Crystalline 1 : 1 Inclusion Complexes between a Roof-Shaped Diamide Host and Methanol or Propionic Acid. Crystal Structures and Modes of Interaction

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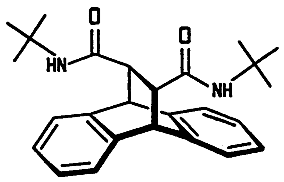
The crystal structures of two inclusion complexes between *anti-N,N'*-di-*t*-butyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide host and methanol [a=11.8893(4), b=18.0943(7), c=12.6322(4) Å, β=108.47(3)°, $P2_1/c$, Z=4] or propionic acid [a=11.4580(8), b=11.7614(9), c=12.4675(8) Å, α=95.37(3), β=109.70(3), γ=113.26(3)°, $P\bar{1}$, Z=2] as guests have been studied by X-ray diffraction. Closed loops of different sizes, formed via hydrogen-bond interactions between host and guest or between the hosts only, characterize both structures. The crystals with the propionic acid guest consist of hydrogen-bonded host : guest associates with 2 : 2 stoichiometry, while the methanol inclusion gives rise to infinite hydrogen-bonded chains.

Carboxylic acids have been noted as powerful crystalline hosts.[1] Due to their distinct hydrogen bonding properties,[2,3] they make possible crystalline complex formation with a wide range of guests.[4–6] Amides corresponding to the carboxylic acids are also crystalline hosts[7] but show different complexation behavior. An example is the diamide **1** which yielded a crystalline 1 : 1 inclusion compound with methanol (**2**) in a highly selective manner,[8] while the corresponding diacid[9] gave crystalline inclusion complexes with higher alcohols only.[8] Apart from this difference, the inclusion ability of the diacid is much more pronounced.[8] Nevertheless, **1** also yields a crystalline inclusion compound with propionic acid (**3**) which has the same stoichiometric ratio (1 : 1) as the corresponding propionic acid complex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2 = **1** · MeOH (1:1)

3 = **1** · EtCOOH (1:1)

Table 1. Crystal Data and Some Details of the Refinement Calculations (esd's, where given, are in Parentheses)

Compound	**2**	**3**
Formula unit	$C_{26}H_{32}N_2O_2 \cdot CH_4O$	$C_{26}H_{32}N_2O_2 \cdot C_3H_6O_2$
Formula weight	436.59	478.63
Unit cell dimensions		
a/Å	11.8893(4)	11.4580(8)
b/Å	18.0943(7)	11.7614(9)
c/Å	12.6322(4)	12.4675(8)
α/deg	90	95.37(3)
β/deg	108.47(3)	109.70(3)
γ/deg	90	113.26(3)
V_c/Å^3	2577.6(5)	1402.4(7)
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
$D_{c,\text{X-ray}}$/g cm^{-1}	1.125	1.133
$\mu_{c,\text{Cu}K\alpha'}$/cm^{-1}	5.44	5.66
F(000)	944	516
Radiation (λ/Å)	Cu $K\alpha$ (1.5418)	Cu $K\alpha$ (1.5418)
θ_{max}/deg	70	60
N_{obs} (unique, non-zero)	4225	3750
N_{ref} with $I>3\sigma(I)$	2595	2322
$N_{variables}$	315	375
Final agreement factors		
$R=\sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.048	0.051
$R_w=[\sum w\cdot\lvert\Delta F\rvert^2/\sum w\cdot\lvert F_o\rvert^2]^{1/2}$	0.073	0.078
Weighting: g in SHELX[a)]	0.00886	0.0091

a) Weights of the structure factors in SHELX[12] are estimated as $w=\text{const}/(\sigma^2(F)+g\cdot F^2)$

formed by the mentioned diacid host.[8] Analogs of **1** with less bulky groups than *t*-butyl are inefficient.[8]

For a better understanding of the inclusion properties of **1**, and to learn the general modes of interaction between host amide and different guest functions,[9] we studied the crystal structures of the 1 : 1 complexes of **1** with methanol (**2**) and propionic acid (**3**).

Experimental

Crystals of the inclusion complexes **2** [**1**·methanol (1 : 1)] and **3** [**1**·propionic acid (1 : 1)] were obtained as described earlier.[8] In order to protect the crystals from possible solvent evaporation during the measurements, each selected single crystal of both **2** and **3** was sealed in a glass capillary.

