A Novel Clathrate Design: Selective Inclusion of Uncharged Molecules via the Binaphthyl Hinge and Appended Coordinating Groups. X-ray Crystal Structures and Binding Modes of 1,1′-Binaphthyl-2,2′-dicarboxylic Acid Host/Hydroxylic Guest Inclusions[1]

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Abstract: 1,1′-Binaphthyl-2,2′-dicarboxylic acid (**1**) is demonstrated as a novel type of clathrate host whose main mode of action is derived from a combination of the steric barrier and the coordinative interaction principle which constitutes the new "coordinatoclathrate" strategy. Inclusion properties of the crystal lattice of **1** are revealed for a variety of uncharged organic guest molecules (30 examples), ranging from OH-, to NH-, to CH-acidic compounds such as alcohols, carboxylic acids, amides, and nitriles to rather unpolar compounds like bromobenzene and toluene. Marked discrimination selectivities in the clathrate formation from solvent mixtures are found in regard to the group functionality, the substitution pattern, and the molecular size of the guest species, making accessible a simple process for chemical compound separation. The stoichiometries and the increased-temperature as well as the reduced-pressure stabilities of the various clathrates are discussed. The principles of structure of five different alcohol clathrates of **1** are determined with the aid of X-ray structure analysis at 273 K: **1**·2MeOH (**10**) [$P2_1/n$, a = 15.642 Å, b = 14.532 Å, c = 9.292 Å, β = 95.14°, Z = 4]; **1**·2EtOH (**11**) [$C2/c$, a = 11.737 Å, b = 14.522 Å, c = 13.769 Å, β = 101.5°, Z = 4]; **1**·2(2-PrOH) (**13**) [$C2/c$, a = 12.051 Å, b = 14.776 Å, c = 14.362 Å, β = 102.53°, Z = 4]; **1**·2-BuOH (**15**) [$P2_1/n$, a = 12.009 Å, b = 12.747 Å, c = 14.982 Å, β = 105.52°, Z = 4]; **1**·ethylene glycol (**24**) [$P2_1/n$, a = 14.276 Å, b = 9.533 Å, c = 15.556 Å, β = 109.19°, Z = 4]. In all these cases, however, hydroxyl groups of the host molecules were found to be intercalated via large pseudo-ring formation between the carboxyl functions of at least two host units of opposite chirality with a different mode of hydrogen bridging. Depending on the host:guest stoichiometry (1:1 or 1:2) and on the nature of the guest molecules, these entities consist of three, four, or eight moieties (COOH, OH). The direction of the strong and cooperative bonds is always *homodromic*. The shape and the size of the cleft formed in the matrix of cooperating host moieties are shown to vary, matching the specific needs of coordinating interactions (hydrogen bonding) and topological requirements (branching, e.g.) of the guest species.

The understanding of weak intermolecular interactions is becoming of central interest in different fields of chemistry.[3] In this regard, host–guest relationships of coronate/cryptate fashion have helped to clarify some of the existing problems.[4] A second approach makes use of the fixation of uncharged guests into the hydrophobic interior of cyclodextrins[5] and analogous cone-, collar-, donut-, picket-fence-, and pumpkin-shaped molecular cavities and clefts.[6] Recently, host–guest compounds of the lattice inclusion type[7] appeared to be more attractive candidates to study weak intermolecular interactions and to translate them into practice.[8-10] Among them, special attention is drawn to the construction of chiral host lattices which may operate in terms of a chiro-differentiating separation process via clathrate inclusions.[11]

Although the phenomenon of lattice inclusion dates back to the middle of the past century,[12] only limited success was made in the directed synthesis of new clathrate hosts,[13,14] and most of the known clathrate compounds were discovered by accident.[15] Here we report on a novel principle for constructing host molecules; a representative example is given by **1**, which allows the entry into a new family of potentially chiral host–guest lattice inclusions. We designate them as "coordinatoclathrates" for reasons illustrated below. The significant and unusual properties of this new host

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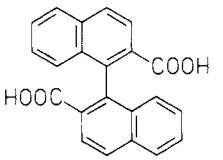

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system in selective inclusion and clathrate stability prompted us to initiate a structure study. Altogether, this paper gives a survey of the different host–guest binding modes detected by X-ray crystallography in five of the thirty isolated clathrates of **1**.

Conception

Topological (steric) interactions represent a domain of neutral-component host–guest compounds.[5-7] Binding selectivity in this case is effected by the steric requirements of the host and guest individuals to form the specific host–guest aggregate. Most of the lattice inclusion compounds known so far respond to this regularity.[16]

Our efforts in developing new strategies in lattice inclusion chemistry refer to the fact that in addition to *topological* interactions, *directed* binding forces, e.g., of dipole–dipole, ion–dipole, and ion–ion type (coordinative interactions), and H-bonding between a host and a guest component[17] give rise to control guest selectivities on a higher level (Figure 1). Consequently, an appropriate host molecule should meet a new constructional principle (Figure 1).

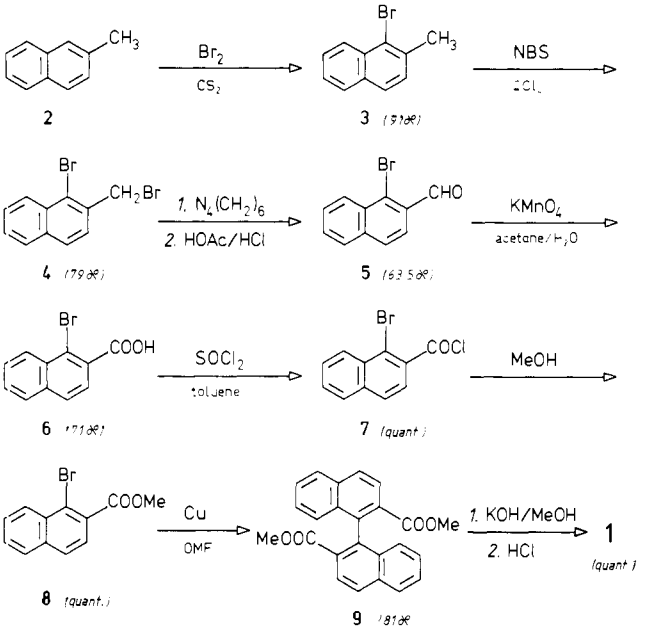
Realization of this concept was through the substituted *1,1'-binaphthyl* system, where the bulky binaphthyl unit displays the required topological barrier[18] and suitably positioned substituents may mediate complementary host–guest coordination. In particular, the 1,1'-binaphthyl-2,2'-dicarboxylic acid (**1**) was expected as a potential host molecule for producing *coordination-assisted* lattice inclusion ("coordinatoclathrate" formation), e.g., via H-bonding.[19] Further advantages which lead us to decide in favor of this system arise from the multivariate possibilities in converting the carboxylic substituents into sensors with other functional group characteristics (e.g., ester, amide, amine, etc.) and from the fact that the binaphthyl hinge allows an easy optical resolution[20] which, besides the programming of guest selectivities, may also effect a chiral discrimination in the future.

The term "coordinatoclathrate" for this specific type of lattice inclusion comes from a new proposal for the nomenclature of host–guest compounds,[21] the basic idea of which is expressed in Figure 1.

Results and Discussion

Synthesis of the Host Compound (1). For the synthesis of the binaphthyldicarboxylic acid host **1**[22-25] we proceeded on the route outlined in Scheme I. This synthesis is composed of a number of well-known steps. The overall yield of **1** obtained for this synthetic pathway amounts to 26%. In the initial step 2-methylnaphthalene (**2**) was converted into the corresponding 1-bromo derivative **3**,[26-29] followed by a side-chain bromination

Scheme I



(**4**),[28-30] a Sommelet reaction (**5**),[25] and an oxidation to give the acid **6**.[25,30,31] The latter was transformed into the corresponding acid chloride **7** and esterified to produce **8**.[30,31] The coupling of the bromo ester **8** to give the binaphthyl diester **9**[24,25,30] was effected under Ullmann conditions,[32] and the saponification of this ester[25] completes the synthesis. The yield for the coupling step could be improved substantially compared with the earlier literature procedure[24,25,30] by using activated copper bronze[33] in carefully dried and degassed boiling dimethylformamide instead of heating up the components without a solvent.[34]

Clathrate Formation. Inclusion Stoichiometry. When 1,1'-binaphthyl-2,2'-dicarboxylic acid (**1**), which is obtained from the synthesis as an amorphous powder,[25] was recrystallized from ethanol, transparent heavy crystals were formed. They were identified as a solvated species of **1** containing ethanol in a strict 1:2 (**1**:EtOH) stoichiometry (NMR integration). From this, its stability toward vacuum drying (ambient temperature), and its behavior on heating (crystals turn opaque with the release of the solvent at 88 °C) we concluded the presence of a clathrate (**11**).[35]

Other kinds of *alcohols* like methanol, 1-propanol, and higher normal alcohols as well as branched derivatives differing in their grade of ramification and in the substitution pattern or being of the mono- or oligovalency type, respectively, reveal analogous inclusions on recrystallization. A list of the different examples (**10–25**) is given in Table I.

