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Solid-State Binding of Dimethyl Sulphoxide Involving Carboxylic Host Molecules. X-ray Crystal Structures of Four Inclusion Species

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Abstract. The crystal structures of four dimethyl sulphoxide (DMSO) inclusion compounds with different carboxylic acid hosts, **1**–**4**, have been studied by single crystal X-ray analysis. Crystals of the *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid inclusion compound (**1a**), [**1** · DMSO (1 : 1)] show monoclinic ($P2_1/n$) symmetry with the unit cell dimensions $a = 11.522(4)$, $b = 18.658(2)$, $c = 8.709(1)$ Å and $\beta = 98.92(2)°$. The clathrate of the 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylic acid (**2a**), [**2** · DMSO (1 : 2)] is triclinic ($P\bar{1}$) with the cell dimensions $a = 15.043(7)$, $b = 9.657(4)$, $c = 8.118(7)$ Å, $\alpha = 101.81(5)$, $\beta = 96.05(4)$ and $\gamma = 100.04(4)°$. Triclinic ($P\bar{1}$) symmetry is shown also by the inclusion compound of 9,10-dihydro-9,10-ethanoanthracene-11-monocarboxylic acid (**3a**) [**3** · DMSO (1 : 1)] with the cell dimensions $a = 6.3132(1)$, $b = 7.9846(2)$, $c = 17.5314(4)$ Å, $\alpha = 96.46(2)$, $\beta = 87.08(2)$ and $\gamma = 106.02(2)°$. The 9,9′-bianthryl-2-monocarboxylic acid clathrate (**4a**) [**4** · DMSO (1 : 1)] is monoclinic ($P2_1/n$) and the cell dimensions are $a = 19.625(18)$, $b = 8.817(1)$, $c = 14.076(8)$ Å and $\beta = 97.92(6)°$. In all these structures, the hosts show the same basic recognition pattern for the DMSO guest, involving a strong O—H···O bond from the COOH to the S=O group, and a possible C—H···O type interaction between the carbonyl O atom of the host and a CH_3 group of the guest. The crystals consist of discrete host-guest aggregates which are mainly held together by weak intermolecular interactions of the Van der Waals' type. The stoichiometries of the aggregates are, however, different.

Key words. Inclusion compounds, X-ray crystal structure analysis, DMSO clathrates, hydrogen bonding.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82075 (53 pages).

1. Introduction

Molecules that recognize and bind to specific substrates are important for analytical applications and for the development of more effective catalysts, carriers and reagents [1]. Exploring interactions at the molecular level is therefore an exciting and challenging aspect of contemporary chemistry [2].

'Coordinatoclathrand' [3] is the name we have given to a particular type of substance which allows specific interactions between host and guest molecules in the

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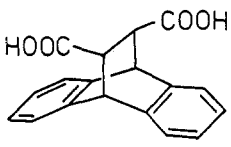
crystalline state. Interactions proceed from functional group relationships involving the host and the guest and include H-bonds as the main factor. Thus far, our studies have focused on the recognition and binding of hydroxylic molecules, mostly alcohols, by different carboxylic hosts [4].

We have now turned our interest towards inclusion of aprotic but dipolar guests, among them dimethylformamide and dimethyl sulphoxide, and have examined a substantial number of structures to help delineate those features which favour solid-state binding. A few structures of dimethylformamide inclusion compounds have already been published by us [5].

Here we discuss X-ray crystal structures of four inclusion compounds, **1a**–**4a**, composed of dimethyl sulphoxide (DMSO) and differently constituted carboxylic hosts (**1**–**4**). The present work comprises also the first structural data on three examples (**2**–**4**) of new host molecules.



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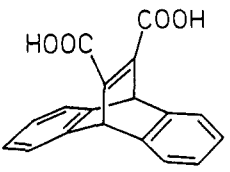

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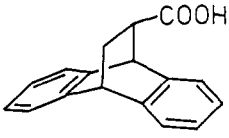

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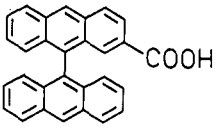

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Inclusion compounds:

1a	: 1 • DMSO (1:1)		3a	: 3 • DMSO (1:1)	
2a	: 2 • DMSO (1:2)		4a	: 4 • DMSO (1:1)	

2. Experimental

2.1. SYNTHESIS AND CRYSTAL GROWTH

Roof-shaped carboxylic host compounds **1**–**3** were prepared as previously described [6]. 9,9′-bianthryl-2-carboxylic acid (**4**) was obtained by the procedure of Bell and Waring [7].

Single crystals of the inclusion compounds **1a**–**4a** were grown by dissolving the respective hosts **1**–**4** in dimethyl sulphoxide (DMSO) and saturating the solutions by slow evaporation at room temperature.

2.2. X-RAY DATA COLLECTION AND PROCESSING

The single crystals selected for X-ray diffraction measurements were sealed in epoxy glue. Intensity data were collected on computer-controlled diffractometers at room temperature, using graphite-monochromated CuK_α radiation ($\lambda = 1.5418$ Å) and the ω–2θ scan technique. The data reduction included corrections for Lorentz and polarization effects, and in the case of compound **3a** also for absorption. The unit cell parameters of compounds **1a** and **4a** were refined using accurately measured line positions (80 for **1a** and 19 for **4a**) on powder photographs, taken with a Guinier-Hägg type focusing camera using strictly monochromated CuK_{α_1} radiation ($\lambda = 1.5406$ Å) and Si ($a = 5.4309$ Å at 298 K) as an internal standard. The angular settings of 30 and 51 well-centred, strong reflections (with $33° < 2\theta < 55°$), accurately measured by the diffractometer, were used in the least-squares refinement of unit cell parameters for the crystals of **2a** and **3a**, respectively. Crystal data and some experimental details are summarized in Table I.