X-Ray Data Collection and Processing. X-Ray diffraction data were collected on a STOE/AED2 diffractometer at room temperature, using the ω–2θ scan technique. Five reference reflections for the crystal of **2** were measured at intervals of about 1 h. No systematic variation of intensity was detected. The six monitor reflections, measured approximately every 45 min for **3**, however, showed a decrease in intensity of about 7%. Moreover, despite the low absorption coefficients of the present crystals (cf. Table 1), significant absorption effects were detected in the case of compound **3**, in all probability due to the mother liquor content of the capillary. Accordingly, the net intensities were corrected for Lorentz and polarization effects, and in the case of **3** also for decay and absorption effects. The absorption correction was based upon ψ scans of eight reflections within the limits $76<\chi<85°$ and $25<2\theta<71°$. The transmission factor varied between 50 and 83%.

The unit cell parameters, listed in Table 1, were refined by least-squares fit to θ values of 57 [$37<2\theta<57°$] and 58 [$16<2\theta<53°$] accurately centered reflections.

Structure Analysis and Refinement

The positions of the non-hydrogen atoms were derived by direct methods [SHELXS][11] and refined by full-matrix least-squares treatment according to Sheldrick.[12] The carbon-bonded hydrogen positions

Table 2. Fractional Atomic Coordinates of Non-Hydrogen Atoms and of the Hydrogens Involved in the Hydrogen Bonds of Compounds **2** and **3**, Respectively (esd's, where given, are in Parentheses)