The stoichiometries found for these host–guest aggregates (Table I) depend on the size and bulkiness of the corresponding guest alcohol. Methanol (**10**) and ethanol (**11**), for example, are taken up by the crystal lattice of **1** in a host:guest stoichiometry of 1:2. The isomeric butanols (**14–16**), however, show 1:1 stoichiometry. The same is valid for the inclusions of benzyl alcohol (**22**) and of trichloroethanol (**23**) as bulky guest substitutes and for those of the bifunctional representatives ethylene glycol (**24**)

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(34) Cf.: Miyano, S.; Tobita, M.; Suzuki, S.; Nishikawa, Y.; Hashimoto, H. *Chem. Lett.* **1980**, 1027.

(35) Cf.: Weber, E.; Vögtle, F. *Angew. Chem.* **1980**, *92*, 1067; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1030.

Table I. Clathrate Inclusion Compounds of **1**: Stoichiometries and Thermal Stability Characterization

compd	guest compd	host:guest mol ratio[a]	thermal dec, °C[d]
10	methanol	1:2	146 (+82)
11	ethanol	1:2	88 (+10)
12	1-propanol	2:1	72 (−25)
13	2-propanol	1:2	86 (+4)
14	1-butanol	1:1	72 (−46)
15	2-butanol	1:1	92 (−7)
16	2-methyl-1-propanol	1:1	71 (−37)
17	2-methyl-2-propanol	1:1	141 (+58)
18	1-pentanol	1:2	123 (−15)
19	2-methyl-1-butanol	2:1	135 (+7)
20	2-methyl-2-butanol	1:2	164 (+62)
21	4-methyl-1-pentanol	1:1	154 (−9)
22	benzyl alcohol	1:1	120 (−85)
23	trichloroethanol	1:1	117 (−34)
24	ethylene glycol	1:1	165 (−32)
25	propylene glycol	1:1	149 (−66)
26	acetic acid	1:1	115 (−3)
27	propionic acid	2:1	139 (−2)
28	lactic acid	1:1	140 ( )[e]
29	formamide	1:2	136 (−74)
30	*N*-methylformamide	1:2	108 (−75)
31	*N,N*-dimethylformamide (DMF)	1:2	117 (−35)
32	dimethyl carbonate	2:1[b]	<25
33	diethyl carbonate	*c*	<25
34	acetylacetone (2,4-pentanedion)	1:1	64 (−70)
35	acetonitrile	1:1	119 (+38)
36	nitromethane	1:1	126 (+25)
37	dimethyl sulfoxide	1:1	155 (−34)
38	diethyl ether	*c*	<25
39	bromobenzene	1:1	116(−40)

[a] Determined by NMR integration (in CD_3CN/Me_2SO-d_6, 2:1) after a drying period of 12 h at 0.5 torr for each compound. [b] Decomposites under vacuum drying at ambient temperature. [c] Unstable at atmospheric pressure. [d] Value indicates the beginning of the clathrate decomposition (either onset of opacity or release of the gaseous guest component). Specification in parentheses gives the relative thermal stability (difference between the decomposition point of the clathrate and the boiling point of the respective neat guest solvent at atmospheric pressure). [e] No description of the boiling point for the neat guest solvent in the literature.

and propylene glycol (**25**) (all 1:1 stoichiometry).

A second type of guest species which shows affinity toward the uptake into the **1** lattice is represented by *carboxylic acids*. Examples belonging to this sort of host–guest inclusion were obtained for acetic (**26**), propionic (**27**), and lactic acids (**28**) (the stoichiometries vary from 1:1 to 2:1). Appropriate guest species were also found in the area of *carboxylic amides* and *esters*, of which formamide (**29**), *N*-methylformamide (**30**), and *N,N*-dimethylformamide (**31**) led to inclusions with 1:2 (host:guest) stoichiometry, whereas the host–guest aggregates formed with esters, e.g., dimethyl carbonate (**32**), diethyl carbonate (**33**), gave no reproducible stoichiometry ratio after drying under conditions as specified in Table I because of their low stability. On the other hand *CH-acidic* solvents such as acetylacetone (**34**), acetonitrile (**35**), nitromethane (**36**), and dimethyl sulfoxide (**37**) yield stable inclusions, each having a strict 1:1 stoichiometry. We were also able to isolate a 1:1 stoichiometrical inclusion compound from the relatively nonpolar bromobenzene, whereas diethyl ether as a guest component seems too volatile to be retained in the host lattice under ambient conditions.

Clathrate Stability (Increased-Temperature and Reduced-Pressure Clathrate Decomposition Properties). With some exceptions, the clathrate compounds are almost indefinitely stable upon storage in air (cf. Table I). Also under vacuum conditions (0.5 torr, 12 h) the majority of the isolated inclusion compounds exhibit a remarkably strong guest fixation. On heating under reduced pressure (0.5 torr), a decomposition with growing opacity is observed within a specific temperature range for each compound (Table I). In the case of the MeOH, EtOH, *t*-BuOH, 2-methyl-2-butanol, acetonitrile, and nitromethane inclusions (**10**, **11**, **17**, **20**, **35**, **36**), these temperature ranges lie above the boiling point of the corresponding guest solvent, most remarkably for MeOH, for which the boiling point and the point for the beginning of the decomposition differ by 70 °C. That indicates a particularly strong clathration.[36] The bulk of the compounds, however, fall into the range of the boiling point of the pertinent pure guest component or shortly below (cf. values given in parentheses in Table I).

Table II. Preference of Guest Binding of Host **1** from a Two-Component Solvent System

entry	recrystallization solvent compd mixt (equimolar ratio)	relative guest excess, % GE
1	MeOH/*EtOH*[a]	46.3[b]
2	MeOH/*t-BuOH*	91.3
3	*MeOH*/toluene	14.3
4	*EtOH*/*i*-PrOH	78.9
5	*EtOH*/*t*-BuOH	92.4
6	EtOH/*$PhCH_2OH$*	19.7
7	EtOH/*$HOCH_2CH_2OH$*	>95.0
8	*EtOH*/CH_3COOH	>95.0
9	*EtOH*/CH_3CN	>95.0
10	EtOH/*DMF*	>95.0
11	*n*-PrOH/*i-PrOH*	29.2
12	*n*-BuOH/*t-BuOH*	73.9
13	*i*-BuOH/*t-BuOH*	78.0
14	CH_3CN/*Me_2SO*	>95.0
15	*CH_3CN*/toluene	41.8

[a] Solvents printed in italics refer to those preferentially enclathrated. [b] Determined by NMR integration (in CD_3CN/Me_2SO-d_6, 2:1) of the isolated crystals after a drying period of 12 h at 0.5 torr.

The determination of solid-state IR spectra (KBr) highlights bands which document a coordinative host–guest interaction according to our concept. The values for the OH-stretching modes of the included alcohols indicate strongly bonded OH groups as they are very close to those found in the pure liquid alcohols rather than in the gaseous (e.g., 3374 cm^{-1} in the clathrated species vs. 3676 cm^{-1} for gaseous ethanol). The bands in the 1700-cm^{-1} region arising from the carbonyl group of the host lattice refer, as expected, to stronger interactions in the alcohol cases than in the others.

Lattice Inclusion Selectivity and Guest Discrimination (Clathrate Formation Selectivity). The host lattice of **1** allows the selective inclusion of guest molecules. The results are summarized in Table II. A selection is derived from steric as well as from chemical points of view. In some instances a practically 100% discrimination of one guest species is achieved from a solvent mixture. One recognizes most distinctly a discrimination for a combination of guest species differing in the functional group characteristics. But also within a series of homologues and different substituted and branched compounds, respectively, belonging to the same class of substances, a discrimination is effected in up to a 90% ratio.[37] For instance, the crystallization of **1** from a 1:1 mixture of MeOH/EtOH preferentially yielded the corresponding EtOH clathrate under the conditions given in Table II in a relative guest excess of 46.3% (entry 1). A discrimination in the two-component system MeOH/*t*-BuOH was found to clearly favor *t*-BuOH (GE 91.3%, entry 2), showing again the preference of the host lattice to the higher homologues of MeOH. However, in the cases of the solvent mixtures EtOH/*i*-PrOH and EtOH/*t*-BuOH the order for the discrimination is inverted; EtOH is now preferred (entries 4, 5). An even more pronounced discrimination (GE 95%) is seen in the solvent pair EtOH/acetic acid (entry 8). The removal of the latter compound from a polar media is normally observed to be difficult. EtOH is also favored in a 95% guest excess rate to

(36) This high thermal stability equals that of the corresponding tri-*o*-thymotide solvent inclusion which is representative of strong clathration. See: Baker, W.; Gilbert, B.; Ollis, W. D. *J. Chem. Soc.* **1952**, 1443.

(37) Guest selectivity properties to this extent are out of the ordinary: cf. ref 8 and 13.

