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Crystalline Inclusion Compounds Derived from Derivatives of Mandelic Acid. Host Synthesis, Inclusion Formation, and X-Ray Structures of a Free Host Compound and of DMSO Inclusion Complexes in Both Racemic and Optically Resolved Forms

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Abstract. New chiral host compounds based on mandelic acid derivatives having methyl (**6a**, **b** and **8a**, **b**) or bromo substituents (**7a**, **b**) attached to the phenyl ring of mandelic acid and involving additional aromatic groups were synthesized. The inclusion properties of both the racemic and the optically resolved host species are reported, including solvent co-crystallization as well as chiroselective and vapour sorptive inclusion. The structures of the free racemic host compound **6b** and of the DMSO inclusion compounds of optically resolved and racemic **8** (**8a** and **8b**, respectively) have been determined by X-ray analysis. Enantiomeric pairs of molecules in **6b** form centro-symmetric dimers by mutual hydrogen bonding of one hydroxyl group while the other is involved in O—H $\cdots$ π interactions. The guest molecules in the DMSO complexes of **8a** and **8b** are bound via hydrogen bonds to two host molecules related by translation along crystallographic axes. Parallels to previous hosts of this type are drawn.

Keywords: host–guest chemistry, crystalline inclusion compounds, racemate resolution, vapour sorption, X-ray structure determination, hydrogen bonding, mandelic acid.

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1. Introduction

Crystal-engineering [1] and crystalline inclusion chemistry [2] are very topical fields due to their impetus on materials science [3], separation techniques [4] and sensing [5]. A particular interest is aimed at the separation of optical isomers using crystalline host-guest chemistry [6]. Diol host compounds such as those derived from natural tartaric acid [7] and lactic acid [8] have proved to have high efficiency in this respect.

Recently we have developed diol host analogues **1**(**a**, **b**) based on mandelic acid [9]. It was shown that these hosts and their substituted derivatives (**2–5**, **a–b**) are also capable of forming crystalline inclusion compounds [10]. The inclusion property was found to strongly depend on the optical species of the host (optically resolved or racemic) as well as on the substituents existing at the bulky diphenylmethanol group. In each case, the optically resolved species proved superior while substitution adversely affected the inclusion properties [9, 10]. The substituents are also connected to a particular phase transition phenomenon discovered in respective DMF complexes [11].

In order to learn more of the general and specific inclusion behaviour of this particular host family, we studied compounds **6**(**a**, **b**)–**8**(**a**, **b**) which are typical of a substitution at the phenyl group of mandelic acid, and compared them to the previous results.

2. Experimental

2.1. SYNTHESIS

2.1.1. *General*

Melting points were taken on a Kofler apparatus (Reichert, Wien). The optical rotations were measured with a Perkin-Elmer 241 polarimeter using a 1 dm cell. The ^{1}H-NMR spectra were recorded on Varian T60A (60 MHz) and Bruker WM-300 (300 MHz) instruments with Me_4Si as internal reference (δ values in ppm). IR spectra were measured with a Perkin-Elmer 1600 FT-IR spectrometer; spectral bands are reported in cm^{-1}. Mass spectra were obtained by GC-MS with a Hewlett-Packard 5890/MS 5989A. The GC determinations of the enantiomer purity were performed using Lipodex columns (Macherey Nagel). Microanalyses were carried out by the Microanalytical Laboratory of the Technical University Bergakademie Freiberg. Compounds **1**–**5** (**a**, **b**) were synthesized as described previously [9, 10].

2.1.2. *Substituted Mandelic Acid Precursors*

4′-Methylmandelic Acid. This compound was prepared from *p*-tolylaldehyde and sodium cyanide followed by acidic hydrolysis of the intermediate nitrile according to the literature [12]. Recrystallization from benzene-chloroform gave colourless crystals in 78% yield; m.p. 143 °C (lit. [13] m.p. 145 °C).

Optical Resolution of 4′-Methylmandelic Acid. Separation of the enantiomers was carried out by using diastereomeric salt formation with (*R*)-(+)-phenylethylamine and subsequent liberation (HCl) of the optically resolved species as described [14]. Recrystallization from chloroform gave colourless crystals of the pure (*R*)-configurated acid in 68% yield; m.p. 140 °C; $[\alpha]_D^{20} - 184°$ (c1, $CHCl_3$) and 61% of the (*S*)-configured acid with $[\alpha]_D^{20} + 178°$ (c1, $CHCl_3$).

(R)- and (R, S)-Methyl 4′-Methylmandelate. Conc. sulphuric acid (2.5 mL) was added to a solution of the optically resolved or racemic 4′-methylmandelic acid (25 g, 0.16 mol) in methanol (75 mL), and the mixture was refluxed for 5 h. On addition of water (125 mL), neutralization with solid potassium carbonate, removal of the methanol under reduced pressure, extraction with chloroform, drying and evaporation of the solvent the crude esters were obtained as oils. Recrystallization from petroleum ether-toluene (1 : 1) yielded the esters as colourless crystals.

(R)-Methyl 4′-Methylmandelate. 91%; m.p. 60 °C; $[\alpha]_D^{20} - 188°$ (c1, $CHCl_3$); ^{1}H-NMR (60 MHz, CDCl) δ 7.4 (d, 4H, Ar—H), 5.1 (d, 1H, OH), 3.7 (s, 3H, CH_3), 3.4 (s, 1H, C—H), 2.3 (s, 3H Ar—CH_3).

(R, S)-Methyl 4′-Methylmandelate. 95%; m.p. 58 °C; spectroscopic data as given for the optically resolved species.

4′-Bromomandelic Acid. This compound was prepared from α,α-dibromo-*p*-bromoacetophenone on treatment with NaOH and water following the literature procedure [15]. Recrystallization from benzene gave colourless crystals in 89% yield; m.p. 115 °C (lit. [15] m.p. 117 °C).

Optical Resolution of 4′-Bromomandelic Acid. Separation of the enantiomers was carried out by using diastereomeric salt formation with (1*R*, 2*S*)-(−)-ephedrine and subsequent liberation (HCl) of the optically resolved species as described [16]. Recrystallization from chloroform yielded 44% of the pure (*R*)-configurated acid; m.p. 96 °C (lit. [16] m.p. 107 °C); $[\alpha]_D^{20}$ – 132° (c1, $CHCl_3$).

(R)- and (R, S)-Methyl 4′-Bromomandelate. The same procedure was used as for methyl 4′-methyl-mandelate.

(R)-Methyl 4′-Bromomandelate. 83%; m.p. 68 °C; $[\alpha]_D^{20}$ – 156° (c1, acetone); ^{1}H-NMR (60 MHz, $CDCl_3$) δ 7.4–7.0 (m, 4H, Ar—H), 5.0 (s, 1H, CH), 4.5 (s, 1H, OH), 2.3 (s, 3H, CH_3).

(R, S)-Methyl 4′-Bromomandelate. 90%; m.p. 72 °C; spectroscopic data as given for the optically resolved species.

