



Novel Two-Component Supramolecular Association Mode between Carboxylic Acids Realized in the Crystalline Complex of 1,1'-Binaphthyl-2,2'-dicarboxylic Acid and Formic Acid

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Abstract. A novel type of two-component H-bonded supramolecular associate (21-membered pseudo-macrocyclic rings) formed between mono- and dicarboxylic acids is found in the crystalline complex of 1,1'-binaphthyl-2,2'-dicarboxylic acid and formic acid. The crystal data are: (C₂₂H₁₄O₄)·(CH₂O₂), $a = 12.904(3)$ Å, $b = 8.829(2)$ Å, $c = 33.348(7)$ Å, $V = 3799(2)$ Å³, orthorhombic, *Pbca*, $Z = 8$, $R = 0.060$ ($F > 4\sigma$), 2649 reflections.

Key words: X-ray crystallography, H-bond, host–guest complex, supramolecular associate, catenated structure.

Supplementary data relevant to this article have been deposited with the British Library as Supplementary Publication 82251 (4 pages).

1. Introduction

Inherent self-complementary and recognition behavior are characteristic features of the carboxylic acid class of compounds, i.e., the carboxylic group of an acid molecule tends to be involved in interaction of its own kind [1]. As a result of this, monocarboxylic acids usually yield a finite hydrogen-bonded dimer or less frequently they form an infinite chain of catenated structure *via* hydrogen bonding [2]. Hence they follow the two basic types of supramolecular synthons [3] which are characteristic for monocarboxylic acids. Dicarboxylic acids may be incorporated in endless chains of carboxylic dimers [1–3] though in rare cases associates of

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other structure are possible dependent on the relative disposition of the carboxylic groups in a molecule [4].

Formation of infinite strands consisting of the dimers of host molecules is observed both for 1,1'-binaphthyl-2,2'-dicarboxylic acid (BNDA) [5] and trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid [6] both of which show remarkable inclusion ability [7]. In two-component host-guest crystals formed between these acids and simple monocarboxylic acids, as a result of the self-assembling, the dicarboxylic components (host) assemble to give an infinite chain of carboxylic dimers while the monocarboxylic acids (guest) yield single dimers, i.e., the acid species are separated and associate in homo-dimer fashion [8]. A hetero-dimer type association is also possible where the molecules of monocarboxylic acids are bound to dicarboxylic acid dimers at one or both sides [9–10]. However, up to the present, more complex structures involving these kinds of acids have not been observed.

Here we report a novel type of two-component supramolecular association involving BNDA and formic acid (1 : 1) that shows neither conventional dimer nor simple catenated structure.

2. Experimental

To prepare single crystals 50 mg BNDA [10] was dissolved in 3 mL formic acid and was kept at room temperature. Crystals suitable for X-ray structure analysis appeared after 20 days. A single crystal with dimension $0.1 \times 0.2 \times 0.5$ mm was used for all measurements on a Syntex-P2₁ diffractometer. The unit cell parameters were determined by a least-squares fitting of the setting angles of 15 reflections (2θ in the range 25–30°). Crystal data are as follows: $(C_{22}H_{14}O_4) \cdot (CH_2O_2)$, $a = 12.904(3)$ Å, $b = 8.829(2)$ Å, $c = 33.348(7)$ Å, $V = 3799(2)$ Å³, orthorhombic, $Pbca$, $Z = 8$, $F(000) = 1584$, $\mu = 0.71$ mm⁻¹, $\rho = 1.31$ g cm⁻³.

Intensities of 2649 reflections were measured with graphite monochromatized CuK_{α} -radiation. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using SHELXS-86 [11]. All nonhydrogen atoms of the structure were located from the E -map. Subsequent difference Fourier synthesis revealed all hydrogen atoms. The refinement of the structure was carried out by SHELXL-93 [12]. The F_c values were corrected for extinction by the function $k[1 + xF_c^2\lambda^2(\sin(2\theta))^{-1/4}]^{-1/4}$, where k is the overall scale factor (1.54) and x is an extinction parameter (0.0015). The weight of the reflections were calculated according to the formula $W = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = [f \text{ maximum of } (0 \text{ or } F_o^2) + (1 - f)F_c^2]$, $a = 0.0008$. The structure was refined to the final R -indices $R_1 = 0.060$ and $wR_2 = 0.058$ for 1413 observations with $F_o > 4\sigma(F_o)$ and $R_1 = 0.139$ and $wR_2 = 0.065$ for all data. In the final ΔF_{map} calculated after the last cycle of refinement the maximum and minimum peaks were 0.17 and -0.13 e Å⁻³, respectively. Final atomic coordinates of the nonhydrogen atoms are given in Table I.

Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the 1 : 1 host–guest complex between BNDA and formic acid. $U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U_{(\text{eq})}$
C(1)	5120(2)	−309(4)	3893(1)	48(1)
C(2)	5300(3)	503(4)	4240(1)	50(1)
C(3)	5897(3)	−144(5)	4555(1)	63(1)
C(4)	6292(3)	−1558(6)	4519(1)	71(1)
C(5)	6455(3)	−3939(6)	4143(1)	79(2)
C(6)	6241(4)	−4782(6)	3819(2)	90(2)
C(7)	5654(4)	−4200(6)	3505(1)	86(2)
C(8)	5289(3)	−2748(6)	3527(1)	71(1)
C(9)	5504(3)	−1811(5)	3856(1)	54(1)
C(10)	6098(3)	−2421(5)	4176(1)	60(1)
C(11)	4582(3)	364(4)	3536(1)	50(1)
C(12)	3535(3)	244(4)	3462(1)	56(1)
C(13)	3086(3)	940(5)	3119(1)	68(1)
C(14)	3670(4)	1733(5)	2861(1)	79(1)
C(15)	5360(4)	2753(5)	2656(1)	76(1)
C(16)	6384(4)	2904(6)	2719(1)	93(2)
C(17)	6854(3)	2186(6)	3042(1)	88(2)
C(18)	6284(3)	1359(5)	3305(1)	66(1)
C(19)	5206(3)	1182(4)	3258(1)	52(1)
C(20)	4748(3)	1883(5)	2921(1)	63(1)
C(21)	4848(3)	2027(5)	4298(1)	60(1)
C(22)	2854(3)	−598(5)	3743(1)	65(1)
O(1)	5063(2)	2609(3)	4646(1)	99(1)
O(2)	4323(2)	2683(3)	4054(1)	84(1)
O(3)	1871(2)	−494(4)	3645(1)	101(1)
O(4)	3139(2)	−1278(3)	4032(1)	99(1)
C(23)	3626(4)	5974(6)	4597(1)	81(2)
O(5)	2836(3)	6866(4)	4635(1)	118(1)
O(6)	3774(3)	4918(4)	4801(1)	106(1)

3. Results and Discussion

3.1. MOLECULAR STRUCTURE

The BNDA molecule conformation is defined by the dihedral angle between the naphthyl moieties, the coplanarity of the atoms of these moieties and the orientation and inclination of the carboxyl groups to the parent naphthyl fragments. The former two characteristics of the BNDA conformation are conserved practically unchanged in all previously studied crystals involving BNDA [7], i.e., the planes of the naphthyl fragments are nearly perpendicular to each other and their atoms are coplanar to a high degree. In our case the naphthyl moieties are tilted at an angle $85.3(0.1)^\circ$ to each other and the coplanarity of atoms is better than $0.029(4)$ Å.

The carboxyl group may be oriented in two ways relative to the neighboring non-bonded H(3) or H(13) atom. In the first orientation the hydroxyl group of the carboxyl moiety is directed towards H(3) while in the other orientation the carbonyl O atom of the carboxyl group is located near to the H(3) atom. The first conformation is found in most crystals involving BNDA while an alternative orientation is characteristic for the clathrates of BNDA with DMFA [13] and DMSO [14]. In the present complex of BNDA with formic acid the more commonly observed conformation is realized for both halves of the host molecule (Figure 1). The carboxyl groups are inclined at $5.3(0.5)^\circ$ and $4.4(0.6)^\circ$ relative to the naphthyl moieties C(1)—C(10) and C(11)—C(20), respectively.

The formic acid molecules have an unusual conformation in the complex. A hydrogen atom H(O5) of the hydroxyl group O(5)—H and carbonyl atom O(6) are expected to be located at one side of the C(23)—O(5) bond in the usual conformation (*cis*-oriented) whereas in the present structure an alternative position is found, i.e., O(6) and H(O5) atoms are located at different sides of the C(23)—O(5) bond (*anti*-orientation). This conformation is a result of the packing forces in the crystal since the guest molecule in a *cis*-conformation would not be able to be incorporated with host molecules to form associates found in the crystal structure.