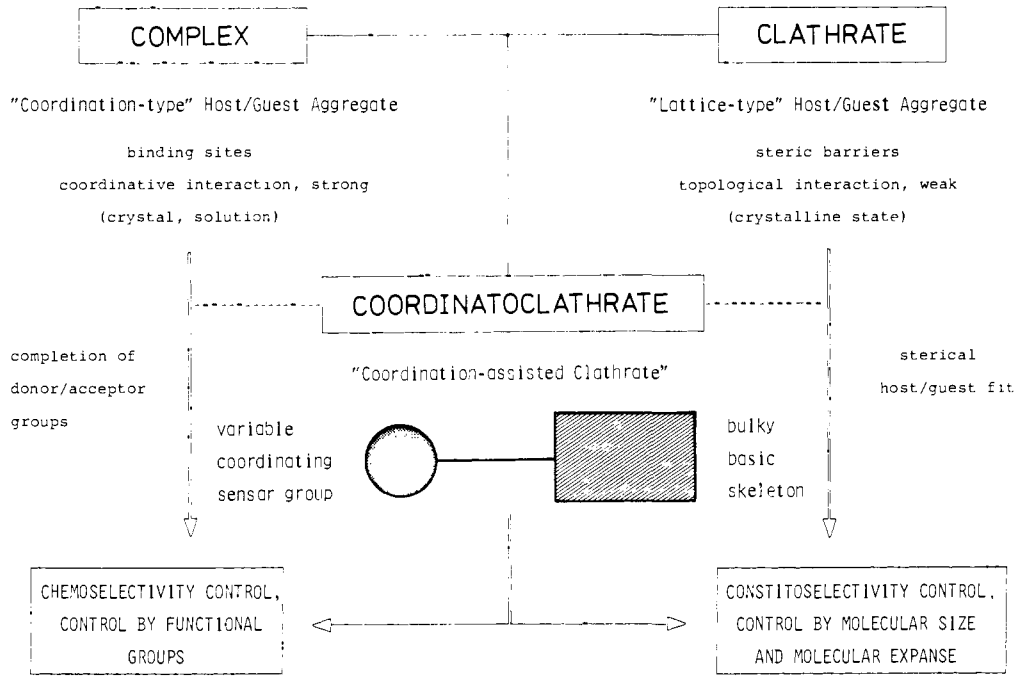

Figure 1. Coordinatoclathrate concept and abstracted structure of a coordinatoclathrate host: definitions, relations, and functions of control.

acetonitrile (entry 9), but not to DMF, the ratio of which is reversed (95% GE of DMF, entry 10). Also EtOH is not the preferred guest entity in the presence of the solvent compounds ethylene glycol and benzyl alcohol (entries 6, 7). Guest preference in the first case may emerge from the more extensive H-bonding pattern due to the bivalency of the guest alcohol, in the latter case from the phenyl group which seems structurally well adapted to the aromatic moieties of the host. Entries 11–13 are distinguished by the fact that the higher branched homologues of PrOH and BuOH, as a rule, are the favored guest components. The practically complete discrimination of acetonitrile vs. dimethyl sulfoxide (entry 14) may also be interpreted as a remarkable result, since both solvent molecules are of the same category (dipolar aprotic) and additionally have comparable polarities.[38] This unexpected finding is retained even when acetonitrile is applied in a 10-fold excess with respect to dimethyl sulfoxide. The preferred uptake of acetonitrile in a mixture with toluene (entry 15), however, does not refer to such an exquisite molecular guest competition process (cf. also entry 3).

Discrepancies which may be recognized from a comparison of the thermal stability for a specific inclusion compound with its selectivity at formation are fictitious, since for both representations different processes should be taken into account. The clathrate formation ("formation selectivity") will normally be kinetically controlled, whereas the thermal stability ("binding selectivity") of a clathrate is pivoted upon the thermodynamics of the guest release.

Description of the Crystal Structures of the Clathrates 10, 11, 13, 15, and 24. (1) Bonding Parameters. Bond lengths in the binaphthyl moieties and those in the carboxyl groups (Table III, deposited) agree with those from earlier studies on binaphthyl and related compounds.[39,40] They generally also conform to the expected values. This, however, does not hold for the dimensions of the guest molecules which show appreciable deviations even in the alcoholic C–O distances.[41] The influence of structural disorder (be it static or dynamic) is usually,[42] though not always,[43] recognized in the crystal chemistry of inclusion compounds. As described in the Experimental Section, we could resolve major disorder sites in the guest molecules of **11** and **13** but not in **15** where an unreasonably short distance (1.16 Å) to the C atom of a methyl terminus obviously indicates disordering of this position. Attempts to correct for thermal motion effects by applying a simple "riding motion" approach[44] led to no substantial improvement in the bonding dimensions of the 2-butanol and ethylene glycol guest molecules in **15** and **24**.

(2) Molecular Conformation. The shape of the molecules is as depicted in Figure 2a–e, indicating some disorder of the guest components for **11** and **13**. The binaphthyl units show appreciable deviations from planarity (Table IV, deposited), which is in agreement with earlier observations for this moiety.[39] The dihedral angles between the naphthyl groups (Table V, deposited) lie in a narrow range centered around its mean value 87.3° (1.5), thus differing from those values determined for racemic (68.6°) and resolved binaphthyl (103.1°),[39a,b] but also for a (+)-dimethyl 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylate bromobenzene solvate (76.6°)[39g] or the recently published structure of 2,2′-dimethoxy-1,1′-binaphthyl (111°)[39i] as similar substitution analogues. Close values, however, were observed in the structure of (−)-2,2′-bis(bromomethyl)-1,1′-binaphthyl (91.6°),[39c] of 2,2′-dihydroxy-1,1′-binaphthyl (89°)[39h] and of 2,2′-diamino-1,1′-binaphthyl (85°).[39h] The spread of these values (68–111°) over the *synclinal/anticlinal* range suggests that the rotation around the C(1)–C(1′) bond is a relatively soft parameter in this angular range which may be influenced by the crystal or by packing forces. The carboxyl groups which are of great stability in the *synplanar* form[40] are slightly inclined to the plane of the respective naphthyl

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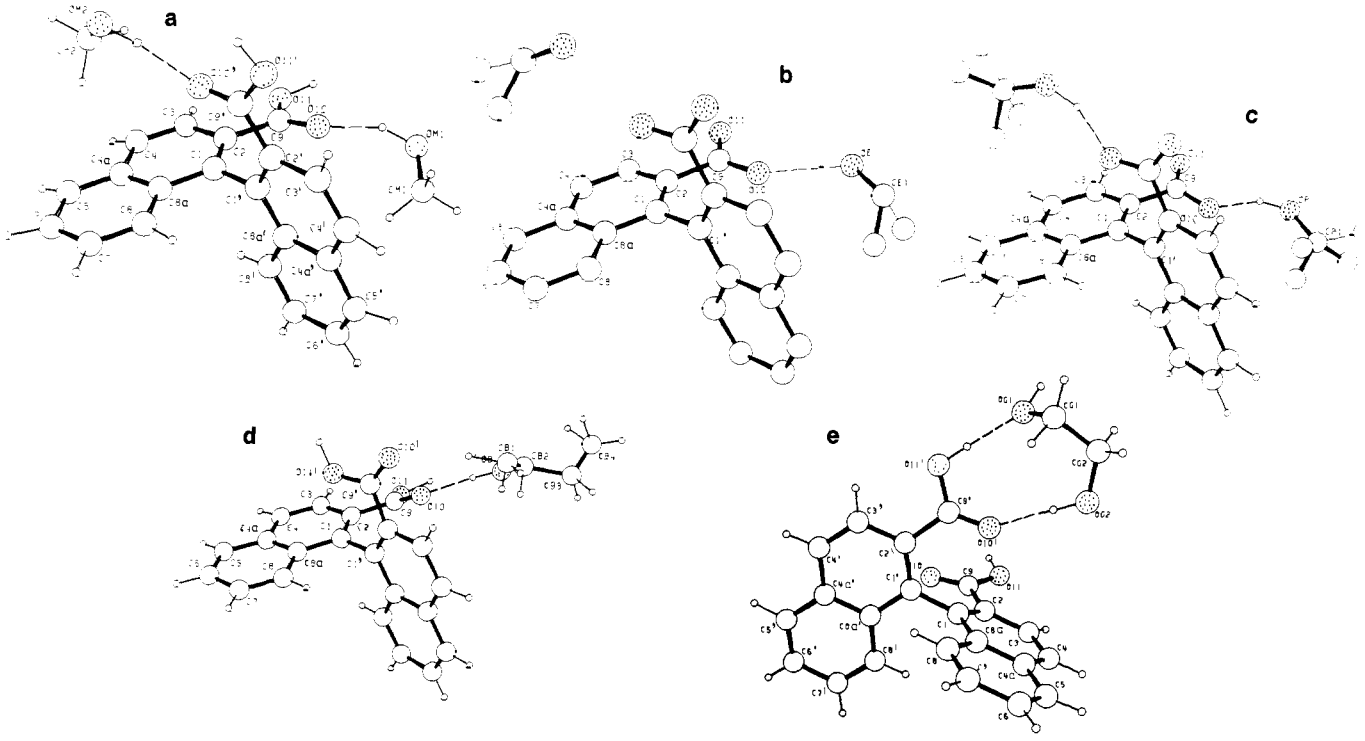

Figure 2. (a–e) Molecular structures of the coordinatoclathrates: (a) 1·2MeOH (**10**), (b) **1**·2EtOH (11), (c) **1**·2(2-PrOH) (**13**), (d) **1**·2-BuOH (**15**), (e) **1**·$HOCH_2CH_2OH$ (**24**). Solid and dashed lines represent covalent and hydrogen bonds, respectively. The structures of 11 (Figure 2b) and of 13 (Figure 2c) show a rotational disorder in the terminal methyl carbon atoms of the guest alcohols.

group (Table V). The dihedral angle between these two moieties however, shows a tendency to increase parallel to the size and the ramification of the guest alcohols.

