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DICARBOXIMIDE-BASED CLATHRATE DESIGN. HOST SYNTHESIS, INCLUSION FORMATION AND X-RAY CRYSTAL STRUCTURES OF A FREE HOST AND OF INCLUSION COMPOUNDS WITH 2- AND 3-METHYLCYCLOHEXANONE, 3-METHYLCYCLOPENTANONE, BUTYRONITRILE, PROPAN-1-OL and (−)-FENCHONE GUESTS

EDWIN WEBER* AND CHRISTIANE REUTEL
Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg/Sachs, Germany

AND

CONCEPCIÓN FOCES-FOCES* AND ANTONIO L. LLAMAS-SAIZ
Departamento de Cristalografía, Instituto de Química-Física 'Rocasolano', CSIC, Serrano 119, E.28006 Madrid, Spain

Crystalline host compounds consisting of a roof-shaped dicarboximide framework and pendant diarylethanol analogous subunits were synthesized and shown to form inclusion complexes with small organic molecules such as alcohols, amines, ketones or polar and apolar organic solvents. Clathrate efficiency and selectivity depend on the particular host structure. The crystal and molecular structures of a free host compound (2a) and inclusion compounds [2a·3-methylcyclohexanone (1 : 1), 1a·3-methylcyclopentanone (1 : 1), 1a·2-methylcyclohexanone (1 : 1), 1b·butyronitrile (1 : 1), 1b·propan-1-ol (2 : 1) and 1b·(−)-fenchone (1 : 1)] were determined by x-ray diffraction analysis. In all the structures, the hydroxyl group is involved in intramolecular hydrogen bonds and the host and guest molecules are held by lattice forces only. The channels and cavities left in the host matrix are large enough to allow disorder or high thermal displacement parameters of the guest molecules. The local packing coefficients for all guests are 0·42 on average.

INTRODUCTION

Host compounds capable of forming crystalline inclusions (clathrates)[1] are a great challenge owing to potential uses such as in enantiomer separation,[2] chemical sensing[3] and topochemical reactivity.[4] Families of clathrate hosts involving designed structural modifications have attracted particular attention since tuning of inclusion properties is feasible. Specific host structures feature a long molecular axle with bulky groups at both ends,[5] a spider type of molecule,[6] a molecular analogue of a pair of scissors[7] or a roof.[8] Among these geometric approaches, the molecular roof mimic has proved to have broad use either as an individual host[8,9] or in a modular building block ('clathratogenic group') fashion.[10] Previously we transferred the natural and racemic amino acid alanine along this line into a corresponding crystalline host. This was done via modification of the amino acid with a roof-shaped dicarboximide clathratogenic group to yield **1a** and **1b**.[11] We have studied their inclusion properties in detail and did part of the structural work, which raised further questions.[11]

We report here on new potential host molecules of this type having additional substituents at the *para*-position of the phenyls (**2**–**4**) or being derived from the amino acids phenylglycine (**5**) and phenylalanine (**6**) instead of alanine. This work involved the synthesis, consideration of inclusion properties and x-ray structures of the free host **2a** (**I**) and of six inclusion compounds [**II** = **2a**·3-methylcyclohexanone (1 : 1), **III** = **1a**·3-methylcyclopentanone (1 : 1), **IV** = **1a**·2-methylcyclohexanone (1 : 1), **V** = **1b**·butyronitrile (1 : 1), **VI** = **1b**·propan-1-ol (2 : 1) and VII = **1b**·(−)-fenchone (1 : 1)], thus making possible a correlation of the present and the previous clathrate properties and structures.

* Corresponding authors.

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RESULTS AND DISCUSSION

Synthesis

Potential host compounds **1–6 (a, b)** (see p. 165 for structures) were synthesized in three steps from the respective amino acids by converting them into the corresponding ethyl ester hydrochlorides **7–9**, followed by a Grignard reaction with the respective bromoaryls to give 2-amino alcohols **10–15**, and reaction with anhydride **16**. The crystalline inclusion compounds were obtained by single recrystallization of the host compound from the respective guest solvent, isolation of the crystals and drying under standard conditions (see Experimental).

