 2$, $R = 0.0446$ for 3171 reflections; for **1b**: monoclinic C2/c, $a = 13.268(3)$ Å, $b = 12.636(3)$ Å, $c = 21.786(4)$ Å, $\beta = 90.56(3)^\circ$, $V = 3652.3(14)$ Å³, $Z = 8$, $R = 0.0618$ for 2365 reflections.

Introduction

Molecules (hosts) that recognize and bind to specific substrates (guests) are important for analytical applications and for the development of more effective catalysts, carriers and reagents [1]. The compound *trans*-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1**) in its nature as a coordinatoclathrate host [2] shows typical structural features, namely:

- a bulky molecular skeleton which gives rise to voids in the crystal lattice,
- appended carboxylic functions (sensor) groups which provide hydrogen bonding to guests or to other host molecules.

This roof-shaped molecule allows stoichiometric, selective inclusions of a great number of different polar organic guests, most of which are able to form hydrogen bonds [3], i.e., it demonstrates versatile host properties. Our investigations of the last years suggest that pseudopolymorphism (or more properly called solvatomorphism, if the guest component represents a solvent) is a characteristic behavior of inclusion (host–guest) complexes derived from versatile host compounds [4–7]. It is known that host compound **1** forms isostructural clathrates with acetic and propionic acid [8].



Scheme 1. Host molecule (**1**).

Here we report a study showing the ability of these clathrates to solvatomorphism and describe the structures of the obtained clathrate modifications.

Experimental

Pseudopolymorphism (solvatomorphism) investigations and preparation of single crystals

As a basis for comparison the conventional (room temperature) clathrates were prepared [8], their powder XRD patterns registered, and cell parameters of single crystals measured. Increased temperature crystallization from corresponding solutions was carried out in thermostats with changing of the temperature by steps of 5 °C up to 50 °C. Sub-room temperature experiments were performed in a refrigerator by 5 °C step lowering of temperature down to –10 °C. For

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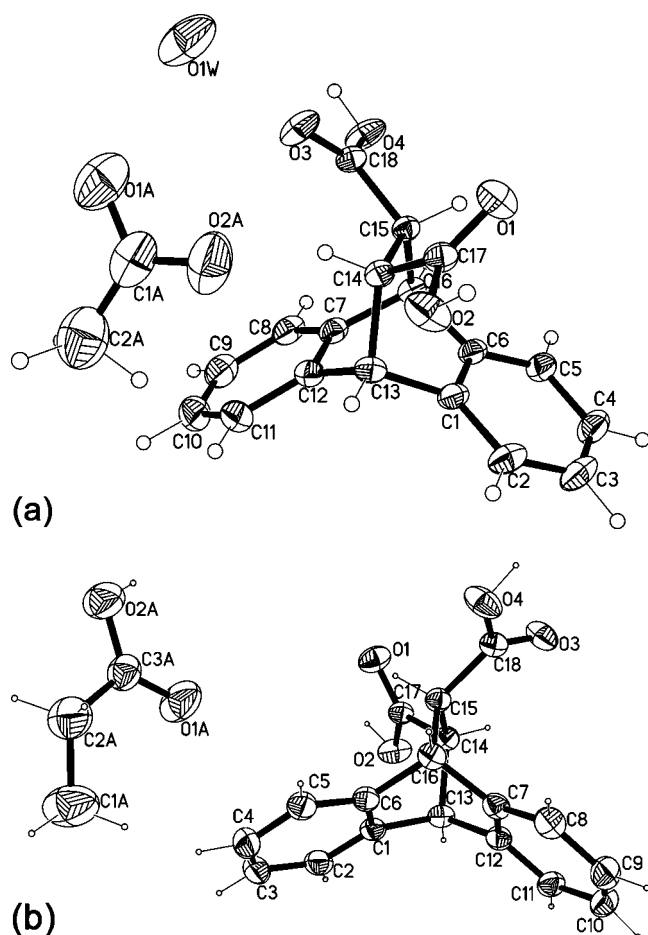


Figure 1. Perspective views of the asymmetric units and numbering scheme in the studied clathrates: (a) **1a**[1-acetic acid-water] and (b) **1b**[1-propionic acid]. The anisotropic displacement parameters are shown at 30% probability level.

each batch, powder XRD patterns were registered or cell parameters determined in case of growth of suitable single crystals. These characteristics of the prepared products were compared with those of the conventional phase in order to establish formation of a new modification.

