

Crystalline Host–Guest Complexes Involving Carboxylic Acid Hosts and a Dimethyl Sulphoxide Guest. X-Ray Crystal Structures of Two Inclusion Species

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Abstract. The host compounds 2,2'-binaphthyl-3,3'-dicarboxylic acid (**1**) and 1,1':3'-1''-terphenyl-2',4,4''-tricarboxylic acid (**2**) have been synthesized, and crystal structures of their inclusion compounds with DMSO {**1a** [1·DMSO(1 : 1)]; **2a** [2·DMSO (1 : 2)]} have been determined from single crystal X-ray diffraction data. The crystals show monoclinic symmetry with $Z = 4$ ($P2_1/n$ for **1a** and $P2_1/c$ for **2a**), with the unit cell dimensions $a = 11.567(1)$, $b = 10.206(1)$, $c = 17.579(1)$ Å, $\beta = 100.50(1)^\circ$ for **1a**, and $a = 14.910(1)$, $b = 6.732(1)$, $c = 26.084(1)$ Å, $\beta = 100.41(1)^\circ$ for **2a**. The structural models were refined to $R = 0.032$ with 3127 reflections for **1a**, and $R = 0.035$ with 3175 observations for **2a**, collected at $T = 173(1)$ K. Both structures comprise a characteristic molecular recognition pattern for DMSO via strong (CO)O—H \cdots O(=S) hydrogen bonds and possible C—H \cdots O contacts, the latter ones from the guest methyl groups to the carbonyl oxygen of the host carboxyl groups. In the crystals H-bonded endless chains of alternating host and guest molecules are formed, which are held together by ordinary van der Waals' forces. Additionally, host **2** binds a second DMSO molecule by a single (CO)O—H \cdots O(=S) bond.

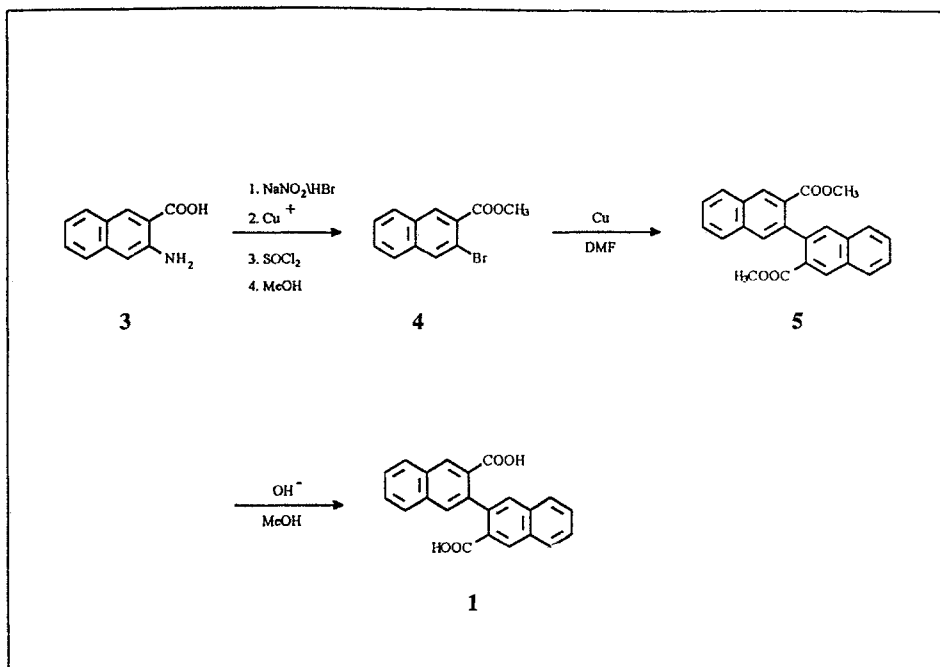
Key words. X-ray structure analysis, crystalline heteromolecular complexes, carboxylic acid hosts, DMSO guest, hydrogen bonding.

Supplementary Data relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82186 (9 pages).

1. Introduction

The use of weak supramolecular interactions [1] is an important approach to developing analytical [2], topochemical [3] and material [4] properties. The principles that govern these interactions are essential in making predictions possible [5].

