Polymorphism of crystalline host–guest complexes and unsolvated hosts. Part 6.[†] Pseudo-dimorphism of complexes between 1,1′-binaphthyl-2,2′-dicarboxylic acid and ethanol. X-Ray crystal structures of the β-form and of the unsolvated host compound

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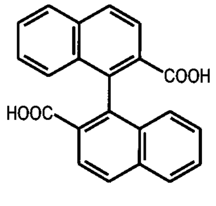
Depending on crystallization conditions, under ordinary conditions or from solution in ethanol at 60 °C, 1,1-binaphthyl-2,2′-dicarboxylic acid (BNDA) yields pseudo-dimorphous inclusion complexes with ethanol: α-form with 1:2 and β-form with 2:1 BNDA–ethanol host–guest ratio, respectively. At 100 °C crystallized from ethanol, unsolvated BNDA is obtained. All three structures are formed as a result of packing of infinite chains which are generated by different types of H-bonding. In the α-form, BNDA molecules are incorporated in 12-membered loops involving host–guest–host (−H···2G···H−) type H-bonds while in the β-form [triclinic ($P\bar{1}$), $a = 9.982(3)$, $b = 13.327(3)$, $c = 14.544(3)$ Å, $\alpha = 81.21(3)$, $\beta = 81.21(3)$, $\gamma = 88.76(3)$°, $Z = 4$, $R = 0.066$ for 3713 reflections] four BNDA molecules are associated by H-bonds typical for dimers of carboxylic acids and these tetramers are incorporated into chains *via* the α-form mode of interaction, establishing −4H···2G···4H···2G− type of association in the chains. In the unsolvated BNDA [orthorhombic (*Pccn*), $a = 24.348(5)$, $b = 11.165(2)$, $c = 12.868(3)$ Å, $Z = 8$, $R = 0.128$ for 849 observations] the structure is formed by chains of carboxylic acid dimers only.

Previous articles of the present series were mainly devoted to polymorphism of the inclusion complexes of gossypol and its dianiline derivative.[1,2] Gossypol, which is a derivative of 2,2′-binaphthyl, is a versatile crystalline host[3,4] and characterized by a unique polymorphism of the host–guest complexes as well as of the unsolvated host species.[5] 1,1′-Binaphthyl-2,2′-dicarboxylic acid (BNDA), a derivative of 1,1′-binaphthyl, is also a versatile crystalline host,[6] *i.e.* it readily forms coordinatoclathrates and conventional clathrates with different guest molecules.[7] As for gossypol we expect that BNDA would give differently structured host–guest complexes involving the same species. Therefore we have studied the behaviour of BNDA in forming polymorphous inclusion complexes under different thermodynamic conditions involving the same constituents. Ethanol was selected from possible guest solvents[6,7] to be the first test. Strictly speaking, this paper is devoted to BNDA complex formation with ethanol up to 100 °C keeping the other parameters fixed. Crystal structures of a new pseudo-dimorphous[‡] modification of a BNDA complex with ethanol (β-form, 2:1 host:guest ratio) and of the unsolvated BNDA host compound, obtained on recrystallization of BNDA at higher temperature (60 or 100 °C) are reported and discussed relative to the known α-form of the 1:2 BNDA–ethanol complex[10] obtained under ordinary crystallization conditions.



BNDA

Results and discussion

Under ambient conditions, BNDA crystallizes from ethanol to yield a 1:2 host–guest coordinatoclathrate (space group *C*2/*c*).[10] In the structure of this complex, host(H)–guest(G) type H-bonds close centrosymmetric 12-membered loops [Fig. 1(*a*)]. By formation of these loops, BNDA molecules are incorporated into infinite chains (−H···2G···H−) defining the structure of the α-form.

At 60 °C, BNDA crystallizes from an ethanol solution as a 2:1 host–guest complex (β-form), *i.e.* here inclusion of the guest component is decreased fourfold relative to the α-form complex. Unlike the α-form of the BNDA complex with ethanol having one molecule in the asymmetric part of the unit cell (host molecules lie on a twofold axis) the β-form of the complex has two host molecules of opposite chirality in the independent part of the unit cell.

The conformation of the two independent molecules I and II in pseudo-dimorph-β is slightly different. The dihedral angles between the naphthyl units (Fig. 2) are 88° and 94° in molecules I and II, respectively. The tilt of the carboxy group planes to the naphthyl moieties to which they belong is also different in molecules I and II. For molecule I the angles are 20° and 33° while for molecule II they are 23° and 3.6°. In the α-form complex the dihedral angle between the naphthyl units and the tilt of the carboxy group plane to the naphthyl moieties is 85° and 9°, respectively. The methylene group of the ethanol molecules is disordered in two positions with nearly equal occupation.

