Versatility of the 1,1′-Binaphthyl-2,2′-dicarboxylic Acid Host in Solid-state Inclusion: Crystal and Molecular Structures of the Dimethylformamide (1 : 2), Dimethyl Sulphoxide (1 : 1), and Bromobenzene (1 : 1) Clathrates

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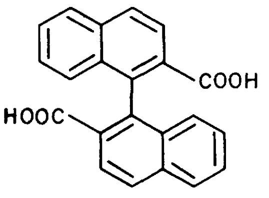
The clathrate structures of the host 1,1′-binaphthyl-2,2′-dicarboxylic acid (**1**) with dimethylformamide, (**2**), dimethyl sulphoxide, (**3**), and bromobenzene, (**4**) as guest molecules have been studied. *X*-Ray structure analyses show that the capacity for inclusion is primarily dependent on the proton donor–acceptor (co-ordinating) ability of the host. Nevertheless, the structures are very different. In (**2**) [crystal data: a = 14.916(13), b = 9.882(10), c = 17.128(13) Å, β = 90.45(7)°, space group $P2_1/c$, Z = 4, R_f = 0.066 for 2 550 observations] the guest molecules can act both as proton donor and acceptor in hydrogen bonding with the host, in (**3**) [a = 12.912(5), b = 17.979(15), c = 9.702(7) Å, β = 110.79(7)°, $P2_1/n$, Z = 4, R_f = 0.080 for 1 932 reflexions] the guest molecule acts as proton acceptor only, and in (**4**) [a = 9.955(2), b = 10.426(3), c = 12.005(3) Å, α = 77.34(2), β = 93.02(2), γ = 104.59(2)°, $P\bar{1}$, Z = 2, R_f = 0.074 for 1 555 observations] a 'true' clathrate structure is established, with bromobenzene being incorporated in a hydrogen-bonded host matrix of (**1**). The decrease in co-ordinating bond strength between host and guest is also manifested in the gradual increase of disorder observed for these guest species. Conclusions concerning the clathrate formation selectivity of (**1**) are derived from the structural observations.

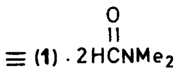
Clathrate compounds and related lattice-controlled host–guest systems† are becoming objects of considerable attention.[2,3] The interest stems from the fundamental information which is provided by those structures about lattice forces and van der Waals potentials and, on a more practical level, from their use to store guest compounds or to separate different types of guest molecules (including enantiomers) from each other.[4,5] Crystalline molecular assemblies may also provide organized environments most convenient for simulating enzyme active sites and chemical transition states.[6]

A major stumbling block in this area of chemistry, however, is the general problem of designing and synthesizing new selective host lattices.[2] Research aimed at overcoming these difficulties has been given priority recently. Clathrate structures have been mainly represented up to now by the 'hexa-host' type compounds.[7] Lately, attention has been paid to symmetry-constrained host molecules,[8,9] and Coulomb interactions with charged ammonium compounds have also been applied to stabilize a crystalline host–guest aggregate.[10]

A recently suggested strategy in selective clathrate design, called the principle of co-ordinatoclathration,[1] combines topological and co-ordinative host–guest interactions.[11,12] 1,1′-Binaphthyl-2,2′-dicarboxylic acid (1), an exponent of this new host design, shows eminent inclusion ability towards a number of chemically different guest substrates.[12] The major effects governing clathrate formation with (1) have been revealed using alcohols as guest components, *i.e.* molecules exhibiting both proton acceptor and donor ability. The present work adds to our previous studies of *X*-ray analysis on the inclusion compounds of (1)[12] by incorporating DMF, DMSO, and bromobenzene as guest species [clathrate compounds (2)—(4), respectively] which have reduced or non-existent proton-donor abilities. The investigations were supplemented with observations on some selectivity properties of DMSO and DMF *vis-à-vis* aliphatic alcohols.[12]



(1)

(2) ≡ (1) · 
$$\mathrm{(1)}\cdot 2\,\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NMe_2}$$

(3) ≡ (1) · Me_2SO

(4) ≡ (1) · PhBr

Results and Discussion

Views of structures (2)—(4) are presented in Figures 1(a)—(c) and 2(a)—(c). Figures 3(a), (b) show electron-density sections in clathrate (4). The crystallographic numbering schemes of the atoms are displayed in Figures 1(a)—(c). Crystal data are given in Table 1.

Molecular Structures.—The general features of host (1) in all three inclusion structures [Figures 1(a)—(c)] agree within experimental error and show similarities with those studied earlier.[12] For example, the planes of the naphthyl groups in (2)—(4) as well are nearly perpendicular to each other [the angle between the plane normals are 92.9(1), 98.1(2), and 92.1(1)°, respectively]. The observed dihedral angles between the planes of the naphthyl rings and their respective COOH

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† For a new proposal for the classification and nomenclature of host–guest-type compounds see ref. 1.