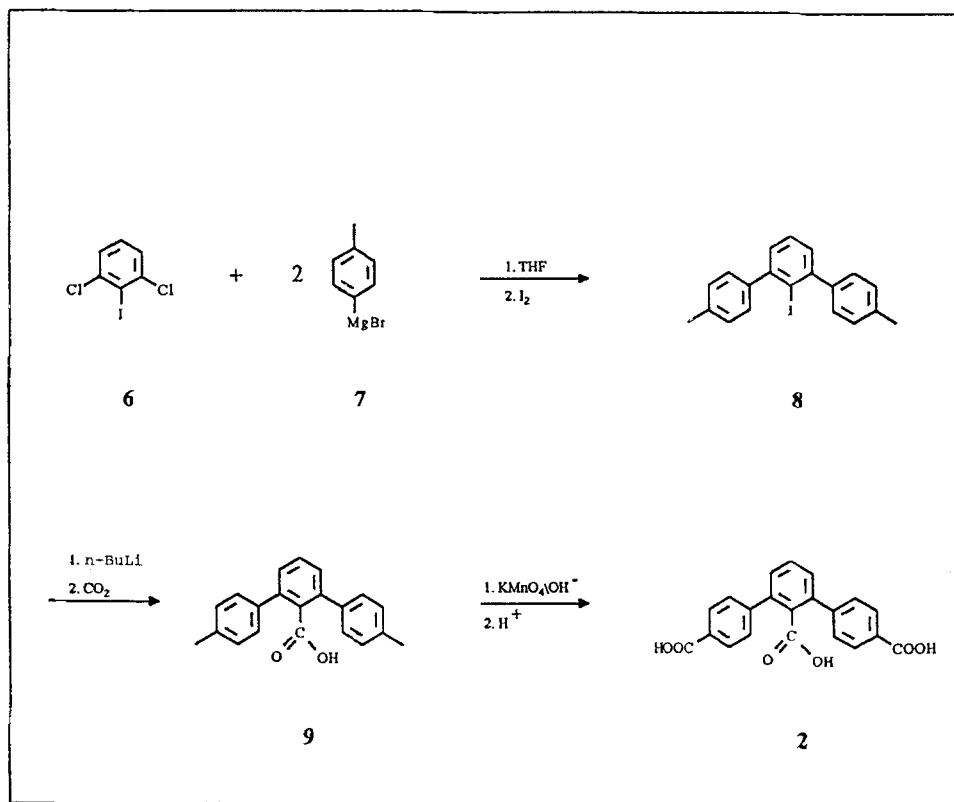
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Scheme 1.

'Coordinatoclathrand' [6] is the name we have given to a particular type of crystalline hosts which allow specific interactions between host and guest functional groups in the solid state. We have examined a substantial number of structures to help delineate those features and to show potential host-guest recognition behavior [7]. One problem we have focused on is the mode of interaction between carboxylic clathrand hosts and DMSO guests [8]. Previous studies have shown that DMSO may interact either in a single O—H···O bond, or in O—H···O and C—H···O types of bonding [9], but the occurrence of one or the other mode of interaction is an unknown feature.

In order to solve this problem, we decided to study crystalline complexes between DMSO and di- and tricarboxylic host molecules **1** and **2** (Schemes 1 and 2, respectively), where **1** is a constitutional isomer of the well documented coordinatoclathrand 1,1'-binaphthyl-2,2'-dicarboxylic acid (2,2'-BNDA) [10]. The structure of its inclusion compound with DMSO has been reported [9c]. The present work comprises synthesis of host molecules **1** and **2**, and X-ray crystal structure determinations of the inclusion compounds with DMSO: **1a** [**1**·DMSO (1:1)] and **2a** [**2**·DMSO(1:2)].



Scheme 2.

2. Experimental

2.1. SYNTHESIS

2.1.1. General

All temperatures are uncorrected. Melting points were obtained with a Kofler apparatus (Reichert, Wien). Infrared spectra (IR) were determined with a UNICAM SP1100 spectrometer (Pye Ltd., Cambridge). 1H - and ^{13}C -NMR spectra were taken with a WH-90 (90 MHz) or AC-200 (200 MHz) (Bruker, Karlsruhe) in the solvent as indicated; chemical shifts are reported in ppm downfield from tetramethylsilane as external reference (s, singlet, d doublet, and m, multiplet). The mass spectra were recorded with an MS-50 spectrometer (A. I. E., Manchester).

2.1.2. Synthesis of Host Compound 1 (Scheme 1)

Methyl 3-Bromo-2-naphthoate (4). This intermediate was prepared from 3 using a Sandmeyer reaction, acid chloride transformation and esterification route as

described in [11]. Column chromatography (silica gel; eluent chloroform/petroleum ether, 60–90 °C, 1:1) yielded 41% of **4** as colourless glass, m.p. 53–55 °C (lit. [11a] not reported).

Dimethyl 2,2'-Binaphthyl-3,3'-dicarboxylate (5). Coupling reaction of **4** with copper bronze in DMF according to the literature procedure [12]. Recrystallization from ethanol yielded 55% of **5** as colourless crystals, m.p. 169 °C (lit. [11a] 173–173.5 °C).

2,2'-Binaphthyl-3,3'-dicarboxylic Acid (1) was obtained by heating **5** with methanoic potassium hydroxide, cooling, acidification with conc. HCl and recrystallization of the white precipitate from ethanol; 93% colourless crystals, m.p. 297–299 °C (lit. [11a] 298–299 °C).