Atom	x/a	y/b	z/c	$B_{eq}{}^{a)}/B/\text{Å}^2$
Compound **2** [**1**·MeOH (1 : 1)]				
C(1a)	0.7146(3)	0.3273(2)	−0.1505(3)	4.4(1)
C(1)	0.6147(3)	0.2853(2)	−0.1984(3)	5.6(1)
C(2)	0.5715(3)	0.2778(2)	−0.3138(3)	6.6(1)
C(3)	0.6266(4)	0.3129(2)	−0.3800(3)	6.4(1)
C(4)	0.7279(3)	0.3559(2)	−0.3324(3)	5.0(1)
C(4a)	0.7709(3)	0.3627(2)	−0.2178(2)	4.1(1)
C(5a)	0.9586(3)	0.3559(2)	−0.0686(3)	4.3(1)
C(5)	1.0776(3)	0.3434(2)	−0.0563(3)	5.5(1)
C(6)	1.1396(4)	0.2918(2)	0.0226(4)	7.2(2)
C(7)	1.0847(4)	0.2537(2)	0.0866(4)	7.4(2)
C(8)	0.9664(3)	0.2674(2)	0.0755(3)	6.1(1)
C(8a)	0.9035(3)	0.3183(2)	−0.0025(3)	4.6(1)
C(9)	0.7755(3)	0.3399(2)	−0.0271(2)	4.3(1)
C(10)	0.7721(2)	0.4258(2)	−0.0074(2)	3.6(1)
C(11)	0.8294(2)	0.4660(2)	−0.0846(2)	3.4(1)
C(12)	0.8778(2)	0.4077(2)	−0.1518(2)	3.9(1)
C(13)	0.8329(2)	0.4421(2)	0.1162(2)	3.7(1)
O(14)	0.9397(2)	0.4556(1)	0.1542(2)	4.8(1)
N(15)	0.7592(2)	0.4386(2)	0.1770(2)	4.3(1)
C(16)	0.7934(3)	0.4447(2)	0.3000(3)	5.6(1)
C(17)	0.6766(4)	0.4408(3)	0.3274(3)	8.2(2)
C(18)	0.8703(4)	0.3791(3)	0.3534(4)	8.8(2)
C(19)	0.8567(5)	0.5174(3)	0.3385(4)	9.4(2)
C(20)	0.7408(2)	0.5173(2)	−0.1658(2)	3.5(1)
O(21)	0.6350(2)	0.5192(2)	−0.1720(2)	5.0(1)
N(22)	0.7839(2)	0.5571(2)	−0.2326(2)	3.9(1)
C(23)	0.7130(3)	0.5996(2)	−0.3316(3)	4.6(1)
C(24)	0.6473(3)	0.6634(2)	−0.2973(3)	6.3(1)
C(25)	0.6240(4)	0.5488(2)	−0.4117(3)	6.4(1)
C(26)	0.8008(4)	0.6293(3)	−0.3853(4)	8.2(2)
O(M)	0.4985(2)	0.5929(2)	−0.0645(3)	7.6(1)
C(M)	0.5688(4)	0.6085(3)	0.0428(4)	7.8(2)
H(15)	0.6604	0.4402	0.1542	12(2)
H(22)	0.8629	0.5560	−0.2202	4.4(6)
H(M1)	0.5440	0.5681	−0.0918	10(2)
Compound **3** [**1**·EtCOOH (1 : 1)]				
C(1a)	0.3450(4)	0.7157(4)	0.1991(3)	4.7(2)
C(1)	0.3405(5)	0.7020(4)	0.0854(3)	6.0(2)
C(2)	0.2477(5)	0.5868(5)	0.0015(4)	7.2(2)
C(3)	0.1593(6)	0.4857(5)	0.0288(4)	8.0(3)
C(4)	0.1637(5)	0.4975(4)	0.1417(4)	6.6(2)
C(4a)	0.2570(4)	0.6140(4)	0.2261(3)	5.2(2)
C(5a)	0.4263(4)	0.6899(3)	0.4296(3)	4.8(2)
C(5)	0.4809(5)	0.6398(4)	0.5202(3)	6.0(2)
C(6)	0.6236(6)	0.6951(5)	0.5831(4)	6.8(2)
C(7)	0.7098(5)	0.7998(5)	0.5590(4)	6.8(2)
C(8)	0.6563(4)	0.8511(4)	0.4697(4)	5.6(2)
C(8a)	0.5152(4)	0.7949(3)	0.4045(3)	4.7(2)
C(9)	0.4389(4)	0.8332(3)	0.3022(3)	4.6(2)
C(10)	0.3390(3)	0.8736(3)	0.3390(3)	4.0(1)
C(11)	0.2410(3)	0.7597(3)	0.3688(3)	4.0(1)
C(12)	0.2746(4)	0.6453(3)	0.3532(3)	4.8(2)
C(13)	0.2588(4)	0.9157(3)	0.2400(3)	4.4(2)
O(14)	0.1321(3)	0.8561(3)	0.1837(2)	6.0(1)
N(15)	0.3375(3)	1.0196(3)	0.2160(2)	5.1(1)
C(16)	0.2903(5)	1.0704(4)	0.1126(3)	6.2(2)
C(17)	0.2305(7)	0.9674(5)	0.0004(4)	9.0(3)
C(18)	0.1795(6)	1.1108(5)	0.1160(4)	8.2(3)
C(19)	0.4187(6)	1.1882(6)	0.1251(6)	10.0(3)
C(20)	0.2507(4)	0.7933(3)	0.4939(3)	4.2(2)
O(21)	0.3615(3)	0.8600(3)	0.5792(2)	5.3(1)
N(22)	0.1274(3)	0.7366(3)	0.5014(2)	4.6(1)
C(23)	0.1009(4)	0.7446(4)	0.6097(3)	5.5(2)
C(24)	−0.0540(5)	0.6578(5)	0.5698(4)	7.4(2)
C(25)	0.1340(6)	0.8808(4)	0.6609(5)	8.2(3)
C(26)	0.1852(6)	0.6963(7)	0.6976(5)	9.4(4)
O(A1)	−0.1209(2)	0.6494(3)	0.2701(3)	7.1(2)
O(A2)	−0.1210(3)	0.7994(3)	0.1762(3)	8.1(2)
C(A1)	−0.1805(4)	0.7042(4)	0.2184(4)	5.9(2)
C(A2)	−0.3304(5)	0.6711(6)	0.1896(5)	8.5(3)
C(A3)	−0.4031(6)	0.5624(5)	0.2316(6)	9.1(3)
H(15)	0.4342	1.0649	0.2663	6.6(9)
H(22)	0.0387	0.6885	0.4295	7.5(10)
H(A2)	−0.0220	0.8234	0.1886	11(2)

a) $B_{eq}=1/3\sum_i\sum_j a^*{}_i a^*{}_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 3. Bond Lengths (Å) and Bond Angles (deg) of Possible Hydrogen Bonds in Compounds **2** and **3**. (esd's, where given,[a] are in Parentheses)