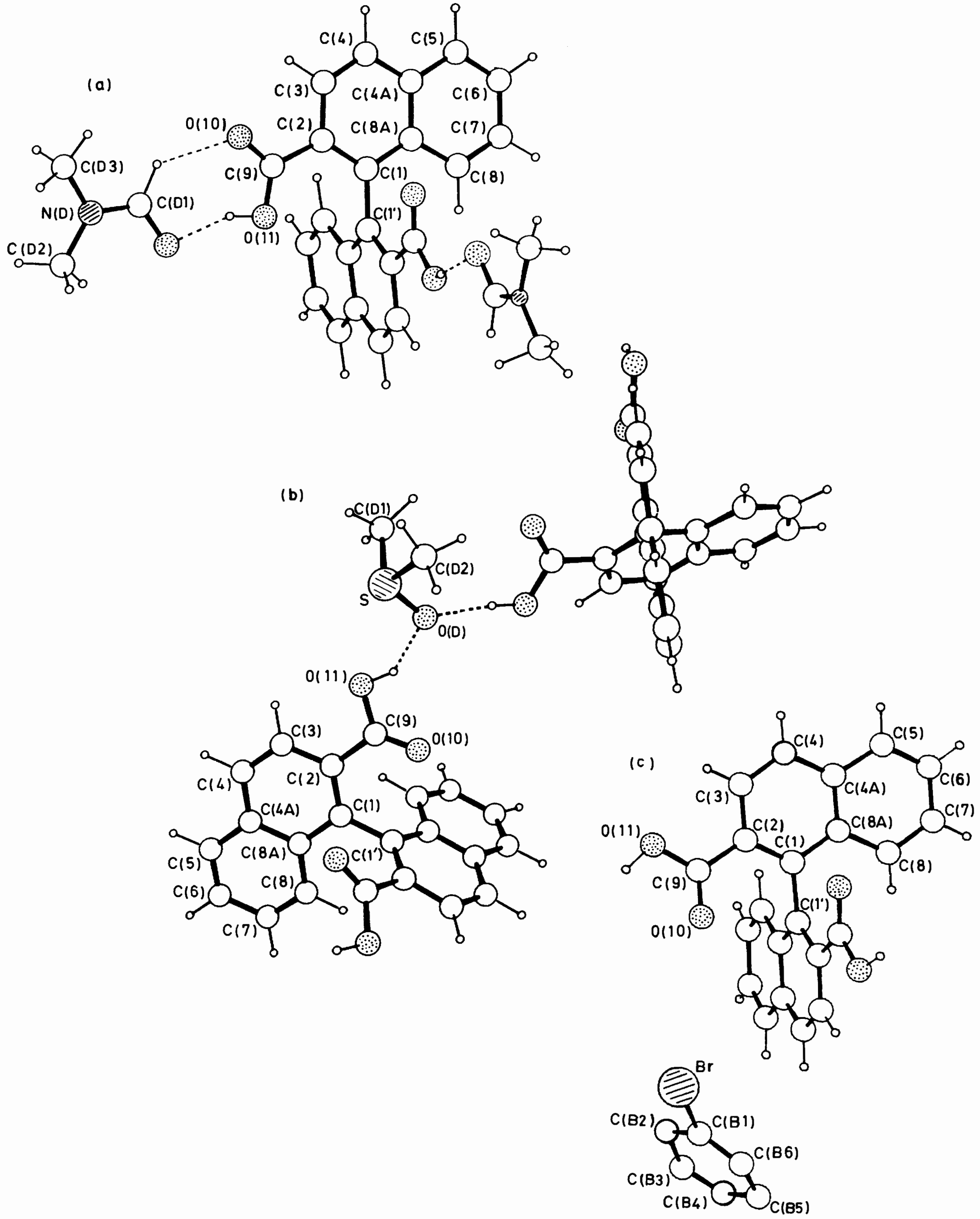

Figure 1. Perspective views of the different inclusion compounds of (**1**) showing the conformation and the relative positioning of host and guest molecules: (a) (**1**)·2 DMF [(**2**)], (b) (**1**)·DMSO [(**3**)], (c) (**1**)·PhBr [(**4**)]. The oxygen atom of DMSO (OD) is a recipient of a second hydrogen bond (broken lines) coming from an enantiomerically related host molecule