Inclusion properties

Previously, host compounds **1a** and **1b** were subjected to a variety of potential guest solvents, and it was found that **1a** and **1b** yielded no less than 56 different crystal inclusions (**1a**, 21; **1b**, 35).[11] In order to make possible an obvious comparison, the compounds, i.e. modified structures **2a–6a**, and **3b**, were tested with the same collection of solvents including alcohols, amines, ketones and examples of other compound classes with molecules of various shapes and sizes. More strictly speaking, the list of solvents shown in Table 1 in Ref. 11 applies, and crystalline inclusion compounds of the present hosts are specified in Table 1 in this paper. A general statement based on Table 1 in Ref. 11 is as follows.

Table 1. Crystalline inclusion compounds

	Host compound				
Guest solvent	**2a**	**3a**	**3b**	**4a**	**5a**
i-BuOH	—	—	—	2 : 1[a]	2 : 1
c-PentOH	—	2 : 1	—	—	2 : 1
c-HexOH	1 : 1	1 : 1	1 : 1	—	1 : 1
2-Me-*c*-HexOH	—	—	—	—	3 : 1
3-Me-*c*-HexOH	—	—	—	1 : 2	3 : 1
1-$PrNH_2$	1 : 1	—	—	—	—
i-$BuNH_2$	2 : 1	—	—	—	1 : 1
s-$BuNH_2$	2 : 1	—	—	—	—
t-$BuNH_2$	—	—	—	—	—
c-$PentNH_2$	2 : 1	—	—	—	—
c-$HexNH_2$	1 : 1	2 : 1	—	—	1 : 1
2-Me-*c*-$HexNH_2$	—	2 : 3	—	—	1 : 1
Piperidine	1 : 1	2 : 1	—	—	1 : 1
2-Methylpiperidine	2 : 1	—	—	—	—
3-Methylpiperidine	—	2 : 1	—	—	1 : 1
Pyrrolidine	—	—	—	—	1 : 1
Morpholine	—	—	—	—	1 : 1
Pyridine	—	—	—	—	1 : 1
2-Picoline	—	—	—	—	1 : 1
4-Picoline	—	—	—	—	2 : 1
Acetone	—	—	—	—	2 : 1 (1 : 1)
Cyclopentanone	1 : 1	—	—	—	1 : 1
3-Methylcyclopentanone	1 : 1	—	—	—	1 : 1
Cyclohexanone	1 : 1	2 : 1	1 : 1	—	1 : 1
2-Methylcyclohexanone	1 : 1	—	—	—	1 : 1
3-Methylcyclohexanone	1 : 1	1 : 2	—	—	—
4-Methylcyclohexanone	1 : 1	—	—	—	2 : 1
Cycloheptanone	1 : 1	1 : 1	1 : 1	—	1 : 1
Acetic acid	—	—	—	1 : 3	—
Dimethylformamide	—	—	—	—	2 : 1
Butyronitrile	—	—	—	—	—
Tetrahydrofuran	—	—	—	—	1 : 1
1,4-Dioxane	2 : 1	—	—	—	1 : 1
Benzene	—	—	1 : 1	—	2 : 1
Toluene	—	—	—	—	2 : 1

[a] Host: guest stoichiometric ratio.

Host compound **2a**, in many respects, is similar to **1a**,[11] but there are also differences. Unlike **1a**, host **2a** yields inclusion compounds with small amine solvents, whereas **2a** is less efficient with pyridines and other aprotic or apolar solvents. Moreover, a 2 : 1 host : guest stoichiometric ratio is fairly frequent in the case of **2a**, unlike **1a**. Compound **3a**, and in particular **4a**, are relatively poor inclusion hosts, the latter giving only three crystalline inclusion under the experimental conditions, and each having different stoichiometric ratio. In comparison, **3a** (optically resolved species) is more efficient than **3b** (racemic species), a finding that is in clear contrast to the behaviour of **1a** and **1b**, where **1b** provides a higher number of inclusion compounds.[11]

By far the most efficient host of the new compounds series is **5a**, although it is still inferior to **1b**.[11] Compound **6a** failed totally to undergo inclusion formation.

A reasoned explanation for the individual results is difficult, but the following directions can be outlined. With reference to the alanine-derived hosts, on going from the less bulky **1** via **2** to more bulkily substituted **3**, the ability to form inclusion compounds gradually diminishes. Replacement of apolar by polar groups of comparable size, such as chloro in **4a** instead of methyl substituents in **3a**, seems to hamper inclusion formation, at least in this particular case of substitution pattern. On the other hand, increasing the bulk at C(2) of the host framework shows a pronounced effect in favour or disfavour of the host efficiency, depending on the nature of the substituent. Thus, compared with parent host compound **1a** (alanine-derived host),[11] the phenylglycine analogue **5a** is definitely superior whereas the phenylalanine analogue **6a** gave no inclusion compounds at all under the experimental conditions. Clearly this suggests conformational, interactive and size effects participating in the lattice build-up and governing the packing structures.