2.1.3. *Synthesis of Host Compounds* **6a**,**b**, **7a**,**b** *and* **8a**,**b** *[17] (General Procedure)*

A Grignard reagent of the respective arylhalide (bromobenzene or 4-*tert*-butylbromobenzene) (0.4 mol) in dry tetrahydrofuran was prepared as usual [18]. The corresponding mandelic acid methyl ester (0.1 mol) was added as a solution in tetrahydrofuran (100 mL) dropwise at 0 °C. The mixture was refluxed for about 3 h. A saturated solution of ammonium chloride was added (150 mL) and the phases were separated. Workup included extraction with diethyl ether, washing (water), drying (sodium sulphate), evaporation of the solvent under reduced pressure and recrystallization. Specific details are given for each compound.

*(S)-2-(4-Methylphenyl)-1,1-diphenylethane-1,2-diol (***6a***).* Recrystallization from cyclohexane-chloroform yielded 63% colourless crystals; m.p. 205 °C; $[\alpha]_D^{20} - 210$ (c1, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.7–6.9 (m, 14H, Ar—H), 5.6 (d, 1H, OH), 3.1 (s, 1H, OH), 2.3 (d, 1H, CH), 2.2 (s, 3H, CH_3); GC-MS area% = 60.3, m/z = 257(5), 183(100), 165(9), 105(90), 77(60), 51(10). *Anal. calcd.* for $C_{21}H_{20}O_2$: C, 82.46; H, 7.55. *Found*: C, 82.76; H, 7.26.

*(R, S)-2-(4-Methylphenyl)-1,1-diphenylethane-1,2-diol (***6b***).* Colourless crystals (75%) from cyclohexane-chloroform; m.p. 209 °C; analytical data correspond to **6a**.

*(S)-2-(4-Bromophenyl)1,1-diphenylethane-1,2-diol (***7a***).* Recrystallization from cyclohexane-acetone yielded colourless crystals (68%); m.p. 207 °C; $[\alpha]_D^{20} - 154$ (c1, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.7–6.9 (m, 14H, Ar—H), 5.6 (d, 1H, OH), 3.1 (s, 1H, OH), 2.3 (d, 1H, CH); GC-MS area% = 94.2, m/z = 334(2), 183(100), 165(9), 105(90), 77(60), 51(10). *Anal. calcd* for $C_{21}H_{20}O_2$: C, 82.46; H, 7.55. *Found*: C, 82.76; H. 7.26.

*(R, S)-2-(4-Bromophenyl)-1,1-diphenylethane-1,2-diol (***7b***).* Colourless crystals (75%) from cyclohexane-acetone; m.p. 215 °C; analytical data correspond to **7a**.

*(R)-1,1-Bis(4-tert-butylphenyl)-2-(4-methylphenyl)ethane-1,2-diol (***8a***).* Recrystallization from cyclohexane-chloroform yielded colourless crystals (68%); m.p. 210 °C; $[\alpha]_D^{20}$ + 156 (c1, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) d 7.6–6.9 (m, 12H, Ar-H), 5.6 (d, 1H, CH), 2.9 (s, 1H, OH), 2.26 (d, 1H, OH), 2.25 (s, 3H, CH_3), 1.26 and 1.24 (s, 9H, *tert*-butyl). GC-MS area% = 94.4, m/z = 294(30), 279(100), 161(26), 118(16). *Anal. calcd.* for $C_{29}H_{36}O_2$: C, 83.61; H, 8.71. *Found*: C, 83.42; H, 8.70.

(R, S)-1,1-Bis(4-tert-butylphenyl)-2-(4-methylphenyl) ethane-1,2-diol **8b**. Colourless crystals (73%) from benzene; m.p. 215 °C; analytical data correspond to **8a**.

Table I. Co-crystallization inclusion compounds (host : guest stoichiometric ratios)[a]

Guest solvent[b]	Host compound					
	6a	**6b**	**7a**	**7b**	**8a**	**8b**
2-Me-*c*-HexNH_2	1 : 1	–	–	–	–	–
3-Me-*c*-HexNH_2	–	1 : 1	–	–	–	–
Cyclohexanone	1 : 1	–	1 : 1	–	–	–
2-Methylcyclohexanone	–	–	–	–	1 : 1	1 : 1
3-Methylcyclohexanone	1 : 1	1 : 1	1 : 1	–	1 : 1	1 : 1
4-Methylcyclohexanone	1 : 1	–	–	–	1 : 1	–
Dimethylformamide	–	–	1 : 1	–	1 : 1	–
Dimethyl sulfoxide	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
3-Methyltetrahydrofuran	1 : 1	–	–	–	1 : 1	–
1,4-Dioxane	–	–	1 : 1	–	–	–
Morpholine	–	–	–	–	1 : 1	–
4-Methylmorpholine	1 : 1	–	–	–	1 : 1	1 : 1
3-Methylpiperidine	–	–	–	–	1 : 1	1 : 1
3-Picoline	1 : 1	–	–	–	1 : 1	–

[a] See Experimental Section for methods of preparation, drying standard and characterization.

[b] The following solvents yielded no inclusion compound: MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, 2-BuOH, *i*-BuOH, *t*-BuOH, *c*-PentOH, *c*-HexOH, *c*-HeptOH, 2-Me-*c*-HexOH, 3-Me-*c*-HexOH, 2-BuNH_2, *i*-BuNH_2, *c*-PentNH_2, *c*-HexNH_2, benzaldehyde, acetone, *c*-pentanone, cycloheptanone, β-butyrolactone, γ-valerolactone, propylene oxide, THF, 2-methyltetrahydrofuran, acetonitrile, propionitrile, butyronitrile, nitromethane, nitroethane, piperidine, pyridine, toluene, xylene.

2.1.4. *Solvent Inclusion Compounds by Crystallization*

The host compound was dissolved by heating in a minimum amount of the respective guest solvent. The solution was allowed to cool slowly. After storage for 12 h at room temperature, the crystals which formed were collected by suction filtration and dried (1 h, 15 Torr, room temperature). The host:guest stoichiometric ratios were determined by ^{1}H-NMR integration. Data for each compound are given in Table I.

2.1.5. *Optical Resolution by Inclusion Crystallization*

The host compound was dissolved in the boiling racemic guest substance. Slow cooling gave crystals of the inclusion compounds which were collected and washed with light petroleum (b.p. 40–60 °C). The enantiomer separation (ee of the included guest) was determined by direct GC analysis or polarimetry. In the latter case,

Table II. Enantioselective inclusion formation (% ee)[a]

Racemic guest compound	Host compound				
	1a	**2a**	**3a**	**6a**	**8a**
3-Me-*c*-HexOH	62[b]	–	–	–	–
2-$BuNH_2$	5[b]	7[b]	–	–	–
2-Me-*c*-$HexNH_2$	4[b]	83[b]	–	–	–
3-Me-*c*-$HexNH_2$	–	92[b]	–	–	–
3-Methylpiperidine	93[b]	–	–	–	90[c]
3-Methylcyclohexanone	95[c]	–	–	90[c]	93[c]
γ-Valerolactone	93[c]	–	58[c]	–	–
3-Methyltetrahydrofuran	–	–	–	67[c]	–

[a] Line mark means: inclusion formation unsuccessful or not tested.
[b] Determined by polarimetry.
[c] Determined by GC.