Atoms involved	Symmetry	Distance			Angle
		Donor ··· Acceptor	D–H	H ··· A	∠D–H ··· A
Compound **2** [**1** · MeOH (1 : 1)]					
O(M)–H(1M) ··· O(21)	*x*, *y*, *z*	2.766(4)	0.86	1.92	172
N(15)–H(15) ··· O(M)	1−*x*, 1−*y*, −*z*	2.995(3)	1.11	1.96	152
N(22)–H(22) ··· O(14)	2−*x*, 1−*y*, −*z*	3.125(3)	0.90	2.24	168
Compound **3** [**1** · EtCOOH (1 : 1)]					
O(A2)–H(A2) ··· O(14)	*x*, *y*, *z*	2.673(5)	1.00	1.68	170
N(22)–H(22) ··· O(A1)	*x*, *y*, *z*	3.012(4)	0.97	2.05	161
N(15)–H(15) ··· O(21)	1−*x*, 2−*y*, 1−*z*	3.154(4)	0.95	2.23	163

a) The H atom positions are not refined (cf. text).

were calculated after each refining cycle, using geometric evidence. The amide H atoms in both structures, together with the hydroxyl H in **2** and the carboxylic one in **3**, were located from difference electron density maps and were held riding on their respective 'mother' atoms during the subsequent calculations.

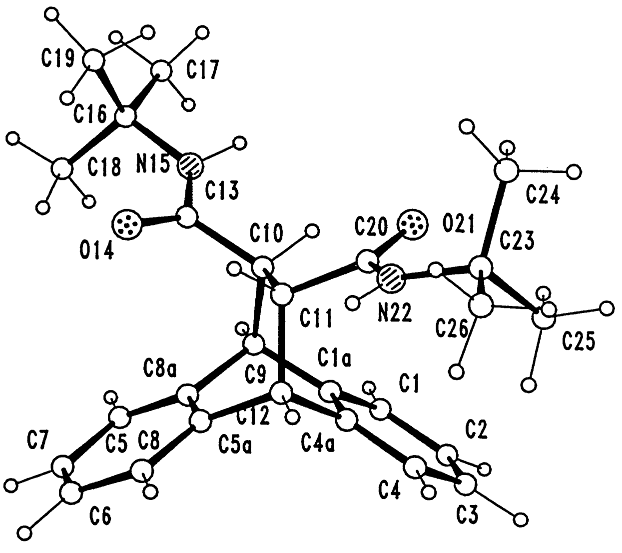

Fig. 1. Perspective view and atom labelling of host molecule **1**.

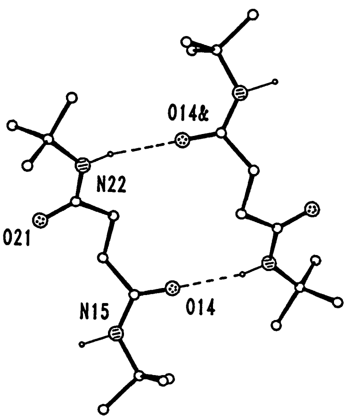

Fig. 2. Diagram of the hydrogen-bonded host–host unit present in the inclusion compounds **2** and **3**. Excerpts of the host molecules including the bridge C-atoms and functional groups only. Hydrogen bonds are indicated by broken lines.

In the last stage of the refinements, the C, O, and N atoms were allowed to vibrate anisotropically, while isotropic temperature factors were refined for the H positions. The methyls were treated as rigid groups with three rotation parameters refined for each of them. The final *R* values together with the crystal data and some details of the refinement calculations are shown in Table 1.