2.1.3. Synthesis of Host Compound **2** (Scheme 2)

4,4''-Dimethyl-2'-iodo-1,1':3',1''-terphenyl (8) was synthesized using an analogous procedure [13]. A solution of 13.6 g (0.05 mol) 1,3-dichloro-2-iodobenzene (**6**) [14] in 200 mL of dry THF was added dropwise over 90 min to a refluxing solution of 39.1 g (0.2 mol) of *p*-tolylmagnesium bromide (**7**) in 400 mL dry THF [prepared from 34.1 g (0.2) mol *p*-bromotoluene in 200 mL dry THF and 4.9 g (0.2 mol) magnesium in 200 mL dry THF]. The resulting mixture was refluxed for 5 h, cooled to 0 °C, quenched with a solution of 57.0 g (0.22 mol) iodine in 200 mL dry THF and stirred for 15 h at room temperature. After addition of a saturated solution of Na₂S₂O₅, to remove excess iodine, the solvent was evaporated in vacuo and the aqueous solution extracted with diethyl ether. The combined organic layers were dried with MgSO₄; the solvent and volatile impurities were distilled off at 65 °C/0.05 Torr. Dissolution of the residue in cyclohexane, filtration through silica gel (6 × 4 cm²) and recrystallization from ethanol yielded 16.2 g (84%) **8** as colourless crystals, m.p. 139–140 °C, ¹H-NMR (CDCl₃) δ 2.41 (s, 6H), 7.18 (m, 11H); ¹³C-NMR (CDCl₃) δ 21.39, 104.24, 127.57, 128.62, 129.31, 137.24, 142.88, 148.04; IR (KBr) 2913, 1512, 1445, 1019, 795 cm⁻¹; high resolution mass spectrum, exact mass calcd. for C₂₀H₁₇I 384.0373, obsd. 384.0377. *Anal. calcd.* for C₂₀H₁₇I (384.26): C, 62.52; H, 4.46. *Found:* C, 63.08; H, 4.13.

4,4''-Dimethyl-1,1':3',1''-terphenyl-2'-carboxylic Acid (9) was prepared according to a general procedure [15]. To a solution of 15.4 g (0.04 mol) **8** in 100 mL dry cyclohexane under argon were added 20.4 g (0.48 mol) lithium chloride (dried at 150 °C/0.05 Torr for 24 h) and 16.5 mL (0.041 mol) of a 2.5 M solution of *n*-butyllithium in *n*-hexane. After stirring for 15 h at room temperature, the solvents were evaporated and the white residue (except lithium chloride) was dissolved in 120 mL of dry THF at –78 °C. At the same temperature dried CO₂ was bubbled

through the mixture for 8 h (30–40 bubbles/min). Stirring was continued overnight while the mixture warmed up to room temperature.

Then the mixture was hydrolyzed with 130 mL 2M HCl and, after removal of THF, the aqueous residue was extracted four times with ethyl acetate. The organic layers were combined, dried with Na₂SO₄ and distilled to dryness. The residue was dissolved in chloroform and filtered through silica gel (6 × 10 cm²) which was washed with chloroform until no more organic byproducts could be detected (UV). The product was eluted with acetone and recrystallized from dichloromethane to yield 9.7 g (80%) of **9** as colourless crystals, m.p. 163 °C; ¹H-NMR (CDCl₃/DMSO-*d*₆) δ 2.28 (s, 6H), 7.09 (d, *J* = 8 Hz, 4H), 7.35 (d, *J* = 8 Hz, 4H), 7.15–7.40 (m, 3H); ¹³C-NMR (CDCl₃/DMSO-*d*₆) δ 20.63, 101.10, 127.48, 129.45, 137.90, 138.19, 171.79; IR (KBr) 2918, 1697, 1566, 1514, 822, 800 cm⁻¹; high resolution mass spectrum, exact mass *calcd.* for C₂₁H₁₈O₂ (302.37) 302.1302, *obsd.* 302.1310.

1,1' : 3',1''-Terphenyl-2',4,4''-tricarboxylic Acid (2). To a solution of 17.4 g (0.44 mol) NaOH in 100 mL water were added 10.0 g (0.033 mol) of **9**. The mixture was treated with 28.0 g (0.176 mol) KMnO₄ in four portions of 7.0 g every 30 min at room temperature and stirred for 5 h. Excess KMnO₄ was destroyed by heating to 80 °C. After acidification with 80 mL 50% sulphuric acid, and, at the same temperature, 180 g Na₂S₂O₇ were added to reduce the MnO₂ formed. The crude product was collected and dissolved in 5M NaOH. The solution was extracted twice with diethyl ether, filtered through celite and acidified with 1 M sulphuric acid to yield a precipitate, which was collected. Recrystallization from toluene yielded 6.1 g (51%) of **2** as colourless crystals, m.p. >300 °C; ¹H-NMR (DMSO-*d*₆) δ 7.50 (d, *J* = 8.4 Hz, 4H), 7.99 (d, *J* = 8.4 Hz, 4H), 7.40–7.70 (m, 3H); ¹³C-NMR (DMSO-*d*₆) δ 128.79, 129.55, 130.11, 133.90, 138.33, 144.69, 167.32, 170.00; IR (KBr) 3132, 1701, 1609, 815, 779 cm⁻¹; high resolution mass spectrum, exact mass *calcd.* for C₂₁H₁₄O₆ (362.34) 362.0786, *obsd.* 362.0781.

2.2. CRYSTALLOGRAPHY

2.2.1. Sample Preparation

Single crystals of inclusion compounds **1a** and **2a** were obtained by dissolution of **1** or **2** in DMSO and saturating the solution by slow evaporation at room temperature.