Table III. Vapour sorptive inclusion compounds (host : guest stoichiometric ratios)[a]

Guest solvent	Host compound				
	1a	**2a**	**3a**	**6a**	**8a**
MeOH	–	–	1 : 1	–	–
2-Me-*c*-$HexNH_2$	–	–	–	1 : 1	–
Cyclopentanone	–	1 : 1	–	–	–
3-Methylcyclohexanone	1 : 1	1 : 1	1 : 1	–	–
Dimethylformamide	1 : 1	–	1 : 1	1 : 1	1 : 1
Dimethyl sulfoxide	–	1 : 1	1 : 1	–	1 : 1

[a] See Experimental Section for methods of preparation, drying standard and characterization.

the crystals were heated in vacuum (100 °C, 15 Torr) to obtain the pure guest component as distillate. The ee data are listed in Table II.

2.1.6. *Solvent Inclusion by Vapour Sorption*

The solid host compound was exposed to the vapour of the guest substance until saturation (several hours, desiccator). Determination of the host:guest stoichiometric ratios was achieved as before. Data are given in Table III.

2.2. CRYSTALLOGRAPHY

X-ray Structure Determination. Details of data collection and those of the refinement procedure are given in Table IV. The crystals used for data collection were obtained by slow evaporation of the host compound in the guest solvent at room temperature. In the case of **6b** acetonitrile was used to crystallize the pure host. All crystals were enclosed in Lindemann capillaries to prevent decomposition and those of **8a**·DMSO and **8b**·DMSO were cooled in the nitrogen gas stream of an Oxford Cryosystems low temperature device [19]. The structures were solved by direct methods using the SIR92 program [20] and the refinements were carried out by full matrix least squares procedures on F_o, using the XTAL3.2 System [21]. Semiempirical absorption corrections (Ψ scan) were performed for **8a**·DMSO and **8b**·DMSO. In **8b**·DMSO, the refinement stopped at high R-values and an empirical absorption correction was applied (DIFABS) [22]. The hydrogen atoms were, mainly, located in the corresponding difference Fourier synthesis and were included in the refinement, although some had to be kept fixed in the last cycles of the refinement. The weighting scheme was calculated with the aid of the PESOS [23] program. Geometrical data were extracted using the PARST [24] program. The absolute configuration of atom C(2) in **8a**·DMSO was found to be *(R)* as verified by the value of the Flack parameter [25] (Table IV). The atomic scattering factors were taken from the literature [26].

Final fractional coordinates of the non-hydrogen atoms for all structures reported herein are listed in Tables V–VII.

3. Results and Discussion

3.1. SOLVENT CO-CRYSTALLIZATION AND INCLUSION

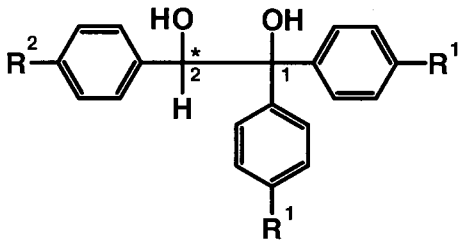
To make a sound comparison between the different species of this type (**1**–**8**) possible, the same series of guest solvents as previously employed [9, 10] is used for testing the crystalline inclusion behaviour of **6**(**a**,**b**)–**8**(**a**, **b**). These include cyclic and acyclic alcohols and amines of different size, dipolar aprotic compounds of different polarities, heterocycles with different numbers and types of heteroatoms, as well as aromatic hydrocarbons. A summary of the inclusion properties is listed in Table I.

As could be expected from the previous results [9, 10], no inclusion compound of an apolar solvent has been obtained while amines, ketones, small heterocycles and simple dipolar aprotic solvents are effective. Nevertheless, compared to the parent host compounds **1**(**a**, **b**), and in a certain way also to the substituted host derivatives of structure **2**–**5** [9, 10], the compounds **6**(**a**, **b**)–**8**(**a**, **b**) are rather low efficient hosts. For instance, not a single inclusion compound is formed with an alcohol, whereas **1a** readily yielded inclusion compounds with different alcohols, but the other derivatives (**2**–**5**) are also poor in this respect.

Table IV. Crystal analysis parameters

Crystal data	**6a**	**8a**·DMSO	**8b**·DMSO
Formula	$C_{21}H_{20}O_2$	$C_{28}H_{36}O_2 \cdot C_2H_6OS$	$C_{28}H_{36}O_2 \cdot C_2H_6OS$
Crystal habit	Colourless, prism	Colourless, prism	Colourless, prism
Crystal size (mm)	0.60 × 0.26 × 0.26	0.46 × 0.33 × 0.33	0.80 × 0.50 × 0.16
Symmetry	Monoclinic, $P2_1/c$	Monoclinic, $C2$	Triclinic, $P\bar{1}$
Unit cell determination:	Least-squares fit from 61, 67 and 73 reflections ($\theta < 45°$)		
Unit cell dimensions (Å, °)	a = 5.9026(2)	a = 28.5478(14)	a = 19.6310(36)
	b = 17.3067(12)	b = 6.0186(1)	b = 12.3061(2)
	c = 16.0590(12)	c = 17.0957(8)	c = 5.9726(4)
	90, 100.27(5), 90	90, 98.995(5), 90	93.85(1), 93.54(1), 95.70(2)
Packing: V (Å^3), Z	1614.1(2), 4	2901.2(2), 4	1429.0(4), 2
Dc (g/cm^3), M, F(000)	1.252, 304.39, 648	1.133, 494.73, 1072	1.149, 494.73, 536
μ (cm^{-1})	6.217	11.990	12.171
T (K)	295	225	225
Experimental data			
Technique	Four circle diffractometer: Philips PW1100, Bisecting geometry. Graphite oriented monochromator: $\omega/2\theta$ scans. Detector apertures 1 × 1°. 1 min./reflex. CuKα radiation, $\theta_{max} = 65°$.		
Scan width:	1.5°	1.5°	1.6°
Number of reflexions:			
Measured	2955	5624	4926
Independent	2751	2045 (Friedel pairs)	4766
Observed ($2\sigma(I)$)	2210	1818 (Friedel pairs)	3955
Standard reflexions:	2 reflexions every 90 minutes. No decay.		
Transmission (max-min)	–	1.000–0.839	1.000–0.467
Extinction coeff. ($\times 10^4$)	0.57(15)	0.96(18)	0.06(2)
Solution		Direct methods: Sir92	
Refinement:		Least-Squares on Fobs, Full matrix	
Parameters:			
Number of variables	288	460*	482
Degrees of freedom	1922	1358	3473
Ratio of freedom	7.7	4.0	8.2
H atoms		From difference synthesis*	
Weighting-scheme	Empirical as to give no trends in $\langle \omega \Delta^2 F \rangle$ vs. $\langle \lvert F\text{obs} \rvert \rangle$ and $\langle \sin\theta/\lambda \rangle$		
Abs. structure parameter	–	0.05(4) (Flack)	–
Max. thermal value (Å^2)	U11[C(37)] = 0.136(3)	U22[C(37)] = 0.205(14)	U22[C(37)] = 0.117(5)
Final ΔF peaks (eÅ^{-3})	−0.17/0.16	−0.33/0.41	−0.47/0.71
Final R and Rw	0.039, 0.044	0.048, 0.059	0.069, 0.090

* See experimental.