(3) Hydrophilic Host–Guest Interactions. Modes of Hydrogen Bonding. Hydrogen bonding is one of the main chemical characteristics of carboxylic acids and alcohols.[45] Accordingly, it also plays a decisive role in the packing pattern of these compounds in the crystalline state.[40] The present clathrate structures give a particularly clear manifestation of this principle in holding together chemically different species within the same crystal lattice (Figure 3a–d).

The H-bonding schemes of compounds **10**, **11**, and **13** display similarity insofar as the alcoholic OH groups are embedded in a symmetrically fashioned *12-membered* (inclusive H-atoms) pseudo-ring (Figure 3a,b; R = Me, Et, *i*-Pr). The 12-membered ring in each case is built up from the OH groups of two alcohol molecules and from two COOH groups of two enantiomerically related host molecules. On the other hand, the clathrate **15** exhibits a dissymmetrical *10-membered* ring system as a building block of the crystal lattice (Figure 3c). Two carboxyl groups of two host molecules of opposite chirality establish a donor···acceptor interaction and only one 2-butanol molecule takes part, with the same donor/acceptor relation as in the former case, in closing this circular H-bond system. The structure of **24** shows again the formation of a symmetrical ring system. The contributing moieties (four hydroxyls of two individual ethylene glycol guest molecules, and four COOH groups belonging to 2 × 2 enantiomerically related host molecules) form a *24-membered* pseudo-ring in this case (Figure 3d).

The general features of the hydrogen-bonding pattern bear importance as far as the outstanding clathrating ability, selectivity, and systematics of the studied compounds are concerned. It is important to note that relatively planar closed loops of hydrogen bonds are formed in all the cases in which at least two molecules of opposite chirality are involved and the guests (OH groups) are embedded. This pattern, which may be termed as an "extended dimer" image, is certainly determined by the ability of the COOH groups and the alcoholic OH function to act as hydrogen donor and acceptor at the same time (cf. ref 40c).

Recently, circular hydrogen bonds which show close topological similarity to those discussed have gained considerable attention, e.g., on the cyclodextrin sector,[42b,46] mainly because of the stability enhancement of such arrangements via the cooperative effect.[47] Consequently, apart from the enthalpy contribution of hydrogen bonding in the binding process of the substrate molecule, there may be a further stabilizing factor operating in the clathrates of **1**. The observed $H\cdots O_A$ vectors characterize the systems of hydrogen bonds as *homodromic*[46b] in each case (Figure 3a–d).

As a further consequence, the geometry of hydrogen bonding displays rather short contact distances compared with the values ($H\cdots O_A$ = 1.82 Å, $O-H\cdots O_A$ = 167°, $O_D\cdots O_A$ = 2.77 Å)[47b] obtained from recent analyses on the geometry of $O_D-H\cdots O_A$ interactions.[47b,48] The dimensions, however, may be classified into two categories according to the types of the donor/acceptor groups (Table VI). Those in type "X" (i.e., where the donor is the carboxylic OH and where the acceptor is the alcoholic one) seem to be shorter [$H\cdots O_A$ = 1.62 (9) Å, $O_D\cdots O_A$ = 2.611 (35) Å] and somewhat more linear [$H\cdots O_A$ = 170 (6)°] than their "Y" counterparts [$H\cdots O_A$ = 1.82 (9) Å, $O_D\cdots O_A$ = 2.761 (84) Å, $O_D-H\cdots O_A$ = 163 (10)°]. The tendency seen in these data may parallel other observations derived from statistically more significant data sets: the shorter a hydrogen bond, the more linear it tends to be.[47b,48] The difference between the two classes may be understood in terms of the acidity/basicity difference of the respective moieties taking part in the formation of these hydrogen-bonded clusters.

These findings suggest that it is not a prerequisite to have larger hydrated molecules to form closed loops of hydrogen bonds.[49]

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Table VI. H-Bonding Dimensions of the Different Clathrates

compd	bond[a] class	bond distance, Å			angle, deg,
		$O_D \cdots O_A$	O_D-H	H$\cdots O_A$	O_D-H$\cdots O_A$
10 (1·2MeOH)[b,c]	X	2.633 (4)	0.98	1.66 (2)	171
	X	2.588 (4)	1.05	1.54 (1)	172
	Y	2.788 (4)	1.05	1.83 (2)	150
	Y	2.734 (4)	0.97	1.79 (5)	161
11 (1·2EtOH)		2.66 (1)			
		2.62 (1)			
13 [1·2(2-PrOH)][b]	X	2.676 (3)			
	Y	2.694 (3)	1.01	1.73 (2)	158
15 (1·2-BuOH)[c]	X	2.565 (3)	1.06 (3)	1.51 (3)	171 (2)
	Y	2.693 (3)	0.95 (4)	1.75 (4)	173 (3)
	Z	2.640 (3)	1.13 (4)	1.55 (4)	161 (3)
24 (1·ethylene glycol)[c]	X	2.615 (3)	1.00 (3)	1.65 (3)	161 (2)
	X	2.654 (2)	0.92 (3)	1.74 (3)	176 (2)
	Y	2.917 (2)	0.97 (3)	1.99 (3)	157 (2)
	Y	2.739 (2)	0.93 (3)	1.81 (3)	176 (2)

[a] Assignment, donor/acceptor characterization: X, –C(O)–OH/R–OH; Y, R–OH/–C(OH)=O; Z, –C(O)–OH/–C(OH)=O. [b] Esd's directly related to H-atom positions are meaningless for these structures because of the nature of the refinement. [c] Mean values[d] and root mean square deviations for structures **10**, **15**, and **24**: $O_D \cdots O_A$, (X) 2.611 (35), (Y) 2.761 (84); O_D-H, (X) 1.00 (6), (Y) 0.98 (4); H$\cdots O_A$, (X) 1.62 (9), (Y) 1.82 (9); O_D-H$\cdots O_A$, (X) 1.70 (6), (Y) 163 (10). [d] Averaged over five and six values for "X" and "Y", respectively.

Table VII. Summary of Crystal Data and Experimental Details

compd	10	11	13	15	24
formula	$C_{22}H_{14}O_4 \cdot 2CH_3OH$	$C_{22}H_{14}O_4 \cdot 2C_2H_5OH$	$C_{22}H_{14}O_4 \cdot 2C_3H_7OH$	$C_{22}H_{14}O_4 \cdot C_4H_9OH$	$C_{22}H_{14}O_4 \cdot C_2H_4(OH)_2$
fw	406.43	434.49	462.54	416.48	404.42
color	colorless	colorless	colorless	colorless	colorless
space group	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$
cell dimensions					
a, Å	15.642	11.737	12.051	12.009	14.276
b, Å	14.532	14.522	14.776	12.747	9.533
c, Å	9.292	13.769	14.362	14.982	15.556
β, deg	95.14	101.50	102.53	105.52	109.19
Z	4	4	4	4	4
cell vol, Å^3	2104	2300	2496	2210	1999
calcd density, g/cm^3	1.283	1.254	1.230	1.252	1.343
$(\sin \xi)/\lambda$ limit, Å^{-1}	0.7035	0.5947	0.5947	0.6278	0.6278
total no. of unique reflections collected	3947	1899	1998	4558	4109
no. of reflections used in refinement	2308 ($I > 2\sigma I$)	842 ($I > 2\sigma I$)	707 ($I > 2.5\sigma I$)	2281 ($I > 2.5\sigma I$)	2261 ($I > 3\sigma I$)
no. of variables refined	279	149	175	281	272
final agreement factors, R	0.068	0.072	0.075	0.062	0.050
R_w	0.062	0.075	0.075	0.046	0.042

Simpler systems can also mimic this phenomenon. To our knowledge, structural data where the donor and the acceptor parts of the hydrogen bridge system are derived from carboxylic acid and alcohol hydroxyls of individual molecules are rather rare.[50] They may open the way to a new field of hydrogen-bonding studies in solids.