Single crystals of the novel clathrate modification composed of **1** and acetic acid (**1a**) were obtained by slow solvent evaporation from a solutions of **1** in acetic acid at 5 °C during 1 week. Crystals of the pseudopolymorphous inclusion complex including **1** and propionic acid (**1b**) were obtained at 50 °C during 10 h.

X-ray data collection and processing

The single crystals selected for X-ray diffraction measurements were sealed in epoxy glue. All single crystal XRD data obtained in this work were collected on a NONIUS KAPPA CCD X-Ray diffractometer in the "Centre de Diffractométrie Automatique Henri Longchambon" (MoK α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at room temperature. The 2763 reflections for **1a** and 3440 reflections for **1b** with $1.00^\circ < \theta < 27.48^\circ$ (resolution between 20.40 Å and 0.77 Å) were used for unit cell refinement. Crystal data and selected experimental details are summarized in Table 1.

Table 1. Selected crystal data and experimental details

Compounds	1a	1b
	Crystal Data	
Crystal system	Triclinic	Monoclinic
Space group	P-1 (No. 2)	C2/c (No. 15)
a, b, c [Å]	8.626(2)	13.268(3)
	9.073(2)	12.636(3)
	12.042(2)	21.786(4)
α, β, γ [°]	76.34(3)	90
	77.41(3)	90.56(3)
	84.13(3)	90
V [Å ³]	892.5(4)	3652.3(14)
Z	2	8
D (calc) [g/cm ³]	1.303	1.340
μ [mm ⁻¹]	0.100	0.098
$F(000)$	366	1552
	Data Collection	
Temperature (K)	293	293
Radiation [Å]	0.71073	0.71073
θ min–max [°]	3.2, 27.5	3.1, 27.5
Dataset	–11:11; –11:10;	–17:17; –15:16;
	–15:13	–28:28
Tot., Uniq. Data, R (int)	5831, 3934, 0.016	6929, 4109, 0.032
Observed data	3171	2365
	Refinement	
$N_{\text{ref}}, N_{\text{par}}$	3934, 294	4109, 301
$R, wR2, S$	0.0446, 0.1235, 1.03	0.0618, 0.1860, 1.06
min. and max. Resd. Dens.	–0.17, 0.26	–0.33, 0.38
	[e/Å ³]	

Structure analysis and refinement

The structures were solved by direct methods (SHELXS program [9]). Practically all non-hydrogen atoms of the investigated structures were located from the best F-map. The structures were refined by the full matrix least-squares method at first with isotropic and then with anisotropic temperature factors using the program SHELXL-93 [10]. The positions of H-atoms were found from difference Fourier maps except for the hydrogen atoms of the solvent molecules in both structures. Coordinates of these H-atoms were generated geometrically (C–H distance fixed at 0.96 Å, O–H at 0.82 Å) and allowed to ride on the carbon or oxygen atoms to which they are bonded. In the structure of **1a** the additional water molecules located at five positions with s.o.f. from 0.12 to 0.33 (totally 1.11 molecules), have been located. Final atomic coordinates are given in the Table 2.

Results and discussion

The atomic positional parameters of the pseudopolymorphs are given in Table 2, atom labeling is in accordance with Figure 1. Hydrogen bond geometries are listed in Table 3.

Table 2. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for **1a** and **1b**. The esd's are given in parentheses

