

Formation of Isolated Guest Dimers vs. Host–Guest Coordination. X-Ray Crystal Structures of Four Carboxylic Acid Inclusion Compounds Formed by Roof-Shaped and Scissor-Like Host Molecules

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(Received: 25 November 1988)

Abstract. The crystal structures of the inclusion compounds of *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid host (**1**) with formic acid (**1a**), acetic acid (**1b**), and propionic acid (**1c**) as guests, and of the coordinatoclathrate of the 1,1'-binaphthyl-2,2'-dicarboxylic acid host (**2**) with acetic acid as guest (**2b**) have been studied by single crystal X-ray diffraction. These studies show that inclusion of small carboxylic acids by carboxylic acid hosts like **1** and **2** results in formation of isolated, hydrogen-bonded guest dimers. Additional H-bond contacts between host and guest carboxylic groups are only formed in cases **1a** and **2b**. The dimeric acidic guest units are sitting in the cavities of the host or host–guest framework and have no other interactions than those of a weak Van der Waals' type with the neighbouring molecules. Crystal data: **1**-formic acid (1:2): triclinic ($P\bar{1}$), $a = 11.6769(6)$, $b = 9.4067(4)$, $c = 9.0020(4)$ Å, $\alpha = 81.522(4)$, $\beta = 100.310(6)$, $\gamma = 104.208(6)^\circ$, $Z = 2$, $R = 0.048$ for 2392 reflections; **1**-acetic acid (1:1): monoclinic ($P2_1/n$), $a = 9.717(2)$, $b = 14.462(2)$, $c = 13.038(3)$ Å, $\beta = 104.27(1)^\circ$, $Z = 4$, $R = 0.046$ for 3042 observations; **1**-propionic acid (1:1): monoclinic ($P2_1/n$), $a = 9.897(4)$, $b = 14.671(7)$, $c = 13.284(7)$ Å, $\beta = 105.92(6)^\circ$, $Z = 4$, $R = 0.056$ for 2302 reflections; **2**-acetic acid (2:3): triclinic ($P\bar{1}$), $a = 12.746(1)$, $b = 17.781(2)$, $c = 11.010(1)$ Å, $\alpha = 105.606(4)$, $\beta = 112.992(8)$, $\gamma = 81.175(6)^\circ$, $Z = 2$, $R = 0.067$ for 4375 observations.

Key words. Inclusion compounds, X-ray structure analysis, carboxylic acid clathrates, H-bonding.

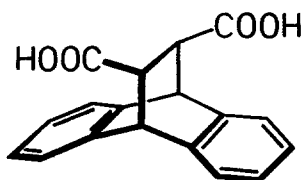
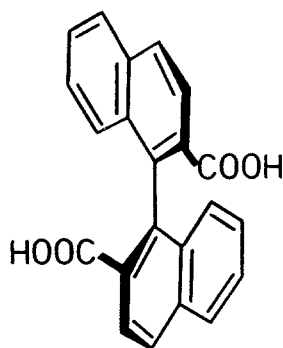
Supplementary Data relating to this article has been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82078 (70 pages).

1. Introduction

The 'coordinatoclathrate principle' was formulated for host molecules endowed with both a bulky skeleton and appended sensor groups [1]. Eminent representatives of this type of hosts are the roof-shaped *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1**) and the scissor-like 1,1'-binaphthyl-2,2'-dicarboxylic acid (**2**). Molecules **1** and **2**, like many other carboxylic host compounds of the coordinatoclathrate type [2–4], trap the guest molecules by steric

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barriers and coordinative interactions. They readily form stoichiometrically composed crystalline inclusion complexes with a large number of small organic molecules, mostly of a polar nature with the possibility of forming hydrogen bonds, such as alcohols, carboxylic acids, amides, sulphoxides or nitriles [6, 7]. The structural principles governing the clathrate formations and host-guest interactions in coordinatoclathrates of **1** and **2** with guests, such as different alcohols, dimethylformamide and dimethyl sulphoxide, have already been revealed by X-ray investigations [4–7]. The present work adds to our previous studies by incorporating carboxylic acids such as formic acid (**1a**), acetic acid (**1b**) and (**2b**), and propionic acid (**1c**) as guest species. The remarkable thing about the resulting compounds is that host and guest molecules have the same type of functional groups with high ability for hydrogen bonds. How do they fit together in the crystal structure?

**1****2**

Inclusion compounds:

- 1a:** 1·formic acid (1:2),
- 1b:** 1·acetic acid (1:1),
- 1c:** 1·propionic acid (1:1),
- 2b:** 2·acetic acid (2:3).

2. Experimental

2.1. SAMPLE PREPARATION

The carboxylic host compounds, **1** [4] and **2** [6a] were prepared as previously described. Crystals of the inclusion compounds were obtained by recrystallization of the respective host from a solution containing the corresponding guest.

2.2. X-RAY DATA COLLECTION AND PROCESSING

The single crystals selected for X-ray diffraction measurements were sealed in epoxy glue for compounds **1a** and **1c** and in a glass capillary for compounds **1b** and **2b**. The net intensities were corrected for Lorentz and polarization effects, and in the case of structure **1b** also for absorption and extinctions effects. The unit cell

parameters were refined using the angular settings of strong, well-centered reflections [38 for **1a**, 25 for **1b**, 25 for **1c**, and 44 for **2b**] accurately measured by the diffractometer within the θ -range $17^\circ < \theta < 42^\circ$. Crystal data and selected experimental details are summarized in Table I.

