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## 1,2-Naphthalenedicarboxylic Acid: Structures of Channel Clathrates and an Unsolvated Crystalline Phase

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### Abstract

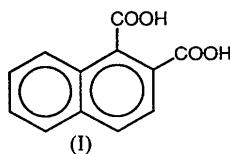
(1) 1,2-Naphthalenedicarboxylic acid–diethyl ether,  $C_{12}H_8O_4 \cdot nC_4H_{10}O$ ,  $M_r = 216.19$ , tetragonal,  $I4_1/a$ ,  $a = 22.086$  (3),  $c = 9.463$  (3) Å,  $V = 4616$  (2) Å<sup>3</sup>,  $Z = 16$ ,  $F(000) = 1792$  (without ether),  $F(000) = 1873$  (with 2.7 molecules of ether per unit cell),  $D_x = 1.24$  g cm<sup>-3</sup> (without ether),  $D_x = 1.31$  g cm<sup>-3</sup> (with 2.7 molecules of ether per unit cell),  $\lambda(Mo K\alpha) = 0.71073$  Å,  $T = 296$  K,  $\mu = 0.88$  cm<sup>-1</sup>,  $R = 0.052$  for 1130 unique reflections having  $I > 3\sigma_I$ . (2) 1,2-Naphthalenedicarboxylic acid,  $C_{12}H_8O_4$ ,  $M_r = 216.19$ , triclinic,  $P\bar{1}$ ,  $a = 9.027$  (1),  $b = 9.234$  (1),  $c = 7.256$  (1) Å,  $\alpha = 106.08$  (1),  $\beta = 90.79$  (1),  $\gamma = 111.80$  (1)°,  $V = 535.0$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 224$ ,  $D_x = 1.34$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $T = 296$  K,  $\mu = 0.95$  cm<sup>-1</sup>,  $R = 0.043$  for 1216 unique reflections having  $I > 3\sigma_I$ . (3) 1,2-Naphthalenedicarboxylic acid–dimethoxyethane,  $C_{12}H_8O_4 \cdot nC_4H_{10}O_2$ ,  $M_r = 216.19$ , tetragonal,  $I4_1/a$ ,  $a = 22.067$  (2),  $c = 9.465$  (2) Å,  $V = 4609$  (1) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.25$  g cm<sup>-3</sup> (without dimethoxyethane),  $D_x = 1.39$  g cm<sup>-3</sup> (with 4.4 molecules of dimethoxyethane per unit cell),  $\lambda(Mo K\alpha) = 0.71073$  Å,  $T = 296$  K. (4) 1,2-Naphthalenedicarboxylic acid–ethyl acetate,  $C_{12}H_8O_4 \cdot nC_4H_8O_2$ ,  $M_r = 216.19$ , tetragonal,  $I4_1/a$ ,  $a = 22.043$  (2),  $c = 9.489$  (2) Å,  $V = 4611$  (2) Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.25$  g cm<sup>-3</sup> (without ethyl acetate),  $D_x = 1.37$  g cm<sup>-3</sup> (with 4.1 molecules of ethyl acetate per unit cell),  $\lambda(Mo K\alpha) = 0.71073$  Å,  $T = 296$  K. Crystalline 1,2-naphthalenedicarboxylic acid has been found in tetragonal and triclinic phases at room temperature. The tetragonal phases are solvent clath-

rates, unit cells having been determined for crystals grown from three solvents: diethyl ether (1), dimethoxyethane (3), and ethyl acetate (4). These three unit cells are quite similar but have statistically different edge lengths. Proton NMR was employed to confirm the presence of solvent in each tetragonal phase and to determine the solvent content of these phases. Triclinic unit cells were determined for two samples, one crystallized from anisole (2), the other from water; these cells agreed with each other to within their combined e.s.d.'s. Data sets were collected from a tetragonal diethyl ether clathrate crystal and from a triclinic crystal grown from anisole. For the tetragonal phase, intermolecular hydrogen bonding by the carboxylic acid groups at the C(1) positions forms infinite helical chains about each fourfold screw axis, with H...O(acceptor) distances of 1.52 (6) Å. These chains are interconnected via cyclic dimer hydrogen bonding of the carboxylic acid groups at the C(2) positions, with H...O(acceptor) distances of 1.74 (6) Å. This framework results in open channels, parallel to the  $z$  direction, in which disordered solvent molecules are located. The electron density of the disordered diethyl ether molecules was treated by a model with uncorrelated C atoms with fixed displacement parameters but variable populations. In the triclinic phase of this acid, intermolecular hydrogen bonding occurs in cyclic dimer fashion for the carboxylic acid groups both at the C(1) and at the C(2) positions. For these hydrogen bonds the H...O(acceptor) distances are 1.53 (5) and 1.71 (4) Å, respectively. This arrangement of hydrogen bonds produces an infinite ribbon of molecules connected in a zigzag pattern.

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### Introduction

As part of a continuing series of investigations of hydrogen bonding in organic solids, investigations of the crystal structures of carboxylic acids of naphthalene and related compounds have become of interest to us. The structure of 1,8-naphthalenedicarboxylic acid has been reported (Fitzgerald, Gallucci & Gerkin, 1991) and was found to have nearly complete disorder in its hydrogen bonds. An investigation of crystalline 1,2-naphthalenedicarboxylic acid, (I), is reported here which shows hydrogen bonding different from that of the 1,8-diacid as well as the presence of two quite different phases of the 1,2-diacid occurring at room temperature.