Atom	x/a	y/b	z/c	$U_{\text{eq}} (\text{\AA}^2)$
1a				
O(1)	−0.67904(12)	0.94719(13)	0.50623(9)	0.0553(4)
O(2)	−0.47938(12)	0.97623(15)	0.35297(10)	0.0603(4)
O(3)	−0.84093(12)	0.59819(10)	0.44363(11)	0.0584(4)
O(4)	−1.09058(11)	0.69072(12)	0.45795(11)	0.0588(4)
C(1)	−0.77991(16)	1.13324(14)	0.21607(11)	0.0405(4)
C(2)	−0.7154(2)	1.27463(17)	0.18651(15)	0.0555(5)
C(3)	−0.8142(2)	1.40160(17)	0.20201(17)	0.0652(6)
C(4)	−0.9740(2)	1.38786(16)	0.24848(15)	0.0592(5)
C(5)	−1.03943(19)	1.24608(15)	0.28016(13)	0.0467(5)
C(6)	−0.94154(15)	1.11926(13)	0.26327(11)	0.0381(4)
C(7)	−0.93710(16)	0.89377(13)	0.18432(11)	0.0401(4)
C(8)	−1.0310(2)	0.82783(16)	0.13091(14)	0.0512(5)
C(9)	−0.9618(3)	0.77915(18)	0.02928(15)	0.0652(6)
C(10)	−0.8023(3)	0.7946(2)	−0.01727(15)	0.0676(7)
C(11)	−0.7074(2)	0.85765(18)	0.03665(13)	0.0570(5)
C(12)	−0.77565(17)	0.90819(14)	0.13737(11)	0.0425(4)
C(13)	−0.69122(16)	0.98329(14)	0.20518(11)	0.0400(4)
C(14)	−0.71314(14)	0.88163(14)	0.33122(10)	0.0352(3)
C(15)	−0.89158(14)	0.86779(13)	0.38402(11)	0.0332(3)
C(16)	−0.99182(15)	0.95706(13)	0.29295(11)	0.0362(3)
C(17)	−0.62407(15)	0.93918(14)	0.40586(11)	0.0390(4)
C(18)	−0.93727(15)	0.70466(13)	0.43010(11)	0.0370(4)
*O(1A)	−0.4373(7)	0.4216(13)	0.2952(9)	0.114(3)
*O(2A)	−0.3758(5)	0.6527(4)	0.2822(5)	0.112(2)
*C(1A)	−0.3912(8)	0.5496(8)	0.2317(9)	0.088(3)
*C(2A)	−0.3523(10)	0.5696(8)	0.1087(8)	0.120(3)
*O(1W)	−0.5312(8)	0.3782(11)	0.5060(9)	0.109(3)
*O(2W)	−0.4828(7)	0.4950(11)	0.4313(8)	0.071(3)
*O(3W)	−0.558(6)	0.402(4)	0.563(9)	0.19(3)
*O(4W)	−0.506(7)	0.392(3)	0.410(11)	0.16(6)
*O(5W)	−0.4296(10)	0.5154(14)	0.3054(13)	0.123(6)
1b				
O(1)	0.23128(11)	0.12969(12)	0.47341(8)	0.0574(6)
O(2)	0.37576(12)	0.21784(12)	0.47603(9)	0.0595(6)
O(3)	0.32840(13)	−0.15060(13)	0.49610(8)	0.0586(6)
O(4)	0.22297(15)	−0.19906(14)	0.42189(9)	0.0675(7)
C(1)	0.41219(15)	0.11415(16)	0.33590(10)	0.0422(7)
C(2)	0.41282(18)	0.21512(19)	0.31176(12)	0.0542(8)
C(3)	0.3585(2)	0.2365(2)	0.25854(13)	0.0659(10)
C(4)	0.3041(2)	0.1582(3)	0.22991(13)	0.0665(10)
C(5)	0.30101(18)	0.0569(2)	0.25393(11)	0.0534(8)
C(6)	0.35444(15)	0.03530(17)	0.30724(9)	0.0441(7)
C(7)	0.46320(16)	−0.10165(16)	0.35104(9)	0.0419(7)
C(8)	0.50617(19)	−0.19699(19)	0.33341(11)	0.0527(8)
C(9)	0.6082(2)	−0.2132(2)	0.34363(12)	0.0607(9)
C(10)	0.6662(2)	−0.1366(2)	0.37095(12)	0.0596(9)
C(11)	0.62427(16)	−0.0403(2)	0.38904(10)	0.0483(8)
C(12)	0.52281(15)	−0.02356(16)	0.37850(9)	0.0417(6)
C(13)	0.46499(15)	0.07643(16)	0.39389(9)	0.0400(7)
C(14)	0.37982(15)	0.04196(16)	0.43833(10)	0.0383(6)
C(15)	0.31061(16)	−0.03977(16)	0.40666(9)	0.0383(6)
C(16)	0.35475(16)	−0.06848(16)	0.34205(10)	0.0421(7)
C(17)	0.32178(15)	0.13425(16)	0.46355(10)	0.0403(6)
C(18)	0.29005(15)	−0.13457(16)	0.44611(10)	0.0414(7)

Table 2. Continued

Atom	x/a	y/b	z/c	U_{eq} (\AA^2)
O(1A)	0.07910(15)	0.0154(2)	0.19281(10)	0.0972(9)
O(2A)	-0.08486(15)	0.00347(19)	0.18413(10)	0.0913(9)
C(1A)	0.0958(3)	0.0643(4)	0.06688(18)	0.125(2)
C(2A)	0.0066(2)	0.0135(3)	0.09350(15)	0.0934(14)
C(3A)	0.0038(2)	0.0106(2)	0.16122(13)	0.0623(9)

U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

Starred atom sites have a s.o.f less than 1.0.