2.3. STRUCTURE ANALYSIS AND REFINEMENT

Reasonable starting models of the structures were derived by direct methods using the program systems SHELXS [8] for **1a** and MULTAN 80 [9] for **1b**, **1c** and **2b**. Difference Fourier syntheses and full-matrix least-squares calculations by means of the SHELX [10] (**1a**, **1c** and **2b**) or of the SDP [11] (**1b**) program systems were then used for completion and refinement of the initial structural models.

The carboxylic hydrogen sites in all cases were taken from electron density maps and held fixed during the subsequent calculations, while the positions of the remaining H atoms were generated after each cycle of the refinement (C—H = 1.08 Å) using geometric evidence. The methyl groups were treated as rigid groups. Non-hydrogen atomic positions were refined together with their anisotropic temperature parameters, except in structure **2b**, where the limitations of the least-squares program ($N_{\text{iso}} + 2N_{\text{aniso}} < 160$) [10] allowed only fifty-six non-hydrogen atoms (14 O and 42 C) to be treated anisotropically. The remaining eight carbon positions in the latter case were refined with isotropic temperature parameters. Concerning the hydrogen atoms, isotropic temperature factors were refined for the carboxylic H positions and group isotropic temperature factors for the calculated C-bonded ones.

Some of the stronger low- θ reflections [3 for **1a**, 12 for **1c** and 25 for **2b**] with F_{obs} considerably less than F_{calc} , most probably due to extinction, were excluded from the last refinements. The final reliability indices are listed in Table I. Unit weights were used in the refinement of structures **1a**, and **1c**, while the weights of the reflections were calculated as $w = 4F_0^2/\sigma(F_0^2)^2$ [11] and $w = 2.3174/(\sigma^2(F) + 0.00224F^2)$ [10], for structures **1b** and **2b**, respectively.

3. Results and Discussion

The atomic positional parameters of the four inclusion compounds **1a**, **1b**, **1c**, and **2b** are given in Table II; atom labelling is in accordance with Figure 1. Hydrogen bond geometries are listed in Table III. Perspective views of the crystallographic asymmetric units of the present four clathrates are shown in Figure 1, and the crystal packings are illustrated in Figures 2, 3, and 4. The list of intramolecular bond lengths and bond angles involving the non-hydrogen atoms (Tables IV and V), fractional atomic coordinates of the calculated H atoms (Table VI), anisotropic thermal parameters of the non-hydrogen atoms (Table VII) as well as the list of the observed and calculated structure factors are included in the Supplementary Material.

3.1. MOLECULAR STRUCTURES

The geometry of the rigid host **1** is almost identical in the present structures (Figures 1a, b and c). Corresponding bond lengths and bond angles are in

Table I. Selected crystal data and experimental details of inclusion compounds **1a**, **1b**, **1c** and **2b** (The e.s.d.'s, where given, are in parentheses.)

Compounds	1a	1b	1c	2b
Formula	$C_{18}H_{14}O_4 \cdot 2(CH_2O_2)$	$C_{18}H_{14}O_4 \cdot C_2H_4O_2$	$C_{18}H_{14}O_4 \cdot C_3H_6O_2$	$2(C_{22}H_{14}O_4) \cdot 3(C_2H_4O_2)$
Formula weight	386.4	354.4	368.4	864.9
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
<i>a</i> , Å	11.6769(6)	9.717(2)	9.897(4)	12.746(1)
<i>b</i> , Å	9.4067(4)	14.462(2)	14.671(7)	17.781(2)
<i>c</i> , Å	9.0020(4)	13.038(3)	13.284(7)	11.010(1)
α , deg.	81.522(4)	90.0	90.0	105.606(4)
β , deg.	100.310(6)	104.27(1)	105.92(6)	112.992(8)
γ , deg.	104.208(6)	90.0	90.0	81.175(6)
V , Å ³	937.5(1)	1175.7(6)	1855(2)	2209.1(4)
<i>Z</i>	2	4	4	2
D_x , g cm ⁻³	1.37	1.33	1.32	1.30
μ , cm ⁻¹	8.62	0.92	7.63	7.55
Radiation used	CuK α	MoK α	CuK α	CuK α
θ limit, deg.	69	25	68	70
No. of unique non-zero refl. collected	3031	3269	3078	7246
No. of refl. used in the refinements	2392	3042	2302	4375
Tot. no. of variables	258	235	252	555
$R = \Sigma \Delta F /\Sigma F_o $	0.048	0.046	0.056	0.067
$R_w = \Sigma\sqrt{w} \Delta F /\Sigma\sqrt{w} F_o $	0.048	—	0.056	0.079
$R_G = [\Sigma w \Delta F ^2/\Sigma w F_o ^2]^{1/2}$	0.063	0.078	0.053	0.104