Bond distances and angles of the BNDA molecules are in good agreement with those found in earlier studied structures [9, 10, 13–15].

3.2. SUPRAMOLECULAR STRUCTURE

In the 1:1 co-crystalline complex of BNDA with formic acid a novel type of supramolecular association is found (Figure 2). Using the H-bond O(3)—H...O(2) ($0.5 - x, -0.5 + y, z$) BNDA molecules are incorporated into an infinite zigzag mode catenated structure with the remaining hydroxyl and carbonyl parts of the —CO(1)O(2)H and —CO(3)O(4)H carboxyl groups respectively, not involved in hydrogen bondings. These groups of the two host molecules related to each other by translation along the *b* axis are H-bonded with complementary parts of the formic acid carboxyl group.

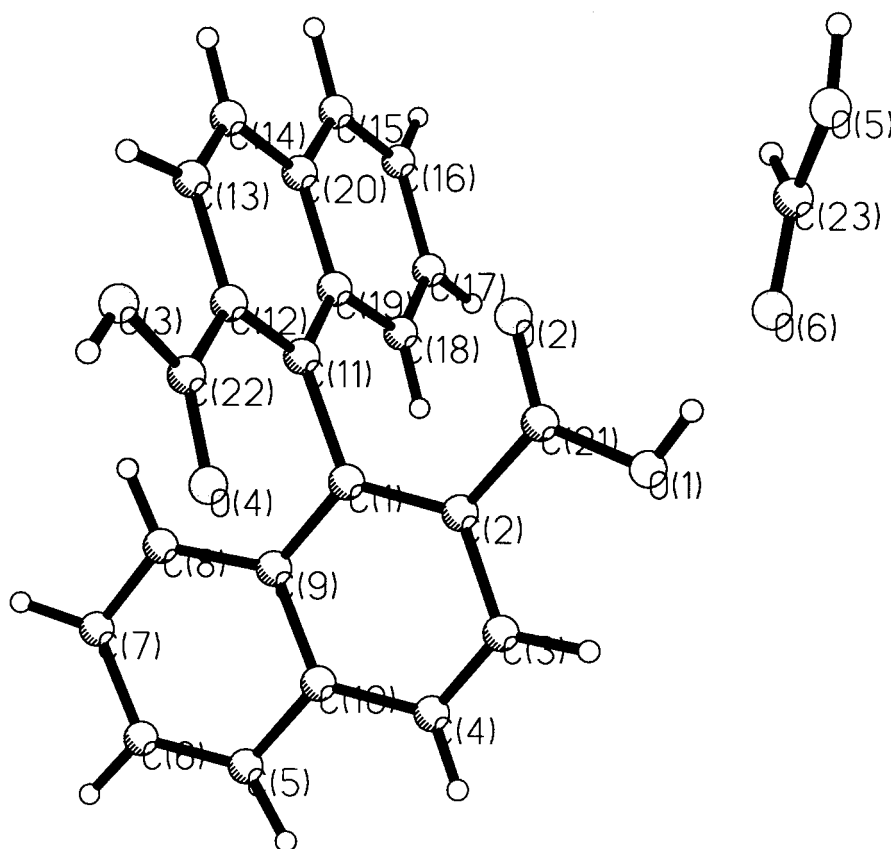


Figure 1. Conformation of the host and guest molecules and the atom labeling scheme.