Respective views of the crystallographic asymmetric units of the present clathrates are shown in Figure 1, and the crystal packings are illustrated in Figure 2.

Investigations carried out show that in both cases of the carboxylic acid guests (acetic or propionic acids) new clathrate modifications are obtained if the formation temperature of the inclusion complexes is varied. The pseudopolymorph of the **1**-acetic acid clathrate is obtained at 5 °C in the form of a ternary complex with participation of water molecules while the novel pseudopolymorph of the propionic acid clathrate is formed at 50 °C. Thus, it is shown that solvatomorphism behavior is characteristic for both studied clathrates.

Molecular structures

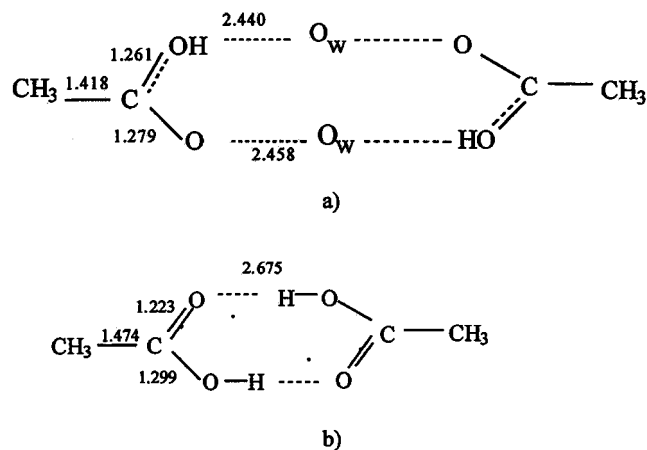
The geometry of the rigid host **1** is almost identical in the present structures (Figure 1a, b). Corresponding bond lengths and bond angles are in good agreement with each other and also with the values published in previous communications on related structures [11, 12]. In the ethano bridge the C(13)–C(14) and C(15)–C(16) bonds are elongated [1.5619(18), 1.5675(18) Å and 1.557(3), 1.572(3) Å for **1a** and **1b**, respectively], while the length of the C(14)–C(15) bond in the middle is comparable with the usual length [1.538(2) and 1.541(3) Å for **1a** and **1b**, respectively]. The dihedral angles between the phenyl rings are 57.7(1)° in **1a** and 55.7(1)° in structure **1b**. The carboxylic groups form dihedral angles with the central ethano bridge plane 130.1(2)° and 134.9(1)° in clathrates **1a** and **1b**, respectively.

A special point of interest of the structure of **1a** arises from the guest component, presented here as a separate species containing acetic acid and water. The H-bond parameters in this carboxylic acid dimer which is formed by participation of two symmetrically related water molecules is very unusual, compared with the conventional acetic acid dimer [8] (Scheme 2).

Involvement of water molecules to dimer formation with short O...O distances between acid and water molecules leads to a strong intermolecular interaction. The H-bond lengths 2.440 and 2.458 Å are an indication to symmetrical H-bonds where the hydrogen atom of the bond is in the middle of the interacting oxygen atoms [13].

Crystal structures

In structures of the conventional clathrates between **1** and acetic or propionic acid there are no H-bonding contacts



Scheme 2. Water-build-in (a) and conventional acetic acid (b) dimers.