### Experimental

1,2-Naphthalenedicarboxylic anhydride from Chem-syn Science Lab was suspended in water, reacted with aqueous NaOH, boiled and combined with additional NaOH until the pH remained above 10. This solution was cooled, filtered, and while in an ice bath, reacted with 1M HCl. The resulting precipitate was filtered and dried in an evacuated desiccator containing KOH pellets. An IR spectrum of the dried precipitate confirmed it to be 1,2-naphthalenedicarboxylic acid.

#### *Tetragonal 1,2-naphthalenedicarboxylic acid–diethyl ether*

1,2-Naphthalenedicarboxylic acid prepared as described above was dissolved in anhydrous diethyl ether. The solution was allowed to evaporate at room temperature over a period of 7 days, producing square-columnar crystals with multi-faceted caps. The experimental sample was a clear multi-faceted chunk having approximate principal dimensions  $0.27 \times 0.27 \times 0.38$  mm. It was mounted with epoxy cement on a glass fiber and X-ray data were collected at room temperature on a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo  $K\alpha$  radiation.

Unit-cell parameters were obtained from a symmetry-restricted least-squares fit of the setting angles for 25 centered reflections with  $21 < 2\theta < 30^\circ$ . Intensity data were measured for 7054 reflections (exclusive of standards) with  $+h$ ,  $+k$ ,  $\pm l$  indices ( $h_{\max} = 31$ ;  $k_{\max} = 31$ ;  $-13 \leq l \leq 13$ ) and  $2\theta$  values in the range  $4 \leq 2\theta \leq 60^\circ$ . The  $\omega$ - $2\theta$  scan technique was employed with scan widths  $(1.15 + 0.35 \tan \theta)^\circ$  in

$\omega$ , and background/scan time-ratio of 0.5. A variance was assigned to each reflection by means of the formula  $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$  in which  $\sigma_{cs}$  is based on counting statistics and  $I$  is the integrated intensity. Six standard reflections (420, 222, 341, 235, 673, 495) were measured after every 150 reflections; they showed, on average, a maximum non-systematic relative intensity variation of  $\pm 3.7\%$ . No decay or absorption correction was applied. The data were corrected for Lorentz and polarization effects. Averaging equivalent reflections gave 3558 independent reflections, with  $R_{\text{int}} = 0.082$ ; weak high-angle reflections contributed significantly to  $R_{\text{int}}$  (up to  $40^\circ$  in  $2\theta$ ,  $R_{\text{int}} = 0.028$ ).

The observed reflection-limiting conditions ( $hkl$ :  $h + k + l = 2n$ ;  $hk0$ :  $h(k) = 2n$ ;  $00l$ :  $l = 4n$ ) uniquely determined the space group as  $I4_1/a$  (No. 88). The direct methods MITHRIL program (Gilmore, 1984) in TEXSAN (Molecular Structure Corporation, 1989) was used to generate an  $E$  map from which the initial positions of the C and O atoms of 1,2-naphthalenedicarboxylic acid were identified. Full-matrix least-squares refinement was performed to minimize the function  $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$  in which  $\sigma_F = \sigma_I/2FLp$ . Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for C and O; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965). After refinement of anisotropic displacement parameters for the C and O atoms of the diacid, a Fourier difference map indicated the positions of the H atoms and unaccounted-for electron density in regions parallel to  $c$  and through the  $\bar{4}$  sites. The H atoms attached to the naphthalene ring were assigned canonical benzene hydrogen geometry (C—H distance =  $0.95 \text{ \AA}$ ;  $B = 1.2 \times B_{\text{eq}}$  of the C atom to which it is attached) and least-squares refinement was performed to convergence, giving  $R = 0.093$ ,  $wR = 0.152$  and  $S = 4.38$  for data having  $I > 3\sigma_I$ . At this stage, a Fourier difference map of a region parallel to  $c$  and through a  $\bar{4}$  site (Fig. 1) showed continuous electron density in a channel approximately  $3.5 \text{ \AA}$  in diameter.

On the basis of these results, proton NMR spectra were collected on 1,2-naphthalenedicarboxylic acid samples before and after recrystallization from diethyl ether. As summarized in Table 4, they revealed the presence of diethyl ether in the recrystallized 1,2-diacid, but not in the starting material. The number of ether molecules per unit cell calculated from the NMR data was 2.7. (The maximum number of ether molecules per unit cell consistent with close packing along the channel is 4.4.) With 2.7 diethyl ether molecules per unit cell the calculated density,  $1.31 \text{ g cm}^{-3}$ , is in better agreement with the measured density,  $1.35 \text{ g cm}^{-3}$  (determined by flotation in aqueous KI), than is the value calculated assuming

that only acid is present,  $1.24 \text{ g cm}^{-3}$ . These data make clear that the electron density unaccounted for in the difference Fourier map arises from diethyl ether solvent molecules disordered along channels parallel to  $c$  and containing  $\bar{4}$  sites. The disorder is apparently somewhat random, since detailed modeling was not possible. However, the positions of the acid hydrogen atoms could not be determined without accounting, at least roughly, for the electron density of the incorporated solvent molecules. Consequently, C atoms were assigned independently within the channels to positions indicated by the Fourier peak interpretation program, and their coordinates and populations were refined by a procedure similar to that described by Boge, Mockler & Sinn (1977) but with fixed displacement parameters. This procedure permitted refinement of the acid hydrogens, and the final refinement for data having  $I > 3\sigma_I$  converged as follows: 1130 observations; 179 variables (including disordered solvent);  $R = 0.052$ ;  $wR = 0.059$ ;  $w = \sigma_F^{-2}$ ;  $S = 1.99$ ;  $(\Delta/\sigma)_{\max} < 0.10$ . While the present modeling of the solvent is oversimplified, the refined 'solvent atom' populations give a value of 2.6 ether molecules per unit cell, a value consistent both with the NMR results and the measured sample density.