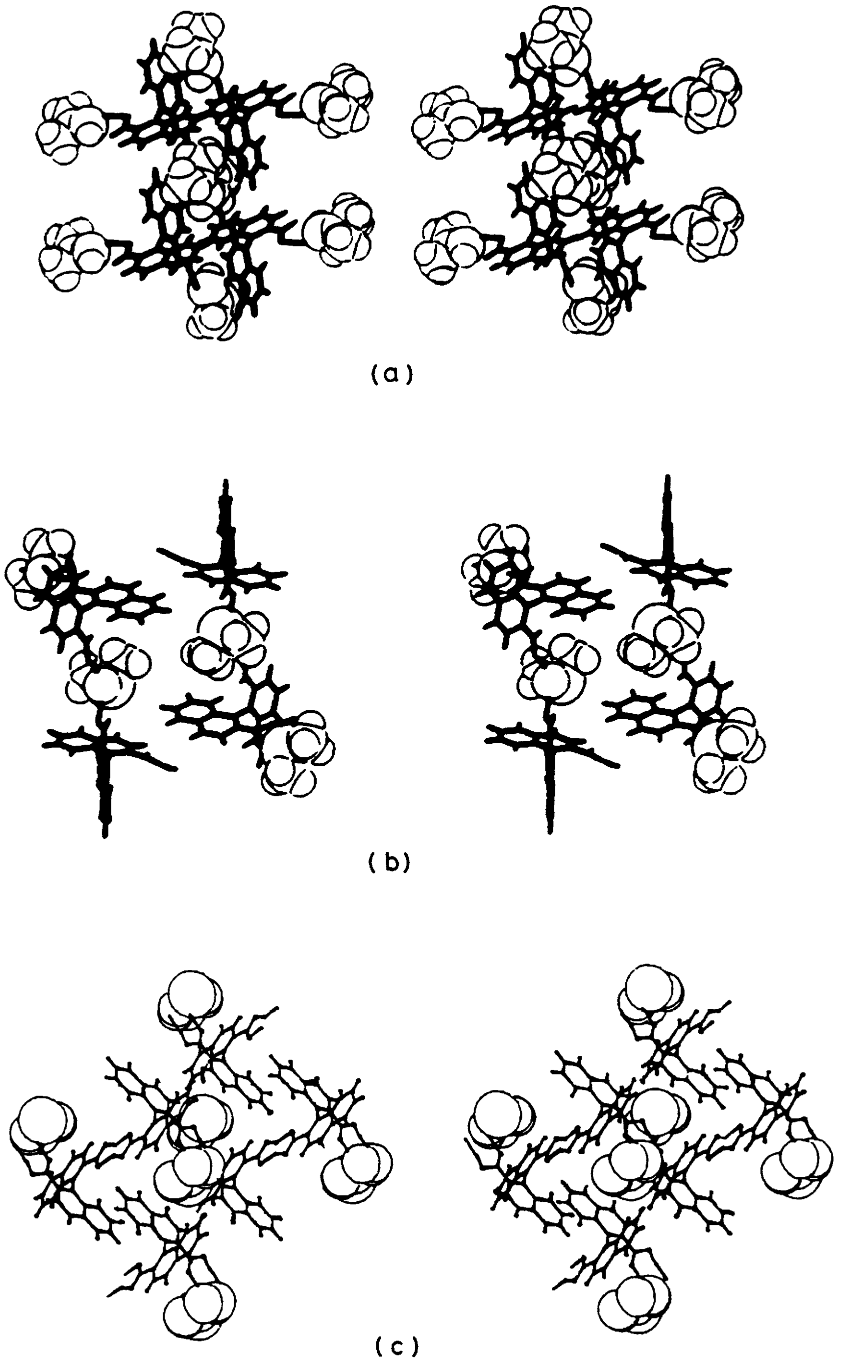

Figure 2. Stereoscopic representations of the crystal packings: (a) (**1**)·2 DMF [(**2**)], (b) (**1**)·DMSO [(**3**)], (c) (**1**)·PhBr [(**4**)]. Atoms of the host molecules are drawn with arbitrary radii, those of the guest molecules with their van der Waals radii

groups are 10.5(6) and 3.1(5)° for (**2**), 9.9(5) and 33.3(3) for (**3**), and 17.1(3) and 3.8(3)° for (**4**).

Guest molecule dimensions in (**2**) and (**3**) generally conform to those expected from structural data on similar entities in a comparable environment. Nevertheless, some peculiar deviations from ideal bonding do arise. Most probably they originate from disordering, especially severe in the case of the guest entity in (**4**). These deviations are to be discussed under the respective packing headings.

Packing Features and Host–Guest Interactions.—The DMF inclusion compound (**2**) displays some interesting differences from a recently described co-ordinatoclathrate with C_2 molecular symmetry.[11] In that structure the C_2 symmetry is perfectly coincident with a crystallographic two-fold rotor; while it is violated in the present (**1**)·DMF structure [Figure 1(a)]. There are differences in the co-ordination of the DMF molecules, too. One of the DMF molecules displays binding identical to that found earlier,[11] with the C=O group hydrogen-bonded to a COOH unit, and forming a seven-membered ring *via* a second interaction of the C–H ··· O type (*cf.* Table 2). The other one, however, does not take part in such an interaction. While its C=O group is hydrogen-bonded to the co-ordinating COOH, the C–H vector of this DMF molecule points away

Table 1. Crystal data for the inclusion compounds of (**1**)