2.2.2. X-Ray Data Collection and Processing

X-ray data were collected on a STOE/AED2 diffractometer. The transparent, light yellow, irregularly shaped single crystals were sealed in epoxy glue in order to prevent possible solvent evaporation. Four (for **1a**) and five (for **2a**) standard reflections, measured with 90 minutes interval, showed no significant intensity

TABLE I. Crystal data and selected experimental details. The esd's are given in parentheses.

Compound	1a [1·DMSO (1 : 1)]	2a [2·DMSO (1 : 2)]
Formula	C ₂₂ H ₁₄ O ₄ ·C ₂ H ₆ OS	C ₂₁ H ₁₄ O ₆ ·2(C ₂ H ₆ OS)
Formula weight	420.48	518.60
Symmetry	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions		
<i>a</i> , Å	11.567(1)	14.910(1)
<i>b</i> , Å	10.206(1)	6.732(1)
<i>c</i> , Å	17.579(1)	26.084(1)
β, deg.	100.50(1)	100.41(1)
<i>V_c</i> , Å ³	2040.6(2)	2574.9(2)
Refinement of the cell dimensions		
No. of θ values used	53	37
2θ-range, deg.	19–38	19–38
<i>Z</i>	4	4
<i>F</i> (000)	880	1088
<i>D_c</i> , g cm ⁻³	1.3687(1)	1.3377(1)
μ, cm ⁻¹	1.83	2.41
Radiation/λ, Å	Mo <i>K</i> _α /0.71069	Mo <i>K</i> _α /0.71069
Temperature, K	173 ± 1	173 ± 1
Approximate crystal size, mm.	0.30 × 0.53 × 0.38	0.34 × 0.38 × 0.22
No. of collected reflections	6260	6663
θ limit, deg.	30	30
No. of unique non-zero reflections	5165	5189
No. of reflections with <i>I</i> /σ(<i>I</i>) > 3	3127	3175
No. of refined variables	351	354
$R = \sum \Delta F / \sum F_0 $	0.032	0.035
$wR = [\sum w \Delta F ^2 / \sum w F_0 ^2]^{1/2}$	0.039	0.042
<i>wR</i> _{tot}	0.045	0.050
Weighting: $w = [\sigma^2(F) + g \cdot F^2]^{-1}$		
with <i>g</i> =	0.00028	0.00024
Final Δρ _{max} /Δρ _{min} , e ⁻ Å ⁻³	0.26/–0.26	0.29/–0.30

variation during the data collections. Data reductions included corrections for background, Lorentz and polarization effects, but the relatively modest absorption effects (*cf.* Table I) were ignored. Crystal data and selected experimental details are given in Table I.

2.2.3. Structure Analysis and Refinement

The structures were solved by application of direct methods (SHELXS) [16] and refined by full-matrix least-squares [LS] calculations (SHELX) [17] based on $|F|$. The non-hydrogen atoms were treated anisotropically in both compounds. The hydrogen positions in **1a** [1·DMSO (1 : 1)], derived from a difference electron density ($\Delta\rho$) map, were refined isotropically, whereas the carboxy H atoms in **2a** [2·DMSO (1 : 2)], also located from a $\Delta\rho$ map, were held riding on their parent oxygens during the subsequent calculations, with isotropic vibrational parameters refined for them. Isotropic displacement parameters were refined also for the carbon-bonded hydrogens of **2a**, which were assumed to be in geometrically idealized positions (C—H = 1.00 Å), calculated after each refinement cycle from geometric evidence. Thirty-four reflections from **1a** and 4 low- θ reflections measured for **2a**, with considerably lower F_o than F_c values, probably due to extinction effects, were excluded from the final refinement calculations, which yielded the final R and wR values listed in Table I. The wR_{tot} values were calculated for the refined structure models using all unique, non-zero observations. The final fractional coordinates of the non-hydrogen atoms are listed in Table II.

3. Results and Discussion

Perspective views of the crystallographic asymmetric units of **1a** [1·DMSO (1 : 1)] and **2a** [2·DMSO (1 : 2)], with atoms labelled as in the text, are shown in Figures 1(a) and (b), respectively. The molecular packings are depicted in Figures 2 and 3. Hydrogen bonds and possible (C)—H···O interactions are listed in Table III.

3.1. MOLECULAR STRUCTURES

1,1'-Binaphthyl-2,2'-dicarboxylic acid [2,2'-BNDA] is a host molecule with well documented, excellent clathrate forming ability and remarkable selectivity [10]. Host **1** (2,2'-binaphthyl-3,3'-dicarboxylic acid, [3,3'-BNDA]) consists of the same fundamental elements as 2,2'-BNDA, but they are connected differently. Nevertheless, X-ray results show these two semi-rigid molecules to have comparable molecular conformations. In their DMSO inclusion compounds, for example, the dihedral angle between the two binaphthyl planes are 70.46(5) and 81.9(2)°, and the carboxyl groups are tilted through 14.3(1)/21.19(1) and 9.9(5)/33.3(3)° with respect to the binaphthyl rings they are linked to in 3,3'-BNDA and 2,2'-BNDA [9c], respectively. The observed differences between corresponding dihedral angles, shown above, possibly indicate that these are relatively soft parameters, which might be affected by the hydrogen bonding scheme and/or by the crystal packing. The carbon atoms of the binaphthyl moieties in the 3,3'-BNDA molecule are coplanar within 0.05 Å (unprimed) and 0.08 Å (primed). The observed intramolecular bond distances and angles generally conform to expected values.