2.3. STRUCTURE ANALYSIS AND REFINEMENT

The sulphur position, derived from a Patterson synthesis, was used as a starting point for solving the structure of compound **1a** by conventional Fourier calculations. The structure of **2a** was solved in the space group $P1$ by a combination of recycling procedures from an initial DMSO fragment and weighted Fourier syntheses. Reasonable structural models of compounds **3a** and **4a** were derived by direct methods using the program systems MULTAN 80 [8] for **3a** and SHELXS [9] for **4a**. The initial models were completed and refined using the SHELX [10] program system. Only the structure factors with $F > 6\sigma(F)$ were used in the latter calculations. The carboxylic hydrogen sites were taken from difference electron density calculations and were held fixed during the subsequent refinements, except in compound **3a** where their positions were also refined. The remaining H atom sites were generated after each cycle using geometrical evidence (C—H = 1.08 Å). The methyl groups of the DMSO molecules in structures **1a**, **2a** and **3a** were treated as rigid groups.

In structure **4a**, the DMSO guest shows partial disorder. The sulphur atom and the methyl carbon atoms had considerably higher temperature factors than the other non-hydrogen atoms, and the difference electron density calculation revealed some prominent peaks in the vicinity of the S and C(D1) atoms. The disorder of the sulphur atom could be resolved into two major disorder sites, with site occupation factors refined in three cycles to 0.56 and 0.32 for S(1) and S(2), respectively. A similar attempt for C(D1), however, did not yield a reasonable model. The methyl groups of this DMSO guest were also refined as rigid groups, but then were held fixed when the S(2) position was included in the calculation.

In the last cycles of the refinements the non-hydrogen atomic positions were refined together with their anisotropic temperature parameters. Isotropic tempera-

Table I. Selected crystal data and experimental details of inclusion compounds **1a**–**4a**. (The esds, where given, are in parentheses.)

Compound	**1a**	**2a**	**3a**	**4a**
Formula	$C_{18}H_{14}O_4 \cdot C_2H_6OS$	$C_{18}H_{12}O_4 \cdot 2(C_2H_6OS)$	$C_{17}H_{14}O_2 \cdot C_2H_6OS$	$C_{29}H_{18}O_2 \cdot C_2H_6OS$
Formula weight	372.4	448.5	328.4	476.6
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	11.522(4)	15.043(7)	6.3132(1)	19.625(18)
b, Å	18.658(2)	9.567(4)	7.9846(2)	8.817(1)
c, Å	8.709(1)	8.118(7)	17.5314(4)	14.076(8)
α, deg.	90.0	101.81(5)	96.46(2)	90.0
β, deg.	98.92(2)	96.05(4)	87.08(2)	97.92(6)
γ, deg.	90.0	100.04(4)	106.02(2)	90.0
V_c, Å^3	1850(1)	1114(1)	843.8(1)	2412(3)
Z	4	2	2	4
D_c, g cm^{-3}	1.34	1.34	1.29	1.31
μ, cm^{-1}	17.49	24.20	17.58	13.98
Radiation used	CuK_α	CuK_α	CuK_α	CuK_α
No. of unique non-zero reflections collected	3111	3566	1796	3759
θ limits, deg.	67	67	70	67
No. of refl. with $F > 6\sigma(F)$, used in the refinement	2489	3292	1636	2103
No. of variables	245	282	220	327
$R = \Sigma \lvert\Delta F\rvert / \Sigma \lvert F_0\rvert$	0.047	0.066	0.045	0.070
$R_w = \Sigma \sqrt{w}\lvert\Delta F - / \Sigma \sqrt{w}\lvert F_0\rvert$	0.052	0.077	0.045	0.079
$R_G = [\Sigma w\lvert\Delta F\rvert^2 / \Sigma w\lvert F_0\rvert^2]^{1/2}$	0.063	0.100	0.045	0.096
Weighting: g i SHELX[a]	0.00035	0.00020	–[b]	0.00152

[a] The weights of the structure factors in SHELX are calculated as $w = k/(\sigma^2(F) + gF^2)$ [10].

[b] All reflections of **3a** have unit weights.