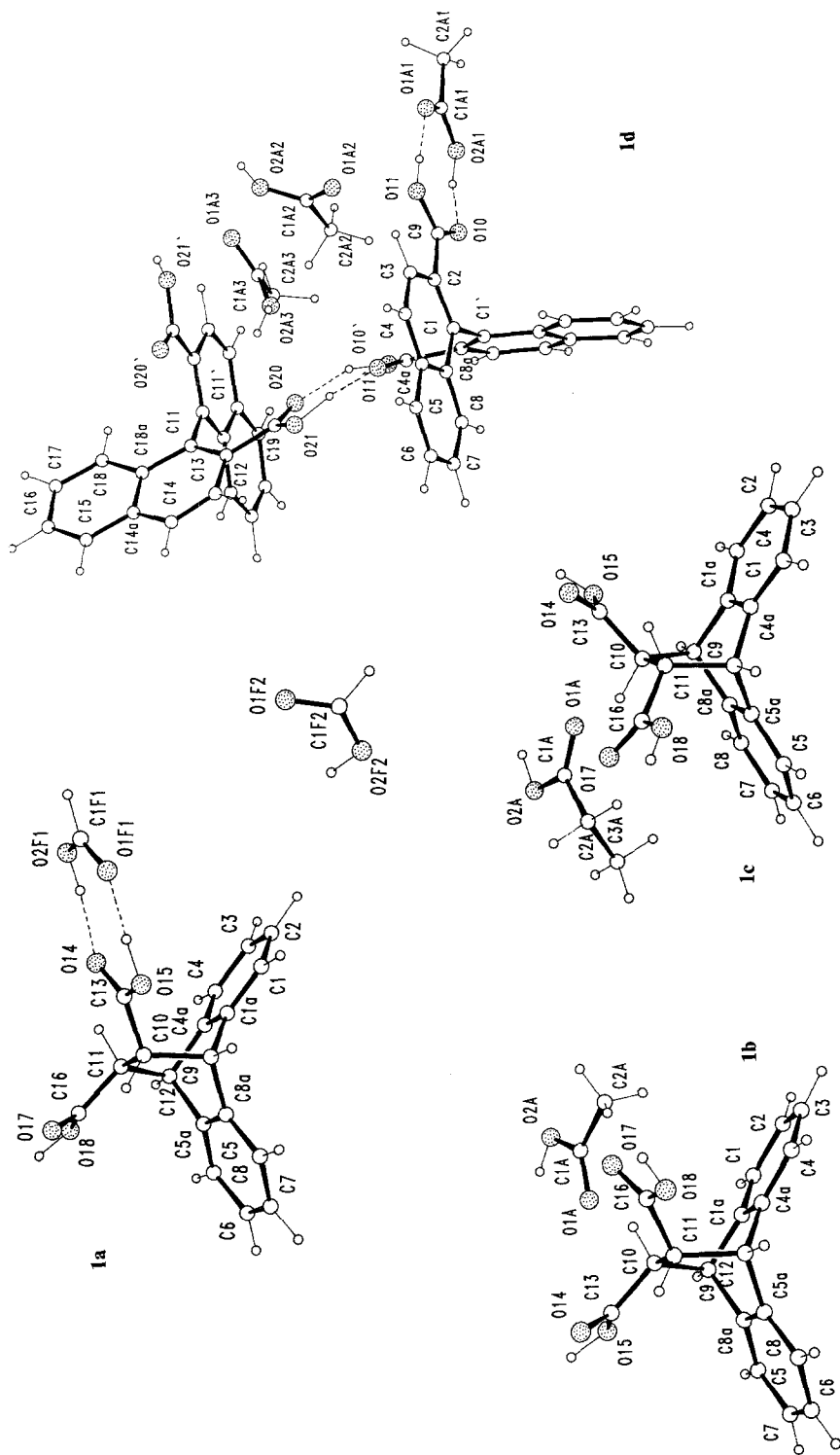


Fig. 1. Perspective view of the asymmetric units of the studied inclusion compounds: (a) **1a** [1-formic acid (1:2)]; (b) **1b** [1-acetic acid (1:1)]; (c) **1c** [1-propionic acid (1:1)] and (d) **2b** [2-acetic acid (2:3)]. O atoms are dotted, solid and dashed lines represent covalent and hydrogen bonds, respectively.

Table II. Fractional atomic coordinates and equivalent isotropic/temperature factors of the non-hydrogen atoms and of the carboxylic hydrogens. The e.s.d.'s, where given, are in parentheses.

