Co-ordination-assisted Inclusion of Neutral Molecules by the Racemic 9,9′-Spirobifluorene-2,2′-dicarboxylic Acid Host Lattice. *X*-Ray Crystal Structure of the Dimethylformamide Clathrate at 170 K

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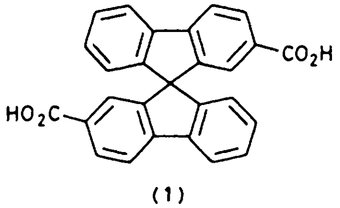
The title compound acts as a clathrate host for dimethylformamide (DMF), ethanol, and propan-2-ol; DMF is held inside a rectangular void of the host lattice *via* hydrogen bonding and steric interaction.

Topological (steric) barriers and more specific, directed forces (co-ordinative interactions, hydrogen bonding, *etc.*) due to pendant functional groups[1] are important in designing new clathrate compounds.[2] 'Co-ordinatoclathrands'† combine a number of these effects and are expected to show pronounced guest-binding stabilities and selectivities which may be varied in a predictable manner. They should also have interesting properties in solid-state chemistry.[3] 9,9′-Spirobifluorene-2,2′-dicarboxylic acid (**1**) is an example of this new type of clathrate host,‡ with a rigid molecular framework of C_2 symmetry[4] which provides two carboxylic groups for co-ordination.[1]



(1)

Compound (**1**) is obtained[5] first as an amorphous powder which can be recrystallized from dimethylformamide (DMF), ethanol or propan-2-ol, but not from methanol, to give transparent crystalline materials. They were identified as solvated species of (**1**) [*i.e.* (**1**)·2DMF; (**1**)·1/2EtOH; (**1**)·Pr^{i}OH].§ These crystalline solvates are relatively stable towards vacuum drying (at 15 Torr) and heating. They turned opaque at the onset of decomposition and solvent was released at higher temperatures [(**1**)·2DMF > 125 °C, (**1**)·1/2 EtOH > 215 °C, (**1**)·Pr^{i}OH > 200 °C]. In the case of the ethanol and propan-2-ol compounds this behaviour points to a particularly strong clathration.

Considering the bulky molecular geometry of (**1**), the packing in the crystal should give a high percentage of free volume into which the DMF, EtOH, or Pr^{i}OH molecules may be

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† Taken from a new proposal for the classification and nomenclature of host–guest-type compounds. (E. Weber and H. P. Josel, *J. Incl. Phenom.*, 1983, **1**, in the press).

‡ In contrast to classical quinol and Dianin inclusions where the functional groups are used exclusively in the construction of the specific host lattice but not in guest binding (ref. 2).

§ Stoicheiometries were determined by n.m.r.-integration and elemental analysis.

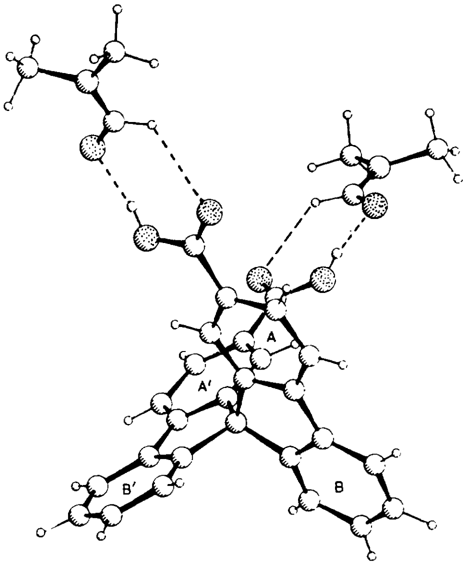

Figure 1. Perspective view of (**1**)·2DMF. Characteristic bond distances and mean bond distances with their e.s.d.s and r.m.d.s, respectively. For the host molecule: C=O 1.218(5), C–O 1.332(5), mean C(Ph)–C(Ph) 1.395(10), mean C(sp^3)–C(sp^2) 1.529(5), mean C(sp^2)–C(sp^2) 1.476(6) Å. For the guest entity: N–C(sp^2) 1.323(5), C=O 1.242(5), mean N–C(sp^3) 1.458(5) Å.