Maximum and minimum peaks on the final electron density difference map had values  $+0.28$  and

$-0.30 \text{ e } \text{Å}^{-3}$ , respectively. The maximum peak was located near  $(0.97, 0.27, 0.75)$  and the minimum peak was located near  $(1.01, 0.20, 0.40)$ , both within approximately  $2.0 \text{ Å}$  of one of the channels along which the disordered solvent lies. Two reflections  $(220, 400)$  had  $(\Delta_F/\sigma_F) > 10$ ; these reflections had large contributions from the disordered solvent regions. [For the final refinement cycle for 1748 independent observations having  $I > \sigma_I$ :  $R = 0.088$ ;  $wR = 0.067$ ;  $S = 1.76$ ;  $(\Delta/\sigma)_{\max} < 0.10$ . Similarly, the final refinement cycle for 2594 independent observations having  $I > 0$ :  $R = 0.130$ ;  $wR = 0.070$ ;  $S = 1.50$ ;  $(\Delta/\sigma)_{\max} < 0.15$ . These latter results are for comparison purposes only.]

Final atomic coordinates, equivalent isotropic and isotropic displacement parameters and their e.s.d.'s for the diacid molecule are given in Table 1.\* The final parameters for the disordered solvent have insufficient physical significance to be included.

Following this analysis of the structure obtained from ether solvent, it appeared that crystals with empty channels might be produced from solvents with molecules too large to fit the channels. On this premise anisole, methyl phenyl ether, was used as a solvent for crystallization of the 1,2-diacid. This, however, resulted in a second form of crystalline 1,2-naphthalenedicarboxylic acid as described below.

#### *Triclinic 1,2-naphthalenedicarboxylic acid*

Upon slow evaporation at 313 K, an anisole solution of 1,2-naphthalenedicarboxylic acid produced plate-like crystals. The experimental sample was a plate having approximate principal dimensions  $0.15 \times 0.23 \times 0.38 \text{ mm}$ . This was mounted with epoxy cement on a glass fiber and X-ray data were collected at room temperature on a Rigaku AFC5S diffractometer utilizing graphite-monochromated  $\text{Mo K}\alpha$  radiation.

Unit-cell parameters were obtained from a least-squares fit of the setting angles for 25 reflections with  $22 < 2\theta < 30^\circ$ . Data collection was performed as described in the preceding section with the following changes of detail: 3300 reflections (exclusive of standards) with  $+h, \pm k, \pm l$  indices ( $h_{\max} = 12$ ;  $-12 \leq k \leq 12$ ;  $-10 \leq l \leq 10$ ); scan widths  $(1.45 + 0.35 \tan \theta)^\circ$  in  $\omega$ ; six standard reflections:  $11\bar{1}, 0\bar{1}1, 220, 222, 6\bar{2}\bar{2}, 5\bar{3}3$ ; average maximum non-systematic relative intensity variation of  $\pm 2.7\%$ . No decay or absorption correction was applied. The data were

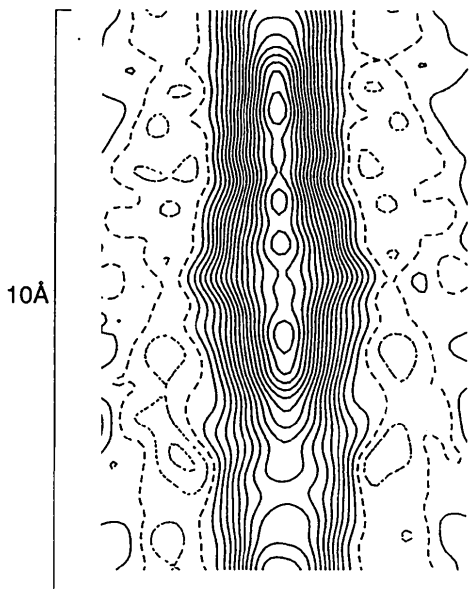


Fig. 1. A section showing residual electron density along an axis parallel to  $c$  and through a  $\bar{4}$  site, which demonstrates continuous residual electron density in this region. Solid lines indicate electron density in steps of  $0.07 \text{ e } \text{Å}^{-3}$ ; dashed lines indicate regions of negative electron density. The center of the map is at  $(1.0, 0.25, 0.50)$  with the long dimension nearly coincident with the  $z$  direction of the crystal.

\* Lists of structure factors, coordinates and isotropic displacement factors for ring hydrogens, anisotropic displacement parameters, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54731 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0547]

Table 1. Final positional parameters and equivalent isotropic and isotropic displacement parameters,  $B_{eq}/B$  ( $\text{\AA}^2$ ), for tetragonal 1,2-naphthalenedicarboxylic acid-diethyl ether, with their e.s.d.'s