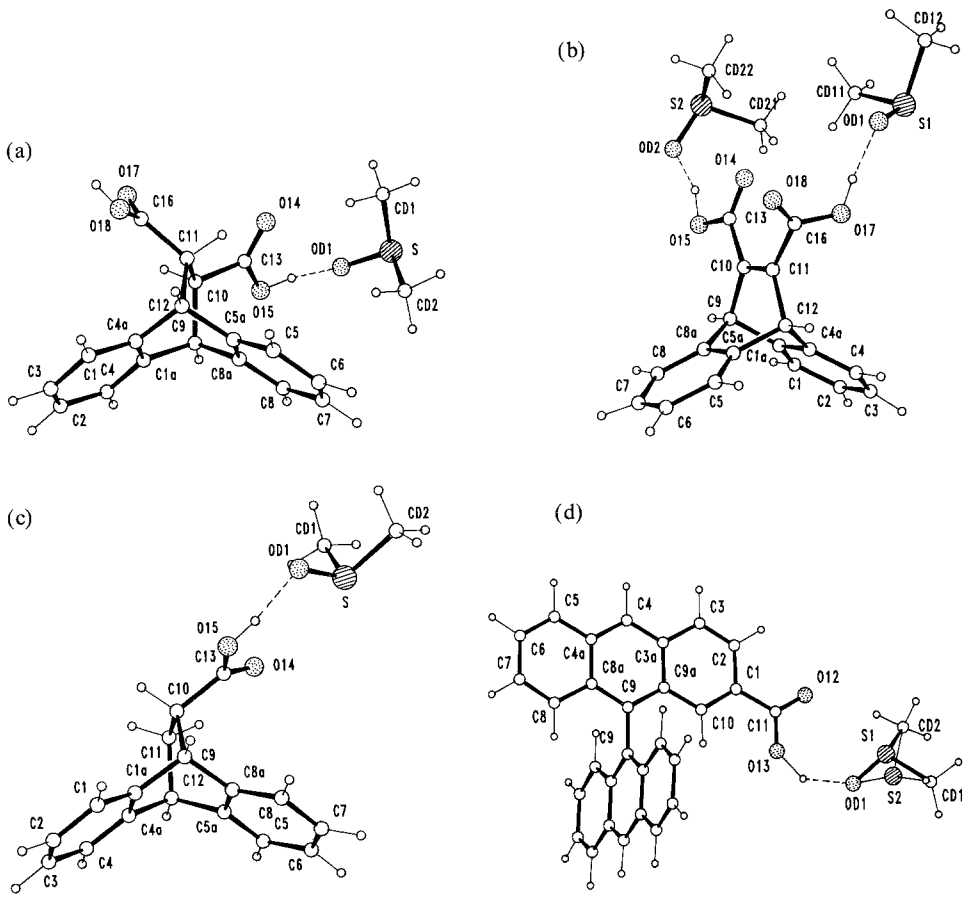


Fig. 1. Perspective view of the asymmetric units of the studied coordinatoclathrates: (a) **1a** [**1** · DMSO (1 : 1)], (b) **2a** [**2** · DMSO (1 : 2)], (c) **3a** [**3** · DMSO (1 : 1)] and (d) **4a** [**4** · DMSO (1 : 1)]. Solid and dashed lines represent covalent and hydrogen bonds, respectively, O atoms are shaded and S atoms hatched. In **4a** the DMSO guest shows partial disorder.

ture factors were refined for the carboxylic hydrogens and group isotropic for the calculated ones. Some of the strongest low-θ reflections (10 for **1a**, 4 for **3a** and 9 for **4a**) with $F_{obs} \ll F_{calc}$ probably due to secondary extinction, were excluded from the final refinements, when the reliability indices (Table I) were obtained. In the case of structure **4a**, however, satisfactory convergence was reached only when the temperature factors of the methyl hydrogens ($U = 0.35$ Å^2) and of the carboxylic H(13) ($U = 0.167$ Å^2) were held fixed.

3. Results and Discussion

The atomic positional parameters of the four inclusion compounds **1a**–**4a** are given in Table II; atom labelling is in accordance with Figure 1. Relevant intermolecular bond distances and angles are listed in Tables III and IV. Perspective views of the crystallographic asymmetric units of compounds **1a**–**4a** are shown in Figure 1, and

Table II. Fractional atomic coordinates and equivalent isotropic/isotropic temperature factors of the non-hydrogen atoms and of the carboxylic hydrogens of the inclusion compounds **1a**–**4a**. (The esds, where given, are in parentheses.)