TABLE II. Fractional atomic coordinates of the non-hydrogen atoms in compounds **1a** and **2a**. The esds are given in parentheses.

Atom	x/a	y/b	z/c
1a [1·DMSO (1 : 1)]			
C(1)	0.3538(2)	0.2208(2)	0.2959(1)
C(2)	0.3817(1)	0.1131(2)	0.2557(1)
C(3)	0.4012(1)	-0.0097(2)	0.2960(1)
C(4)	0.3926(2)	-0.0169(2)	0.3728(1)
C(4a)	0.3655(1)	0.0939(2)	0.4149(1)
C(5)	0.3579(2)	0.0876(2)	0.4944(1)
C(6)	0.3349(2)	0.1984(2)	0.5331(1)
C(7)	0.3178(2)	0.3194(2)	0.4945(1)
C(8)	0.3228(2)	0.3281(2)	0.4174(1)
C(8a)	0.3467(1)	0.2159(2)	0.3756(1)
C(9)	0.4330(1)	-0.1296(2)	0.2556(1)
O(10)	0.4218(1)	-0.1419(1)	0.1866(1)
O(11)	0.4744(1)	-0.2254(1)	0.3051(1)
C(1')	0.2837(2)	0.1574(2)	0.1219(1)
C(2')	0.3870(1)	0.1300(2)	0.1720(1)
C(3')	0.4942(1)	0.1264(2)	0.1414(1)
C(4')	0.4908(2)	0.1436(2)	0.0637(1)
C(4a')	0.3841(2)	0.1642(2)	0.0110(1)
C(5')	0.3799(2)	0.1758(2)	-0.0700(1)
C(6')	0.2748(2)	0.1958(2)	-0.1183(1)
C(7')	0.1698(2)	0.2064(2)	-0.0890(1)
C(8')	0.1707(2)	0.1954(2)	-0.0112(1)
C(8a')	0.2781(2)	0.1734(2)	0.0409(1)
C(9')	0.6101(2)	0.1023(2)	0.1933(1)
O(10')	0.6222(1)	0.0530(2)	0.2566(1)
O(11')	0.7007(1)	0.1398(2)	0.1617(1)
S	0.94668(4)	-0.03818(5)	0.29833(3)
O(D)	0.9103(1)	0.0806(1)	0.2475(1)
C(D1)	0.8665(2)	-0.0289(3)	0.3754(2)
C(D2)	1.0882(2)	0.0029(3)	0.3510(2)

The novel host compound **2** consists of three benzoic acid moieties, linked together by covalent bonds. The C atoms of each phenyl ring are co-planar within 0.014 Å [C(1)—C(6) ring 1], 0.015 Å [C(10)—C(15) ring 2] and 0.013 Å [C(19)—C(24) ring 3]. The carboxyl groups are tilted through 65.9(1)° [at C(1)], 11.9(1)° [at C(13)] and 10.3(2)° [at C(22)] with respect to the phenyl ring planes they are bonded to. The high value of the tilt angle involving the carboxyl group at C(1) is a consequence of the proximity of the two *meta*-positioned, bulky *p*-benzoyl substituents, which force the carboxyl group in the middle out of the C(1)—C(6)

TABLE II. Continued

Atom	x/a	y/b	z/c
2a [2-DMSO (1 : 2)]			
C(1)	0.2503(2)	1.4410(4)	0.1640(1)
C(2)	0.3276(2)	1.5632(4)	0.1763(1)
C(3)	0.3561(2)	1.6726(4)	0.1368(1)
C(4)	0.3089(2)	1.6631(4)	0.0860(1)
C(5)	0.2334(2)	1.5409(4)	0.0737(1)
C(6)	0.2034(2)	1.4280(4)	0.1122(1)
C(7)	0.2141(2)	1.3287(4)	0.2058(1)
O(8)	0.1409(1)	1.3665(3)	0.2181(1)
O(9)	0.2691(1)	1.1881(3)	0.2277(1)
C(10)	0.3765(2)	1.5914(4)	0.2310(1)
C(11)	0.3290(2)	1.6430(4)	0.2703(1)
C(12)	0.3742(2)	1.6776(4)	0.3206(1)
C(13)	0.4687(2)	1.6571(4)	0.3330(1)
C(14)	0.5173(2)	1.6058(4)	0.2940(1)
C(15)	0.4715(2)	1.5754(4)	0.2434(1)
C(16)	0.5153(2)	1.6989(4)	0.3873(1)
O(17)	0.4771(1)	1.7749(3)	0.4198(1)
O(18)	0.6020(1)	1.6440(3)	0.3970(1)
C(19)	0.1234(2)	1.2948(4)	0.0960(1)
C(20)	0.0432(2)	1.3724(4)	0.0671(1)
C(21)	-0.0319(2)	1.2521(4)	0.0508(1)
C(22)	-0.0280(2)	1.0507(4)	0.0625(1)
C(23)	0.0524(2)	0.9719(4)	0.0908(1)
C(24)	0.1270(2)	1.0916(4)	0.1078(1)
C(25)	-0.1085(2)	0.9186(4)	0.0457(1)
O(26)	-0.1060(1)	0.7398(3)	0.0496(1)
O(27)	-0.1840(1)	1.0191(3)	0.0271(1)
S(1)	0.09955(5)	0.96684(10)	0.28457(3)
O(D1)	0.2009(1)	1.0099(3)	0.2995(1)
C(D11)	0.0449(2)	1.1309(5)	0.3223(1)
C(D12)	0.0831(2)	0.7414(4)	0.3173(1)
S(2)	0.62249(5)	1.86117(12)	0.52281(3)
O(D2)	0.6674(1)	1.6955(3)	0.4966(1)
C(D21)	0.5385(3)	1.7417(6)	0.5516(2)
C(D22)	0.7022(3)	1.9234(11)	0.5788(2)