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}/B$
O(1)	0.8408 (1)	0.0936 (1)	-0.0524 (3)	3.1 (1)
O(2)	0.7500 (1)	0.0736 (1)	0.0351 (3)	3.2 (1)
O(3)	0.8015 (2)	0.2830 (1)	-0.1182 (4)	5.1 (2)
O(4)	0.7563 (2)	0.1936 (1)	-0.1385 (3)	4.2 (2)
C(1)	0.8065 (2)	0.1584 (2)	0.1257 (4)	2.5 (2)
C(2)	0.8073 (2)	0.2167 (2)	0.0748 (4)	2.9 (2)
C(3)	0.8228 (2)	0.2651 (2)	0.1654 (5)	3.6 (2)
C(4)	0.8352 (2)	0.2545 (2)	0.3034 (5)	3.9 (2)
C(5)	0.8448 (2)	0.1842 (2)	0.5059 (5)	4.4 (3)
C(6)	0.8418 (2)	0.1271 (3)	0.5584 (5)	4.7 (3)
C(7)	0.8276 (2)	0.0784 (2)	0.4708 (5)	4.1 (2)
C(8)	0.8170 (2)	0.0872 (2)	0.3300 (4)	3.2 (2)
C(9)	0.8188 (2)	0.1462 (2)	0.2717 (4)	2.6 (2)
C(10)	0.8334 (2)	0.1958 (2)	0.3607 (4)	3.2 (2)
C(11)	0.7947 (2)	0.1053 (2)	0.0311 (4)	2.4 (2)
C(12)	0.7869 (2)	0.2294 (2)	-0.0702 (4)	3.1 (2)
H(1)	0.831 (2)	0.052 (3)	-0.111 (5)	8 (2)†
H(2)	0.779 (3)	0.291 (3)	-0.202 (6)	8 (2)†

† Refined isotropically.

corrected for Lorentz and polarization effects. Averaging equivalent reflections gave 3115 independent reflections with  $R_{int} = 0.018$ .

The crystal system was found to be triclinic, thus allowing two space groups:  $P1$  and  $P\bar{1}$ . Initial preference was given to the centrosymmetric alternative  $P\bar{1}$  (No. 2) and since refinement proceeded well it was adopted.

The direct methods *MITHRIL* program (Gilmore, 1984) in the *TEXSAN* package (Molecular Structure Corporation, 1989) was used to generate an *E* map from which the initial positions of the C atoms were identified. Fourier difference methods were used to locate the O atoms and the H atoms. Least-squares refinement proceeded as described above for the diethyl ether clathrate. Ring hydrogens were assigned canonical benzene hydrogen geometry as described above.

The results of the final refinement cycle were: 1216 observations having  $I > 3\sigma_I$ ; 153 variables;  $R = 0.043$ ;  $wR = 0.045$ ;  $w = \sigma_F^{-2}$ ;  $S = 1.46$ ;  $(\Delta/\sigma)_{max} < 0.01$ . Maximum and minimum peaks on the final electron density difference map had values  $+0.17$  and  $-0.22 e \text{\AA}^{-3}$ , respectively. The maximum peak was located midway between C(1) and C(9); the minimum peak was located approximately  $1.4 \text{\AA}$  from C(9). [For the final refinement cycle for 1479 data having  $I > \sigma_I$ :  $R = 0.058$ ;  $wR = 0.050$ ;  $S = 1.48$ ;  $(\Delta/\sigma)_{max} < 0.01$ . Similarly, for the final refinement cycle for 2371 independent reflections having  $I > 0$ :  $R = 0.111$ ;  $wR = 0.056$ ;  $S = 1.27$ ;  $(\Delta/\sigma)_{max} < 0.02$ . These latter results are for comparison purposes only.]

The structure solution for this triclinic phase of 1,2-naphthalenedicarboxylic acid proceeded in a

Table 2. Final positional parameters and equivalent isotropic and isotropic displacement parameters,  $B_{eq}/B$  ( $\text{\AA}^2$ ), for triclinic 1,2-naphthalenedicarboxylic acid, with their e.s.d.'s

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}/B$
O(1)	0.1000 (2)	0.1479 (2)	0.7228 (3)	4.3 (1)
O(2)	0.1759 (2)	0.0964 (2)	0.4273 (3)	4.2 (1)
O(3)	0.2008 (3)	0.6466 (3)	0.6385 (3)	5.0 (1)
O(4)	0.0753 (2)	0.3759 (2)	0.5275 (3)	4.8 (1)
C(1)	0.3442 (3)	0.3374 (3)	0.6723 (3)	3.0 (1)
C(2)	0.3433 (3)	0.4877 (3)	0.6824 (3)	3.1 (1)
C(3)	0.4855 (3)	0.6308 (3)	0.7548 (4)	3.8 (1)
C(4)	0.6233 (3)	0.6186 (4)	0.8129 (4)	4.1 (1)
C(5)	0.7730 (3)	0.4523 (4)	0.8591 (4)	4.7 (1)
C(6)	0.7754 (4)	0.3045 (5)	0.8451 (5)	5.8 (1)
C(7)	0.6356 (4)	0.1620 (4)	0.7770 (5)	5.4 (1)
C(8)	0.4948 (3)	0.1698 (4)	0.7214 (4)	4.3 (1)
C(9)	0.4872 (3)	0.3221 (3)	0.7308 (3)	3.3 (1)
C(10)	0.6290 (3)	0.4669 (4)	0.8018 (4)	3.5 (1)
C(11)	0.1955 (3)	0.1831 (3)	0.5977 (4)	3.2 (1)
C(12)	0.1939 (3)	0.4979 (4)	0.6104 (4)	3.5 (1)
H(1)	-0.013 (6)	0.043 (6)	0.66 (1)	13 (1)†
H(2)	0.103 (4)	0.638 (4)	0.577 (5)	8 (1)†

† Refined isotropically.

straightforward manner, with no unaccounted-for electron density. Final atomic coordinates, equivalent isotropic and isotropic displacement parameters and their e.s.d.'s are given in Table 2. The molecule is shown in Fig. 2. In both the tetragonal and triclinic structures, the asymmetric unit is an entire molecule, so there are no symmetry constraints among any intramolecular distances or angles.