(4) Hydrogen Bonding and C_2 Molecular Symmetry. The important role of hydrogen bonding in establishing crystal lattices[41,51] and especially in the building-up of host matrixes is well accepted.[7,13] A characteristic feature for those clathrate structures, however, is that the hydrogen bonding serves for the building-up of the host lattices *only*, and the guest species are not involved in any direct hydrophilic interaction with the included host molecules.[52] At best, a partial incorporation of the guest molecules into the H-bonding system of a host lattice may occur at the trimesic acid clathrates.[53] Nevertheless, the hydrogen-bonding schemes formed in this class of compounds (2-D ribbon-like type) do not restrict oneself to the maximum acceptor rule recently postulated,[40c] as the present clathrates do.

The C_2 molecular symmetry of **1**, which coincides with crystallographic 2-fold axes in the clathrates **11** and **13** (Figure 3b), bears consequences in building up each of the host–guest lattices. All these structures contain crystallographic glide planes (either c or n; cf. Table VII) which, in accord with former findings,[40a,57] are orthogonal to the direction of the 2-fold rotor inherent in these structures and which serve to propagate the building block of the hydrogen bonding through the crystal. The deviation in the host molecules from ideal C_2 symmetry in **10**, **15**, and **24** is not very large, and most often it is represented by the slightly misaligned carboxyl groups. This is the effect most pronounced in the structure of **15** which has the most dissymmetric hydrogen-bonded ring system, with the largest tilt angle of the carboxyl group in this line of compounds.

(49) Cf.: Jeffrey, G. A. In "Molecular Structure and Biological Activity"; Griffin, J. F., Duax, W. L., Eds.; Elsevier-Biomedical: New York, 1982; p 134. (b) Sudhakar, V.; Bhat, T. N.; Vijayan, M. *Acta Crystallogr., Sect. B* **1980**, *B36*, 125.

(50) A fragment search of independent COOH and COH moieties in the Cambridge Crystallographic Data Base (CCDB) which includes 35 256 entries (state May 1983) reveals 15 cases[59] out of 309 hits which contain these groups in independent molecules (adducts and solvates). Of these cases the analyzed 13 available structure show the following pattern: 6 cases (ref codes AMTBUB, CHOLET, CHOPAL, CTBGLU, DCAET10, and DXCHET) where no interaction between COOH and ROH occur, 4 cases (ADRTAR, BAMANT10, MIPROF, and CAMANX) in which a chain-like involvement of COOH and ROH is mentioned, 3 cases [TPTPCM, SULFZC, and SERASC10 (cf. ref 49b)] where an H-bonded ring system similar to that in, e.g., **10** is formed. This fact was, however, not recognized in TPTPCM.

(51) Lifson, S.; Hagler, A. T.; Dauber, P. *J. Am. Chem. Soc.* **1979**, *101*, 5111.

(52) (a) Flippen, J. L.; Karle, J.; Karle, I. L. *J. Am. Chem. Soc.* **1970**, *92*, 3749. (b) Cf. also: Hardy, A. D. U.; McKendrick, J. J.; MacNicol, D. D.; Wilson, D. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 729.

(53) Herbstein, F. H.; Kapon, M. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1614 and former contributions of this series.

(5) Hydrophobic Interactions, Shape, and Dimension of the Host Cages. Hydrophobic interactions as an active principle are widely recognized in biochemistry[54] and, for obvious reasons, also in the rapidly growing field of artificial enzyme mimicry.[3b,5d,55] The systematic use of the idea of "coordinatoclathration" also takes advantage of hydrophobic interactions by offering a lipophilic environment to the aliphatic portions of the guest substrates. In the present structures, *apolar channels* delimited by the bulky binaphthyl moieties are observed running through the host lattice (Figure 4, deposited). They are regularly broken by the coordinated COOH and OH groups which represent the *polar* environment. How frequently this occurs is closely related to the nature of the guest molecules and the disposition of the size and shape of the hydrophobic cavities (Figure 5).

In clathrate **10**, a guest molecule faces only its counterparts through the polar region of the 12-membered pseudo-ring of hydrogen bonding (cf. Figure 3a). The dimensions of the cleft formed by the surrounding groups are 6.5 Å ("height") and 5.6 Å ("width"), perpendicular to the O(α)–C(α) vector (Figure 5a).

On accommodating the larger guests in **11** and **13** the width of the cage is increased to 6 Å with a depth of 4.1 Å (Figure 5b). Maintaining a relation in the polar region analogous to that in **10** (cf. Figure 3a,b), there is somewhat more room for all the aliphatic parts of both guest molecules, resulting in a somewhat looser packing as reflected in the densities of these crystals (cf. Table VII).

Clathrate **15**, however, uses another way to build up its structure. The asymmetrical ring of hydrogen bonding cannot accommodate a center of symmetry (cf. Figure 3c), and this is now found in between the aliphatic moieties of neighboring guest molecules. The walls of the participating naphthyl moieties are not parallel any longer, thus giving rise to a parallelepiped-shaped cavity with dimensions as shown in Figure 5c. The depth of the cleft in **15** is approximately twice as large as in **11** and **13** (8.8 vs. 4.1 Å).

Groupings of the polar and apolar regions as observed in these crystals may directly favor the rotational disorder of the guest molecules as established for **11** and **13** and suspected for **15**. It thus represents a possibility for increasing the entropy of the molecular aggregate and thereby having a small stabilizing contribution in the energy term. The "observed" degree of freedom (59° for the EtOH and 45° and 55°, respectively, for the *i*-PrOH guest molecules) contributes a moderate entropy change of $\Delta S \simeq 0.4$ kJ/mol. This is also an interesting analogy to larger, more complicated clathrate systems, where such a change may also contribute favorably to the Gibbs free energy of clathrate formation.[5e,42b]

In **24** the situation is again different. The guest molecule has a relatively small lipophilic surface and is partly turned inwards toward the center of a huge 24-membered hydrogen-bonded ring (cf. Figure 3d). The guest molecules seem to fit partly into a preformed void of host molecules maintained by the atoms in the vicinity of the C(1)–C(1′) bond (Figure 5d). In contrast to the building blocks in **10**, **11**, **13**, and **15** the hydrophilic cavity in **24** is formed *intra-* rather than intermolecularly.

Conclusions and Prospects

1,1′-Binaphthyl-2,2′-dicarboxylic acid (**1**) is shown to be a new type of clathrate host for a variety of uncharged organic guest molecules. Guest components preferentially range from OH-, to NH-, to CH-acidic compounds such as alcohols, carboxylic acids, amides, and nitriles. Other polar substances and even rather unpolar compounds like bromobenzene and toluene are also clathrated into the host lattice of **1**. Marked selectivities in the clathrate formation of up to or >95% guest excess are demonstrated with regard to the group functionality, the substitution pattern, and the molecular size of the guest compound. Thus, our concept of *chemo-* and *regioselective* guest control via "coordinatoclathration" has become an active principle in chemical compound separation.

As demonstrated by the structural studies, we succeeded in designing host molecules which build up crystal lattices systematically by using the following principles: (1) a strong hydrogen bonding between host and guest molecules arranged in closed loops (cooperative effect in unidirectional circular H-bonds) where full donor/acceptor capability is utilized; (2) hydrophobic interactions between host and guest which are established by a well-defined void, and as a consequence (3) the disordering of certain guest regions, thereby increasing the entropy of the system (in part at least); (4) the assistance of the lattice buildup by the interaction of partially overlapping aromatic systems. A fundamental finding from the X-ray study is that similar factors which appear in these remarkably simple systems are basic requirements for the design of more complicated host–guest aggregates (e.g., cyclodextrin inclusion compounds[5a]).

Do the alcohol clathrates of the binaphthyl diacid **1** represent a snapshot of the short-distance prereaction of an esterification and can the host **1** allow catalyzed and controlled proton-transfer and group-transfer reactions, respectively?[56] These are stimulating questions waiting for an answer. Reserved to later structure analyses is the determination of whether the host molecules, free of hydroxyl, are combined in the cavities of the host lattice of **1** according to a similar scheme.

Another object refers to a simple chemical modification of the carboxylic sensor group, which may result in a drastic change of the inclusion selectivity. Priority investigations, however, will concentrate on the interesting problem of if and to what an extent the present host system, which readily is fissionable into optical antipodes,[25] can be used for the enantiomeric separation of racemic guest compounds.