Atom	x/a	y/b	z/c	U_{eq}/U (\AA^2)	Atom	x/a	y/b	z/c	U_{eq}/U (\AA^2)
1a: 1-Formic acid (1:2)									
C(1a)	0.7319(2)	0.7428(3)	0.5494(3)	0.035(1)	C(1a)	0.3129(1)	0.2688(1)	0.7490(1)	0.0408(4)
C(1)	0.6797(3)	0.7313(3)	0.6791(3)	0.044(1)	C(1)	0.1759(1)	0.2954(1)	0.7465(1)	0.0581(6)
C(2)	0.7483(3)	0.7076(4)	0.8207(3)	0.052(1)	C(2)	0.1446(2)	0.3247(1)	0.8394(1)	0.0712(6)
C(3)	0.8646(3)	0.6966(3)	0.8315(3)	0.050(1)	C(3)	0.2479(2)	0.3281(1)	0.9331(1)	0.0686(6)
C(4)	0.9178(3)	0.7100(3)	0.7015(3)	0.041(1)	C(4)	0.3864(4)	0.3022(1)	0.9362(1)	0.0510(5)
C(4a)	0.8493(2)	0.7321(3)	0.5607(3)	0.033(1)	C(4a)	0.4193(1)	0.2741(1)	0.8435(1)	0.0388(4)
C(5a)	0.8040(3)	0.6365(3)	0.3131(3)	0.037(1)	C(5a)	0.5980(1)	0.2925(1)	0.7406(1)	0.0380(4)
C(5)	0.8327(3)	0.5307(3)	0.2432(3)	0.048(1)	C(5)	0.7222(1)	0.3386(1)	0.7428(1)	0.0515(5)
C(6)	0.7398(4)	0.4338(4)	0.1625(4)	0.058(2)	C(6)	0.7410(2)	0.3797(1)	0.6516(1)	0.0678(6)
C(7)	0.6241(3)	0.4454(4)	0.1516(4)	0.059(1)	C(7)	0.6350(2)	0.3746(1)	0.5590(1)	0.0699(6)
C(8)	0.5950(3)	0.5532(3)	0.2200(3)	0.050(1)	C(8)	0.5107(2)	0.3281(1)	0.5558(1)	0.0556(5)
C(8a)	0.6870(3)	0.6480(3)	0.3019(3)	0.037(1)	C(8a)	0.4911(1)	0.2863(1)	0.6466(1)	0.0398(4)
C(9)	0.6717(2)	0.7684(3)	0.3868(3)	0.036(1)	C(9)	0.3656(1)	0.2297(1)	0.6586(1)	0.0378(4)
C(10)	0.7480(2)	0.9169(3)	0.3161(3)	0.034(1)	C(10)	0.4224(1)	0.1314(1)	0.6954(1)	0.0341(4)
C(11)	0.8784(2)	0.9034(3)	0.3297(3)	0.032(1)	C(11)	0.5443(1)	0.1383(1)	0.7973(1)	0.0343(4)
C(12)	0.8921(2)	0.7479(3)	0.4075(3)	0.034(1)	C(12)	0.5623(1)	0.2424(1)	0.8321(1)	0.0355(4)
C(13)	0.7367(3)	1.0429(3)	0.3947(3)	0.038(1)	C(13)	0.4640(1)	0.0775(1)	0.6091(1)	0.0370(4)
O(14)	0.8201(2)	1.1197(3)	0.4671(3)	0.064(1)	O(15)	0.3876(1)	0.0899(1)	0.5154(1)	0.0606(4)
O(15)	0.6277(2)	1.0611(3)	0.3787(3)	0.066(1)	O(14)	0.5644(1)	0.0217(1)	0.6310(1)	0.0608(4)
C(16)	0.9266(2)	0.9409(3)	0.1800(3)	0.036(1)	C(16)	0.5197(1)	0.0787(1)	0.8857(1)	0.0384(4)
O(17)	0.8789(2)	1.0115(3)	0.0708(2)	0.052(1)	O(17)	0.4185(1)	0.0281(1)	0.8789(1)	0.0602(4)
O(18)	1.0241(2)	0.8990(3)	0.1807(2)	0.055(1)	O(18)	0.6223(1)	0.0861(1)	0.9726(1)	0.0600(4)
C(1F)	0.7048(4)	1.3492(4)	0.6135(5)	0.062(2)	O(1A)	1.082(1)	0.0487(1)	0.6051(1)	0.0683(5)
O(1F1)	0.6201(2)	1.2786(3)	0.5376(3)	0.067(1)	O(2A)	-0.1026(1)	-0.0135(1)	0.5973(1)	0.0658(5)
O(2F1)	0.8113(2)	1.3284(3)	0.6345(4)	0.085(1)	C(1A)	0.0142(2)	0.0266(1)	0.6477(1)	0.0553(6)
C(2F)	0.3789(4)	0.9816(5)	1.1207(5)	0.075(2)	C(2A)	0.0279(2)	0.0423(2)	0.7615(1)	0.0905(11)
O(1F2)	0.4290(3)	1.1043(3)	1.0684(3)	0.077(1)	H(15)	0.395	0.043	0.459	0.108(8)
O(2F2)	0.3995(3)	0.8602(3)	1.0981(4)	0.092(2)	H(18)	0.616	0.046	1.032	0.072(5)
H(15)	0.630	1.149	0.444	0.15(2)	H(1A)	-0.106	-0.027	0.525	0.166(9)
H(18)	1.060	0.937	0.088	0.18(2)					
H(OF1)	0.816	1.250	0.584	0.19(3)					
H(OF2)	0.488	0.870	1.071	0.24(3)					

1b: 1-Acetic acid (1:1)