	R^1	R^2	*
1a	H	H	(2 *R*)
b	H	H	(2 *R*, 2 *S*)
2 a	Me	H	(2 *R*)
b	Me	H	(2 *R*, 2 *S*)
3 a	t-Bu	H	(2 *R*)
b	t-Bu	H	(2 *R*, 2 *S*)
4 a	Ph	H	(2 *S*)
5 a	F	H	(2 *S*)
6 a	H	Me	(2 *S*)
b	H	Me	(2 *R*, 2 *S*)
7 a	H	Br	(2 *R*)
b	H	Br	(2 *R*, 2 *S*)
8 a	t-Bu	Me	(2 *R*)
b	t-Bu	Me	(2 *R*, 2 *S*)

Scheme 1.

A similar finding is for the aliphatic amines. While **1a** and **2a** are very efficient hosts for the inclusion of amines [9], **3a** and **4a** are less efficient [10], **6**(**a**, **b**) are very poor (Table I), and **7**(**a**, **b**), **8**(**a**, **b**) like **5a** [10] failed to form inclusion compounds with amines. Nevertheless, compound **6b**, which is the racemic species, differs in that it is the only case of a racemic host of this type to include an amine. It is also remarkable to see that **6a** (optically resolved species) selectively yields an inclusion compound with 2-methylcyclohexylamine while for **6b** it is the positional

Table V. Atomic coordinates and U_{eq} values of non-hydrogen atoms for **6b**

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.3539(3)	0.46023(9)	0.3466(1)	0.0402(5)
C(2)	0.2366(3)	0.4082(1)	0.4051(1)	0.0430(6)
C(31)	0.2995(3)	0.3237(1)	0.4018(1)	0.0436(5)
C(32)	0.1411(4)	0.2700(1)	0.3638(1)	0.0554(7)
C(33)	0.1972(4)	0.1919(1)	0.3626(1)	0.0640(8)
C(34)	0.4117(4)	0.1655(1)	0.3999(1)	0.0574(7)
C(35)	0.5694(4)	0.2193(1)	0.4378(1)	0.0631(8)
C(36)	0.5150(4)	0.2967(1)	0.4388(1)	0.0580(7)
C(37)	0.4739(7)	0.0800(1)	0.4019(2)	0.081(1)
O(4)	0.5984(2)	0.45376(7)	0.3717(8)	0.0463(4)
O(5)	0.2984(3)	0.43719(8)	0.49014(8)	0.0551(5)
C(11)	0.2866(3)	0.5458(1)	0.3488(1)	0.0418(5)
C(12)	0.0981(3)	0.5728(1)	0.3810(1)	0.0542(6)
C(13)	0.0427(4)	0.6511(1)	0.3767(1)	0.0612(8)
C(14)	0.1729(4)	0.7026(1)	0.3408(1)	0.0593(7)
C(15)	0.3625(4)	0.6767(1)	0.3094(1)	0.0592(7)
C(16)	0.4181(4)	0.5989(1)	0.3137(1)	0.0491(6)
C(21)	0.2899(3)	0.43116(9)	0.2557(1)	0.0409(5)
C(22)	0.0716(3)	0.4445(1)	0.2103(1)	0.0559(7)
C(23)	0.0087(4)	0.4183(1)	0.1279(1)	0.0649(8)
C(24)	0.1635(4)	0.3786(1)	0.0899(1)	0.0622(8)
C(25)	0.3801(4)	0.3644(1)	0.1345(1)	0.0607(7)
C(26)	0.4440(4)	0.3901(1)	0.2170(1)	0.0511(6)

isomeric guest, 3-methylcyclohexylamine, showing the influence of the chirality of the host.

Moreover both these isomeric amines are alicyclic amines containing a six-membered ring unit which is a structural feature almost generally exhibited by the guests in Table I. This preference of the six membered ring structure of guests is not unusual but rather common and frequently found in crystalline inclusion compounds [2, 4] suggesting favourable molecular dimensions and flexible behaviour. Exceptions from this rule are only DMF, DMSO and 3-methyltetrahydrofuran, with DMSO being included by all hosts regardless of the optical species and the substituents involved.

Another interesting case are the host compounds **7**(**a**, **b**). Although the bromo substituent in **7** in its steric demand is similar to the methyl groups of **6**(**a**, **b**), the inclusion capability of **7**(**a**, **b**) is distinctly reduced. On the other hand, there is an

Table VI. Atomic coordinates and U_{eq} values of non-hydrogen atoms for the **8a**·DMSO crystalline complex

Atom	x/a	y/b	z/c	U_{eq}
S(1)	0.53817(5)	0.2439(8)	0.5937(1)	0.0676(7)
O(3)	0.4928(1)	0.342(1)	0.6092(3)	0.069(2)
C(3)	0.5771(3)	0.469(2)	0.5933(7)	0.100(4)
C(4)	0.5637(2)	0.119(2)	0.6830(6)	0.089(3)
C(1)	0.4217(1)	0.8999(8)	0.7086(3)	0.032(2)
C(2)	0.4226(1)	0.747(1)	0.6365(3)	0.036(2)
C(31)	0.3797(1)	0.773(1)	0.5713(4)	0.042(2)
C(32)	0.3475(2)	0.603(1)	0.5580(4)	0.058(3)
C(33)	0.3083(2)	0.624(2)	0.4966(5)	0.074(3)
C(34)	0.3026(2)	0.808(2)	0.4486(4)	0.064(3)
C(35)	0.3358(2)	0.976(1)	0.4630(5)	0.069(3)
C(36)	0.3739(2)	0.959(1)	0.5217(4)	0.057(2)
C(37)	0.2611(2)	0.824(3)	0.3813(5)	0.111(5)
O(4)	0.4215(1)	1.1285(9)	0.6834(2)	0.039(1)
O(5)	0.4651(1)	0.793(1)	0.6047(3)	0.048(1)
C(11)	0.4649(1)	0.862(1)	0.7729(3)	0.034(2)
C(12)	0.4889(2)	0.660(1)	0.7821(4)	0.040(2)
C(13)	0.5273(2)	0.630(1)	0.8417(4)	0.044(2)
C(14)	0.5435(1)	0.798(1)	0.8948(4)	0.042(2)
C(15)	0.5184(2)	0.996(1)	0.8859(4)	0.042(2)
C(16)	0.4799(1)	1.027(1)	0.8263(4)	0.041(2)
C(17)	0.5853(1)	0.754(1)	0.9614(4)	0.049(2)
C(18)	0.5688(2)	0.593(1)	1.0217(5)	0.065(3)
C(19)	0.6259(2)	0.642(2)	0.9264(6)	0.081(3)
C(20)	0.6034(2)	0.964(1)	1.0054(6)	0.067(3)
C(21)	0.3760(1)	0.863(1)	0.7428(3)	0.032(2)
C(22)	0.3666(1)	0.654(1)	0.7720(4)	0.040(2)
C(23)	0.3251(1)	0.612(1)	0.8020(3)	0.039(2)
C(24)	0.2915(1)	0.779(1)	0.8055(3)	0.038(2)
C(25)	0.3020(2)	0.987(1)	0.7775(4)	0.047(2)
C(26)	0.3428(2)	1.026(1)	0.7461(4)	0.044(2)
C(27)	0.2456(1)	0.742(1)	0.8400(4)	0.047(2)
C(28)	0.2030(2)	0.830(2)	0.7814(5)	0.065(3)
C(29)	0.2485(2)	0.875(2)	0.9178(5)	0.058(3)
C(30)	0.2381(2)	0.499(1)	0.8591(6)	0.069(3)