The binaphthyl diacid **1** is considered to be only one of the first universal representatives of a whole family of new clathrate hosts whose main mode of action is derived from a combination of the two concepts: coordination and topological interactions, constrained with a special (C_2) symmetry. A further example in line with this new strategy has recently been published by us.[57]

Experimental Section

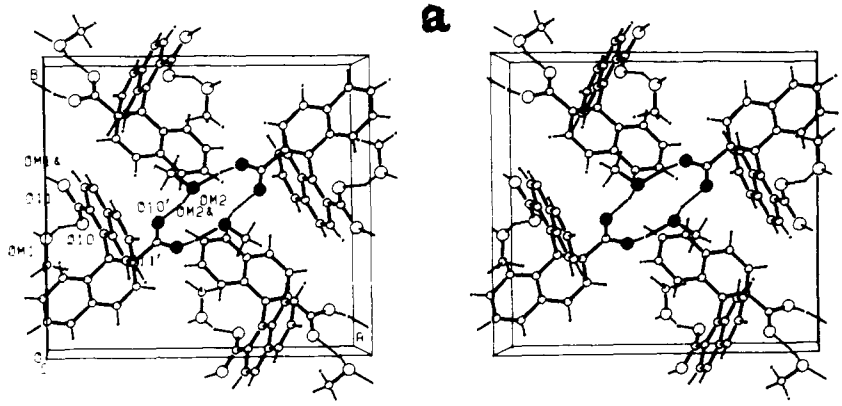
(1) General. All temperatures are uncorrected. Melting points were obtained on a Kofler apparatus (Reichert, Wien). Infrared spectra (IR) were determined on a Perkin-Elmer 267 spectrometer and are reported in cm^{-1}. ^{1}H NMR spectra were taken on a Jeolco MH-100 (100 MHz) or a Varian EM-360 (60 MHz) in the solvent as indicated. Chemical shifts are reported in ppm downfield from tetramethylsilane as internal reference. Splitting patterns are designated as s, singlet, and m, multiplet. The mass spectrum was recorded on a AEI MS-50 mass spectrometer.

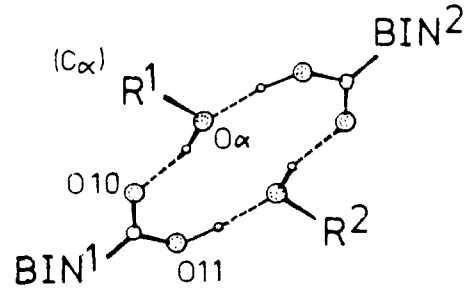
(2) Synthesis of the Host Compound. (a) 1-Bromo-2-methylnaphthalene (3) was prepared from 2-methylnaphthalene (**2**) (Aldrich Chemical Co.) and bromine according to the literature:[26,29] 91% yield; colorless liquid, bp 104–106 °C/0.6 torr (lit.[29] bp. 157 °C/15 torr); ^{1}H NMR ($CDCl_3$) δ 8.55–8.40 (m, 1 H), 7.96–7.30 (m, 5 H), 2.49 (s, 3 H); IR (film) 3045, 2910, 1625, 1600, 1560, 1500, 1440, 1380, 1350, 1330, 1260, 1225, 1140, 1035, 970, 895, 810, 770, 740, 645 cm^{-1}.

(b) 1-Bromo-2-(bromomethyl)naphthalene (4) was obtained following a combination of literature procedures.[28-30] A stirred suspension of **3** (176.8 g, 0.80 mol), *N*-bromosuccinimide (158.0 g, 0.80 mol), and dibenzoyl peroxide (0.5 g, radical starter) in 1 L of dry CCl_4 was refluxed for 3 h while being irradiated (150-W bulb). Completeness of the reaction was indicated by the presence of only succinimide which covers the surface of the solution. The hot mixture was filtered and the collected precipitate was extracted twice with 200-mL portions of boiling CCl_4. Evaporation of the combined filtrates under reduced pressure left a brownish solid which was recrystallized from hexane to give 79% yield of **4** as colorless cubic crystals: mp 107–109 °C (lit.[29] mp 106–108 °C); ^{1}H NMR ($CDCl_3$) δ 8.40–8.23 (m, 1 H), 7.83–7.40 (m, 5 H), 4.83 (s,

(54) "Intermolecular Interactions and Biomolecular Organization"; Hopfinger, A. J., Ed.; Wiley-Interscience: New York, 1977.
(55) "Catalysis in Micellar and Macromolecular Systems"; Fendler, J. H., Fendler, E. J., Eds.; Academic Press: New York, 1975.
(56) There is at least one direct evidence concerning the transfer of an H^+ from the acid. The crystal structure of a recently obtained complex of **1** with imidazole and H_2O (1:1:2) shows unambiguously the presence of COO^- and an imidazolium cation.
(57) Czugler, M.; Stezowski, J. J.; Weber, E. *J. Chem. Soc., Chem. Commun.* **1983**, 154.

a





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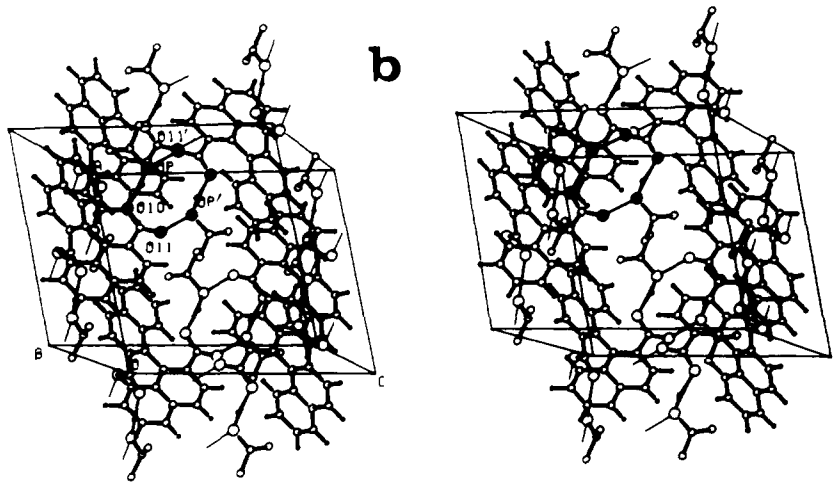

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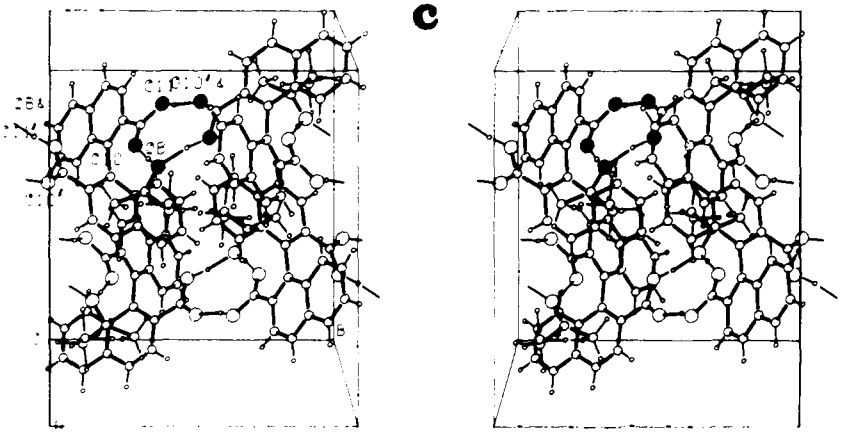
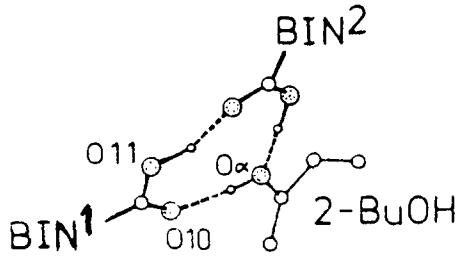
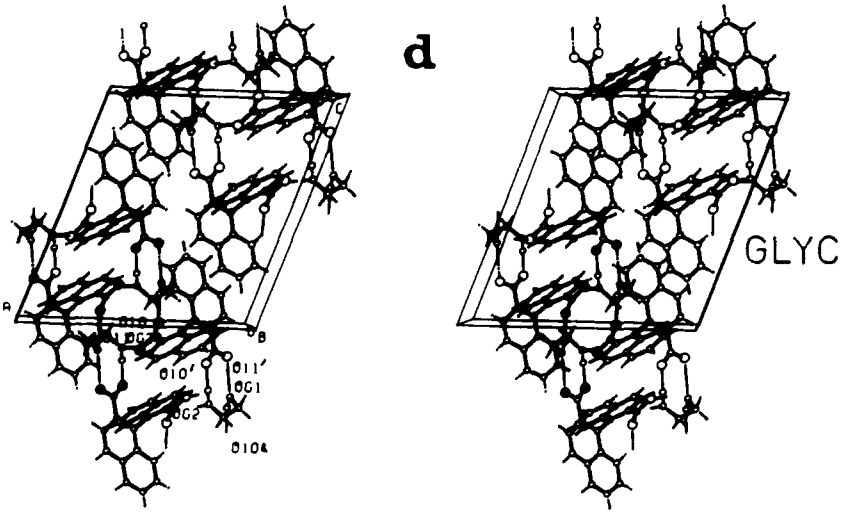
R = i-Pr