Ic: 1-Propionic acid (1:1)		2b: 2-Acetic acid (2:3)	
C(1)	1.0243(4)	C(1)	0.0779(3)
C(1a)	1.0043(3)	C(2)	0.1138(3)
C(2)	1.1511(4)	C(3)	0.1461(4)
C(3)	1.2550(4)	C(4)	0.1094(3)
C(4)	1.2354(4)	C(5)	0.1077(4)
C(4a)	1.1094(3)	C(6)	0.0810(5)
C(5)	0.9035(4)	C(7)	0.0509(4)
C(5a)	0.9332(3)	C(8)	0.0482(4)
C(6)	0.7680(4)	C(8a)	0.0772(3)
C(7)	0.6655(4)	C(9)	0.1217(3)
C(8)	0.6930(4)	O(10)	0.0954(3)
C(8a)	0.8281(3)	O(11)	0.1598(3)
C(9)	0.8761(3)	C(1)	0.0321(3)
C(10)	0.9279(3)	C(2)	0.1002(3)
C(11)	1.0491(3)	C(3)	0.0511(4)
C(12)	1.0734(3)	C(4)	-0.0635(4)
C(13)	0.9656(3)	C(4b)	-0.1365(3)
O(14)	1.0610(2)	C(5)	-0.2552(4)
O(15)	0.8889(3)	C(6)	-0.3250(4)
C(16)	1.0242(3)	C(7)	-0.2772(4)
O(17)	0.9197(2)	C(8)	-0.1638(3)
O(18)	1.1269(2)	C(8b)	-0.0885(3)
O(1A)	0.6144(3)	C(9)	0.2210(3)
O(2A)	0.4061(2)	O(10)	0.2665(2)
C(1A)	0.5227(4)	O(11)	0.2795(3)
C(2A)	0.5403(4)	C(11)	0.7106(3)
C(3A)	0.4246(5)	C(12)	0.6172(3)
H(15)	0.902	C(13)	0.6232(3)
H(18)	1.126	C(14)	0.7190(3)
H(1A)	0.407	C(14a)	0.8172(3)
		C(15)	0.9195(3)
		C(16)	1.0168(4)
		C(17)	1.0159(3)
		C(18)	0.9169(3)
		C(18a)	0.8146(3)
		C(19)	0.5107(3)
		O(20)	0.4829(2)
		O(21)	0.4482(3)
			0.067(1)
			0.049(1)
			0.086(2)
			0.080(2)
			0.061(1)
			0.2462(2)
			0.4358(3)
			0.3442(2)
			0.4291(3)
			0.3366(4)
			0.2448(3)
			0.2501(2)
			0.1610(2)
			0.1965(2)
			0.3742(2)
			0.3696(2)
			0.2678(2)
			0.4266(2)
			0.4111(2)
			0.4273(2)
			0.3864(2)
			0.3781(2)
			0.4715(2)
			0.1056(2)
			0.4548(2)
			0.5160(2)
			0.4782(3)
			0.4657(3)
			0.4154(5)
			0.457
			0.455
			0.528
			0.014
			0.13(2)
			0.0624(3)
			0.1522(2)
			0.0683(3)
			0.1613(3)
			0.2523(3)
			0.051(1)
			0.2462(2)
			0.4358(3)
			0.048(1)
			0.048(1)
			0.079(2)
			0.084(2)
			0.066(1)
			0.050(1)
			0.047(1)
			0.042(1)
			0.041(1)
			0.044(1)
			0.046(1)
			0.068(1)
			0.074(1)
			0.046(1)
			0.0180(2)
			0.3864(2)
			0.3781(2)
			0.4715(2)
			0.1056(2)
			0.4548(2)
			0.0946(2)
			0.1456(2)
			0.2612(3)
			0.2806(4)
			-0.027
			0.014
			0.528
			0.13(2)
			0.0624(3)
			0.4014(2)
			0.4450(3)
			0.4130(3)
			0.3368(2)
			0.3024(3)
			0.2269(3)
			0.1828(3)
			0.1424(4)
			0.2149(2)
			0.2696(4)
			0.070(2)
			0.3370(4)
			0.6734(4)
			0.7452(3)
			0.7156(3)
			0.5097(2)
			0.2806(2)
			0.2327(2)
			0.1944(2)
			0.2013(2)
			0.6520(4)
			0.2452(2)
			0.2494(3)
			0.2939(3)
			0.3364(3)
			0.3335(2)
			0.2874(2)
			0.5023(4)
			0.2153(2)
			0.2326(2)
			0.1788(2)
			0.0689(2)
			0.7356(3)
			0.7368(3)
			0.6244(3)
			0.0819(2)
			0.0580(2)
			0.4934(3)
			0.0205(2)
			0.4757(4)
			0.0087(2)
			-0.0264(2)
			-0.0325(3)
			-0.0031(3)
			0.8308(4)
			0.0284(2)
			0.8122(4)
			0.9169(3)
			0.8146(3)
			0.0358(2)
			0.1229(2)
			0.1269(2)
			0.1552(2)
			0.5368(3)
			0.5706(4)
			0.6811(4)
			0.8122(4)
			0.8308(4)
			0.7198(3)
			0.6374(4)
			0.061(2)
			0.7343(3)
			0.074(1)
			0.085(2)
			0.050(1)
			0.061(2)
			0.067(2)
			0.059(1)
			0.079(2)
			0.083(2)
			0.3816(4)
			0.4127(4)
			0.503(1)
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			0.6395(4)
			0.5711(3)
			0.087(2)
			0.092(2)
			0.049(1)
			0.054(2)
			0.063(2)
			0.064(2)
			0.4757(4)
			0.5862(3)
			0.5706(4)
			0.6811(4)
			0.8122(4)
			0.8308(4)
			0.7198(3)
			0.6374(4)
			0.061(2)
			0.7343(3)
			0.074(1)
			0.085(2)

Table II. (continued for compound 2b)