Compound Number	(**1**)·2 DMF (**2**)	(**1**)·DMSO (**3**)	(**1**)·Bromobenzene (**4**)
Formula	$C_{22}H_{14}O_4$·2 C_3H_7NO	$C_{22}H_{14}O_4$·C_2H_6SO	$C_{22}H_{14}O_4$·C_6H_5Br
M	488.5	420.5	499.4
a/Å	14.916(13)	12.912(5)	9.955(2)
b/Å	9.882(10)	17.979(15)	10.426(3)
c/Å	17.128(13)	9.702(7)	12.005(3)
α/°	90	90	77.34(2)
β/°	90.45(7)	110.79(7)	93.02(2)
γ/°	90	90	104.59(1)
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	4	4	2
D_c/Mg m^{-3}	1.285	1.326	1.410
λ/Å	1.5418	0.710 73	0.710 73
μ/m^{-1}	0.0707	0.0177	0.1758
$\theta_{max.}$/°	67	32	25
N_{TOT}	4 989	7 729	4 120
N_{obs} [$I > 3\sigma(I)$]	2 560	1 932	1 500
N_{ref}	2 550	1 932	1 555
R_f	0.066	0.080	0.074

Table 2. Possible intermolecular hydrogen-bonding contacts (Å) in (**2**)—(**4**)

O ··· O/C ··· O	d(Å)	Donor-H	d(Å)[a]	H ··· Acceptor	d(Å)[a]	Donor-H ··· Acceptor	(°)[a]
(**2**)							
O11 ··· O1D[b]	2.692(6)	O11–H11	0.86	H11 ··· O1D[b]	1.90	O11–H11 ··· O1D[b]	152
O11′ ··· O1D′[b]	2.613(6)	O11′–H11′	0.84	H11′ ··· O1D′[b]	1.81	O11′–H11′ ··· O1D′[b]	159
C1D ··· O10[b]	3.054(8)	C1D–H1D	1.08	H1D ··· O10[b]	2.26	C1D–H1D ··· O10[b]	129
(**3**)							
O11 ··· O1D[b]	2.652(9)	O11–H11	0.98	H11 ··· O1D[b]	1.78	O11–H11 ··· O1D[b]	146
O11′ ··· O1D[c]	2.635(8)	O11′–H11′	0.99	H11′ ··· O1D[c]	1.70	O11′–H11′ ··· O1D[c]	155
C2D ··· O10′[d]	3.308(11)	C2D–H2D3	1.08	H2D3 ··· O10′[d]	2.27	C2D–H2D3 ··· O10′[d]	161
(**4**)							
O11 ··· O10[e]	2.670(8)	O11–H11	1.03	H11 ··· O10[e]	1.65	O11–H11 ··· O10[e]	171
O11′ ··· O10′[e]	2.616(9)	O11′–H11′	0.80	H11′ ··· O10′[e]	1.89	O11′–H11′ ··· O10′[e]	150

[a] E.s.d.s are not given because they tend to be fairly underestimated in this type of refinement.[13] Symmetry operators: [b] x,y,z. [c] $x - 0.5, 0.5 - y, z + 0.5$. [d] $x + 0.5, 0.5 - y, z - 0.5$. [e] $1 - x, -y, 1 - z$.

from the COOH group and thus remains nonbonding. A looser binding of this DMF molecule may also be seen in the shortening of its C=O and C–N bonds [C(1D)–O(1D) = 1.284(7), C(1D′)–O(1D′) = 1.246(7), C(1D)–N(1D) = 1.328(8), C(1D′)–N(1D′) = 1.300(5) Å], which may result from its enhanced mobility as compared with that of the other more tightly bound one. Both DMF molecules, however, are practically co-planar with the COOH groups, to which they are co-ordinated. In the case of the first, 'normally' bound DMF, it is likely that this specific arrangement is partly organized *via* the enhanced co-ordination through the C–H ··· O bond, while for the other it may be enforced by the packing. The packing requirements may also explain why the co-ordinations of the two DMF molecules are different. An assumed 'correctly oriented' binding of the second DMF would result in packing conflicts with the binaphthyl skeleton, as seen in Figure 2(a), which reveals that the guest molecules are held in approximately rectangular voids in the structure.

The crystal structure of the DMSO inclusion compound (**3**) [Figure 1(b)] is most appropriately termed a double-acceptor guest-molecule pattern, which is recognized as a characteristic motif for DMSO complexes.[13] Alternating enantiomers of (**1**) and intercalated DMSO molecules are stacked to form hydrogen-bonded infinite chains, as seen in Figure 2(b). These chains are repeated in the crystal by the *n* glide plane. One more feature of this structure that merits mention is the difference in the 'shortened' S–C_{sp^3} bond lengths [S–C(1D) = 1.68(2) and S–C(2D) = 1.77(1) Å]. The decrease with respect to ideal values is in the range found for similar structures and is due to a weaker fixation of the terminal methyl groups, as clearly indicated by the elevated temperature factors for the atoms of the guest units. The observed discrepancy between the thermal parameters of C(1D) and C(2D) possibly indicates slight differences in the interaction of these groups with their environment. Unfortunately, this hypothesis cannot be confirmed from the present experimental data. Nevertheless, a close contact found for C(2D), indicating a possible C–H ··· O-type interaction (*cf.* Table 2), may explain how this peculiar difference in S–C_{sp^3} length could arise. A further indication is that the COOH group that co-ordinates to the C(2D) methyl shows the largest dihedral angle with its naphthyl ring [33.3(1)°].