ATOM[a]	*x/a*	*y/b*	*z/c*	U^{b}_{eq}/U (Å^2)	ATOM[a]	*x/a*	*y/b*	*z/c*	U^{b}_{eq}/U (Å^2)
1a : **1** · DMSO (1 : 1)					**2a** : **2** · DMSO (1 : 2)				
C(1a)	0.7704(2)	0.3160(1)	0.1336(3)	0.040(1)	C(1a)	0.8152(2)	−0.0023(3)	0.5203(3)	0.037(1)
C(1)	0.7100(3)	0.2642(2)	0.2018(3)	0.052(1)	C(1)	0.8734(2)	−0.0766(4)	0.5950(4)	0.048(1)
C(2)	0.7733(3)	0.2143(2)	0.3006(4)	0.062(1)	C(2)	0.8382(3)	−0.2159(4)	0.6155(5)	0.057(1)
C(3)	0.8939(3)	0.2166(2)	0.3284(4)	0.061(1)	C(3)	0.7470(3)	−0.2791(4)	0.5600(5)	0.058(1)
C(4)	0.9552(3)	0.2688(1)	0.2605(3)	0.050(1)	C(4)	0.6885(2)	−0.2052(3)	0.4832(4)	0.047(1)
C(4a)	0.8930(2)	0.3186(1)	0.1625(3)	0.039(1)	C(4a)	0.7233(2)	−0.0671(3)	0.4649(3)	0.037(1)
C(5a)	0.8958(2)	0.3698(1)	−0.0944(3)	0.040(1)	C(5a)	0.7219(2)	0.0685(3)	0.2420(3)	0.034(1)
C(5)	0.9612(3)	0.3661(1)	−0.2142(3)	0.051(1)	C(5)	0.6868(2)	0.0408(3)	0.0712(4)	0.042(1)
C(6)	0.9027(3)	0.3587(2)	−0.3666(3)	0.065(1)	C(6)	0.7452(3)	0.0770(4)	−0.0436(4)	0.050(1)
C(7)	0.7820(3)	0.3569(2)	−0.3972(3)	0.064(1)	C(7)	0.8365(2)	0.1373(4)	0.0126(4)	0.051(1)
C(8)	0.7162(3)	0.3611(2)	−0.2759(3)	0.053(1)	C(8)	0.8719(2)	0.1669(3)	0.1848(4)	0.044(1)
C(8a)	0.7732(2)	0.3668(1)	−0.1250(3)	0.041(1)	C(8a)	0.8140(2)	0.1319(3)	0.2984(3)	0.036(1)
C(9)	0.7164(2)	0.3731(1)	0.0204(3)	0.039(1)	C(9)	0.8399(2)	0.1508(3)	0.4897(4)	0.037(1)
C(10)	0.7559(2)	0.4473(1)	0.0932(3)	0.038(1)	C(10)	0.7735(2)	0.2348(3)	0.5740(3)	0.036(1)
C(11)	0.8915(2)	0.4497(1)	0.1285(3)	0.036(1)	C(11)	0.6858(2)	0.1719(3)	0.5202(3)	0.035(1)
C(12)	0.9444(2)	0.3783(1)	0.0769(3)	0.038(1)	C(12)	0.6704(2)	0.0302(3)	0.3841(3)	0.037(1)
C(13)	0.7081(2)	0.5087(1)	−0.0136(3)	0.044(1)	C(13)	0.8019(2)	0.3713(3)	0.7088(4)	0.040(1)
O(14)	0.7622(2)	0.5627(1)	−0.0274(3)	0.078(1)	O(14)	0.7498(2)	0.4282(3)	0.7884(3)	0.060(1)
O(15)	0.6025(2)	0.4965(1)	−0.0865(3)	0.065(1)	O(15)	0.8903(2)	0.4235(3)	0.7330(3)	0.059(1)
C(16)	0.9369(2)	0.4692(1)	0.2950(3)	0.040(1)	C(16)	0.6056(2)	0.2257(3)	0.5844(4)	0.042(1)
O(17)	0.8766(2)	0.5033(1)	0.3737(2)	0.056(1)	O(17)	0.5685(2)	0.3103(4)	0.5276(4)	0.070(1)
O(18)	1.0443(2)	0.4510(1)	0.3440(2)	0.059(1)	O(18)	0.5781(2)	0.1621(3)	0.7041(3)	0.065(1)
S	0.5564(1)	0.6301(1)	−0.4073(1)	0.073(0)	S(1)	0.5108(1)	0.2779(1)	1.0867(1)	0.049(0)
O(D1)	0.5030(2)	0.5912(1)	−0.2843(3)	0.077(1)	O(D1)	0.4792(2)	0.2845(3)	0.9046(3)	0.060(1)
C(D1)	0.6773(4)	0.6800(2)	−0.3135(6)	0.100(2)	C(D11)	0.6162(3)	0.4038(5)	1.1521(6)	0.068(2)
C(D2)	0.6383(5)	0.5654(3)	−0.4944(7)	0.121(3)	C(D12)	0.4403(3)	0.3739(6)	1.2084(5)	0.071(2)
H(15)	0.577	0.535	−0.159	0.10(1)	S(2)	0.9189(1)	0.7043(1)	1.1325(1)	0.051(0)
H(18)	1.074	0.465	0.432	0.14(2)	O(D2)	0.9510(2)	0.6571(2)	0.9643(3)	0.054(1)