ring plane. The dihedral angles between the phenyl ring planes are $52.4(1)^\circ$ (rings 1 and 2), $53.0(1)^\circ$ (rings 1 and 3), and $65.9(1)^\circ$ (rings 2 and 3). No anomalous bond lengths or bond angles were detected.

The DMSO guests show the usual pyramidal shape with 309.1° (**1a**) and $309.3/310.5^\circ$ (unprimed/primed guests in **2a**) as the sum of the angles around

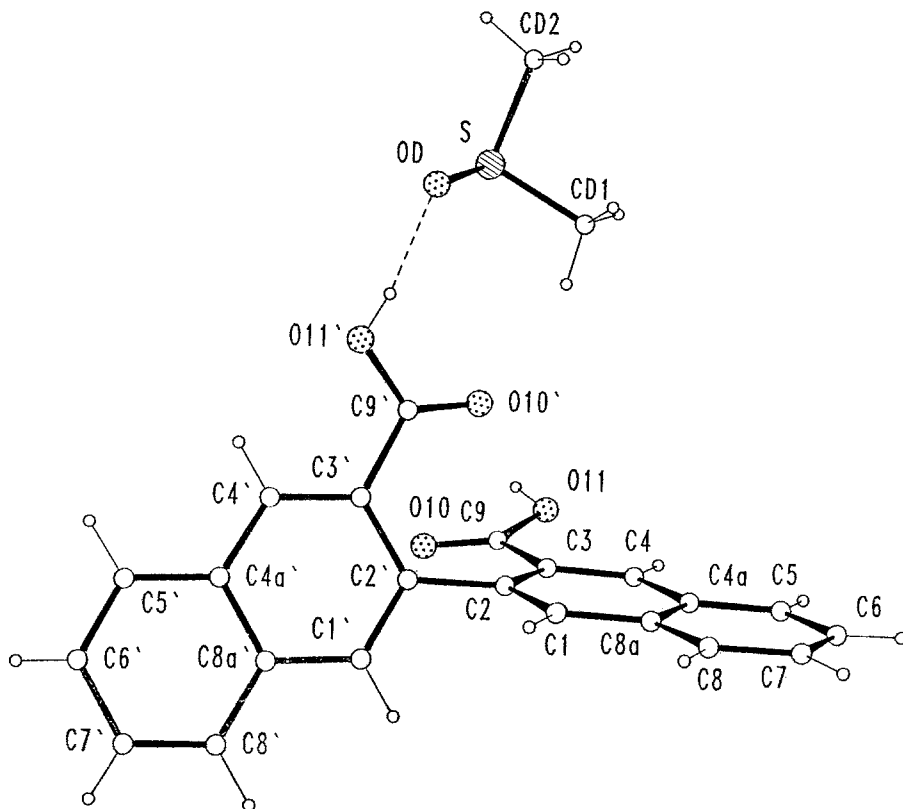


Fig. 1a.

Fig. 1. Perspective views of the asymmetric units of **1a** [1·DMSO (1:1)] (a), and **2a** [2·DMSO (1:2)] (b), with crystallographic labelling of the atoms. O atoms are dotted, S atoms are shaded.

the S atom. The two S—C(D) bonds in each molecule are equal within experimental errors. The mean S—C(D) bond length is 1.772[8] Å (with the r.m.s. deviation in angular brackets), calculated for the three crystallographically independent DMSO guests in the present two inclusions.

3.2. PACKING RELATIONS AND HOST-GUEST INTERACTIONS

The two closely related host molecules, 2,2'- and 3,3'-BNDA, show similar complexation of the DMSO guest. Besides the ordinary O—H_(carboxy) ··· O(=S) hydrogen bond there is also a C—H_(methyl) ··· O(=C) interaction from the guest to the host within the same crystallographic asymmetric unit (*cf.* Table III). Earlier X-ray studies of different crystalline DMSO inclusion compounds [9b, 9c] have shown this type of two-point host-guest interaction to be a common mode of recognition and binding of a DMSO guest by different simple carboxylic host molecules.