By means of a pair of centrosymmetric H-bonds [O(3)−H ···

[†] For Part 5 see ref. 2.

[‡] Polymorphism is generally defined as the existence of chemical substances in two (dimorphism) or more physical forms.[8] However, especially in pharmaceutical chemistry, solvates have also been designated as polymorphs, an obviously erroneous practice.[9] To avoid confusion, we use the term pseudo-polymorphism.

Table 1 Intermolecular H-bonds in the structure of (*a*) BNDA–ethanol (2:1) (β-form) and (*b*) unsolvated BNDA

	Distance/Å			Angle (°)
Atoms involved	O···O	O–H	H···O	∠ O–H···O
(*a*)				
O(1e)–H···O(4)	2.892(7)	0.76(5)	2.15(6)	169(5)
O(3)–H ···O(1e)^{i}	2.617(8)	0.86(6)	1.79(6)	166(6)
O(1′)–H···O(2)	2.667(5)	1.16(5)	1.51(5)	178(4)
O(1)–H···O(2′)	2.603(5)	1.09(5)	1.53(5)	170(4)
O(3′)–H···O(4′)^{ii}	2.634(5)	1.02(6)	1.62(6)	172(4)
(*b*)				
O(1)–H···O(4)^{iii}	2.60(1)	0.85	1.76	169
O(3)–H···O(2)^{iv}	2.67(1)	0.85	1.82	178

Symmetry codes: i, $1 - x, -y, -z$. ii, $-x, 1 - y, 1 - z$. iii, $1.5 - x, y, -0.5 - z$. iv, $1.5 - x, y, 0.5 + z$.

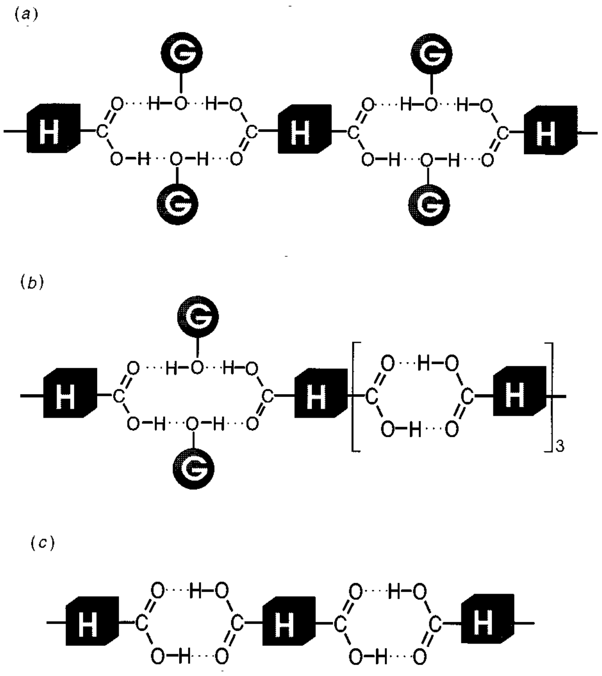


Fig. 1 Infinite hydrogen-bonded chains existing in (*a*) the α-, (*b*) the β-form host–guest crystalline complexes of BNDA (H) with ethanol (G), and (*c*) in the unsolvated BNDA crystal

O(1e) and O(1e)···O(4)] (Table 1) two guest molecules (ethanol) join the host molecules I and I′ together when a 12-membered H-bonded loop similar to the loop in the structure of the α-form [Fig. 1(*a*)] is formed. Molecules I using the second carboxy group are associated with host molecules II by a pair of non-centrosymmetric H-bonds [O(1)–H···O(2′) and O(1′)–H···O(2) (Table 1) when an eight-membered loop is formed [Fig. 1(*b*)]. Molecules II through other carboxy groups are H-bonded with centrosymmetrically related molecules II′. Such bonds closing eight-membered loops are typical for dimers of carboxylic acids.[11] Moreover, molecules II′ using the second carboxy groups form an eight-membered non-centrosymmetric loop during H-bonding with molecules I′. Only here, the BNDA molecules I′ using the second carboxylic functions interact with the ethanol molecules to yield the 12-membered loops. As a consequence, infinite chains parallel to [111] direction in which three eight-membered hydrogen-bonded loops alternate with one 12-membered hydrogen-bonded ring [Fig. 1(*b*)]. In other words, the host molecules are joined by means of three eight-membered loops to tetramers being associated by 12-membered loops to yield the infinite chains of (–4H···2G···4H···2G–) interaction type. Packing of such chains gives rise to the crystal structure of the β-form (Fig. 3). The described type of the supramolecular host–guest interaction is not new for BNDA coordinatoclathrates, *e.g.* being realized in the propanol complex of this host.[12]