C(D21)	0.8803(3)	0.5420(4)	1.2012(6)	0.065(2)
C(D22)	0.8099(3)	0.7471(4)	1.0832(5)	0.066(2)
H(15)	0.905	0.513	0.842	0.06(3)
H(18)	0.541	0.213	0.772	0.06(3)
3a : 3 · DMSO (1 : 1)				
C(1a)	0.8625(6)	0.7025(5)	0.4106(2)	0.040(2)
C(1)	0.7132(6)	0.6845(5)	0.4716(2)	0.047(2)
C(2)	0.7890(7)	0.7355(5)	0.5460(3)	0.056(2)
C(3)	1.0133(7)	0.8031(5)	0.5590(3)	0.058(2)
C(4)	1.1641(7)	0.8201(5)	0.4977(3)	0.051(2)
C(4a)	1.0895(6)	0.7709(5)	0.4234(2)	0.042(2)
C(5a)	1.1368(5)	0.8850(5)	0.2982(2)	0.039(2)
C(5)	1.2557(6)	1.0312(5)	0.2634(2)	0.045(2)
C(6)	1.1458(6)	1.1094(5)	0.2168(2)	0.053(2)
C(7)	0.9215(7)	1.0406(5)	0.2046(2)	0.050(2)
C(8)	0.8033(6)	0.8945(5)	0.2391(2)	0.043(2)
C(8a)	0.9108(5)	0.8169(5)	0.2861(2)	0.037(2)
C(9)	0.8072(5)	0.6565(4)	0.3270(2)	0.038(2)
C(10)	0.9294(5)	0.5171(5)	0.2949(2)	0.039(2)
C(11)	1.1801(6)	0.5921(5)	0.3089(2)	0.045(2)
C(12)	1.2266(6)	0.7817(5)	0.3496(2)	0.041(2)
C(13)	0.8744(6)	0.4624(5)	0.2113(3)	0.046(2)
O(14)	1.0031(4)	0.4827(4)	0.1576(2)	0.062(2)
O(15)	0.6608(4)	0.3859(4)	0.2026(2)	0.061(2)
S	0.7115(2)	0.3262(2)	−0.0002(1)	0.063(1)
O(D1)	0.5638(5)	0.2456(4)	0.0644(2)	0.081(2)
C(D1)	0.8994(8)	0.1995(7)	−0.0205(3)	0.087(3)
C(D2)	0.5511(8)	0.2524(8)	−0.0840(3)	0.095(3)
H(15)	0.627(10)	0.344(8)	0.152(4)	0.14(3)
4a : 4 · DMSO (1 : 1)				
C(1)	0.8003(3)	0.1640(6)	0.3067(3)	0.073(2)
C(2)	0.7380(3)	0.0856(7)	0.2925(4)	0.084(2)
C(3)	0.6968(3)	0.0867(6)	0.3601(4)	0.086(2)
C(3a)	0.7143(3)	0.1662(6)	0.4490(4)	0.074(2)
C(4)	0.6721(3)	0.1703(6)	0.5198(4)	0.080(2)
C(4a)	0.6899(3)	0.2437(6)	0.6064(4)	0.075(2)
C(5)	0.6469(3)	0.2491(6)	0.6787(5)	0.087(2)
C(6)	0.6655(3)	0.3182(7)	0.7632(5)	0.094(3)
C(7)	0.7285(3)	0.3927(7)	0.7823(4)	0.097(3)
C(8)	0.7715(3)	0.3951(6)	0.7148(4)	0.082(2)
C(8a)	0.7543(2)	0.3193(6)	0.6241(3)	0.069(2)
C(9)	0.7978(2)	0.3173(5)	0.5536(3)	0.063(2)
C(9a)	0.7792(2)	0.2429(5)	0.4654(3)	0.063(2)
C(10)	0.8204(2)	0.2403(5)	0.3921(3)	0.064(2)
C(1′)	0.9737(3)	0.1025(7)	0.7057(4)	0.100(3)
C(2′)	1.0349(3)	0.1798(10)	0.7276(5)	0.112(3)
C(3′)	1.0392(3)	0.3274(10)	0.6988(4)	0.108(3)
C(3a′)	0.9836(3)	0.4045(7)	0.6469(3)	0.077(2)
C(4′)	0.9872(3)	0.5544(7)	0.6175(4)	0.082(2)
C(4a′)	0.9329(3)	0.6276(6)	0.5655(4)	0.078(2)
C(5′)	0.9381(4)	0.7804(8)	0.5346(5)	0.102(3)
C(6′)	0.8837(6)	0.8501(8)	0.4844(5)	0.126(4)
C(7′)	0.8217(4)	0.7721(8)	0.4616(4)	0.110(3)
C(8′)	0.8148(3)	0.6274(6)	0.4891(4)	0.081(2)
C(8a′)	0.8703(3)	0.5475(6)	0.5425(3)	0.067(2)
C(9′)	0.8645(2)	0.3978(6)	0.5730(3)	0.062(2)
C(9a′)	0.9209(2)	0.3230(6)	0.6244(3)	0.064(2)
C(10′)	0.9184(3)	0.1693(6)	0.6567(4)	0.080(2)
C(11)	0.8429(3)	0.1617(7)	0.2286(4)	0.082(2)
O(12)	0.8293(2)	0.0840(6)	0.1566(3)	0.123(2)
O(13)	0.8968(2)	0.2464(5)	0.2410(3)	0.107(2)
S(1)	0.9083(2)	0.2732(4)	−0.0023(3)	0.111(2)
S(2)	0.9562(4)	0.2094(11)	−0.0068(5)	0.148(4)
O(D1)	0.9557(3)	0.2709(8)	0.0845(4)	0.173(3)
C(D1)	0.9480(7)	0.3500(14)	−0.0923(8)	0.227(7)
C(D2)	0.8892(7)	0.1078(15)	−0.0491(8)	0.266(8)
H(13)	0.944	0.260	0.195	0.17

[a] Atom labelling is in accordance with Figure 1.

[b] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} \cdot \alpha_i^* \cdot \alpha_j^* \cdot a_i \cdot a_j$.

Talbe III. Distances (Å) and angles (deg) in O—H···O type interactions of inclusion compounds **1a**–**4a**. (The esds, where given, are in parentheses.)