Table VII. Atomic coordinates and U_{eq} values of non-hydrogen atoms for the **8b**·DMSO crystalline complex

Atom	x/a	y/b	z/c	U_{eq}
S(1)	0.04867(4)	0.12443(7)	0.8028(1)	0.0404(3)
O(3)	0.0968(1)	0.0541(2)	0.9148(4)	0.0501(9)
C(3)	0.0084(2)	0.1888(4)	1.0279(8)	0.055(1)
C(4)	0.1007(3)	0.2418(4)	0.728(1)	0.070(2)
C(1)	0.2318(1)	−0.0059(3)	0.5071(5)	0.0305(9)
C(2)	0.1738(2)	−0.0461(2)	0.3245(5)	0.0308(9)
C(31)	0.1520(2)	−0.1681(3)	0.3130(5)	0.0344(9)
C(32)	0.1674(2)	−0.2347(3)	0.1296(6)	0.042(1)
C(33)	0.1441(2)	−0.3453(3)	0.1089(7)	0.052(1)
C(34)	0.1054(2)	−0.3924(3)	0.2685(8)	0.051(1)
C(35)	0.0901(2)	−0.3256(3)	0.4526(7)	0.052(1)
C(36)	0.1125(2)	−0.2145(3)	0.4733(6)	0.045(1)
C(37)	0.0810(3)	−0.5137(4)	0.245(1)	0.081(2)
O(4)	0.2110(1)	−0.0339(2)	0.7244(3)	0.0338(7)
O(5)	0.1162(1)	0.0132(2)	0.3714(4)	0.0395(7)
C(11)	0.2495(1)	0.1189(3)	0.5118(5)	0.0304(8)
C(12)	0.2389(2)	0.1790(3)	0.3274(5)	0.037(1)
C(13)	0.2568(2)	0.2920(3)	0.3400(6)	0.038(1)
C(14)	0.2861(2)	0.3492(3)	0.5363(5)	0.0340(9)
C(15)	0.2972(2)	0.2879(3)	0.7205(5)	0.037(1)
C(16)	0.2792(2)	0.1755(3)	0.7091(5)	0.0348(9)
C(17)	0.3946(2)	0.4732(3)	0.5566(6)	0.040(1)
C(18)	0.3006(3)	0.5231(3)	0.3297(7)	0.054(1)
C(19)	0.3773(2)	0.5021(4)	0.6662(9)	0.060(2)
C(20)	0.2536(3)	0.5262(4)	0.7053(8)	0.063(2)
C(21)	0.2960(1)	−0.0618(2)	0.4621(5)	0.0306(9)
C(22)	0.3278(2)	−0.0476(3)	0.2623(6)	0.044(1)
C(23)	0.3884(2)	−0.0922(3)	0.2218(6)	0.044(1)
C(24)	0.4200(2)	−0.1534(3)	0.3767(5)	0.0325(9)
C(25)	0.3866(2)	−0.1701(3)	0.5710(6)	0.0354(9)
C(26)	0.3254(2)	−0.1256(3)	0.6135(5)	0.0328(9)
C(27)	0.4879(2)	−0.1995(3)	0.3292(5)	0.0360(9)
C(28)	0.4730(2)	−0.3050(3)	0.1754(8)	0.052(1)
C(29)	0.5343(2)	−0.1169(4)	0.2112(9)	0.056(1)
C(30)	0.5267(2)	−0.2255(5)	0.5456(7)	0.059(2)

evident preference of hosts **7** for the small dipolar aprotic guest solvents including DMF, DMSO and 1,4-dioxane attributable to the polarity and polarizability of the bromo atom (Table I). Notwithstanding the rather different inclusion behaviour of the hosts exhibited in Table I, there is one feature common to all inclusion compounds *viz* the host:guest stoichiometric ratio is always 1 : 1 unlike the previous cases of inclusion compounds [9, 10].

3.2. CHIROSELECTIVE INCLUSION

As has been shown in Table I for compounds **6a**–**8a** and in previous papers for **1a**–**5a** [9, 10] these hosts are able to include chiral guests. In order to reveal potential enantioselectivity involving these guest inclusions we studied the chiral discrimination behaviour. The results of the optical resolution experiments obtained under one step co-crystallization conditions are summarized in Table II.

The hosts, in general, are rather efficient for optical resolution of various amines but also of some other chiral compounds. The resolution efficiency in particular, however, appears to be rather sensitive to the nature, the size and the geometry of the guest. For instance, host compound **1a** shows low efficiency with 2-methylcyclohexylamine (4% ee), whereas 3-methylpiperidine is resolved to 93% ee. On the other hand, **2a** yielded only 7% ee for 2-butylamine but 83% for 2-methylcyclohexylamine. Moreover, the most efficient guests in optical resolution using the mandelic acid type hosts are mostly cyclic in the basic skeleton, e.g., six-membered cyclic structures. In this respect, the mandelic acid and the lactic acid derived host compounds are similar [8].

3.3. VAPOUR SORPTIVE INCLUSION

Interestingly, solid organic host compounds are capable of sorptive clathrate formation [27, 28] making possible a new development of chemically sensitive materials [8, 29]. Host compounds derived from lactic acid and bulky bisfluorenols have proven to be particular useful in this respect [5, 30]. Hence a potential ability of sorptive clathrate formation is also expected for the present host compounds. The results of the vapour sorption experiments are summarized in Table III.

Considering the relatively wide range of guests giving co-crystalline inclusions (Table I and previous reports [9, 10]) only a limited number of solvents are efficient in the sorptive clathrate formation. Moreover, when comparing the data of Table III with that of Table I and previous reports [9, 10] it is obvious that co-crystalline and sorptive inclusion formation are different processes [5b]. This is the reason for some apparent differences arising from the two modes of inclusion. For instance host **3a** does not yield an inclusion compound with methanol under the experimental co-crystallization conditions but is indicated in Table III as being efficient in the sorptive uptake of methanol. On the other hand, **1a** and **2a** are sorptively inefficient with methanol but yield inclusion compounds on co-crystallization. The

hosts **6a** and **8a** gave inclusion compounds with 3-methylcyclohexanone on co-crystallization (Table I) but failed on sorption (Table III). Inclusion formation of **6a** with dimethylformamide proved inefficient on co-crystallization but efficient on sorption, while dimethyl sulfoxide was found efficient with reference to both kinds of inclusion formation using **6a**. In order to understand this complex behaviour knowledge of the structural features might be valuable.