An analogous DMSO–clathrate with 9,9′-bianthryl-1-carboxylic acid has a molecular arrangement rather similar to that in (**3**).[14] A pseudo-ring is formed by two possible hydrogen bonds, involving the COOH group and one of the methyl groups of the DMSO molecule.

The building principle of the bromobenzene inclusion compound (**4**) [Figure 1(c)] is seen in the infinite chains of

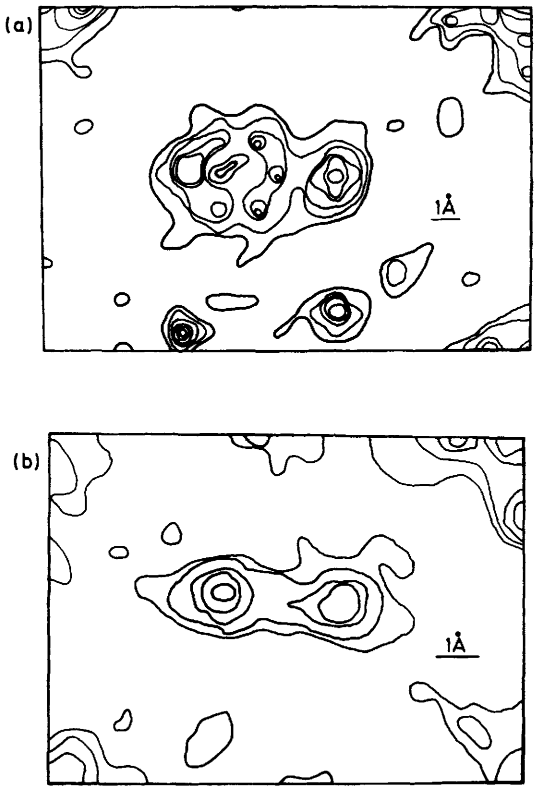

Figure 3. Cross-sections of electron density through the van der Waals surfaces of (**1**)·PhBr [(**4**)]: (a) in the plane of the PhBr molecule; (b) perpendicular to (a) in the height of the atoms in ortho position of the phenyl ring. Electron density contours are from 0 eÅ^{-3}, with arbitrary spacing

hydrogen-bonded (**1**) molecules of alternating chirality. Owing to the shape of the host, the chains consist of segments in a zig-zag-like arrangement, which offers the possibility of having the guest molecules included in the apolar clefts formed between these chains [Figure 2(c)]. The host molecules are hydrogen-bonded in pairs related by centres of symmetry, very similar to a well known pattern in carboxylic acids.[15] The nearest neighbour contacts (Table 2) clearly show the feasibility of hydrogen bonding in this dimer-like arrangement. The Br atom is asymmetrically positioned with respect to the O(11) atoms of the COOH groups (3.39 *versus* 3.62 A), the more tilted COOH having the shorter contact distance. It is thus possible that a hydrogen bond is accepted by the bromine atom, and this type of bonding would lead to disorder in the hydrogen atom position at O(11). Since there are several problems associated with the structure and since it is always difficult to locate hydrogen atoms by *X*-ray experiments, the hypothesis cannot be confirmed directly. The loose attachment of the bromobenzene molecule gives rise to apparent disorder, which is well exemplified by the quite unacceptable bonding dimensions observed for the major disorder- (OD-)site. Though other electron density features were incorporated in the final scattering model, and in spite of numerous efforts, we were not able to set up a reasonable model for the disorder. It seems to be composed of several closely overlapping in-plane and out-of-plane rotations of the benzene nuclei, impossible to distinguish by a room-temperature *X*-ray experiment. Cross-sections of the electron density around this major OD-site [Figures 3(a), (b)] display an abundance of free space around the guest molecule, thereby giving a direct indication of the possible cause of disorder.

Conclusion concerning Two-component Solvent Mixture Selectivity of Clathrate Formation.—The present [(**2**)—(**4**)] and former structures of inclusion compounds[12] indicate that (**1**) is a versatile host which can adapt to very different guests. Depending upon the nature of the offered guest solvent, *e.g.* if it has proton donor or acceptor ability or neither, inclusion compounds of different types will be formed. In the first case 'co-ordinatoclathrates' result, *e.g.* (**2**) and (**3**), and the second case constitutionally favours 'true' clathrates which are mainly formed *via* van der Waals' interactions [*cf.* (**4**)]. An explanation for this versatility of (**1**) as a host is certainly the amphoteric molecular backbone: The bulky aromatic part, as a matter of fact, is responsible for the loose lattice build-up, while the COOH groups provide binding sites for co-ordinative interaction with suitable guests or, on the other hand, contact among one another to form the hydrogen-bonded host matrix. Moreover, selectivity in guest inclusion is retained in both cases (*cf.* Table 2 in ref. 12).