Atoms involved	Symmetry	Donor···Acceptor	Donor—H	H···Acceptor	∢Donor—H···Acceptor
1a : **1** · DMSO (1 : 1)					
O(15)—H(15)···O(D1)	x, y, z	2.606(3)	0.97	1.65	167
O(18)—H(18)···O(17)	$-x+2, -y+1, -z+1$	2.625(3)	0.83	1.80	174
2a : **2** · DMSO (1 : 2)					
O(18)—H(18)···O(D1)	x, y, z	2.563(4)	0.95	1.62	172
O(15)—H(15)···O(D2)	x, y, z	2.562(3)	1.07	1.52	161
3a : **3** · DMSO (1 : 1)					
O(15)—H(15)···O(D1)	x, y, z	2.582(4)	0.92(6)	1.67(6)	173(6)
4a : **4** · DMSO (1 : 1)					
O(13)—H(13)···O(D1)	x, y, z	2.634(7)	1.22	1.60	138

Table IV. Distances (Å) and angles (deg) in possible C—H···O type interactions between host and guest molecules of five different DMSO inclusion compounds.

Inclusion compound	C···O	C—H	H···O	∢C—H···O
1a:**1** · DMSO (1:1)	3.35	1.08	2.38	148
2a:**2** · DMSO (1:2)	3.38	1.08	2.48	140
	3.29[b]	1.06	2.37	144
3a:**3** · DMSO (1:1)	3.32	1.08	2.47	134
4a:**4** · DMSO (1:1)	3.28	1.11	2.47	129
BNDA[a] · DMSO (1:1)	3.31	1.08	2.27	161

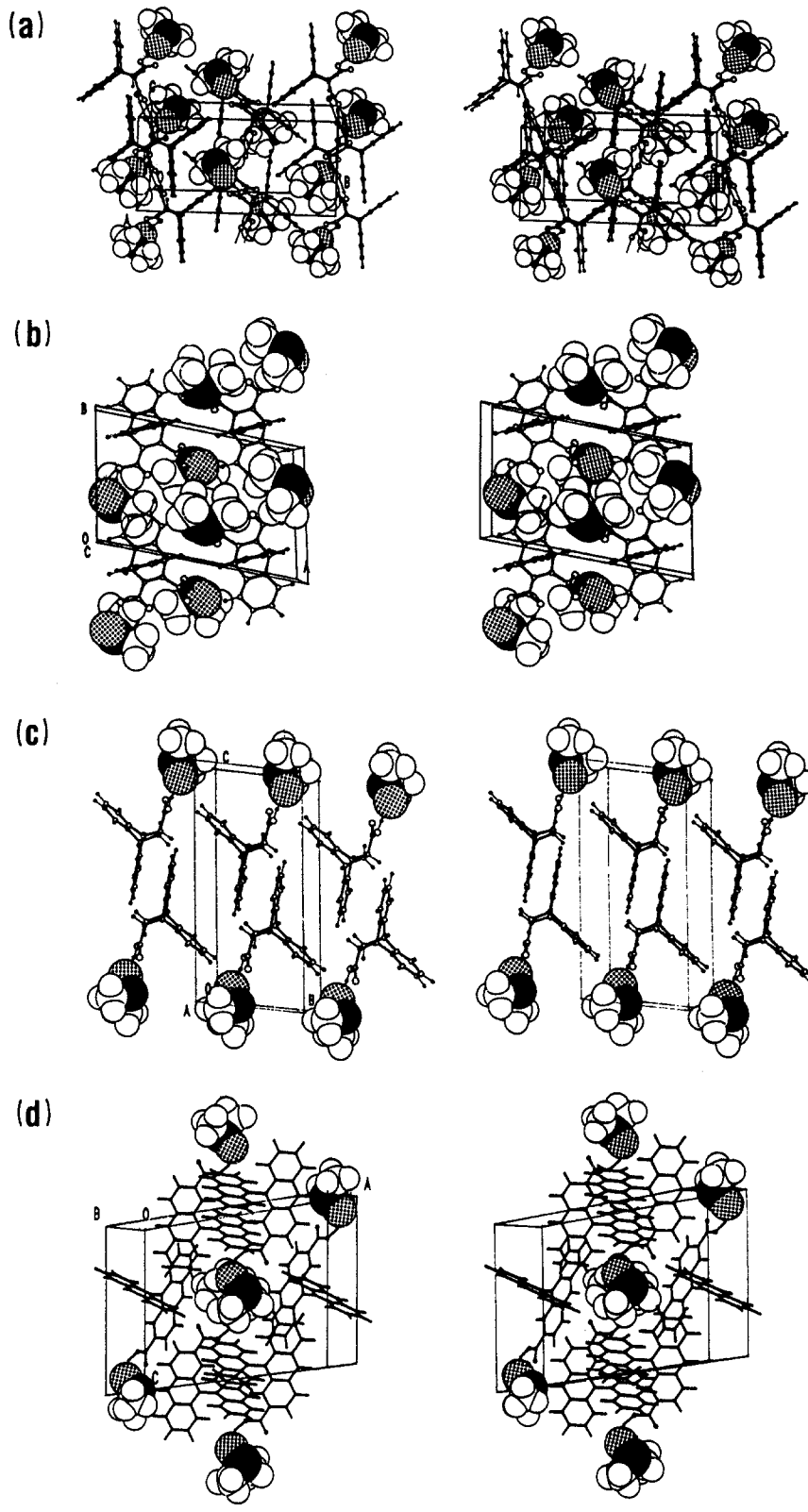
[a] 1,1′-Binaphthyl-2,2′-dicarboxylic acid (cf. Ref. 5b).
[b] Contact between symmetry-related host–guest aggregates (see the text for explanation).

the crystal packings are illustrated in Figure 2. The lists of intramolecular bond distances and bond angles, involving the non-hydrogen atoms (Tables V and VI), fractional atomic coordinates of the calculated hydrogen atoms (Table VII), anisotropic thermal parameters of the non-hydrogen atoms (Table VIII) as well as the lists of the observed and calculated structure factors are deposited with the British Library as Supplementary Publication. No. SUP 82075.