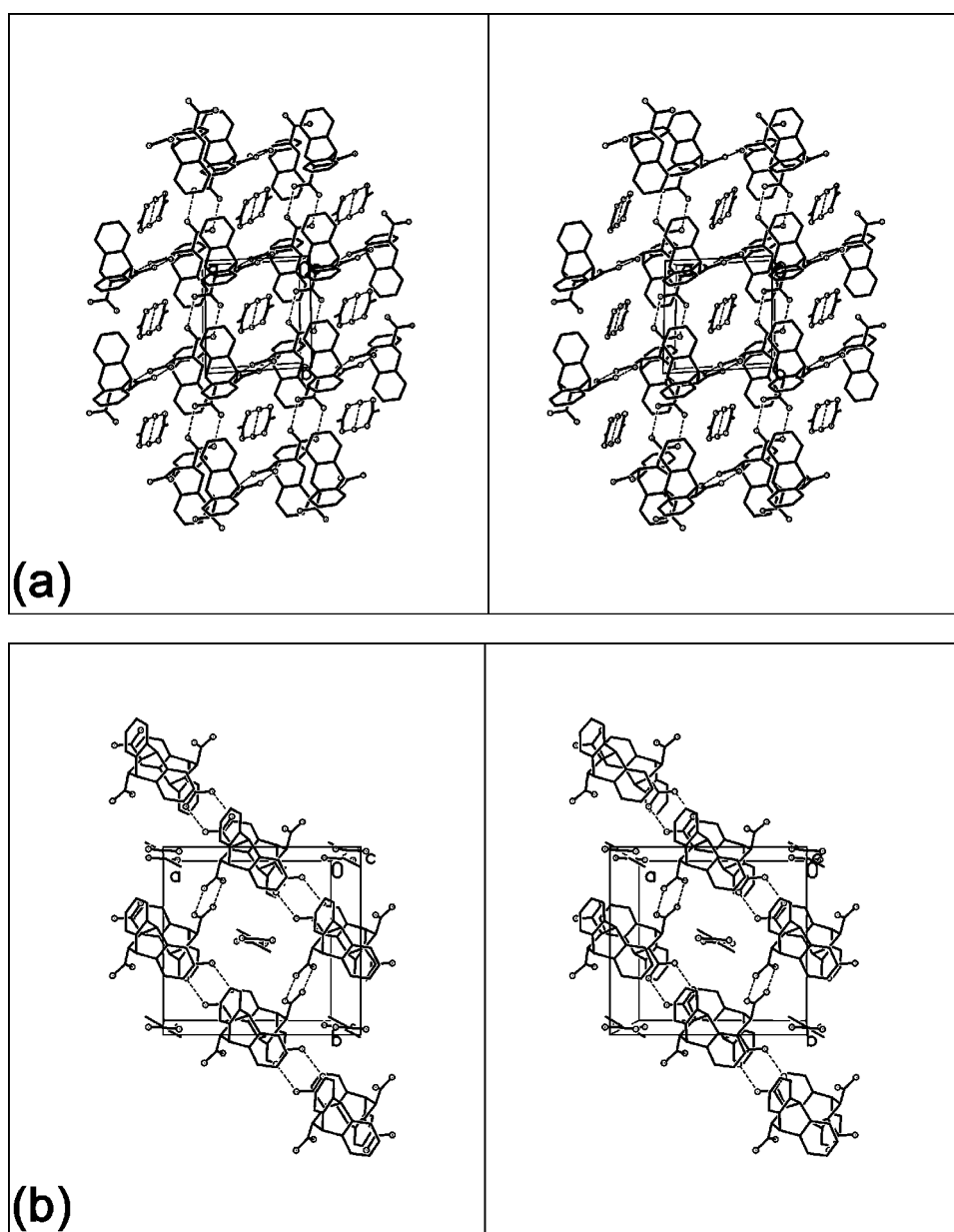
between host and guest components [8]. On the contrary the acid molecules are included into the clathrates in the form of classical dimers. The framework is build up of hydrogen bonded zigzag chains of the host. These chains run parallel to the c -axis and form tunnels, in which the guest dimers are located (Figure 3).

In both new pseudodimorphs, the tendency of the small carboxylic acids to form centrosymmetric dimers is retained, preventing the guest molecules from host–guest H-bonding. The host molecules are incorporated to endless columns through intermolecular H-bonds in direction of the [110] diagonal in **1a** and [010] in **1b**. In the channels of **1a**, resultant from the packing of the host columns, the above-mentioned dimers (constructed from acid and water molecules) are located. Guest positions in channels, however, are half-filled by dimers (s.o.f. is 0.5) remaining another half of sites for occupation by water molecules. Water molecules are disordered over five positions with s.o.f. from 0.12 to 0.33 leading to formation of the special “aqueous region”. All water molecules are located within one plane with accuracy of 0.029 Å and form a rhomb with diagonal of 4.55 and 2.29 Å.