Atom	x/a	y/b	z/c	$U_{eq}/U(\text{Å}^2)$	Atom	x/a	y/b	z/c	$U_{eq}/U(\text{Å}^2)$
C(11')	0.7043(3)	0.0827(2)	0.8738(3)	0.047(1)	C(2A1)	0.1623(6)	0.5903(3)	1.1806(5)	0.116(3)
C(12)	0.7246(3)	0.1527(2)	0.9689(3)	0.051(2)	C(1A2)	0.4552(7)	0.4081(5)	1.0261(9)	0.157(5)
C(13')	0.7143(3)	0.1604(2)	1.0961(4)	0.064(2)	O(1A2)	0.3832(4)	0.4505(4)	0.9567(7)	0.182(4)
C(14)	0.6851(3)	0.0993(3)	1.1258(4)	0.067(2)	O(2A2)	0.5576(5)	0.4239(3)	1.0841(7)	0.177(4)
C(14b)	0.6672(3)	0.0255(2)	1.0334(4)	0.057(1)	C(2A2)	0.4198(8)	0.3389(6)	1.0464(12)	0.218(8)
C(15')	0.6385(4)	-0.0389(3)	1.0628(4)	0.079(2)	C(1A3)	0.4870(12)	0.4288(8)	0.5984(17)	0.209(10)
C(16)	0.6226(4)	-0.1096(3)	0.9724(5)	0.090(3)	O(1A3)	0.5404(8)	0.4845(5)	0.6569(10)	0.248(7)
C(17)	0.6340(4)	-0.1188(3)	0.8490(5)	0.081(2)	O(2A3)	0.4427(6)	0.4133(4)	0.4677(12)	0.198(6)
C(18')	0.6610(3)	-0.0577(2)	0.8155(4)	0.064(2)	C(2A3)	0.4750(13)	0.3649(8)	0.6576(15)	0.274(13)
C(18b)	0.6778(3)	0.0167(2)	0.9061(3)	0.049(1)	H(11)	0.164	0.537	0.808	0.12(2)
C(19')	0.7528(3)	0.2223(2)	0.9393(4)	0.064(2)	H(11')	0.364	0.173	0.750	0.22(4)
O(20')	0.7621(3)	0.2242(2)	0.8372(3)	0.103(2)	H(21)	0.374	0.191	0.568	0.17(3)
O(21')	0.7697(3)	0.2838(2)	1.0414(3)	0.103(2)	H(21')	0.777	0.336	1.009	0.25(4)
C(1A1)	0.1533(4)	0.5481(3)	1.0411(4)	0.075(2)	H(1A1)	0.128	0.444	0.913	0.21(3)
O(1A1)	0.1674(3)	0.5784(2)	0.9629(4)	0.088(2)	H(1A2)	0.585	0.476	1.066	0.40(4)
O(2A1)	0.1297(3)	0.4739(2)	1.0060(3)	0.098(2)	H(1A3)	0.435	0.429	0.406	0.33(4)

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

Table III. Distances (Å) and angles (deg.) in hydrogen bonds. The e.s.d.s, where given, are in parentheses.

Atoms involved	Symmetry	Donor...Acceptor	Donor—H	H...Acceptor	∠ Donor—H...Acceptor
1a: 1:Formic acid (1:2)					
O(15)—H(15)...O(1F1)	(x, y, z)	2.690(4)	1.07	1.62	174
O(2F1)—H(O(1F1))...O(1A)	(x, y, z)	2.676(4)	0.94	1.74	172
O(18)—H(18)...O(17)	(-x + 2, -y + 2, -z)	2.647(3)	0.98	1.67	175
O(2F2)—H(O(1F2))...O(1F2)	(-x + 1, -y, -z)	2.640(5)	1.09	1.67	146
1b: 1:Acetic acid (1:1)					
O(15)—H(15)...O(1A)	(-x + 1, -y, -z + 1)	2.628(2)	1.02	1.62	169
O(18)—H(18)...O(17)	(-x + 1, -y, -z + 2)	2.647(2)	0.99	1.67	171
O(2A)—H(1A)...O(1A)	(-x, -y, -z + 1)	2.676(2)	0.95	1.72	178
1c: 1:Propionic acid (1:1)					
O(15)—H(15)...O(1A)	(-x + 2, -y + 1, -z)	2.661(4)	0.93	1.76	163
O(18)—H(18)...O(17)	(-x + 2, -y + 1, -z + 1)	2.651(4)	0.89	1.78	165
O(2A)—H(1A)...O(1A)	(-x + 1, -y + 1, -z)	2.647(4)	1.08	1.59	167
2b: 2:Acetic acid (2:3)					
O(11)—H(11)...O(1A1)	(x, y, z)	2.638(4)	0.98	1.66	176
O(11')—H(11')...O(20)	(x, y, z)	2.618(5)	1.02	1.65	156
O(21)—H(21)...O(10')	(x, y, z)	2.613(4)	1.17	1.46	166
O(2A1)—H(1A1)...O(10)	(x, y, z)	2.673(4)	1.01	1.68	165
O(21')—H(21')...O(1A1)	(-x + 1, -y + 1, -z + 2)	2.710(5)	1.12	1.67	152
O(2A2)—H(1A2)...O(1A2)	(-x + 1, -y + 1, -z + 2)	2.662(10)	1.13	1.53	176
O(2A3)—H(1A3)...O(1A3)	(-x + 1, -y + 1, -z + 1)	2.632(17)	0.77	1.96	146

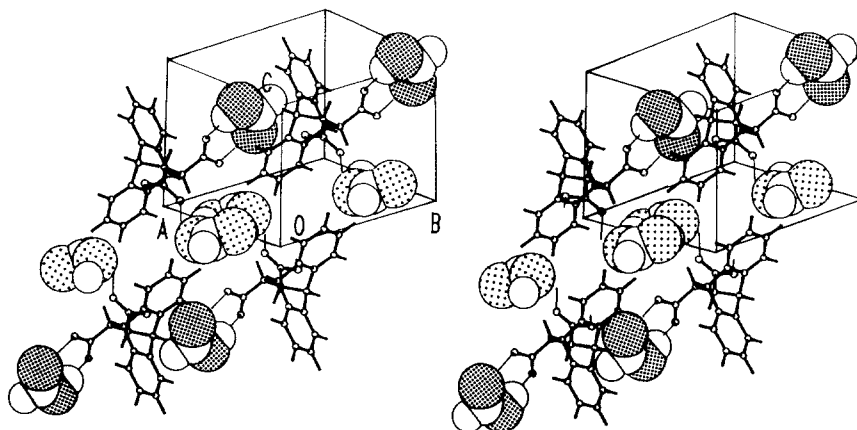


Fig. 2. Stereo view of the molecular packing of the 1-formic acid (1:2) clathrate (**1a**). The host molecules are shown in stick style, the atoms of the formic acid guests are drawn with Van der Waals radii. The O atoms of the host-coordinated formic acid are shaded and those of the isolated guest dimers are dotted. H bonds in lightfaced lines.