Results and Discussion

The final fractional coordinates and the hydrogen bond dimensions for **2** and **3** are listed in Tables 2 and 3, respectively. The crystallographic labelling of the atoms of the host is shown in Fig. 1. Figure 2 is a schematic representation of the H-bonded host-host interaction found in the complexes. Figures 3 and 4 illustrate the H-bonded host-guest units in **2** and **3**, while the respective crystal packings are shown in Figs. 5 and 6. Intramolecular bond distances and angles and the thermal parameters of the non-hydrogen atoms are collected in Tables 4, 5, and 6.[13)]

Molecular Structures. The dihydroanthracene moiety of the diamide host **1**, in both structures, shows the expected roof-shaped form with bond lengths and bond angles in agreement with the data published earlier for related carboxylic host molecules.[8,14,15)] Accordingly, the elongated C(9)–C(10) and C(11)–C(12) bonds

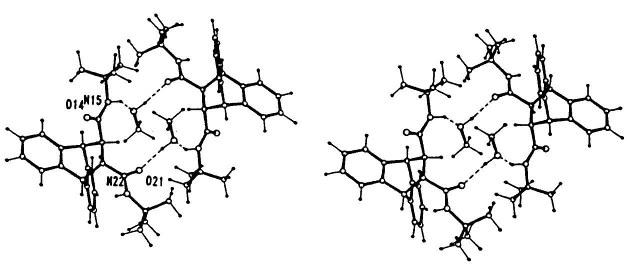

Fig. 3. Stereoscopic view of the hydrogen-bonded host–guest unit in **2** (methanol inclusion complex of **1**). Hydrogen bonds are indicated by broken lines.

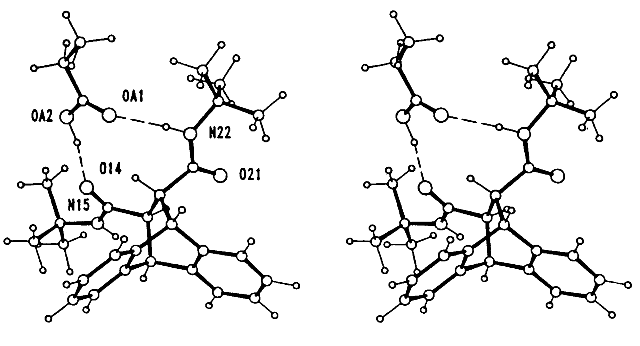

Fig. 4. Stereoscopic view of the hydrogen-bonded host-guest unit in **3** (propionic acid inclusion complex of **1**). Hydrogen bonds are indicated by broken lines.

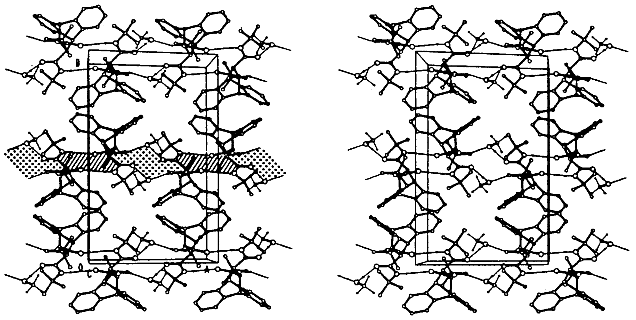

Fig. 5. Stereoscopic view of the crystal packing of **2** (inclusion complex with methanol). The nonrelevant hydrogen atoms of the host are omitted for clarity. Hydrogen bonds as thin lines. Individual cases of zones with host-host and host-guest hydrogen bond contacts are indicated by hatched and dotted areas, respectively.

of the ethano bridge in the present structures have the average length values of 1.577 and 1.562 Å, respectively; the mean C(10)-C(11) bond distance is 1.540 Å, and the dihedral angles[16)] between the two aromatic ring planes are 121.0(1)° in **2** and 122.8(2)° in **3**. The bond dimensions in the amide groups, with the calculated mean values of 1.336 Å for $N\text{-}C_{(sp^2)}$, 1.486 Å for $N\text{-}C_{(sp^3)}$ and 1.231 Å for C=O, also conform to the common values for such bonds.[17)] The guest molecules, (methanol in **2** and propionic acid in **3**) have ordered structures with acceptable bond dimensions.

Packing Relations and Host-Guest Interactions. The host **1** as well as the guests (methanol and propionic acid) in the present inclusion complexes are equipped with functional groups (carbamoyl, hydroxyl or carboxyl) possessing both proton donor and proton acceptor ability. Consequently, hydrogen bonds are expected to play an important role in these structures. There are hydrogen bonds between the amide moieties of symmetry-related host molecules (Table 3). These relatively weak N(-H)···O bonds form 14-membered (including the hydrogen atoms) closed loops when linking the hosts pairwise in both compounds (Fig. 2). The 1 : 1 clusters of hosts comprise two proton donor (NH) and two proton acceptor sites (C=O) for potential H bond interaction with the guests (see Fig. 2).