As an example, the selectivity of (**1**) for DMF and DMSO relative to alcohols apparently is the effect of interactions between C–H groups of the guest molecule and oxygen atoms of the host matrix. The occurence of such weaker hydrogen bonds was recently proved by extensive statistical analysis.[16]

Such bonds might give a small, favourable enthalpy or entropy contribution to the Gibbs free energy of formation. Interactions of this type are seen in the structure of (**2**), and possibly also in (**3**), and may contribute to the enthalpy term. For example, to build an associate with a closed system of hydrogen bonds, only one molecule of (**1**) and two molecules of DMF are needed in an ideally symmetrical model,* as revealed by structure analyses. However, a topologically closed hydrogen-bonding system in a simple alcohol clathrate of (**1**) with similar 1:2 stoicheiometry (*e.g.* with EtOH)[12] requires a more intricate structure with additional restrictions (*e.g.* the presence of a symmetry centre in the hydrogen-bonding loop). This involves unfavourable entropy cost of organizing more molecules, generally two of (**1**) and two guest alcohols.

Comparing solvent selectivities observed for a second category of dipolar aprotic solvents which produce 1:1 host–guest stoicheiometry with (**1**), *e.g.* DMSO *versus* CH_3CN as guest solvent, one may also conclude that a possible C–H ··· O contact should shift the equilibrium towards the former solvent, although both solvents appear as relatively strong hydrogen-bond acceptors, which may even have the same pattern of hydrogen bonds. However, due to the rod-like shape of acetonitrile, interactions of the C–H ··· O type probably disfavour the bonding enthalpy of this molecule relative to DMSO.

The role of hydrogen-bonding, including its topology, therefore explains the observed inclusion selectivity of (**1**) also in cases where different alcoholic guest substrates are concerned. In addition, the favoured inclusion of MeOH over toluene could be explained, at least in part, on the basis of hydrogen-bonding ability. If the structure of (**4**) is accepted as a possible analogue of the toluene example, the preference of the hydroxy component clearly follows from the change in hydrogen-bonding between host and guest.

In the future, these considerations, based on available three-dimensional information about the present structures, will undoubtedly become more important for interpretation of solid-state inclusion selectivities.

Experimental

Sample Preparation.—The syntheses of (**1**) and of its inclusion compounds (**2**) [(**1**)·2DMF], (**3**) [(**1**)·DMSO], and (**4**)

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* The structure of the 9,9′-spirobifluorene-2,2′-dicarboxylic acid·DMF (1:2) clathrate exhibits exact C_2 molecular symmetry.[11]

[(**1**)·C_6H_5Br] are described in ref. 12. Suitable crystals for *X*-ray diffraction were grown from solutions of (**1**) in the corresponding solvents. Crystals used for the experiments were sealed in an epoxy resin for (**2**) and (**3**), and in a glass capillary for (**4**).

Data Collection and Processing.—Diffraction data for the crystals of (**2**) and (**3**) were recorded on a PW 1100 diffractometer with graphite-monochromatized Cu-K_α radiation for (**2**) and Mo-K_α for (**3**), respectively. The data for the crystals of (**4**) were collected on an Enraf–Nonius CAD-4 diffractometer. All measurements were carried out at 293 K.

Structure Analysis and Refinement.—Initial structural models were obtained by direct methods [17] and completed by successive difference electron density syntheses. All hydrogen atoms but those of the COOH groups in (**2**) and (**3**), which were located in difference Fourier maps, were generated in assumed positions.[18]

In the refinement of (**2**), the reliability index *R* converged to 0.082 for 2 560 structure factors, all with $F > 6\sigma(F)$ and unit weights. It was, however, noticed that the large observed structure factors were considerably weaker than the calculated ones at low $\sin\theta/\lambda$, which suggested extinction. Therefore, in the final refinement 10 reflections with $\Delta F/\sigma(F) > 5[\sin\theta_{max.}/\lambda < 0.16]$ were omitted, which reduced the final *R* to 0.066 for 2 550 reflections. The refinement of (**3**) resulted in a final *R* index of 0.080 for 1 932 structure factors, all with $F > 6\sigma(F)$ and unit weights.