agreement with each other and also with the values published in our previous communications about related structures [3–5]. In the ethano bridge the C(9)—C(10) and C(11)—C(12) bonds are elongated, while the dimension of the C(10)—C(11) bond in the middle is comparable with the usual length. The mean values calculated for eight different molecules in seven different crystal structures [3–5] (with r.m.s. deviations in square brackets) are 1.567[7] Å for the elongated bonds and 1.548[5] Å for the C(10)—C(11) bond. The standard value for a $C_{(sp^3)}-C_{(sp^3)}$ bond is 1.541(± 3) Å [12]. The dihedral angles between the phenyl rings are 58.8(1)° in **1a**, 51.7(1)° in **1b** and 52.0(1)° in structure **1c**.

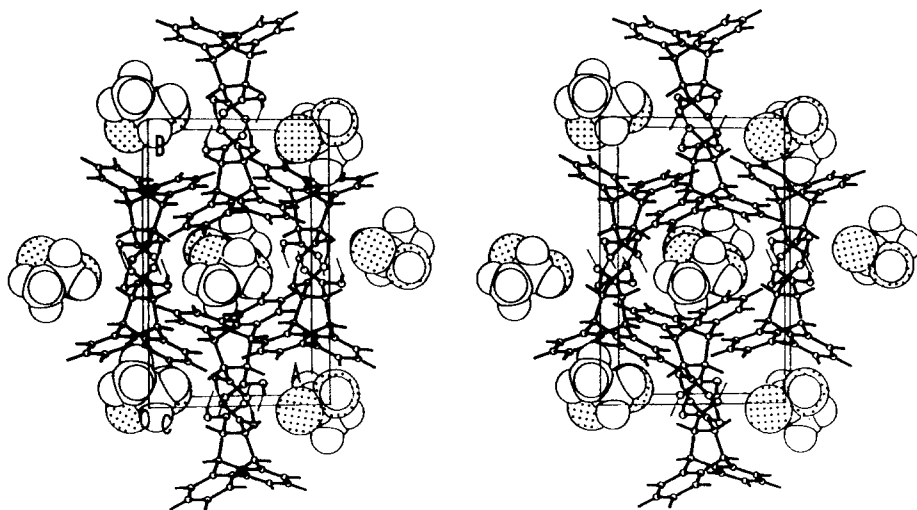


Fig. 3. Stereo packing illustration of the 1-propionic acid (1:1) clathrate (**1c**). The framework formed by H-bonded host molecules is shown in stick model fashion. The guest dimers in the tunnels are represented as space-filling models with the O atoms dotted.

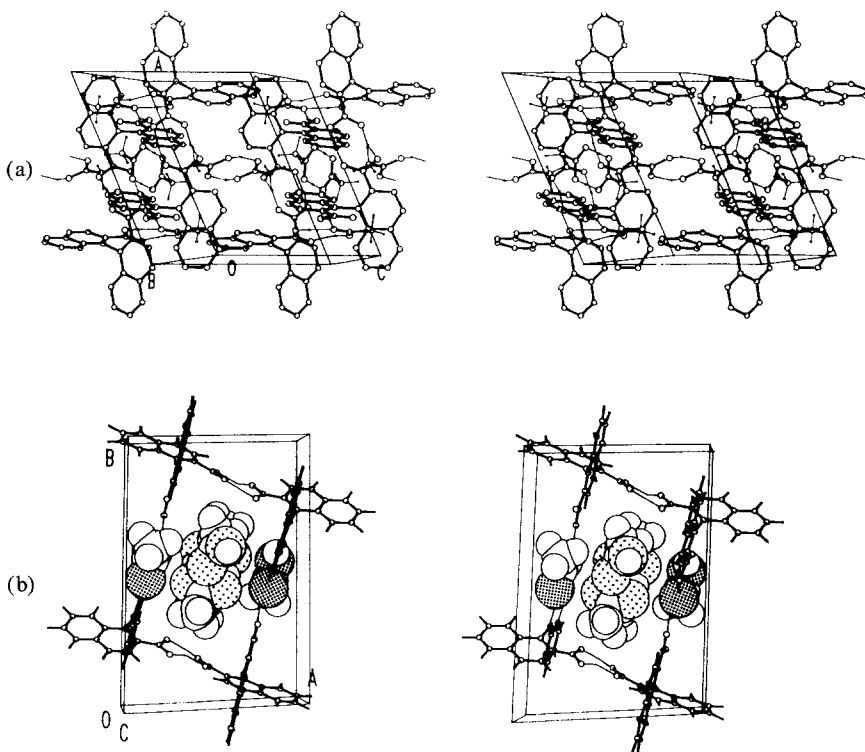


Fig. 4. Stereoscopic packing diagram of the 2-acetic acid (2:3) clathrate (**2b**) from two different points of view and in different fashion: (a) seen along the *b* axis in stick style only, and (b) seen along the *c* axis with the guest molecules in space-filling representation. In (a) the H atoms of the host are omitted for clarity, H bonds in lightfaced lines. In (b) the O atoms of the host-coordinated guest acid are shaded and those of the isolated guest dimers in the tunnel are dotted. H bonds in lightfaced lines.