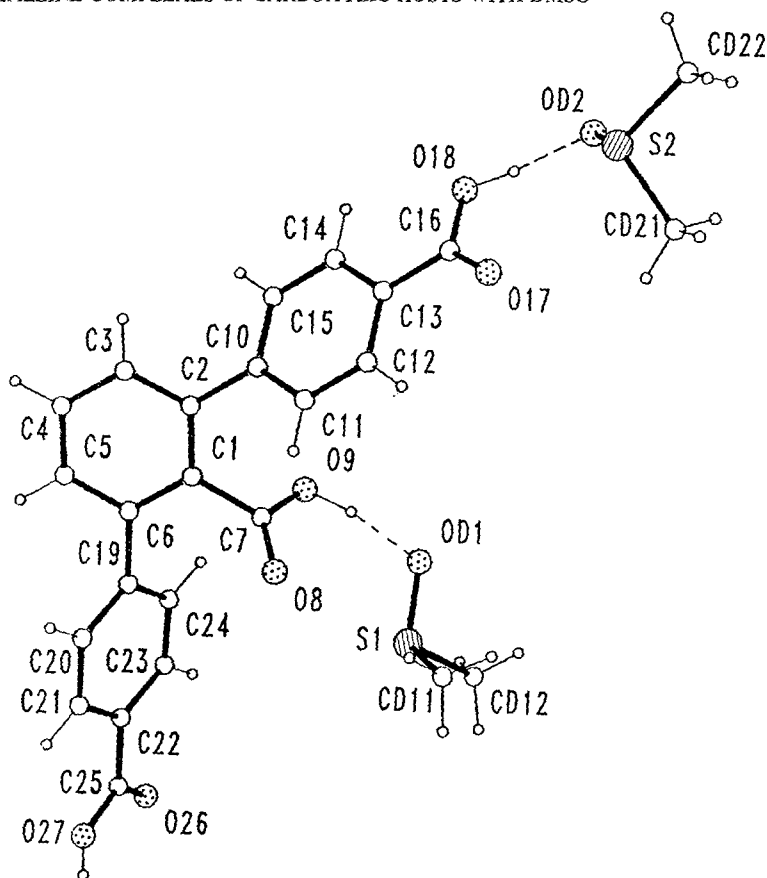


Fig. 1b.

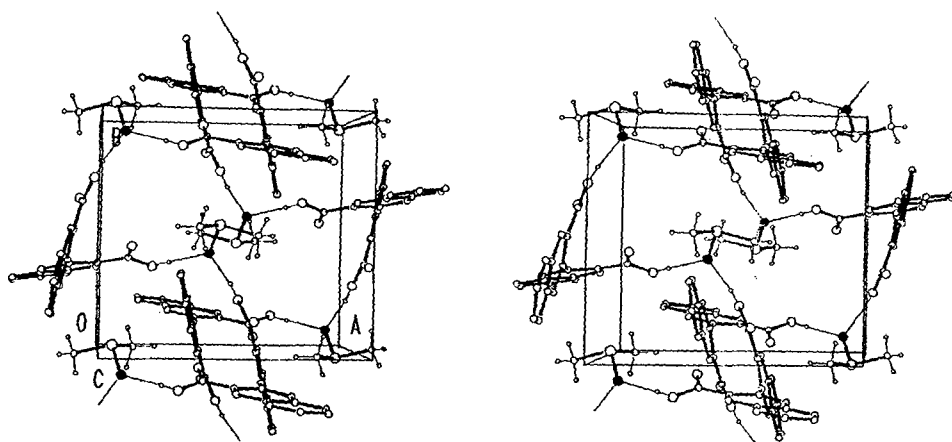


Fig. 2. Stereo packing diagram showing the H-bonded zig-zag \cdots host \cdots guest \cdots host \cdots chains in **1a** [1-DMSO (1 : 1)]. The carbon-bonded H atoms of the hosts are omitted for clarity. Thin lines represent hydrogen bonds. O atoms of the DMSO guests are indicated as filled spots.

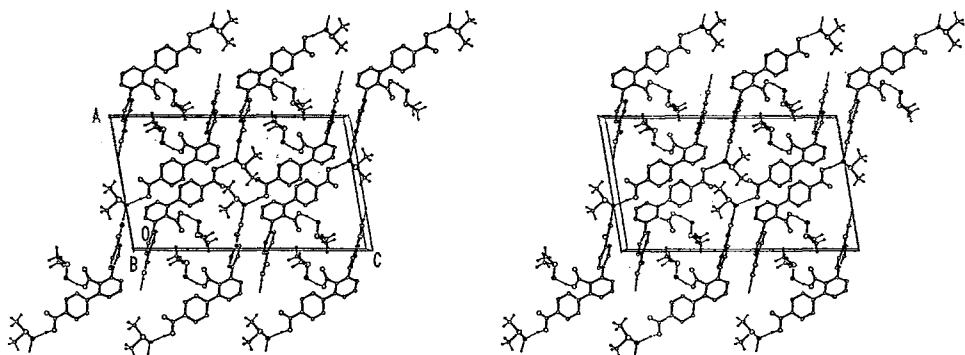


Fig. 3. Stereo packing illustration of **2a** [2·DMSO (1 : 2)]. The carbon bonded H atoms of the host are omitted for clarity. Thin lines represent hydrogen bonds.