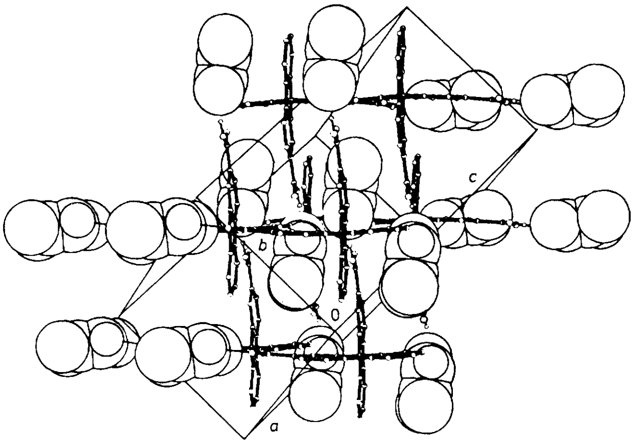

Figure 2. Packing in the (**1**)·2DMF clathrate. All but two H atoms belonging to the CO_2H group and that of the DMF C–H are omitted from this drawing. Atoms of the DMF molecules are represented with their van der Waals radii, those of the host with arbitrary values.

enclosed. In view of this general interest we studied the structure of the (**1**)·2DMF host–guest aggregate by *X*-ray diffraction. Crystals for *X*-ray analysis were grown from DMF by evaporation. A suitable crystal was sealed in a glass capillary and cooled to 170 K.

Crystal data: (**1**)·2DMF, $C_{27}H_{16}O_4\cdot 2Me_2NCHO$, M = 858.91, monoclinic, space group $C2/c$, a = 15.748(3), b = 9.968(2), c = 17.866(2) Å, β = 91.91(2)°, resulting from the refinement with 2θ values for 33 high-angle reflections, Z = 4. 3207 Unique reflections ($2\theta_{max}$ = 55°) were collected on a Syntex P$\bar{1}$ diffractometer using monochromatized Mo-K_α radiation. The structural model was refined with 2085 observed reflections to a final R value of 0.044. All hydrogen atoms were located by the difference Fourier technique and refined.¶

The molecular structure of (**1**)·2DMF is shown in Figure 1. The bifluorenyl host displays crystallographic two-fold symmetry with the spiro-carbon atom in a special position. The fluorene moiety is slightly bowed, the normals between the benzene rings A and B forming an angle of 6.9°.[6] The carboxy-groups adopt the common *syn*-periplanar conformation[7] with an intramolecular dihedral angle of 5.3° with respect to ring A. The guest molecules are held by strong hydrogen bonding to the carboxy-groups of (**1**) [O–H 0.92(6), H ··· O 1.69(6) Å, O–H ··· O 167(6)°]. These dimer units are further stabilized by the proximity of the carboxylic C=O and the C(sp^2)–H hydrogen atom of DMF thus forming a seven-membered pseudo-ring [C–H 0.99(5), H ··· O 2.42(6) Å, C–H ··· O 126(4)°]. The two bridging hydrogens are also close (0.14 and 0.26 Å) to the best plane defined by the five non-hydrogen ring atoms.**

The packing scheme (Figure 2) shows the DMF molecules encapsulated in nearly rectangular cages and also points to a tight spatial fit between host and guest molecules.

Strong i.r. absorptions for C=O at 1685 cm^{-1} indicate that the host–guest compounds of (**1**) with ethanol and propan-2-ol are also of the co-ordinatoclathrate-type (OH-hydrogen bonded to the host),[8] although the stoicheiometries are different. This agrees with our structural findings in another series of alcohol-containing host–guest systems, having the same functional group attached to the structurally related binaphthyl hinge as the steric barrier.[9]

Based on these results we anticipate that further systematic variation in the design principle (*e.g.* changing the shape, size, and relative position of the aromatic groups with respect to the symmetry site) or chemical modification of the pendant functional groups will enable us to engineer new clathrate hosts. The bifluorene derivative (**1**) may be considered only as a first representative of a series of host compounds having characteristically twofold symmetry, and which follow our concept of 'co-ordination-assisted clathrate formation.'

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¶ Atomic co-ordinates for this work may be obtained upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

** This particular behaviour is in clear contrast to a similar clathrate recently described by Dobler *et al.* (ref. 6).