In the **1b** conformation of the propionic acid molecules is different from that in conventional phase – dihedral angle between planes of the carboxylic group and carbohydrate chain is equal to 54.8 and 23.8° in the clathrate modifications obtained at room and high temperatures, respectively. Moreover, guest molecules are incorporated into dimers through an inversion center or twofold axis in conventional phase and **1b**, respectively. Dimers of propionic acid molecules are closely packed in channels of **1b**: interdimer

Table 3. Hydrogen bond parameters (Å, deg) for the investigated structures

1a	Symmetry	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (deg)
O2A–H2AD...O1W	$-1-x, 1-y, 1-z$	0.82	1.60	2.458(8)	177.0
O2–HO2...O1	$-1-x, 2-y, 1-z$	0.94(3)	1.71(3)	2.643(2)	174(2)
O4–HO4...O3	$-2-x, 1-y, 1-z$	0.94(3)	1.74(3)	2.678(2)	175(2)
1b					
O2A–H2AC...O1A	$-x, y, 1/2-z$	0.82	1.87	2.686(3)	177.0
O4–HO4...O3	$1/2-x, -1/2-y, 1-z$	0.90(4)	1.80(4)	2.700(3)	177(3)
O2–HO2...O1	$1/2-x, 1/2-y, 1-z$	1.10(4)	1.56(4)	2.641(2)	167(3)

Figure 2. Stereo packing of **1a** (a) and **1b** (b) viewed along the c axis. Hydrogen atoms are omitted for clarity.

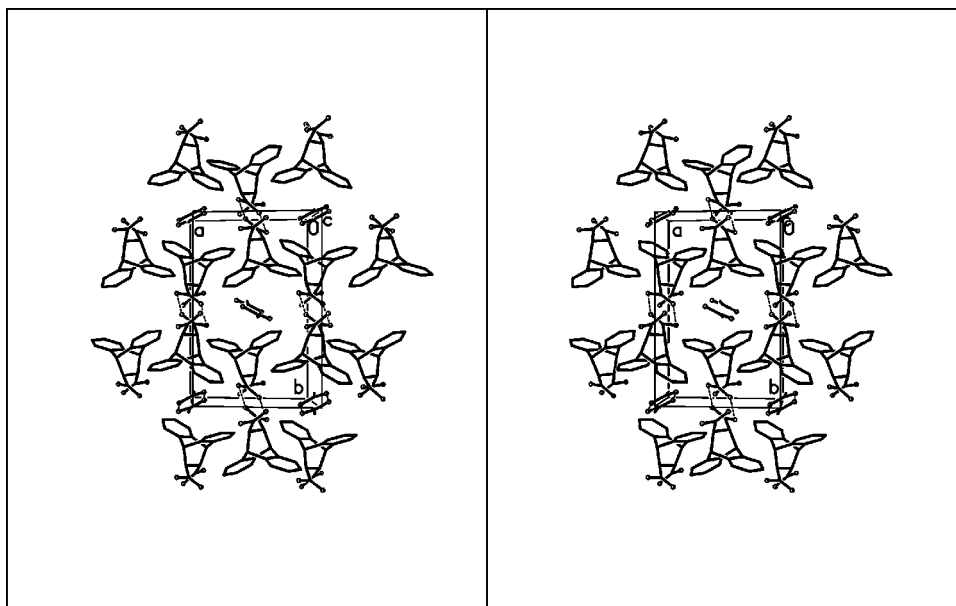


Figure 3. Stereo packing of the **1**-acetic acid clathrate (conventional 1:1 phase [8]).

C–C distances are decreased from 6.13 in the conventional pseudodimorph until 4.18 Å in the high temperature modification.

Conclusions

For the clathrates of trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid **1** with acetic or propionic acids a solvatodimorphism phenomenon is a characteristic feature. This shows another proof of the suggested connection between host versatility and pseudopolymorphism behavior. In order to obtain the new modifications of clathrates the crystallization temperature used for the conventional phases (room temperature) should be decreased in case of **1a** whereas for preparation of the novel solvatodimorph **1b** it should be increased. In all clathrate modifications talked about, dimers typical for carboxylic acids or dimers with participation of water molecules are observed. There are no direct host-guest H-bonds between host and guest acid groups in the structures, and therefore instead of coordinatoclathrates true clathrates are formed, underling the penchant of host compound **1** for homodimerization.

Acknowledgements

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