c





d



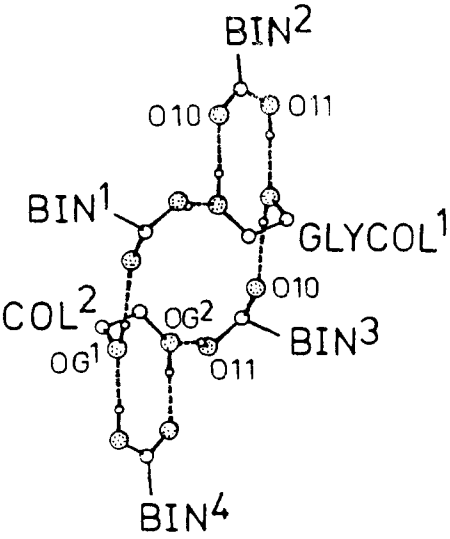


Figure 3. (a–d) Molecular packing and hydrogen-bonding schemes in the coordinatoclathrate crystals (stereoscopic views): (a) of **10** [1·2MeOH], (b) of **13** [1·2(2-PrOH)], (c) of **15** [1·2BuOH], (d) of **24** [1·$HOCH_2CH_2OH$]. The clathrates **11** and **13** are isomorphous. Thus, the structural principles shown in Figure 3b for **13** also count for **11**. In each figure the unit cell boundaries are indicated. Minor disordered atomic sites in **13** are omitted from the drawing. The O-atoms that are part of the hydrogen-bonded ring system are marked with bold circles in the packing schemes. Individual units of the hydrogen-bonded pseudo-ring constitution for each compound are shown separately with O–H···O interactions represented by dashed lines. That unit given under Figure 2a demonstrates the general situation found in the clathrates **11** (R = Et) and **13** (R = *i*-Pr) as well.

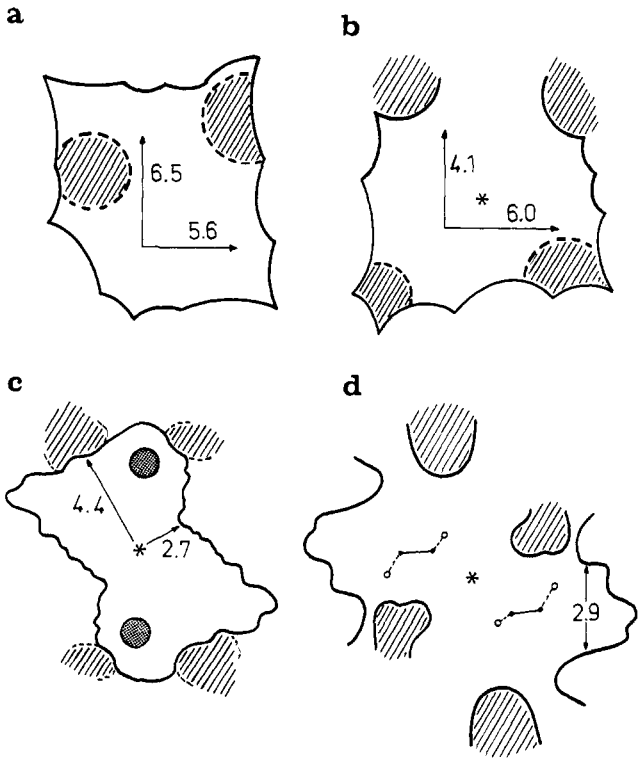


Figure 5. Contour lines resulting from cross sections of electron densities of the respective host voids (idealized representations): (a) in **10** [1·2MeOH], (b) in **13** [1·2(2-PrOH)], (c) in **15** [1·2-BuOH], (d) in **24** [1·$HOCH_2CH_2OH$]. Dimensions are in Å. Asterisks in (b), (c), and (d) indicate centers of symmetry. Cross sections given for **10** (a) and **13** (b) are approximately perpendicular/parallel to the O(α)–C(α) vectors (cf. Figures 3a,b), respectively. Hatched regions indicate O-atoms of coordinating COOH groups, midway of which O(α) should appear. Cross section for **15** (c) is in the 100 plane around a center of symmetry. Dimensions are understood from this center. Polar regions representing O-atoms of –COOH groups are hatched while the positions of the symmetry-dependent O(α) atoms (shown with half van der Waals radii) are shaded. Cross section for **24** (d) is given perpendicular to the plane of the symmetry-center related C atoms of the guest molecules (projected onto this plane as stick models). O atoms of COOH groups are marked as before. Apolar regions appear in these drawings as continuous solid lines, which are not concatenated in **24**, however.

2 H); IR (KBr) 3055, 2910, 1500, 1330, 1260, 1225, 1205, 985, 870, 860, 820, 760, 675 cm^{-1}.

(c) **1-Bromo-2-naphthaldehyde** (**5**) was synthesized from **4** under Sommelet conditions as described.[25] Recrystallization from hexane yielded 63.5% of **5** as colorless needles: mp 118–119 °C (lit.[25] mp 119–120 °C); ^1H NMR ($CDCl_3$) δ 10.72 (s, 1 H), 8.68–8.46 (m, 1 H), 8.10–7.60 (m, 5 H); IR (KBr) 3060, 3020, 2920, 2870, 1685, 1620, 1600, 1430, 1330, 1260, 1220, 895, 875, 815, 775, 755, 700 cm^{-1}.

(d) **1-Bromo-2-naphthoic acid** (**6**) was prepared from **5** using a blend of literature procedures.[25,30] The aldehyde **5** (30.0 g, 128 mmol) was dissolved in 400 mL of acetone by gentle heating, and under stirring a hot solution of potassium permanganate (35.0 g, 222 mmol) in a mixture of 75 mL of H_2O/500 mL of acetone was dropped in within 0.5 h. Stirring was continued for an additional 2 h at about 40 °C. After cooling, the MnO_2 precipitate was removed by suction filtration and the filtrate was freed from acetone by evaporation under reduced pressure. After cooling with ice the mixture (precipitate in water) was acidified with concentrated HCl. The precipitate was separated, thoroughly washed with water, and dried under vacuum at 80 °C for 12 h. Recrystallization from toluene yielded 71% of **6** as colorless needles: mp 189–190 °C (lit.[25] mp 189–191 °C); ^1H NMR (CD_3CN/Me_2SO-d_6, 2:1) δ 8.60–8.38 (m, 1 H), 8.13–7.61 (m, 5 H), 4.19 (s, broad, 1 H); IR (KBr) 3010, 2910, 1695, 1620, 1595, 1460, 1250, 975, 760, 700 cm^{-1}.

(e) **1-Bromo-2-naphthoic Acid Chloride** (**7**). The usual thionyl chloride method[58a] was followed.[31] A mixture of acid **6** (150.0 g, 0.60 mol), thionyl chloride (300 mL, excess), and toluene (300 mL) was gradually heated to boiling, whereupon the acid chloride dissolved. After refluxing for 3 h, the solvents (toluene, thionyl chloride) were removed by vacuum distillation. The solid residue was recrystallized from hexane to give a quantitative yield of pure acid chloride **7** as colorless needles; mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 8.63–8.47 (m, 1 H), 8.03–7.68 (m, 5 H); IR (KBr) 1780, 1620, 1590, 1545, 1450, 1320, 1260, 1220, 1200, 1035, 1000, 930, 820, 760 cm^{-1}. High-resolution chemical ionization mass spectrum, exact mass calcd for $C_{11}H_6BrClO$ 267.9290, obsd 267.9292.

(f) **Methyl 1-bromo-2-naphthoate** (**8**) was synthesized from acid chloride **7** and methanol by the common procedure.[58b] A suspension of **7** (162.3 g, 0.602 mol) in 750 mL of methanol was stirred at room temperature until dissolution had occurred. The solution was then heated to reflux for 5 h, followed by evaporation under reduced pressure to give a crystalline solid. Recrystallization from hexane and workup of the mother liquor led to a quantitative yield of pure **8** as colorless platelets: mp 53–55 °C (lit.[30] mp 58–59 °C); ^1H NMR ($CDCl_3$) δ 8.70–8.56 (m, 1 H), 8.06–7.64 (m, 5 H), 4.06 (s, 3 H); IR (KBr) 2930, 2910, 1715, 1455, 1265, 1235, 1125, 1005, 760 cm^{-1}.

(g) **Dimethyl 1,1′-Binaphthyl-2,2′-dicarboxylate** (**9**). Into a three-necked flask equipped with a mechanical stirrer, gas inlet tube, and reflux condenser was placed freshly activated copper bronze[33] (25.0 g, excess), followed by **8** (flushed with nitrogen) (13.3 g, 50 mmol). The system was brought under an atmosphere of nitrogen, and 200 mL of DMF (freshly distilled over CaH_2 and saturated with nitrogen) was added. The stirred mixture was gently refluxed for 12 h, cooled, and then filtered. The residue was extracted with 1 L of boiling toluene. The combined filtrates were washed thoroughly with 2 N HCl (4 × 200 mL), then with water (4 × 500 mL), and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure and subsequent crystallization from methanol yielded 81% of colorless platelets: mp 157–158 °C (lit.[25] mp 158 °C); ^1H NMR ($CDCl_3$) δ 8.40–7.12 (m, 12 H), 3.52 (s, 6 H); IR (KBr) 3060, 2940, 1725, 1620, 1600, 1460, 1435, 1335, 1285, 1245, 1190, 1140, 1070, 835, 770 cm^{-1}.