In order to elucidate these parameters, we studied the crystal structures of free host compound **2a**, its inclusion compound with 3-methylcyclohexanone (1 : 1) and five relevant inclusion compounds of **1a** and **1b**, i.e. **1a**·3-methylcyclopentanone (1 : 1), **1a**·2-methylcyclohexanone (1 : 1), **1b**·(−)-fenchone (1 : 1), **1b**·butyronitrile (1 : 1) and **1b**·propan-1-ol (2 : 1). The last two solvents are not accommodated by any host lattice of compounds **2–5**.

Structural studies

Bond lengths and angles (Tables 2 and 3) show good agreement with those found for the previously reported

Table 2. Selected geometrical parameters and hydrogen bond interactions (Å, °) for **I–IV**[a]

	I	**II**	**III**		**IV**	
Bond			Mol. 1	Mol. 2	Mol. 1	Mol. 2
C(1)—C(2)	1·558(4)	1·545(13)	1·544(11)	1·580(10)	1·563(11)	1·550(12)
N(5)—C(31)	1·382(3)	1·370(13)	1·379(7)	1·343(10)	1·367(9)	1·382(11)
N(5)—C(35)	1·396(3)	1·407(12)	1·430(8)	1·419(9)	1·412(9)	1·426(11)
C(31)—O(32)	1·223(4)	1·218(18)	1·212(10)	1·241(11)	1·198(10)	1·203(12)
C(35)—O(36)	1·206(3)	1·205(16)	1·186(10)	1·205(11)	1·181(11)	1·195(11)
C(2)—N(5)—C(31)	126·3(2)	127·0(8)	127·9(4)	127·7(6)	125·9(5)	128·3(7)
C(2)—N(5)—C(35)	121·2(2)	120·6(7)	120·4(4)	119·9(6)	119·5(5)	118·6(7)
O(4)—C(1)—C(2)—C(3)	45·2(3)	52·0(11)	50·1(8)	47·0(8)	53·3(9)	45·9(10)
O(4)—C(1)—C(2)—N(5)	−81·3(2)	−76·0(9)	−73·9(7)	−79·6(7)	−74·1(8)	−78·8(8)
C(11)—C(1)—C(2)—N(5)	41·6(3)	46·6(11)	49·7(8)	44·8(8)	49·6(9)	46·2(9)
C(21)—C(1)—C(2)—N(5)	164·5(2)	170·2(7)	169·6(5)	166·1(6)	170·2(6)	165·3(7)
C(3)—C(2)—N(5)—C(31)	−69·0(3)	−66·7(12)	−63·8(8)	−67·7(9)	−58·8(9)	−72·0(11)
C(3)—C(2)—N(5)—C(35)	100·3(3)	98·2(10)	107·1(6)	100·0(8)	107·1(8)	96·4(9)
C(1)—C(2)—N(5)—C(31)	60·3(3)	63·1(11)	63·0(7)	60·6(9)	69·6(9)	54·1(11)
Intramolecular contact						
O(4)···O(32)	2·710(3)	2·661(9)	2·681(7)	2·664(8)	2·697(8)	2·663(9)
H(4)···O(32)	1·94(3)	1·77(10)	1·84(9)	1·93(9)	1·85(−)	1·91(10)
O(4)—H(4)	0·79(3)	0·94(10)	0·84(10)	0·77(10)	0·93(−)	0·87(10)
O(4)—H(4)···O(32)	166(3)	157(11)	172(9)	158(10)	150(−)	144(9)
Intermolecular contact						

Compound	X—H···centroid	X—H	X···Y	H···Y	X—H···Y	Symmetry
III	C(241)—H(241)···C(11–16) Mol. 1	0·87(12)	3·636(16)	2·89(12)	145(10)	*x*, *y*, *z*

[a] C(11–16) stands for the centroid of the corresponding phenyl group. **I** = **2a**; **II** = **2a**·3-methylcyclohexanone (1 : 1); **III** = **1a**·3-methylcyclopentanone (1 : 1); **IV** = **1a**·2-methylcyclohexanone (1 : 1).