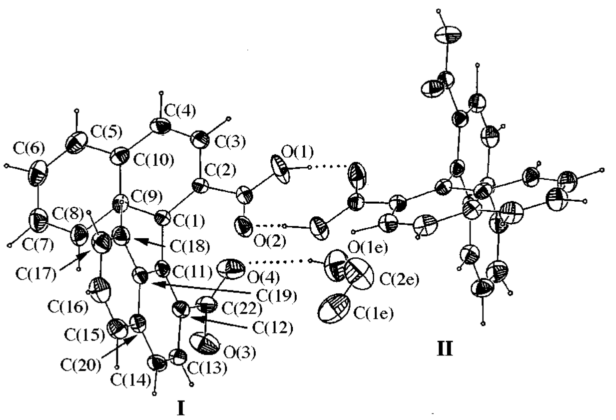


Fig. 2 View of the asymmetric unit of the β-form of the complex between BNDA and ethanol, and atom labelling scheme. For clarity only one of the two positions of the disordered methylene group of the ethanol molecule is shown. The hydrogen bonds are indicated as dotted lines.

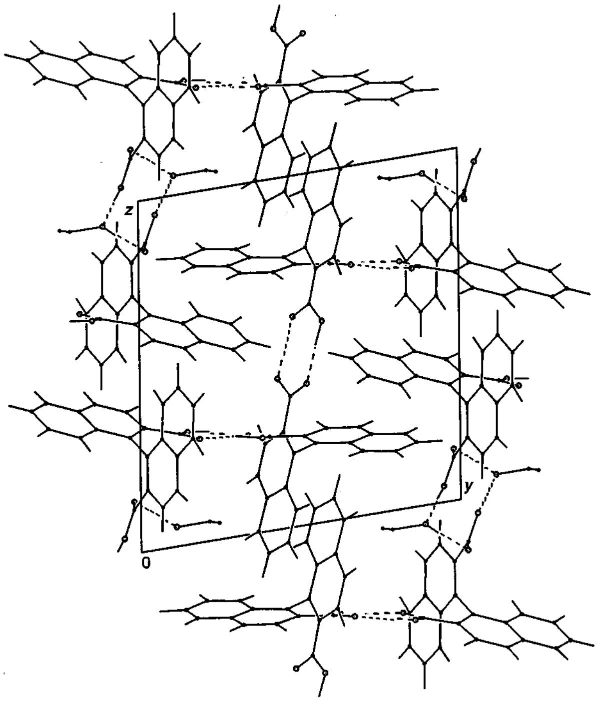


Fig. 3 Packing structure of the β-form of the complex between BNDA and ethanol. For clarity only one of the two positions of the disordered methylene group of the ethanol molecule is shown. The hydrogen bonds are indicated as dashed lines.

At 100 °C, BNDA crystallizes from solution in ethanol as the unsolvated form. In it the dihedral angles between the naphthyl units and the tilt of the carboxy group planes to appropriate naphthyl moieties are 76°, 28° and 26°, respectively. A pair of the unsymmetric H-bonds (Table 1), which may be caused by poor experimental data, associate the BNDA molecules *via* carboxylic group dimers to infinite chains [Fig. 1(*c*)] running in the direction of the *z*-axis. Packing of these chains forms the structure of the unsolvated BNDA host (Fig. 4).

Conclusions

By changing the crystallization conditions of BNDA from solution in ethanol three different crystal modifications are obtained. Under ordinary conditions, BNDA is crystallized as typical coordinatoclathrate (α-form) with host–guest ratio 1:2

Table 2 Crystal data for the 2:1 BNDA complex with ethanol and of unsolvated BNDA

	BNDA–ethanol (2:1) (β-form)	Unsolvated BNDA
Formula	$2C_{22}H_4O_4 \cdot C_2H_5OH$	$C_{22}H_4O_4$
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pccn*
a/Å	9.982(3)	24.348(5)
b/Å	13.327(3)	11.165(2)
c/Å	14.544(3)	12.868(3)
α/°	81.21(3)	90.00
β/°	81.21(3)	90.00
γ/°	88.76(3)	90.00
V/Å^3	1890	3498
D_c/g cm^{-3}	1.284	1.300
Z	4	8
Radiation	Cu-Kα	Cu-Kα
Adsorption coefficient/mm^{-1}	0.73	0.73
Crystal size/mm	0.08 × 0.1 × 0.2	0.06 × 0.05 × 0.1
2θmax/°	116	116
Unique data collected	5317	2234
No. of reflections with $I > 2\sigma(I)$	3724	853
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.076$, $wR2 = 0.231$	$R1 = 0.122$, $wR2 = 0.144$
R indices (all data)	$R1 = 0.112$, $wR2 = 0.261$	$R1 = 0.278$, $wR2 = 0.175$
Goodness of fit on F^2	1.21	1.26
Largest diff. peak/hole/e Å^{-3}	0.36/−0.32	0.16/−0.17
F(000)	764.00	1424