3.4. STRUCTURAL STUDIES

The molecular and crystal structures of the free host compound **6b** and the two solvent inclusion compounds **8a**·DMSO and **8b**·DMSO, containing the same guest but involving different optical species of the host have been determined.

Perspective views of the molecular structures including the numbering scheme are displayed in Figure 1, and the crystal packing showing the hydrogen bond interactions in the **6b**, **8a**·DMSO and **8b**·DMSO structures are presented in Figure 2. The relevant intra- and intermolecular geometrical parameters are provided in Table VIII.

3.4.1. *Molecular Structures*

The molecular structures of the three host molecules display similar structural characteristics among them (Table VIII) and with the analogous compounds [9–11]. The significant differences only involve the angles at C(1) and C(11) and the twist of the phenyl rings. The external angles at these two atoms are enlarged as a result of the steric strain. The C(2) atom in all hosts is very close to being coplanar with the C(11–16) phenyl ring; the lower the C(2)—C(1)—C(11)—C(12) torsion angle, the greater the angular distortion. The *tert*-butyl substitution at the para position on the phenyl rings closes the angles by at least 3.5° [C(14), C(24)] in the 115.9(6)–116.5(3)° range. However, the decrease at C(34) due to the methyl group is in the 0.5–2.2° range; the upper limit is in agreement with the value of −1.9(2)° reported by Domenicano and Murray-Rust [31] for the *ipso* angle.

3.4.2. *Packing Relations and Host–Guest Interactions*

The crystal structure of **6b** consists of cyclic hydrogen-bonded dimers with the two molecules related by an inversion center (Figure 2a). As in the parent host compound **1b** (Figure 2b) [9] only one hydroxyl group [O(4)—H(4)] is involved in O—H···O hydrogen bonding while the other [O(5)-H(5)] contributes to the stabilization of the dimer through an O—H···π-electron cloud contact [32, 33] with the C(11–16) ring of the centrosymmetric molecule. The addition of the methyl group at C(34) does not affect the packing mode (cf. Figures 2a and 2b) and the only noticeable fact is the elongation of the *b* axis and to a lesser extent of the *c* axis [compound **1b** in ref. [9]: space group $P2_1/c$, a = 5.9565(2), b = 16.5149(12), c =

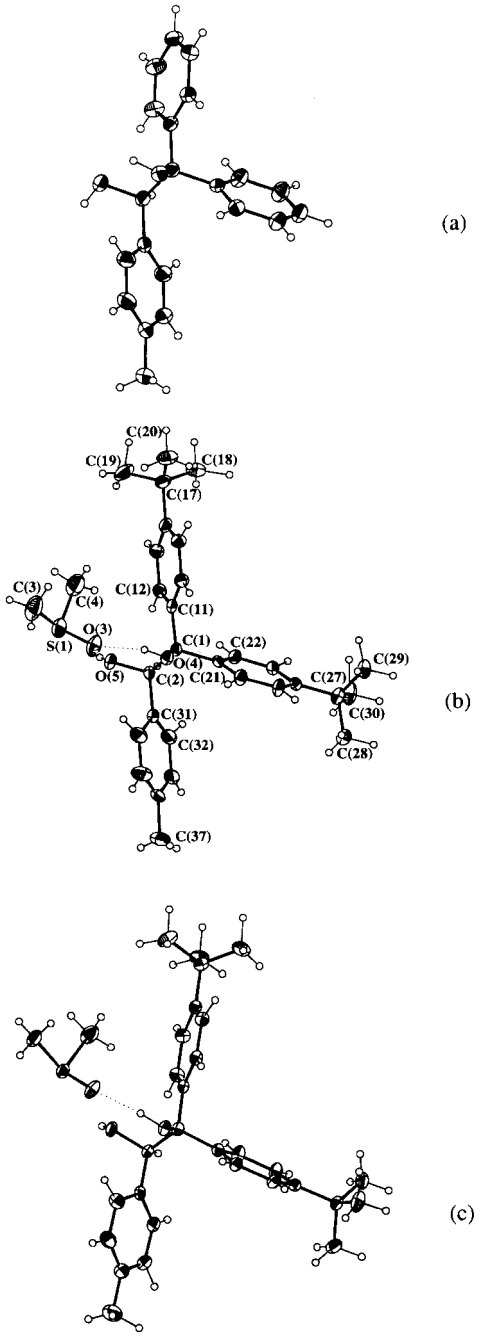


Figure 1. Perspective views of the independent molecules of **6b** (a), **8a**·DMSO (b) and **8b**·DMSO (c), showing the atom numbering system with 30% probability level. Dotted lines indicate hydrogen bonds.