Following analysis of the two preceding crystals, selected additional solvents were used for crystal growths of 1,2-naphthalenedicarboxylic acid. Two particular goals of this experimentation were: (a) to produce the tetragonal phase solvent-free and (b) to

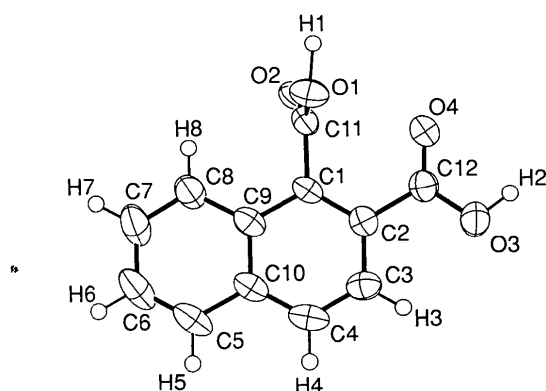


Fig. 2. A view of the 1,2-naphthalenedicarboxylic acid molecule, as it occurs in the triclinic phase, drawn using *ORTEP*II (Johnson, 1976). The molecule as it occurs in the tetragonal phase is not shown here since it is indistinguishable except for the dihedral angles between the carboxyl groups and naphthalene ring. Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

Table 3. Unit-cell data, solvent abundance and densities for five crystalline samples of 1,2-naphthalenedicarboxylic acid

Crystallization occurred at room temperature except in the case of anisole solvent, for which  $T = 313$  K. The tetragonal cell was symmetry constrained

Solvent	Crystal system	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	No. of solvent molecules per unit cell*	Density ( $\text{g cm}^{-3}$ )	
									Calc.†	Obs.‡
Diethyl ether	Tetragonal	22.086 (3)	22.086	9.463 (3)	90	90	90	2.7	1.31	1.35
Dimethoxyethane	Tetragonal	22.067 (2)	22.067	9.465 (2)	90	90	90	4.4	1.39	1.41
Ethyl acetate	Tetragonal	22.043 (2)	22.043	9.489 (2)	90	90	90	4.1	1.37	1.41
Anisole	Triclinic	9.027 (1)	9.234 (1)	7.256 (1)	106.08 (1)	90.79 (1)	111.80 (1)	–	1.34	1.36
Water	Triclinic	9.028 (3)	9.238 (4)	7.254 (3)	106.06 (3)	90.85 (3)	111.79 (3)	–	1.34	1.34

\* Determined by proton NMR; see Table 4 for details.

† For the tetragonal cells, the solvent content has been included in the calculated density.

‡ By flotation in aqueous KI; estimated uncertainty,  $\pm 0.02 \text{ g cm}^{-3}$ .

Table 4.  $^1\text{H}$  NMR data for tetragonal-phase solvent clathrates of 1,2-naphthalenedicarboxylic acid with estimated uncertainties given in parentheses

NMR spectra obtained on Bruker AM-250 spectrometer at 250 MHz; samples prepared in DMSO- $d_6$ .

Solvent	Aryl-H $\delta\text{H}$	Integrated intensity	Protons used for solvent peak	$\delta\text{H}$	Integrated intensity	Derived No. of solvent molecules per unit cell
Diethyl ether	7.64–8.08	110 (5)	$\text{H}_3\text{CCH}_2\text{OCH}_2\text{CH}_3$	1.05–1.10	19 (1)	2.7 (2)
Dimethoxyethane	7.66–8.08	297 (15)	$\text{H}_3\text{COCH}_2\text{CH}_2\text{OCH}_3$	3.22	82 (4)	4.4 (3)
Ethyl acetate	7.65–8.07	258 (13)	$\text{H}_3\text{CCOOCH}_2\text{CH}_3$	1.97	33 (2)	4.1 (2)
Diethyl ether; 51 days in vacuum	7.63–8.07	328 (16)	$\text{H}_3\text{CCH}_2\text{OCH}_2\text{CH}_3$	1.05–1.11	51 (3)	2.5 (2)

produce an ordered-solvent tetragonal clathrate by choosing a solvent whose molecular length is commensurate with the channel length per unit cell. Although neither of these goals has yet been achieved, additional crystals were produced. Unit-cell parameters were determined for these additional samples and these data are summarized in Table 3 with other selected experimental results. Single-crystal specimens were used in each case, and the unit-cell determinations were carried out in the same manner as described above. The presence of solvent in each tetragonal case was determined by proton NMR data, which were also used to estimate the relative amount of solvent, as listed in Table 4. Densities were measured by flotation in aqueous KI solutions; for the tetragonal cases, these measurements were more difficult than usual (presumably due to uptake of solvent during the measurements), hence the estimated uncertainties are larger than for the triclinic crystals.