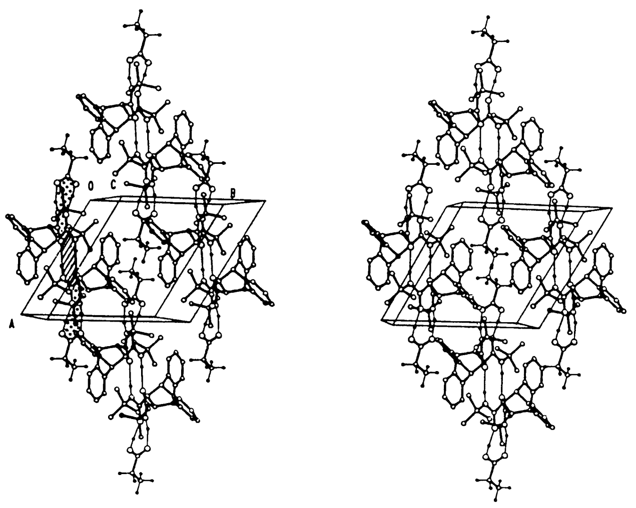

Fig. 6. Stereoscopic view of the crystal packing of **3** (inclusion complex with propionic acid). The nonrelevant hydrogen atoms of the host are omitted for clarity. Hydrogen bonds as thin lines. Individual cases of zones with host-host and host-guest hydrogen bond contacts are indicated by hatched and dotted areas, respectively.

Although both guest molecules have typical proton donor and acceptor functions, the H bond interactions between host and guest show different topologies in the present two complexes. In **2**, each methanol is H-bonded to two different host molecules (or host-host clusters), and the two amide moieties of the host are involved in H-bonding with two different guests. Accordingly, a large, 18-membered (including the H atoms) loop is formed around the center of symmetry via two O-H···O and two N-H···O interactions (Fig. 3). In the case of **3**, however, an 11-membered loop is closed via H-bond interactions involving the two amide moieties of one host and the carboxyl group of the guest molecule (Fig. 4).

Thus, in the methanol inclusion crystal, the total hydrogen bonding scheme results in a framework which is infinite in one dimension. It includes 'double chains' of opposite O-H···O and N-H···O hydrogen-bonded strings, running in the crystallographic *a* direction (Fig. 5). By way of contrast, in the propionic acid inclusion, discrete hydrogen-bonded host-guest associates with 2 : 2 stoichiometry are created (Fig. 6). They include a large 24-membered ring with O-H···O and N-H···O hydrogen bonds. Both the supramolecular strings in **2** and the discrete clusters of host-guest units in **3** are shielded by a smooth cover of lipophilic groups, which makes possible a quite dense packing in the crystal. The host-guest associates are held together by van der Waal's forces.

Conclusions

Elucidations of the crystal structures in the present study provides a rationale for the host properties of **1** and analogous compounds. Normally, amide molecules use their self-complementary hydrogen bonding functionality to form dimers (8-membered hydrogen-bonded rings) in the crystal.[10] Obviously, this causes severe sterical problems for the bulky molecules **1**, both in the intra- and intermolecular sense, except for the extended dimer formation specified in Fig. 2. On the other hand, it is a general rule[10] that good proton donors and acceptors, such as provided by the amide function, are always involved in hydrogen bonding in a crystal structure. Consequently, **1** makes use of suitably shaped proton donor and acceptor guest molecules to accomplish hydrogen bonding in a densely packed host–guest co-crystal. The analogues of **1** with substituents less bulky than *t*-butyl are different.[8] They do not need the aid of a guest molecule for crystallization, and they make no space available for guest molecules. Thus, the present inclusion structures are determined primarily by the bonding characteristics between host and guest and steric requirements in the crystal structure. On the same line, other host molecules with amide functions for selective crystal inclusion may be designed, and the observed interaction patterns are also a promising approach for engineering organic solids.[18]

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