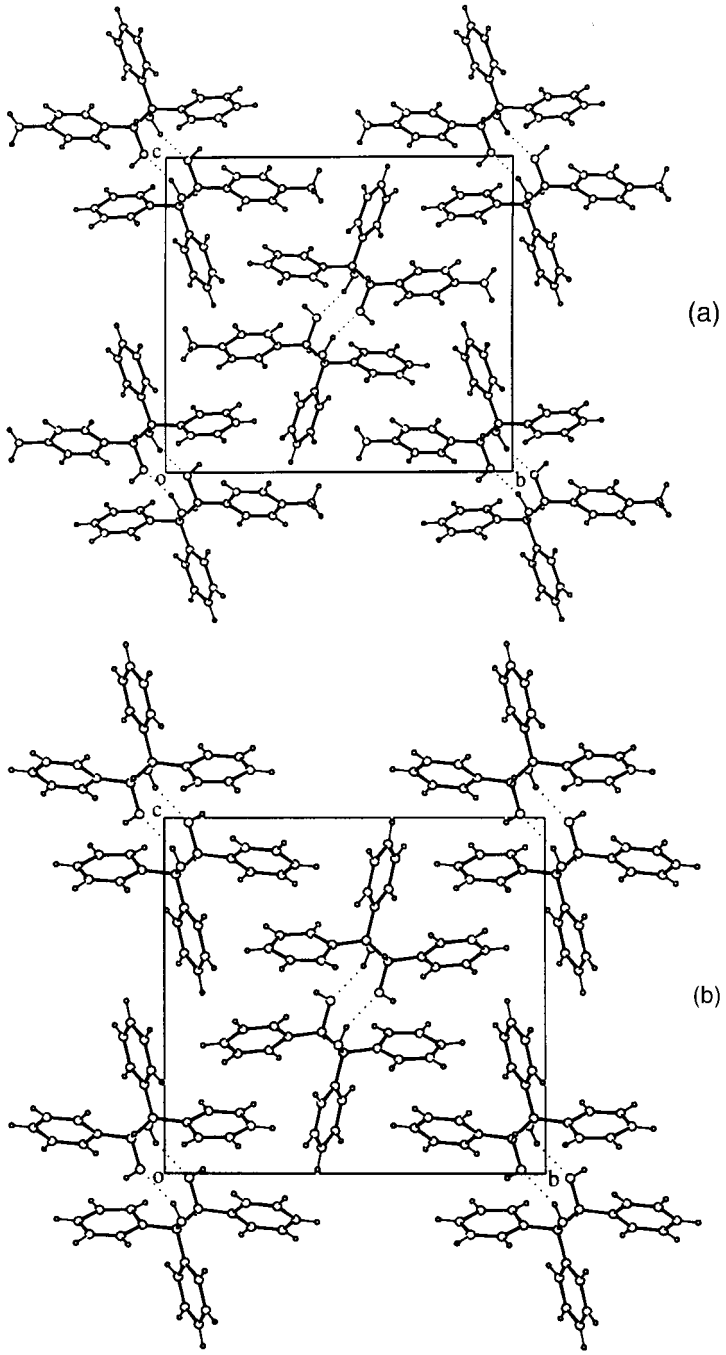


Figure 2. Packing diagrams for the **6b** (a), **8a**·DMSO (c) and **8b**·DMSO (d) structures; (b) represents the packing of the parent host compound **1b** [9] for comparison purposes. Dotted lines indicate hydrogen bonds.

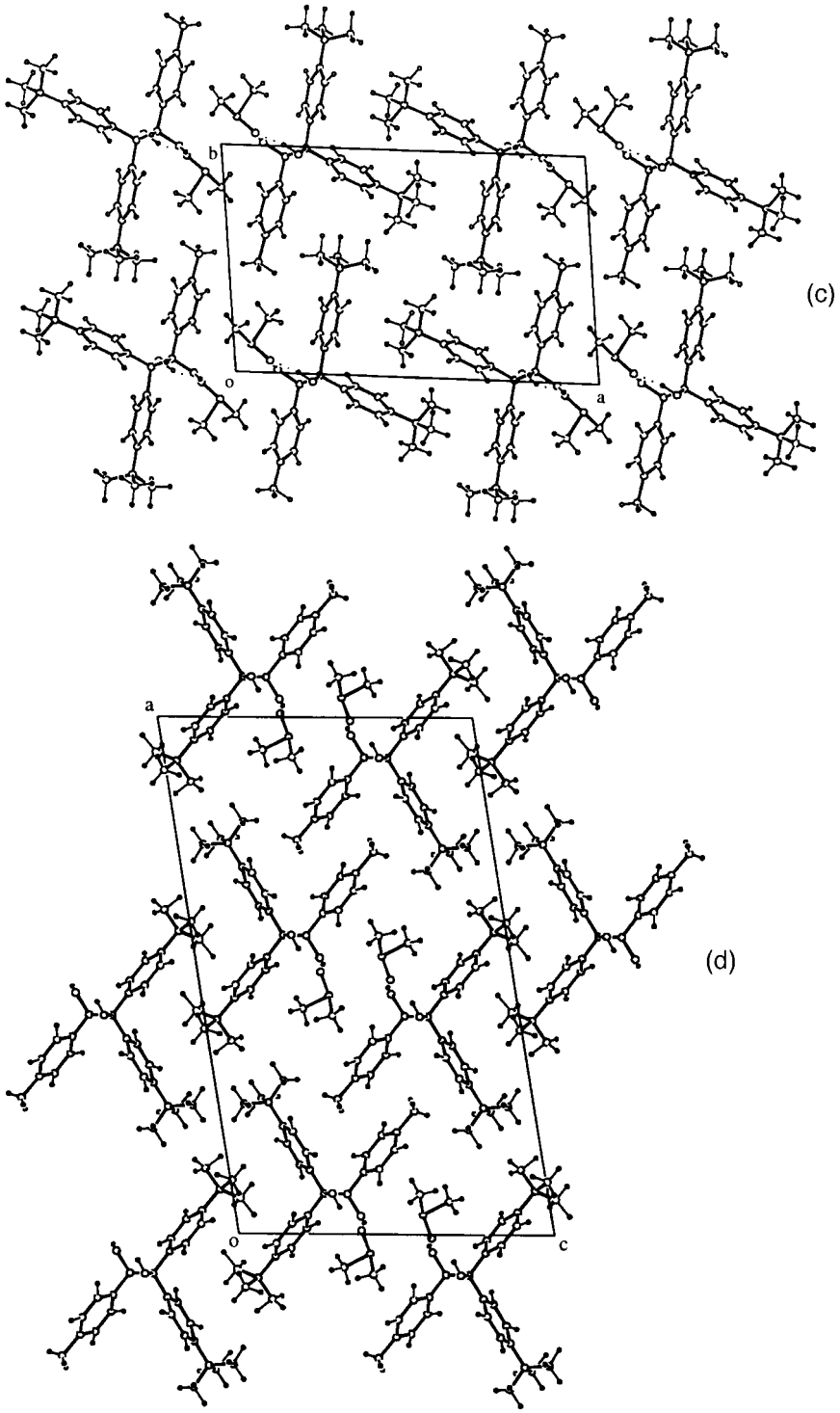


Figure 2.

Table VIII. Selected geometrical parameters for compounds **6b**, **8a**·DMSO, **8b**·DMSO (Å, °)