Values of bond lengths and bond angles in the two crystallographically independent molecules of **2** agree with each other within experimental errors and generally conform to the values published earlier for this host [6]. The two naphthyl moieties are approximately perpendicular to each other. The dihedral angles between the least-squares planes of the naphthyl rings are $86.78(8)$ and $87.31(3)^\circ$. Noteworthy is the variation in the inclination angles of the different carboxyl groups with respect to the plane of the attached naphthyl moiety. The dimer (Figure 1d) has two sensor groups available for binding, for which the angles are $3.1(3)$ and $2.2(3)^\circ$. The two other carboxyl groups, which connect the two molecules to each other by forming the eight-membered hydrogen-bonded ring, are inclined to the respective naphthyl planes through $15.0(4)$ and $25.7(2)^\circ$.

The different carboxylic acid guests generally show the expected geometries [13, 14]. In structure **2b**, however, the bond dimensions of the guest molecules, especially those which form the isolated dimeric guest entities, have larger uncertainties than those of the hosts. This is probably because they have higher thermal mobility than the remaining non-hydrogen atoms of this structure, as shown by

their temperature parameters (cf. Table II and VII), which indicates a looser packing in this region of the crystal.

3.2. PACKING RELATIONS AND HOST-GUEST INTERACTIONS

X-ray studies of seven crystal structures containing **1** revealed that this roof-shaped host always retains at least one of its two carboxyl groups for binding to another host molecule [4, 5, 7]. Such a dimer with two sensor groups free for binding of the guests is the basic motif also in the formic acid inclusion compound of **1** (**1a**) with 1:2 stoichiometry, which is unusual for this host. The two guests of the asymmetric unit (cf. Figure 1a) are very different crystallographically. Only one of them is coordinated to the host, thus forming H-bonded host-guest associations with 2:2 stoichiometry. These 2:2 aggregates are then linked together by Van der Waals' type forces to form the crystal structure, just as in the 1-dimethyl sulphoxide (1:1) compound [5, 7]. In the case of the formic acid inclusion compound, however, there are cavities in the structure, in which hydrogen bonded dimers of the other guest acid reside (Figure 2). The guest dimer has only weak Van der Waals' type interaction with the host or the host-bonded guest molecules which constitute the structural framework.

The acetic acid and propionic acid inclusion compounds of **1**, compounds **1b** (preliminary communication in Ref. [3]) and **1c**, respectively, are isomorphous. Therefore, the packing diagram of only one of them is shown (Figure 3). Eight-membered H-bonded loops interlink the host acids to infinite, parallel zig-zag chains, like in the crystal structure of the free host [4]. The packing of the chains in the inclusion compounds is, of course, different from that in the free host. The host chains of the clathrates are arranged so that tunnels are created between them parallel to the *c* axis. The small guest acids form H-bonded dimers residing in these tunnels. There is no specific interaction between host and guest; the guest dimers are retained only by steric barriers caused by the host matrix. Accordingly, they are organized as classical clathrates [1a, 1b].

The versatility and eminent clathrate-forming ability of host **2** has already been demonstrated by eight crystal structures [6]. The present acetic acid inclusion compound (**2b**) with the unusual 3:2 stoichiometry, however, reveals a new type of construction among the coordinato-clathrates of **2**. At the same time it shows pronounced similarity with the structures of the carboxylic acid inclusion compounds of **1**. Molecules **2** in **2b** form hydrogen-bonded dimers in a way which is characteristic for host **1**. The dimer of **2**, however, uses only one of its sensor groups for coordination of a guest acid (Figure 1d), the other carboxyl group functions as a proton donor in an H bond [O(21)—H(21)···O(1A1), cf. Table III] which links two centrosymmetrically related 2:1 host-guest associations to each other. In the crystal, the so formed 4:2 aggregates (cf. Figure 4b) are further connected by weak packing forces of the Van der Waals type so that tunnel-like cavities are created in the direction of the *c* axis (Figure 4a). The guest acids that are not coordinated by the host make dimers with their respective centrosymmetric equivalents in the usual way. These dimers are placed in the tunnels, which are wide enough to allow high thermal mobility for the weakly bonded guest entities.

3.3. CONCLUDING REMARKS

The four structures presented here may suggest a principle in the formation of inclusion crystals between carboxylic acids, which is 'similar binds to similar' or host prefers bonding to host, and guest to guest, before bonding is established between host and guest. Accordingly, isolated guest dimers are formed, which are trapped in the cavities of the structural framework formed by host molecules or host-guest aggregates.

The finding raises the question whether this behaviour is confined to carboxylic acids only or does it also apply to molecules with other functional groups of high H-bond capability, such as amides [15]. Another moot point is to what extent the difference in pK_a -values of the host and guest acids play a role in the formation of a particular aggregate structure. Studies along these lines are in progress. It is promising, since designed aggregate structures of H-bonded acids [16] and amides [17] in the crystalline state can be expected to become useful tools for different problems in organic solid state chemistry [18] and materials science [19].

Acknowledgements

M.C. thanks the Swedish Institute (SI) for a fellowship (Grant Nr. 4149-1) and also with I.C. acknowledges the stimulating interest and encouragement of Prof. Peder Kierkegaard (Univ. of Stockholm). This work was supported by the Swedish Natural Science Research Council (NFR), the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie.

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