### Discussion

Each of the tetragonal-phase channel clathrates of 1,2-naphthalenedicarboxylic acid observed in this research, as described in Table 3, involved a solvent containing one or two O atoms and having its longest dimension considerably greater than its transverse dimensions. The three tetragonal unit cells are of

quite similar, but not identical, dimensions, the  $a$  axis decreasing from the diethyl ether to the dimethoxyethane to the ethyl acetate clathrate by approximately  $0.02 \text{ \AA}$  per step, a value six times as large as the greatest  $a$ -axis e.s.d.; the  $c$ -axis lengths are essentially equal for two of these cells, while for the third it is  $0.025 \text{ \AA}$  longer. The two triclinic cells observed for the acid crystallized from anisole and from water are of respectively equal dimensions, within their combined e.s.d.'s. The triclinic forms resulted from these crystallizations presumably because anisole (methyl phenyl ether) is too large to be accommodated within the tetragonal-phase channels and because water is incompatible with the channel in some manner yet to be understood. All relevant evidence to date suggests that without appropriate solvent molecules to occupy the tetragonal-phase channels, the triclinic phase is preferred. Thus, for example, it was found that holding crystals of the diethyl ether clathrate in a vacuum of approximately  $10^{-3}$  Torr for 51 days did not appreciably change the number of ether molecules per unit cell, as determined by proton NMR (see Table 4); this result suggests that the ether molecules are not very loosely bound in the clathrate structure and that indeed this interaction may be critical to the existence of the tetragonal structure.

Complete structures for the diacid were determined for the tetragonal diethyl ether clathrate

Table 5. Bond lengths (Å) and angles (°) for a tetragonal phase (with diethyl ether) and the triclinic phase of 1,2-naphthalenedicarboxylic acid, with their e.s.d.'s

	Tetragonal phase	Triclinic phase		Tetragonal phase	Triclinic phase
<b>Naphthalene core</b>					
C(1)—C(2)	1.374 (5)	1.372 (3)	C(9)—C(1)—C(2)	120.8 (4)	120.9 (2)
C(2)—C(3)	1.412 (6)	1.416 (3)	C(1)—C(2)—C(3)	119.9 (4)	120.1 (2)
C(3)—C(4)	1.355 (6)	1.362 (4)	C(2)—C(3)—C(4)	120.3 (4)	119.8 (3)
C(4)—C(10)	1.407 (6)	1.401 (4)	C(3)—C(4)—C(10)	121.7 (4)	121.6 (3)
C(5)—C(10)	1.420 (6)	1.424 (4)	C(4)—C(10)—C(9)	119.3 (4)	119.4 (2)
C(5)—C(6)	1.358 (7)	1.349 (5)	C(10)—C(9)—C(1)	118.1 (4)	118.2 (2)
C(6)—C(7)	1.393 (7)	1.399 (5)	C(5)—C(10)—C(9)	118.5 (4)	118.5 (3)
C(7)—C(8)	1.367 (5)	1.362 (4)	C(10)—C(5)—C(6)	120.8 (4)	120.9 (3)
C(8)—C(9)	1.416 (5)	1.416 (4)	C(5)—C(6)—C(7)	120.7 (4)	120.7 (3)
C(9)—C(10)	1.418 (6)	1.421 (3)	C(6)—C(7)—C(8)	120.6 (4)	120.6 (3)
C(1)—C(9)	1.434 (5)	1.422 (3)	C(7)—C(8)—C(9)	120.4 (4)	120.6 (3)
			C(8)—C(9)—C(10)	119.0 (4)	118.7 (2)
Mean C—C	1.396 (26)	1.395 (27)	Mean interior	120.0 (10)	120.0 (10)
			C(4)—C(10)—C(5)	122.2 (4)	122.1 (3)
			C(8)—C(9)—C(1)	122.9 (4)	123.1 (2)
			C(9)—C(1)—C(11)	117.5 (3)	117.5 (2)
			C(2)—C(1)—C(11)	121.7 (4)	121.6 (2)
			C(1)—C(2)—C(12)	120.1 (4)	119.4 (2)
			C(3)—C(2)—C(12)	119.8 (4)	120.5 (2)
<b>Carboxyl groups</b>					
C(1)—C(11)	1.499 (5)	1.503 (3)	O(1)—C(11)—O(2)	122.4 (4)	124.8 (3)
C(2)—C(12)	1.471 (5)	1.484 (3)	O(1)—C(11)—C(1)	112.2 (4)	115.5 (2)
C(11)—O(1)	1.316 (4)	1.284 (3)	O(2)—C(11)—C(1)	125.2 (4)	119.6 (2)
C(11)—O(2)	1.210 (4)	1.242 (3)	O(3)—C(12)—O(4)	122.5 (4)	123.0 (3)
C(12)—O(3)	1.310 (5)	1.309 (3)	O(3)—C(12)—C(2)	114.9 (4)	115.0 (3)
C(12)—O(4)	1.224 (5)	1.220 (3)	O(4)—C(12)—C(2)	122.6 (4)	122.0 (3)
O(1)—H(1)	1.09 (6)	1.10 (5)	C(11)—O(1)—H(1)	108 (3)	113 (2)
O(3)—H(2)	0.95 (5)	0.95 (4)	C(12)—O(3)—H(2)	110 (3)	108 (2)

and for the triclinic form obtained from anisole; these results form the basis of the following discussion. Fig. 2 shows an *ORTEP* (Johnson, 1976) drawing, with our numbering, of the 1,2-naphthalenedicarboxylic acid molecule determined from the triclinic data. A similar drawing based on the tetragonal data is virtually indistinguishable, except for the dihedral angles of the carboxyl groups, and was therefore omitted. Selected bond lengths and angles from these two data sets are listed in Table 5. Comparison of these results demonstrates that within the naphthalene core all bond lengths and angles agree within their combined e.s.d.'s except for the C(1)—C(9) bond lengths. The C atoms of the naphthalene core have a mean deviation from the best-fit least-squares plane describing these atoms of 0.013 (7) Å (tetragonal phase) or 0.008 (5) Å (triclinic phase); these values are considerably smaller than the corresponding value for the C atoms of 1,8-naphthalenedicarboxylic acid: 0.055 (30) Å (Fitzgerald, Gallucci & Gerkin, 1991). This greater degree of planarity arises from the smaller steric interaction of the carboxylic acid groups in the present case.