Atoms	**6b**	**8a**·DMSO	**8b**·DMSO	
C(1)—C(2)	1.551(2)	1.540(8)	1.546(4)	
C(1)—O(4)	1.431(2)	1.441(6)	1.437(4)	
C(1)—C(11)	1.535(2)	1.534(6)	1.539(4)	
C(1)—C(21)	1.526(2)	1.527(7)	1.524(4)	
C(2)—C(31)	1.512(2)	1.527(6)	1.515(4)	
C(2)—O(5)	1.439(5)	1.432(6)	1.436(4)	
C(12)—C(11)—C(16)	118.1(2)	117.2(6)	117.3(3)	
C(22)—C(21)—C(26)	118.3(2)	117.2(6)	117.4(3)	
C(32)—C(31)—C(36)	117.4(2)	118.9(6)	118.5(3)	
C(13)—C(14)—C(15)	119.5(2)	115.9(6)	116.5(5)	
C(23)—C(24)—C(25)	119.3(2)	116.3(6)	116.2(3)	
C(33)—C(34)—C(35)	117.6(2)	117.8(8)	118.0(4)	
C(2)—C(1)—C(11)	113.6(1)	111.7(3)	111.0(2)	
C(1)—C(11)—C(12)	124.1(2)	122.8(4)	123.4(3)	
C(2)—C(1)—C(21)	109.0(1)	109.9(3)	110.1(2)	
C(1)—C(21)—C(22)	119.8(1)	119.5(4)	119.8(3)	
O(4)—C(1)—C(2)—O(5)	62.9(2)	60.8(5)	64.0(3)	
C(21)—C(1)—C(2)—C(31)	57.6(2)	55.9(6)	60.6(3)	
C(11)—C(1)—C(2)—C(31)	178.9(1)	178.3(4)	−178.3(2)	
C(1)—C(2)—C(31)—C(32)	−109.1(2)	−111.0(6)	−110.0(3)	
C(2)—C(1)—C(11)—C(12)	−16.0(2)	−26.6(7)	−26.0(4)	
C(2)—C(1)—C(21)—C(22)	74.3(2)	61.3(6)	60.8(4)	
Hydrogen interactions	X—H	H···Y	X···Y	X—H···Y
6b:				
O(4)—H(4)···O(5)$_{(1-x,1-y,1-z)}$	0.93(3)	1.99(3)	2.892(2)	159(2)
O(5)—H(5)···C(11–16)$_{(1-x,1-y,1-z)}$	0.90(4)	2.88(4)	3.640(1)	142(3)
C(36)—H(36)·C(11–16)$_{(1-x,1-y,1-z)}$	0.94(2)	3.09(2)	3.779(2)	130(2)
C(33)—H(33)···C(11–16)$_{(-x,-1/2+y,1/2-z)}$	0.98(3)	3.17(2)	3.978(2)	139(2)
8a·DMSO:				
O(5)—H(5)·O(3)	0.85(9)	2.00(10)	2.827(8)	160(8)
O(4)—H(4)···O(3)$_{(x,1+y,z)}$	0.86(8)	2.07(8)	2.864(7)	151(7)
C(3)—H(3a)···C(31–36)$_{(1-x,y,1-z)}$	0.93(–)	3.18(–)	3.681(10)	115(7)
C(4)—H(4b)···C(21–26)$_{(x,1-y,z)}$	0.93(–)	2.93(–)	3.742(10)	145(16)
C(18)—H(18b)···C(11–16)$_{(1-x,y,2-z)}$	0,90(10)	2.88(10)	3.744(9)	159(7)
C(20)—H(20c)···C(21–25)$_{(1-x,y,2-z)}$	1.03(8)	3.05(8)	3.999(9)	151(6)
8b·DMSO:				
O(4)—H(4)···O(3)	0.94(5)	1.95(5)	2.850(5)	157(4)
O(5)—H(5)···O(3)$_{(x,y,z-1)}$	0.91(7)	1.97(7)	2.815(4)	152(6)
C(3)—H(3a)···C(31–36)$_{(-x,-y,1-z)}$	0.96(8)	2.71(7)	3.518(6)	140(5)
C(4)—H(4c)···C(21–26)	1.06(6)	2.69(6)	3.579(7)	140(4)
C(29)—H(29a)···C(21–26)$_{(1-x,-y,1-z)}$	0.92(6)	3.05(5)	3.813(5)	139(4)
C(30)—H(30a)···C(11–16)$_{(1-x,-y,1-z)}$	0.99(6)	3.14(5)	4.087(4)	159(4)

C(i1–i6) stands for the centroids of the corresponding rings.

15.7004(12) Å and β = 99.355(5)°]. The dimers are linked by C—H$\cdots\pi$ electron cloud interactions [34, 35] (Table VIII).

The secondary structures of the two inclusion complexes **8a**·DMSO (optically resolved host species) and **8b**·DMSO (racemic host) are similar. Both hydroxyl groups of the host are involved in hydrogen bond interactions with the O atom of the guest molecule resulting in chains parallel to the *b* and *c* axes, respectively, as illustrated in Figures 2c and 2d. The chains, related in **8a**·DMSO by a twofold axis, are held together by C—H$\cdots\pi$ electron cloud interactions, while in **8b**·DMSO this kind of weak interaction reinforces the host-guest pair and join chains of molecules related by inversion centers. The C—H(guest)$\cdots\pi$(host) interactions seem to be stronger in the racemic compound (Table VIII). The guest molecules related by binary axes, **8a**·DMSO, or by symmetry centers, **8b**·DMSO, are located in barrel shaped channels [36], along the *b* and *c* axes. The total packing coefficients for **6b**, **8a**·DMSO and **8b**·DMSO are 0.68, 0.65 and 0.64, respectively.

A statistical survey for DMSO molecules acting as acceptors of an OH hydrogen bond (H$\cdots$O distance between 1.4–2.7 Å) has been performed using the Cambridge Structural Database [37], (CSD October 1996 release), in order to characterize this type of interaction. Only structures with $R < 0.05$, with neither disorder nor error reported and with the hydrogen atoms located have been selected. In **8a**·DMSO and **8b**·DMSO the hydrogen bonds are longer (this will suggest weaker H-bonding) and less linear than the mean values found in the CSD [O$\cdots$O = 2.632(69) Å and OH$\cdots$O = 169(5)°; the standard derivation of the sample is in parentheses]. The S=O double bond distances in **8a**·DMSO and **8b**·DMSO [1.483(5) and 1.500(3) Å versus 1.512(9) Å] are neither significantly different between them nor with respect to the CSD average value. These values are gathered closely around the lower limit of the range [1.494–1.525 Å], and may be as a consequence of the weakness of the hydrogen bonds.

4. Summary and Conclusions

Chemical transformation of mandelic acid into bulky diol derivatives such as **1**–**8** provides a good facility for both highly specific and rather universal clathrate hosts, depending on the optical species and the substituents involved, thus establishing the framework of a new robust host family allowing for structural modifications.

As far as the number of inclusion compounds is concerned the parent host molecule **1** (in particular **1a**) is the most versatile [9, 10], while substitution either at the diphenylhydroxymethyl moiety (**2**–**5**) [10] or the phenyl group of mandelic acid (**6**, **7**) or at both of these groups (**8**) (Table I) give rise to a reduced inclusion property with substitution at the phenyl ring of mandelic acid being mostly affected. This illustrates the superiority of compound **1** in its ability to form inclusion compounds, but from the selectivity point of view the substituted derivatives are more effective. As to the nature of the substituents (e.g. **2** –**5**) the inclusion ability is also differently affected. However, in all cases, irrespective of the particular substituent and its

position at the aromatic rings, the optically resolved compound (**1a**–**8a**) is much more efficient compared to the racemic analogue (**1b**–**8b**).

This superiority may be explained by considering the crystal structures. In the optically resolved free hosts (cf. **1a** [9], **2a** and **3a** [10], the structures do not meet the optimum hydrogen bonding rule in crystals according to Etter [38] and others [39], but exhibit a compromise between close packing and hydrogen bonding. By way of contrast, the racemic host compounds (cf. **1b** [9] and **6b**, Figure 2a, b) tend to form stable hydrogen-bonded dimers of enantiomeric host molecules allowing a relatively densely packed crystal without recourse to solvent molecules, thus exhibiting inferior inclusion behaviour. This is probably the situation in the case of the racemic hosts and solvents not competing with the dimer units, unlike the strong hydrogen acceptor solvents such as in the present dimethyl sulfoxide complex of **8b** (Figure 2d), presumably overruling the dimer formation of hosts to give inclusion compounds.

Moreover it is shown (Table II) that the optically resolved hosts described here can effect enantiomer separation of racemic guests complementary to the lactic acid analogues [8] which is a special merit of these chiral selectors. And last but not least, as manifested in Table III, the solid host compounds of this type are promising materials for sensing of solvent vapours [5, 30].

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