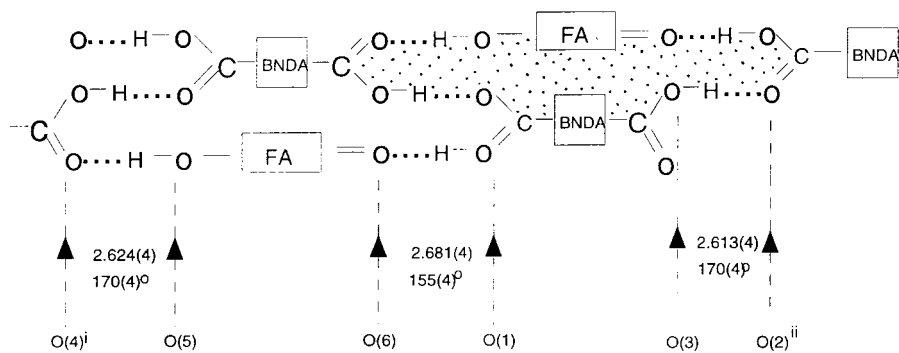


Figure 2. The scheme of supramolecular association between BNDA and formic acid (FA). The 21-membered pseudo-macrocyclic ring is dotted. The lengths and angles of intermolecular H-bonds are shown. The symmetry operations are: (i) $-x, 1+y, z$; (ii) $-0.5-x, -0.5+y, z$.

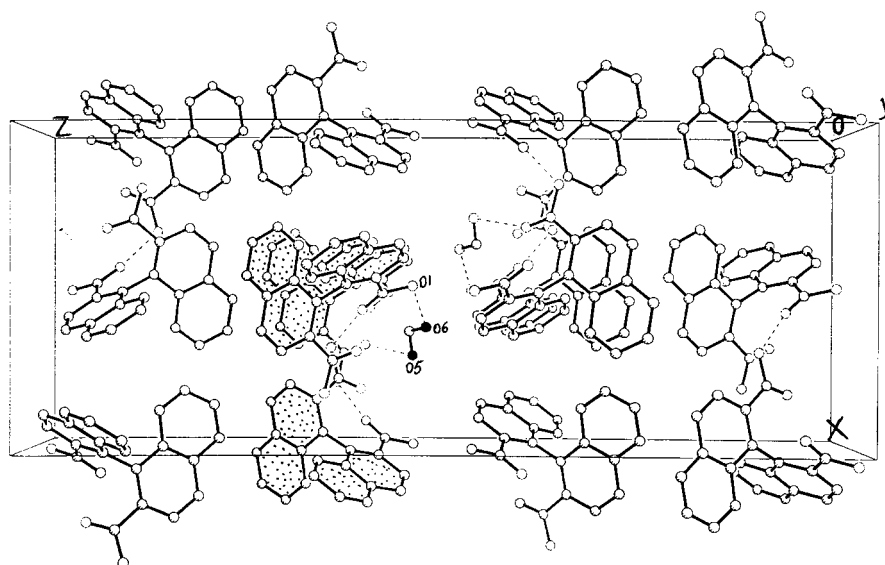


Figure 3. Packing of the supramolecular hydrogen bonded strands (one of them is marked) in the BNDA-formic acid complex directed parallel to the y -axis. The hydrogen bonds are specified as dotted lines.

Considering the bridges of BNDA framework atoms, 21-membered pseudo-macrocyclic rings are formed that border on each other by means of one hydrogen bond for each contact, i.e., the —OH and C=O parts of the carboxylic groups, respectively, show proton donor and proton acceptor abilities only in one bond. Moreover, the strands extending along the b -axis of the crystal, as far as the association of BNDA is concerned, are reminiscent of an endo-polar channel with the molecules of formic acid being accommodated (Figure 3). By size and shape the molecules of formic acid fit well to the channel. As a result the columns feature a surface with three hydrophobic sides typical of the aromatic groups and one hydrophilic side where the formic acid is bound. During packing of these columns hydrophobic sides contact with hydrophobic ones and hydrophilic parts are directed to such parts giving rise to a layer structure with alternating hydrophilic and hydrophobic contact surfaces.

The supramolecular association of carboxylic acids presented here is likely to be rather strong as suggested by the geometrical parameters of the H-bonds. Additional confirmation is seen in the fact that the crystallization of BNDA from solution in formic acid at higher temperature (60 °C) does not change the mode of this particular association pattern unlike other supramolecular structures of BNDA [5].

4. Conclusions

To the best of our knowledge this catenated type of interaction involving a system of dicarboxylic and monocarboxylic acids has not been reported in previous examples thus showing a new supramolecular association.

In view of the attention attached to the carboxylic function in host-guest chemistry both as a site for molecular recognition and docking of substrates[16], and considering the efficiency of the carboxylic groups based supramolecular synthon [3] in self-assembly, crystal-engineering and solid state design including materials properties [17], the structural motif described here is very important.

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