(h) **1,1′-Binaphthyl-2,2′-dicarboxylic Acid** (**1**). The diester **9** (10.0 g, 27 mmol) was refluxed in a solution of 50.0 g of KOH in 250 mL of methanol for 15 h. The solvent was removed under reduced pressure, and after the addition of ice, the mixture was acidified carefully with concentrated HCl to cause a voluminous colorless precipitate. This was collected by suction filtration and thoroughly washed with water to neutrality. Drying under vacuum and over P_4O_{10} gave **1** in quantative yield as a colorless powder: mp 272–274 °C (lit.[25] mp 272–274 °C); ^1H NMR (CD_3CN/Me_2SO-d_6, 2:1) δ 8.17–6.83 (m, 12 H), 3.94 (s, br, 2 H); IR (KBr) 3040, 2900, 1690, 1620, 1596, 1465, 1410, 1285, 1250, 1155, 1140, 836, 770, 700 cm^{-1}.

(3) Preparation of the Clathrates. General Procedure. The host compound **1** was dissolved under heating in a minimum amount of the respective guest solvent. The solution was placed into a heated water bath to prevent it from rapid cooling and to ensure slow crystallization of the clathrate. After storage for 12 h at 4 °C, the crystals which formed were collected by suction filtration and dried at room temperature under reduced pressure (0.5 torr) for 12 h. Data for each compound are given in Table I.

(58) "Methoden der Organischen Chemie" (Houben-Weyl); Müller, E., Ed.; Thieme: Stuttgart, 1952; Vol. VIII, (a) p 467 ff (b) p 543 ff.

(59) List of the retrieved relevant entries from the CCDB. Each compound is uniquely defined by its reference code (given in parentheses) and a shortened literature reference (only the first author's name is cited): (ADRTAR) Carlstrom, D. *Acta Crystallogr., Sect. B* **1973**, *B29*, 161. (AMTBUB) Bigoli, F. *Ibid.* **1981**, *B37*, 1258. (CHOLET) Johnson, *P. L. Ibid.* **1972**, *B28*, 3083. (CHOPAL) Coiro, V. M. *Ibid.* **1980**, *B36*, 848. (CTBGLU) Hata, T. *Ibid.* **1975**, *B31*, 312. (DCAETO 10) Candeloro, S. *Ibid.* **1978**, *B34*, 1928. (DXCHET) Coiro, V. M. *Ibid.* **1979**, *B35*, 2941. (TPTPCM) Gartland, G. L. *Ibid.* **1974**, *B30*, 1841. (SULFZC) Kamiya, K. *Ibid.* **1981**, *B37*, 1626. (SERASC 10) See ref 49b. (BAMANT 10) Konstansek, E. C. *Biochemistry* **1978**, *17*, 3790. (MIPROF) Little, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 4532. (CAMANX) Cameron, T. S. *Cryst. Struct. Commun.* **1977**, *6*, 453. The following two entries have no coordinates deposited with CCDB: (BACXIM) Ricci, J. *Acta Crystallogr., Sect. A* **1981**, *A37*, C61. (TITPRA) Cody, V. *Ibid.* **1978**, *A34*, S87.

(4) Crystallography. (a) Sample Preparation and Data Collection. Crystals of the clathrate compounds **10**, 11, **13**, **15**, and **24** suitable for crystallographic study were obtained as described in section 3 of the Experimental Section. Well-developed crystals appear usually in 1–2 days. Nevertheless, crystallization of **24** took ~2 weeks. As the crystals tend to become opaque in a few hours when exposed to air, selected probes of **10**, **11**, and **13** for measurement were sealed in an epoxy glue, those of **15**, and **24** in a cyanoacrylate resin. Diffraction data were collected for **10**, **11**, and **13** on a Philips PW 1100 automated diffractometer, while for **15** and **24** an Enraf-Nonius CAD-4 instrument was used. All data sets were measured at room temperature with graphite monochromated Mo Kα radiation using an ω–2θ scan technique. The cell constants and pertinent details of the experimental conditions are summarized in Table VII. Intensities were corrected neither for absorption nor for extinction effects.

(b) Structure Determination and Refinement. Initial structural models for all structures but **13** were obtained by direct methods (MULTAN 80 for **10**, SHELX 76 for **11**, and MULTAN 76 for **15** and **24**). An initial model for **13** was obtained from a single isomorphous replacement using atomic coordinates of **11**. Typically, all atoms of the host molecules could be deduced from difference electron density syntheses.

Adjustment of the structural parameters for **10**, 11, and **13** was performed by the blocked full-matrix least-squares procedure of the SHELX 76 system. All H-atoms in **10**, except those generated in assumed positions to the methyl termini, were localized in difference Fourier map and kept riding during the refinement. The refinement smoothly converged, all shift/esd ratios being <0.3. In contrast to **10**, the refinement of the structural models for **11** and **13** posed somewhat more problems partly because in the refinement procedure unreasonably short C–C distances were observed in the guest molecules of 11 and **13**. Difference Fourier calculations revealed prominent peaks in the vicinity of the terminal methyl groups of the ethanol and 2-propanol molecules. They were assigned partial occupancies together with the formal atomic sites and refined. The final occupancies were 0.49 and 0.51 for C(21E) and C(22E) in **11** and 0.62 and 0.38 for C(21P) and C(22P), 0.65 and 0.35 for C(31P) and C(32P) in the 2-propanol molecule of **13**, respectively. No other constraints than the one for the sum of occupancies were, however, applied to these atoms. At the termination of the refinement one still finds unreasonably short C–C bond distances in the guest molecules, especially in **11**. No other plausible interpretation of these facts could be made than that disorder is more extensive in **11** than the model assumes. Most probably, a larger amount of dynamic disorder is present in the structure of **11** than in the sterically more hindered substrate of **13**. The C–C bond distances in the guest of **13** tend to be more "normal" than the one in **11**. With "cum grano salis" we could accept even a localized possible H-atom site for the alcohol OH function in **13**, as shown in Figure 2c. No attempt, however, was made to assign H-atoms to the carbon atoms of the guest molecules in **11** and 13. The skeletal H-atoms of **11** and **13** were placed in assumed positions and constrained toward their carbon atoms throughout the refinement.

Refinement of **15** and **24** was carried out by full-matrix least-squares techniques using a program incorporated in the ENX-SDP package. Positions of all hydrogen atoms other than those of the OH moieties were generated by using geometrical evidence. Those belonging to oxygen atoms were unambigously located in difference Fourier maps. Temperature factors 20% higher than for the respective heavy atoms were assigned to each hydrogen atom and near the completion of the procedure positional parameters of hydrogen atoms were allowed to vary except for those of the terminal methyl groups in **15**. The largest parameter shift was 0.17 and 0.33 times its esd when the final R values were reached.

The final atomic coordinates for the structures of **10**, **11**, **13**, **15**, and **24** are summarized in Tables VIII–XII, and anisotropic thermal parameters, in Tables XIII–XVII (supplementary material).

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Registry No. 1, 746-46-3; **3**, 2586-62-1; **4**, 3378-82-3; **5**, 3378-82-3; **6**, 20717-79-7; **7**, 76373-11-0; **8**, 89555-39-5; **9**, 85464-88-6; **10**, 89555-40-8; **11**, 89555-41-9; **12**, 89555-42-0; **13**, 89555-43-1; **14**, 89555-44-2; **15**, 89555-45-3; **16**, 89555-46-4; **17**, 89555-47-5; **18**, 89555-48-6; **19**, 89555-49-7; **20**, 89555-50-0; **21**, 89555-51-1; **22**, 89555-52-2; **23**, 89555-53-3; **24**, 89555-54-4; **25**, 89555-55-5; **26**, 89555-56-6; **27**, 89555-57-7; **28**, 89577-84-4; **29**, 89555-58-8; **30**, 89555-59-9; **31**, 89555-60-2; **32**, 89555-61-3; **33**, 89555-62-4; **34**, 89555-63-5; **35**, 89555-64-6; **36**, 89555-65-7; **37**, 89555-66-8; **38**, 89555-67-9; **39**, 89555-68-0.

Supplementary Material Available: Tables containing bond lengths for the non-hydrogen atoms, deviations from the least-squares planes of the naphthyl groups, dihedral angles between different planes, final relative atomic coordinates, and anisotropic thermal parameters for the non-hydrogen atoms (Tables III–V, VIII–XVII, respectively) as well as observed and calculated structure factors for all structures studied, and figures with space filling packing diagrams for the clathrates **10**, **13**, and **15** (Figure 4) and for the atomic numbering employed (Figure 6) (74 pages). Ordering information is given on any current masthead page.