The isotropic refinement of a 33 atom model for (**4**) terminated at the relatively high *R* value of 0.18, and inspection of the geometry and *B* values of the carbon atoms in the guest unit revealed major discrepancies, thereby indicating an inadequate treatment of the bromobenzene moiety. These observations, along with the relatively low number of observed reflections, pointed towards a possible severe disorder of this moiety. To introduce a reasonable model for the suspected disorder we tried first to interpret the spurious peaks in the vicinity of the bromine and some of the carbon atoms. Thus, we assumed a rotational disorder in the plane of the benzene ring, resulting in the 'overlap' of two mutually rotated positions. This attempt, however, did not essentially improve either the *R* value or the geometry. An attempted 'regularization' of the distorted benzene ring(s) to hexagons also failed to work. Attempts to treat the bromine atom as anisotropic proved only partially successful, leading to an *R* value of 0.14. Trying to find an ordered or at least reasonable model for the benzene rings with *P*1 symmetry, failed, too. Anisotropic refinement for the host atoms in the presence of generated hydrogen atoms and all atoms except the hydrogens of the guest (which were never included) yielded an *R* of 0.084. At this stage, an attempted localization of the carboxylic hydrogen atoms in a difference map enabled us to define two geometrically reasonable atomic sites which were tentatively retained as the hydrogen positions sought. These peaks also show acceptable hydrogen-bonding characteristics. The model, however, included some surplus atomic sites in the vicinity of the benzene ring of the guest with partial occupancies and isotropic thermal parameters. Independent treatment of these extra variables for all disordered sites was attempted in the next few cycles, but the behaviour of both the major and the minor atomic sites was remarkably unstable. Difference electron density maps showed the presence of residual density inclined to the plane of the bromobenzene ring. This suggested that besides one (or more) molecules rotationally disordered around a vector perpendicular to a mean plane of the guest, there could be additional orientations present rotated about the longitudinal axis of the bromobenzene molecule. Since the behaviour of the ordered models is far removed from reality, we abstained from making any further

Table 3. Fractional atomic co-ordinates of the non-hydrogen atoms ($\times 10^4$) for the different inclusion compounds. The e.s.d.s, where given, are in parentheses. For inclusion compound (**4**) the relative co-ordinates for the disordered phenyl group are multiplied by 10^3 due to the value of the e.s.d.s

(a) Inclusion compound (**2**)

Atom	*x*	*y*	*z*
C(1)	2 266(3)	−381(4)	10 462(3)
C(2)	1 477(3)	−984(4)	10 191(3)
C(3)	976(3)	−1 811(5)	10 702(4)
C(4)	1 228(4)	−2 029(5)	11 445(3)
C(4A)	2 026(4)	−1 440(5)	11 738(3)
C(5)	2 316(5)	−1 640(6)	12 531(3)
C(6)	3 090(5)	−1 060(7)	12 794(3)
C(7)	3 612(4)	−275(5)	12 304(3)
C(8)	3 358(3)	−48(5)	11 550(3)
C(8A)	2 548(3)	−622(4)	11 241(3)
C(9)	1 100(4)	−838(6)	9 383(3)
O(10)	467(3)	−1 538(5)	9 190(3)
O(11)	1 431(3)	37(4)	8 935(2)
C(1′)	2 815(3)	592(4)	9 993(2)
C(2′)	3 542(3)	202(4)	9 558(2)
C(3′)	4 087(3)	1 195(5)	9 203(3)
C(4′)	3 923(3)	2 533(5)	9 302(3)
C(4A′)	3 189(3)	2 977(4)	9 741(3)
C(5′)	3 017(4)	4 381(5)	9 858(3)
C(6′)	2 317(4)	4 788(5)	10 291(3)
C(7′)	1 747(4)	3 837(6)	10 623(3)
C(8′)	1 889(3)	2 469(5)	10 523(3)
C(8A′)	2 621(3)	2 009(4)	10 084(2)
C(9′)	3 789(3)	−1 267(5)	9 461(3)
O(10′)	3 402(3)	−2 187(3)	9 743(3)
O(11′)	4 487(2)	−1 142(4)	9 019(2)
O(1D)	480(3)	137(5)	7 594(2)
N(1D)	−719(3)	−748(5)	6 945(3)
C(1D)	−190(3)	−679(6)	7 571(4)
C(2D)	−631(4)	136(8)	6 267(4)
C(3D)	−1 421(4)	−1 741(6)	6 931(5)
O(1D′)	5 111(3)	−3 871(4)	8 760(3)
C(1D′)	5 789(4)	−3 778(6)	8 343(3)
C(2D′)	7 047(4)	−4 658(7)	7 620(3)
C(3D′)	6 026(4)	−6 161(6)	8 337(5)
N(1D′)	6 258(3)	−4 798(5)	8 097(3)

(b) Inclusion compound (**3**)