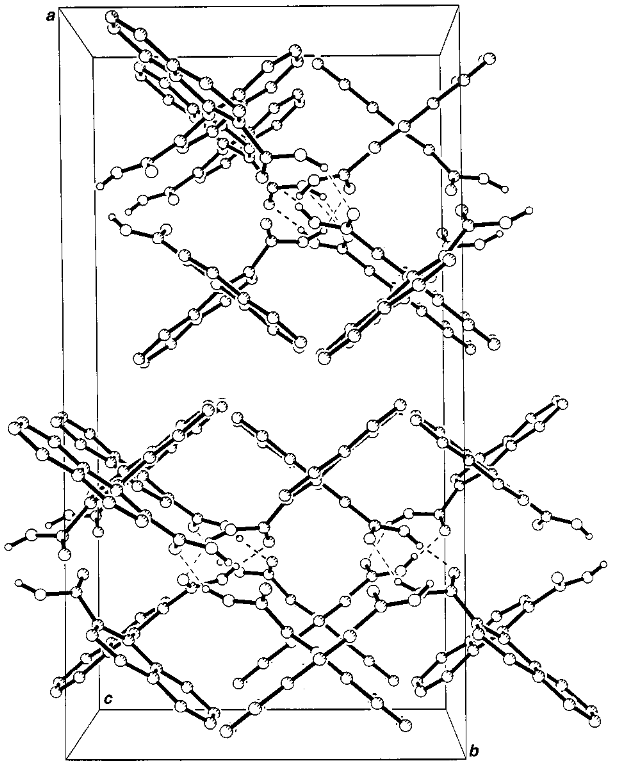


Fig. 4 Packing structure of unsolvated BNDA. The hydrogen bonds are indicated as dashed lines. For clarity non-relevant H atoms are omitted.

and $-\mathrm{H}\cdots2\mathrm{G}\cdots\mathrm{H}-$ type hydrogen bonds. At 60 °C the content of the guest component is decreased relative to the α-form complex (β-form) and the host–host interaction is dominated ($-4\mathrm{H}\cdots2\mathrm{G}\cdots4\mathrm{H}\cdots2\mathrm{G}-$). At 100 °C, crystals are free from guest molecules and in the crystal only host–host interaction is observed ($-\mathrm{H}\cdots\mathrm{H}-$). Thus, the β-form may be understood to be an intermediate between the structures of the conventional coordinatoclathrate of BNDA with ethanol and its unsolvated form.

In summary, BNDA and its crystalline complexes with ethanol show interesting behaviour of a temperature-dependent pseudo-polymorphism. These facts in general may be connected with the remarkable property of solid host–vapour guest inclusion formation observed for many clathrates[13] providing future access to understand the mechanism of the sorptive clathrate process[14] useful for chemical sensing.[15]

Experimental

Single crystals of the β-form of the BNDA complex with ethanol and of the unsolvated host were obtained by evaporation of the solvent from BNDA solution in ethanol in a thermostat at 60 and 100 °C, respectively. The crystals which formed were colourless and prism shaped. All crystallographic measurements were performed on a Syntex-P2, diffractometer. Lattice parameters were determined by a least-squares fitting of the setting angles of 15 reflections within the 2θ range 25–30°. Two standard reflections monitored every 100 intensity measurements during the data collection varied by up to 3%. No corrections for extinction or absorption were applied. Crystal data for the β-pseudo-dimorph of the BNDA complex with ethanol and of the unsolvated BNDA host as well as some details concerning data collection and structure solution are given in Table 2.

The structures were solved by direct methods using the program SHELXS-86.[16] All non-hydrogen atoms were located from the 'best' E-map. The structures were refined first with isotropic displacement parameters and then with anisotropic ones using SHELXL-93.[17] At this stage, all hydrogen atoms of the BNDA complex with ethanol were located on the difference map. Hydrogen atoms of the unsolvated BNDA were placed at the calculated positions because of the poor experimental data.

Supplementary data

The tables of final fractional atomic coordinates, bond lengths and angles involving all the non-hydrogen and hydrogen atoms, and anisotropic displacement parameters for the non-hydrogen atoms have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.§ Lists of the observed and calculated structure factors and the anisotropic displacement

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§ For details of the CCDC deposition scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/70.

parameters for the non-hydrogen atoms may be obtained from the authors (B. I.).

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