3.1. MOLECULAR STRUCTURES

The rigid roof-shaped host molecules in crystals **1a**, **2a** and **3a** are very similar to each other (Figures 1a, 1b and 1c). The corresponding bond angles in structures **1a** and **3a** are in agreement with each other and also with the values found earlier for related structures [6, 11, 12]. The bond lengths and bond angles in the host molecule of structure **2a** also resemble those of the previous complexes except, of course, the bond distances between the C(9)—C(10)—C(11)—C(12) atoms. In the ethano bridges of **1a** and **3a**, the C(9)—C(10) and C(11)—C(12) bonds are elongated, while the C(10)—C(11) bond length in the middle is normal for a $C_{(sp^3)}$—$C_{(sp^3)}$ bond [1.541(±3) Å] [13]. The mean values calculated for structures **1a** and **3a** (with rmsds in square brackets) are 1.559[3] Å for the elongated bonds and 1.548[4] Å for the C(10)—C(11) bond. In the etheno bridge of **2a** the C(9)—C(10) and C(11)—C(12) distances are 1.521(4) and 1.527(4) Å, and the double-bond length is 1.336(4) Å, all in agreement with the standard values of 1.53(±1) and 1.337(±6) Å, respectively, for these bond types [13]. The dihedral angles between the phenyl rings are 57.4(2) and 57.1(1)° in structures **1a** and **3a**, respectively, and 62.9(1)° in structure **2a**.

In the bianthryl monocarboxylic acid molecule, **4** of **4a** (Figure 1d), the bond distances and angles conform to the expected values. The fourteen ring atoms of each of the two aromatic tricyclic groups are coplanar within 0.058 and 0.035 Å, respectively. The dihedral angle between the calculated least-squares planes of these anthryl moieties is 94.96(6)°, and the carboxyl group is inclined through 7.6(3)° to the attached anthryl plane.


(a)
(b)
(c)
(d)

The DMSO molecules have the usual pyramid shape [5b]. The sum of the angles around the S atoms is 311.1° in **1a**, 310.1°/309.6° in **2a** for molecules 1 and 2; 308.5° in **3a**, and 323.1/325.2° in structure **4a** for the disorder sites S(1) and S(2), respectively.

3.2. PACKING RELATIONS AND HOST–GUEST INTERACTIONS

The DMSO oxygen atom is a potent proton acceptor in hydrogen bonding [14]. Thus, in host–guest aggregates involving a carboxylic component, it can readily form a C(O)O—H···O=S interaction. This is the case in all the present structures (Figure 1 and Table III) and has also been observed in the DMSO inclusion compound of 1,1′-binaphthyl-2,2′-dicarboxylic acid [BNDA] [5b].

Inspection of the intermolecular distances in these five structures shows that there is an additional host–guest contact worth mentioning. In each of the five crystals listed in Table IV, the DMSO molecules are arranged so that in addition to the (O—)H···O contact one of the methyl groups approaches a carbonyl O atom of the host. All the C—(H)···O interactions in Table IV except one involve host and guest molecules that are H-bonded to each other. In structure **2a**, however, only one of the DMSO molecules can from its C—H···O interaction with the same —COOH group to which it is H-bonded (Figure 1b). A steric barrier forces the other one into a different arrangement. Thus, its methyl group approaches a carbonyl oxygen of another host molecule instead of its 'own', resulting in a relatively short (<3.3 Å) contact between two asymmetric units. The ability of carbon atoms to act as proton donors in C—H···O type interactions is possibly somewhat controversial [15]. Nevertheless, a survey of 113 accurately determined crystal structures led Taylor and Kennard to the conclusion that the majority of shorter C—H···X (X = O, N or Cl) contacts are attractive interactions and may thus be significant factors in determining the packing arrangement of small organic molecules [15]. Recently, Kumpf and Damewood Jr. demonstrated, using *ab initio* methods, that malonitrile is capable of forming C—H···O bonds by its methylene group, that may be as stable as $-22.6\ \text{kJ mol}^{-1}$ [16]. Because of the uncertainty in the methyl hydrogen positions in the structures **1a**–**4a** and also in BNDA · DMSO (1 : 1) [5b] an unequivocal conclusion is not possible, but consideration of the repeated appearance of largely identical patterns for the binding of the DMSO guests by different carboxylic acid hosts makes it seem likely that these contacts (*cf.* Table IV) are weak C—H···O type interactions which may play an important role in the recognition of DMSO guests by hosts with carboxylic sensor groups.

Another common feature of the present crystal structures is the existence of discrete host–guest aggregates which have, however, different stoichiometries (Figures 2a–2d). The host molecule of **1a** retains at least one of its sensor groups for binding to another host molecule. Such a dimer, with two carboxylic groups free for binding to the guest, seems to be a basic characteristic of inclusion compounds of

Fig. 2. Stereoscopic representation of the crystal packings: (a) **1a** [**1** · DMSO (1 : 1)], (b) **2a** [**2** · DMSO (1 : 2)], (c) **3a** [**3** · DMSO (1 : 1)], and (d) **4a** [**4** · DMSO (1 : 1)]. The host molecules are drawn in stick model fashion, the guest molecules are given as space filling models, O atoms are dotted and the S atoms shaded.