The largest bond-length and bond-angle differences for these two phases of the 1,2-diacid are found in the carboxylic acid groups, as expected. The C—O bond lengths for the two inequivalent acid groups of the tetragonal form are close to the values typical for aromatic carboxylic acids: C—O double bond,

1.226 (20) Å; C—O single bond, 1.305 (20) Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The C(11), O(1), O(2) carboxylic acid group in the triclinic form of the diacid, however, has C—O bond lengths intermediate to the values for single and double C—O bond lengths, and thus similar to values reported for 1,4-naphthalenedicarboxylic acid (Derissen, Timmermans & Schoone, 1979), which indicates that the electrons are partially delocalized, presumably as a result of hydrogen bonding. On the other hand, the C—O bond lengths for the C(12), O(3), O(4) carboxylic acid group of the triclinic form of the diacid agree with typical values for aromatic acids, and thus with the values for the tetragonal form as well.

The dihedral angles formed between the planes of the carboxyl groups and the least-squares best-fit planes of the naphthalene cores are 71.3 (2) and 20.3 (3)° (tetragonal phase) and 82.7 (1) and 7.6 (2)° (triclinic phase) for the C(11) and C(12) carboxyl groups, respectively. Thus, in each case one of the carboxyl-group planes lies nearly parallel to the ring plane while the other lies nearly perpendicular to the ring plane. In contrast, in the 1,8-diacid the planes of the two carboxylic acid groups make nearly equal angles with the ring plane: 42.0 (2) and 43.2 (2)°, approximately halfway between parallel and perpendicular orientations (Fitzgerald, Gallucci & Gerkin, 1991).

Table 6. *Hydrogen-bond parameters for a tetragonal phase (diethyl ether channel clathrate) and the triclinic phase of 1,2-naphthalenedicarboxylic acid, with their e.s.d.'s*

Oxygen-acceptor oxygen	Distance (Å)	H-acceptor oxygen	Distance (Å)	Oxygen-H-acceptor oxygen	Angle (°)
<b>Tetragonal phase</b>					
O(1)—O(2) <sup>i</sup>	2.604 (4)	H(1)—O(2) <sup>i</sup>	1.52 (6)	O(1)—H(1)—O(2) <sup>i</sup>	170 (4)
O(3)—O(4) <sup>ii</sup>	2.683 (4)	H(2)—O(4) <sup>ii</sup>	1.74 (6)	O(3)—H(2)—O(4) <sup>ii</sup>	176 (5)
Symmetry codes: (-) $x, y, z$ ; (i) $\frac{1}{2} + y, \frac{1}{2} - x, -\frac{1}{2} + z$ ; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} - z$ .					
<b>Triclinic phase</b>					
O(1)—O(2) <sup>i</sup>	2.621 (3)	H(1)—O(2) <sup>i</sup>	1.53 (5)	O(1)—H(1)—O(2) <sup>i</sup>	176 (4)
O(3)—O(4) <sup>ii</sup>	2.665 (3)	H(2)—O(4) <sup>ii</sup>	1.71 (4)	O(3)—H(2)—O(4) <sup>ii</sup>	178 (3)
Symmetry codes: (-) $x, y, z$ ; (i) $-x, -y, 1-z$ ; (ii) $-x, 1-y, 1-z$ .					

Hydrogen-bond parameters for the tetragonal and triclinic phases of 1,2-naphthalenedicarboxylic acid are given in Table 6. The hydrogen-bonding pattern is quite different in the two phases. In the tetragonal phase, the acid group at the C(1) position is involved in an infinite helical array of intermolecular hydrogen bonds around fourfold screw axes parallel to the  $z$  direction (see Fig. 3) in which O(1)—H(1) acts as the donor, O(2)<sup>i</sup> as the acceptor in each case, while the acid group at the C(2) position is involved in an intermolecular cyclic dimer hydrogen bond across an inversion center. In the triclinic phase, both carboxylic acid groups are involved in cyclic dimer hydrogen bonding across inversion centers in such a way as to produce an infinite zigzag pattern (see Fig. 5). The shortest oxygen-acceptor oxygen distance occurs as a result of the hydrogen bonding at the C(1) position of the tetragonal phase: 2.604 (4) Å. The three cyclic dimer hydrogen bonds have oxygen-acceptor oxygen distances ranging from 2.621 (3) to 2.683 (4) Å with the carboxylic acid group involved in the shortest of these, the C(1) group of the triclinic phase, showing partial disordering of its C—O bond

lengths. That the carboxyl group of the infinite helical array shows no evidence of disorder is consistent with the fact that the entire array would be required to participate in the disordering rather than just two acid groups as in the cyclic dimers. However, the correlation between oxygen-acceptor oxygen distance and carboxyl-group disorder is tenuous; this is evident when 1,8-naphthalenedicarboxylic acid, which is completely disordered with an average

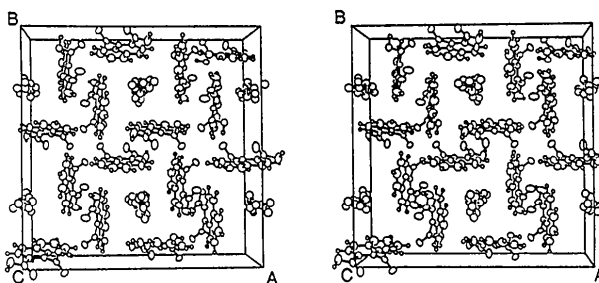


Fig. 4. A stereoview of a unit cell of the tetragonal phase of 1,2-naphthalenedicarboxylic acid crystallized from diethyl ether drawn using ORTEPII (Johnson, 1976). The view is down the  $c$  axis. The partially occupied C atoms used to model the disordered diethyl ether (see text for details) are shown to indicate the presence of the solvent in the channels. The origin was chosen to be at  $i$ .