C(1)	8 113(5)	4 283(4)	−3 868(7)
C(2)	9 241(5)	4 298(4)	−3 586(7)
C(3)	9 925(6)	4 811(4)	−2 557(8)
C(4)	9 503(6)	5 302(5)	−1 842(9)
C(4A)	8 359(6)	5 327(4)	−2 123(8)
C(5)	7 896(8)	5 849(4)	−1 412(9)
C(6)	6 781(8)	5 879(5)	−1 732(10)
C(7)	6 078(7)	5 390(5)	−2 767(9)
C(8)	6 489(6)	4 867(4)	−3 453(8)
C(8A)	7 647(6)	4 816(4)	−3 151(7)
C(9)	9 755(6)	3 742(5)	−4 230(8)
O(10)	9 289(4)	3 225(3)	−5 032(6)
O(11)	10 815(4)	3 894(3)	−4 025(7)
C(1′)	7 326(5)	3 759(4)	−4 928(7)
C(2′)	6 894(5)	3 148(4)	−4 467(7)
C(3′)	6 060(6)	2 711(4)	−5 489(8)
C(4′)	5 706(6)	2 864(4)	−6 955(8)
C(4A′)	6 130(6)	3 478(4)	−7 483(8)
C(5′)	5 754(6)	3 656(5)	−9 011(9)
C(6′)	6 116(7)	4 276(6)	−9 485(9)
C(7′)	6 879(7)	4 758(5)	−8 491(9)
C(8′)	7 294(6)	4 600(4)	−7 022(8)
C(8A′)	6 926(5)	3 951(4)	−6 470(8)
C(9′)	7 312(6)	2 936(4)	−2 875(8)
O(10′)	8 237(4)	3 023(3)	−2 028(6)
O(11′)	6 530(4)	2 603(3)	−2 493(6)
S	13 122(2)	2 907(2)	−3 427(3)

Table 3 (*continued*)

(b) Inclusion compound (**3**)

Atom	x	y	z
O(1D)	12 059(4)	2 924(5)	−4 796(6)
C(1D)	13 962(10)	3 417(8)	−4 036(16)
C(2D)	13 739(7)	2 029(5)	−3 440(9)
(c) Inclusion compound (**4**)			
Br	2 557(2)	3 259(1)	3 632(2)
C(1)	8 075(8)	1 762(6)	2 345(6)
C(2)	7 867(8)	790(7)	3 313(6)
C(3)	8 812(9)	−38(8)	3 605(7)
C(4)	9 882(9)	79(9)	2 902(8)
C(4A)	10 096(8)	1 058(8)	1 890(7)
C(5)	11 173(8)	1 219(9)	1 077(8)
C(6)	11 376(9)	2 173(9)	111(8)
C(7)	10 498(9)	3 015(9)	−151(8)
C(8)	9 449(8)	2 940(8)	576(7)
C(8A)	9 204(7)	1 929(7)	1 607(6)
C(9)	6 660(8)	498(7)	4 069(6)
O(10)	5 640(5)	921(5)	3 786(5)
O(11)	6 747(6)	−258(6)	5 063(5)
C(1′)	7 170(8)	2 786(7)	2 044(6)
C(2′)	6 023(8)	2 615(7)	1 355(6)
C(3′)	5 229(9)	3 589(8)	1 136(7)
C(4′)	5 599(8)	4 669(9)	1 603(7)
C(4A′)	6 792(8)	4 939(7)	2 291(7)
C(5′)	7 247(10)	6 121(8)	2 760(7)
C(6′)	8 430(11)	6 338(9)	3 358(8)
C(7′)	9 254(10)	5 361(9)	3 565(8)
C(8′)	8 794(9)	4 221(7)	3 169(7)
C(8A′)	7 603(8)	3 954(7)	2 523(6)
C(9′)	5 615(8)	1 449(9)	803(7)
O(10′)	6 216(6)	522(5)	942(5)
O(11′)	4 545(6)	1 447(6)	160(5)
C(B11)	290(1)	519(1)	326(1)
C(B21)	352(1)	581(1)	410(1)
C(B31)	378(1)	729(1)	383(1)
C(B41)	371(1)	807(1)	293(1)
C(B51)	273(1)	709(2)	197(2)
C(B61)	253(1)	579(1)	228(1)
C(B12)	325(4)	492(4)	383(3)
C(B22)	297(2)	762(2)	228(2)
C(B32)	328(1)	818(1)	307(1)
C(B42)	409(6)	625(6)	465(5)
C(B52)	241(6)	613(6)	164(5)
C(B62)	312(9)	630(9)	305(7)
C(B72)	225(7)	439(6)	219(6)
C(B82)	352(12)	890(11)	238(10)
C(B92)	248(10)	781(9)	137(8)

physically interpretations of the structural disorder. In a final model we included all major electron density features around the benzene carbon atoms and refrained from interpreting these. We also did not apply contraints to the sum of occupancies in general or to the 'pairs' of electron density features in particular. Although this procedure may be debatable, we felt that we could only reasonably account for the scattering properties of the bromobenze moiety. The final structural model for (**4**), illustrated in Figure 1(c), shows major OD sites for the guest molecule.

Final stomic co-ordinates for compounds (**2**)—(**4**) are given in Table 3. Equations of the calculated least square planes and the atomic displacements from these planes have been deposited as Supplementary Publication No. SUP 56442, (2 pp.*).

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* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, Issue 1.