1 since five other inclusion compounds of **1** [6, 12] also show this behaviour. It leads to a 2:2 stoichiometry for the host–guest aggregate (Figure 2a). Host molecule **2**, however, uses both of its carboxyl groups in host–guest interactions; thus the stoichiometry of the host–guest unit is 1:2 (Figure 2b). The hosts **3** and **4** have only one sensor group each. Consequently, one host and one guest molecule make the structural units which build up the crystals of **3a** and **4a** (Figures 2c and 2d).

As shown in Figures 2b and 2c, the triclinic crystals of **2a** and **3a** are built up of rows of identically oriented host–guest aggregates parallel to the *b* axis. By virtue of the centre of symmetry, adjacent rows contain aggregates with opposite orientations. In the crystals of **4a**, the bulky bianthryl skeletons form a framework with channel-like cavities where the guest molecules reside (Figure 2d). In all these crystal structures, the host–guest aggregates are held together by weak intermolecular interactions of the Van der Waals' type, except in **2a** where weak C—H···O type interactions between different host–guest units are also observed, as has been discussed before.

In summary, the structures may be understood to reveal a general mode of recognition and binding of DMSO by simple carboxylic hosts in crystalline host–guest compounds, there weak interactions of C—H···O type may also play an important role.

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References

1. (a) E. Weber (Ed.): *Molecular Inclusion and Molecular Recognition – Clathrates I* (Topics in Current Chemistry, vol. 140). Springer-Verlag, Berlin-Heidelberg-New York (1987); part II (vol. 149) (1988).
   (b) R. M. Izatt and J. J. Christensen (Eds.): *Synthesis of Macrocycles – The Design of Selective Complexing Agents* (Progress in Macrocyclic Chemistry, vol. 3), Wiley, New York (1987).
   (c) G. Van Binst (Ed.): *Design and Synthesis of Organic Molecules Based on Molecular Recognition.* Springer Verlag, New York (1986).
   (d) J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Eds.): *Inclusion Compounds* vols. I–III. Academic Press, London (1984).
2. (a) J. M. Lehn: *Angew. Chem.* **100**, 91 (1988); *Angew. Chem., Int. Ed. Engl.* **27**, 89 (1988).
   (b) D. J. Cram: *Angew. Chem.* **100**, 1041 (1988); *Angew. Chem., Int. Ed. Engl.* **27**, 1009 (1988).
   (c) H. Grünewald (Ed.): *Chemistry for the Future.* Pergamon Press, Oxford–New York (1984).
3. E. Weber and H. P. Josel: *J. Incl. Phenom.* **1**, 79 (1983).
4. E. Weber, I. Csöregh, B. Stensland, and M. Czugler: *J. Am. Chem. Soc.* **106**, 3297 (1984).
5. (a) M. Czugler, J. J. Stezowski, and E. Weber: *J. Chem. Soc., Chem. Commun.* 154 (1983).
   (b) I. Csöregh, A. Sjögren, M. Czugler, and E. Weber: *J. Chem. Soc., Perkin Trans.* **2**, 507 (1986).
   (c) E. Weber, M. Hecker, E. Koepp, W. Orlia, M. Czugler, and I. Csöregh: *J. Chem. Soc., Perkin Trans.* **2** (1988), 1251.
6. E. Weber, I. Csöregh, J. Ahrendt, S. Finge, and M. Czugler: *J. Org. Chem.* **53**, 5831 (1988).
7. F. Bell and D. H. Waring: *J. Chem. Soc.* 2689 (1949).

8. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerq, and M. M. Woolfson: *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data.* University of York, England (1980).
9. G. M. Sheldrick: *SHELXS 84. Program for Crystal Structure Solution.* University of Göttingen, FR-Germany, personal communication.
10. G. M. Sheldrick: *SHELX 76. Program for Crystal Structure Determination.* Univ. of Cambridge, England (1976).
11. M. Czugler, E. Weber, and J. Ahrendt: *J. Chem. Soc., Chem. Commun.* 1632 (1984).
12. I. Csöregh, M. Czugler, and E. Weber: in *Molecular Structure: Chemical Reactivity and Biological Activity* (Ed. J. J. Stezowski) pp. 390–395. Oxford University Press (1988).
13. O. Kennard: in *International Tables for X-ray Crystallography*, vol. III, pp. 275–276. Kynoch Press, Birmingham, England (1968) [Distributed by Kluwer Academic Publishers, Dordrecht and Boston.]
14. S. N. Vinogradov and R. H. Linnell (Eds.): *Hydrogen Bonding*, Van Nostrand Reinhold, New York (1971).
15. R. Taylor and O. Kennard: *J. Am. Chem. Soc.* **104**, 5063 (1982).
16. (a) J. R. Damewood, Jr., J. J. Urban, T. C. Williamson, and A. L. Rheingold: *J. Org. Chem.* **53**, 167 (1988).
    (b) R. A. Kumpf and J. R. Damewood, Jr.: *J. Chem. Soc., Chem. Commun.* 621 (1988).