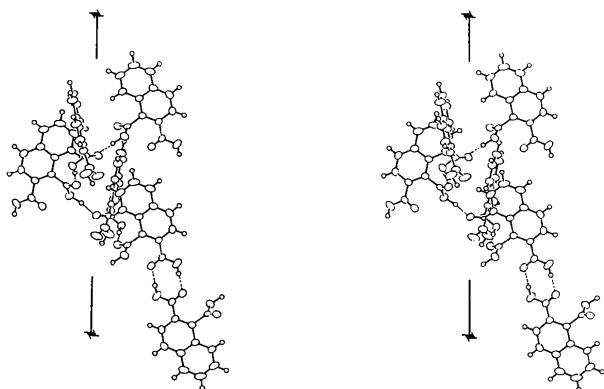


Fig. 3. A stereoview of the hydrogen-bonding arrangement in the tetragonal phase of 1,2-naphthalenedicarboxylic acid crystallized from diethyl ether, drawn using ORTEPII (Johnson, 1976). The view is perpendicular to the  $z$  direction; hydrogen bonds are indicated by dashed lines; approximate location of the fourfold screw axis is indicated. One cyclic dimer hydrogen bond is shown along with the helical hydrogen bonding.

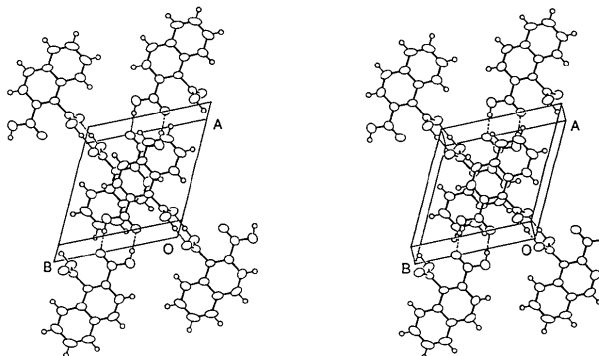


Fig. 5. A stereoview of a unit cell of the triclinic phase of 1,2-naphthalenedicarboxylic acid, drawn using ORTEPII (Johnson, 1976). Four molecules outside the unit cell are shown to permit illustration of the hydrogen bonding (dashed lines).

oxygen-acceptor oxygen distance of 2.663 (4) Å (Fitzgerald, Gallucci & Gerkin, 1991), is compared with the present case.

A unit cell for the tetragonal phase of 1,2-naphthalenedicarboxylic acid containing diethyl ether is shown in Fig. 4 and a unit cell of the triclinic phase of the diacid is shown in Fig. 5. For the tetragonal unit cell, infinite helical chains form about each fourfold screw axis as a result of the hydrogen bonding at the C(1) position as described above. These chains parallel to the *z* direction are interconnected through cyclic dimer hydrogen bonding at the C(2) position. This framework results in open channels parallel to *c*, the walls of which are composed principally of naphthalene rings. Within these channels are solvent molecules, in this case, disordered diethyl ether molecules. The channels are also the location of the  $\bar{4}$  sites, which virtually assures that solvent molecules will be incompatible with the site symmetry even if they are at fixed locations within the channel. In Fig. 4, the partial-occupancy C atoms used to account for the electron density along the columns parallel to *c* and through the  $\bar{4}$  sites are drawn to illustrate the presence of the disordered solvent in the channels. In the triclinic unit cell (Fig. 5), intermolecular hydrogen bonding occurs across inversion centers at both carboxylic acid positions, producing a cyclic dimer at the C(1) position nearly perpendicular to the naphthalene ring and a cyclic dimer at the C(2) position nearly co-planar with the naphthalene ring. This arrangement produces infinite

ribbons of molecules hydrogen bonded in a zigzag pattern and overlapped in such a manner as to occupy the space created above and below the naphthalene rings by the carboxylic acid dimers at the C(1) positions.

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## Structures of Three Biologically Active Conjugates of $\omega$ -Amino Acids and Plant Growth Hormone (Auxin)

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#### Abstract

The crystal structures of biologically active conjugates of the plant growth hormone, indole-3-acetic acid (IAA = auxin) with the non-natural  $\omega$ -amino

acids  $\beta$ -alanine (1),  $\gamma$ -aminobutyric acid (2) and  $\epsilon$ -aminohexanoic ( $\epsilon$ -aminocaproic) acid (3) have been determined. (1) *N*-(IAA)- $\beta$ -Ala,  $C_{13}H_{14}N_2O_3$ ,  $M_r = 246.27$ , orthorhombic, *Pbca*,  $a = 9.114$  (2),  $b = 23.933$  (4),  $c = 11.034$  (4) Å,  $V = 2406.8$  (9) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.359$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 0.92$  cm<sup>-1</sup>,  $F(000) = 1040$ ,  $T =$

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