The two guests in **2a** [2·DMSO (1 : 2)] are also connected to the host via O—H···O hydrogen bonds [Figure 2(b)], and the guest methyl groups seem to be engaged in several possible C—H_(methyl)···O(=C) interactions (Table III). Nevertheless, this latter approach is between symmetry-related molecules and not between those connected by the O—H···O bond. Thus, the pattern of host–DMSO interaction in **2a** differs somewhat from the ‘common’ mode of binding of DMSO by carboxylic hosts. Compound **2a**, together with the earlier studied 9,10-dihydroethenoanthracene-11,12-dicarboxylic acid·DMSO (1:2) [9b] and *trans*-3,3′-bis(4-methylphenyl)cyclopropane-1,2-dicarboxylic acid·DMSO (1 : 2) clathrates [9a], well demonstrate the fact that the relatively weak C—H···O interactions may easily be affected by packing forces. At the same time, C—H···O interactions may play an important role in organization of heteromolecular aggregates. As a consequence, it proved to be difficult to predict a reliable model for molecular recognition and organization in heteromolecular complexes.

The crystal packing in **1a** [3,3′-BNDA·DMSO (11)] is similar to that in 2,2′-BNDA·DMSO (1 : 1) [9c]. Both can be described as a double-acceptor guest-molecule pattern, in which alternating host enantiomers and intercalated DMSO molecules are linked to form infinite, hydrogen-bonded zig-zag chains (*cf.* Figure 2). The chains are held together by ordinary van der Waals’ forces.

Investigation of the molecular packing in **2a** revealed the two guest molecules playing different roles. Guest 1 is only H-bonded to one host molecule, whereas the oxygen of guest 2, O(D2), accepts two hydrogen bonds from two different hosts (Table III), thus linking the host acids into endless chains in a similar way

TABLE III. Distances (Å) and angles (deg) in (O)—H··O hydrogen bonds and in possible (C)—H··O interactions. Esds, where given,^a are in parentheses.

Atoms involved	Distance			Angle
	Donor—H	Donor—Acceptor	H—Acceptor	<Donor—H··Acceptor
1a [1·DMSO (1:1)]				
O(11')—H(11')··O(D)	0.83(2)	2.680(2)	1.86(2)	171(2)
C(1D)—H(D12)··O(10')	0.95(3)	3.300(3)	2.43(3)	152(2)
O(11)—H(11)··O(D) ¹	0.90(3)	2.646(2)	1.76(3)	167(2)
C(5')—H(5')··O(10) ²	1.02(2)	3.360(3)	2.38(2)	159(2)
C(6)—H(6)··O(11) ³	0.96(2)	3.277(2)	2.68(2)	121(2)
C(6)—H(6)··O(11') ⁴	0.96(2)	3.396(3)	2.77(2)	123(2)
Superscript	Symmetry operation			
none	<i>x, y, z</i>			
1	$-x + 1.5, y - 0.5, -z + 0.5$			
2	$-x + 1, -y, -z$			
3	$-x + 1, -y, -z + 1$			
4	$x - 0.5, -y + 0.5, z + 0.5$			
2a [2·DMSO (1:2)]				
O(9)—H(9)··O(D1)	0.97	2.582(3)	1.63	168
O(18)—H(18)··O(D2)	1.00	2.628(2)	1.64	173
C(11)—H(11)··O(8)	1.00	3.435(3)	2.75	126
C(20)—H(20)··O(26) ¹	1.00	3.302(3)	2.62	125
C(14)—H(14)··O(9) ²	1.00	3.380(3)	2.53	142
O(27)—H(27)··O(D2) ³	0.86	2.644(3)	1.79	175
C(D11)—H(111)··O(8) ⁴	1.00	3.301(3)	2.43	145
C(D12)—H(121)··O(8) ⁵	1.00	3.406(3)	2.59	139
C(D11)—H(113)··O(26) ⁵	1.00	3.381(3)	2.45	154
C(D22)—H(222)··O(26) ⁶	1.00	3.279(5)	2.55	129
Superscript	Symmetry operation			
none	<i>x, y, z</i>			
1	$x, y + 1, z$			
2	$-x + 1, y + 0.5, -z + 0.5$			
3	$x - 1, -y + 2.5, z - 0.5$			
4	$-x, y - 0.5, -z + 0.5$			
5	$-x, y + 0.5, -z + 0.5$			
6	$x + 1, -y + 2.5, z + 0.5$			

^aThe H atom positions in **2a** were not refined (see text).

as in **1a** (Figure 3). The parallel H-bonded chains pack so as to form electrostatically favourable contacts, i.e. C—H··O interactions, besides the ordinary van der Waals' connections.

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