Table 3. Selected geometrical parameters and hydrogen bond interactions (Å, °) for **V**–**VII**[a]

Bond	**V**	**VI** Mol. 1	**VI** Mol. 2	**VII**
C(1)—C(2)	1·466(9)	1·563(4)	1·527(6)	1·552(7)
N(5)—(31)	1·386(6)	1·393(5)	1·384(5)	1·383(6)
N(5)—C(35)	1·406(6)	1·389(5)	1·486(6)	1·391(6)
C(31)—O(32)	1·212(6)	1·214(5)	1·209(7)	1·212(6)
C(35)—O(36)	1·216(6)	1·216(6)	1·206(5)	1·213(6)
C(2)—N(5)—C(31)	123·3(4)	126·3(3)	125·5(4)	126·0(4)
C(2)—N(5)—C(35)	123·2(4)	120·8(3)	121·5(4)	122·0(4)
O(4)—C(1)—C(2)—C(3)	68·0(7)	−48·5(4)	53·7(6)	40·8(6)
O(4)—C(1)—C(2)—N(5)	−73·3(6)	77·8(4)	−78·2(5)	−86·1(5)
C(11)—C(1)—C(2)—N(5)	49·8(7)	−46·2(4)	43·5(5)	37·0(6)
C(21)—C(1)—C(2)—N(5)	167·8(4)	−166·1(3)	162·9(4)	157·5(4)
C(3)—C(2)—N(5)—C(31)	−69·8(6)	61·9(5)	−62·8(5)	−70·5(6)
C(3)—C(2)—N(5)—C(35)	93·5(5)	−104·1(4)	109·4(5)	106·6(5)
C(1)—C(2)—N(5)—C(31)	75·7(6)	−66·3(5)	72·0(5)	58·1(6)
Intramolecular contact				
O(4)···O(32)	2·662(6)	2·762(4)	2·807(5)	2·733(5)
H(4)···O(32)	1·71(−)	1·94(6)	2·01(13)	1·65(−)
O(4)—H(4)	1·00(−)	0·86(7)	0·88(11)	1·10(−)
O(4)—H(4)···O(32)	157(−)	159(5)	150(13)	167(−)
Intermolecular contact				

Compound	X—H···centroid	X—H	X···Y	H···Y	X—H···Y	Symmetry
VI	C(140)—H(140)···C(11–16) Mol. 1	0·86(6)	3·566(5)	2·76(6)	158(5)	$-x, -y, 1-z$
VI	C(213)—H(213)···C(21–26) Mol. 1	1·18(7)	3·876(6)	2·77(6)	156(4)	x, y, z
VI	C(133)—H(133)···C(38–43) Mol. 1	0·86(6)	3·566(5)	2·76(6)	159(4)	$-x, -y, 1-z$
VII	C(48)—H(48)···C(21–26)	0·97(−)	3·864(7)	2·95(−)	158(−)	$-x, -y, 1-z$

[a] C(11–16), C(21–26), C(38–43) stand for the centroid of the corresponding phenyl group. **V** = **1b**·butyronitrile (1 : 1); **VI** = **1b**·propan-1-ol (2 : 1); **VII** = **1b**·(−)-fenchone (1 : 1).

structures.[11] The shortening of the C(1)–C(2) bond in **1b**·butyronitrile could be due to the disorder presented by the host [Figure 1(a)], in such a way that both enantiomers are present at the same position sharing the tetracyclic rigid group (the values retained in Table 3 correspond to the most populated enantiomer). All host molecules have as a common feature the OH···O=C intramolecular hydrogen bond (Figure 1), analogously to that previously studied.[11] For the compounds in this work, the O···O weighted distance is 2·721(2) Å and they present values in the 2·661(9)–2·807(5) Å range. The strength of the interaction presented here appears to be stronger than the only intramolecular hydrogen bond reported so far, for the succinimide ring (2·826 Å).[12] Besides, although this ring forms part of 134 crystal structures (data retrieved from the Cambridge Structural Database),[13] just seven C=O···HO intermolecular interactions occur[10,14–20] (mean 2·826 Å, range 2·632–2·946 Å). There are also 22 corresponding to C=O···HN hydrogen bonds (2·914 Å on average). All of them are linear, showing O···HO angles in the range 149–177° for the intermolecular interactions and 160° for the intramolecular interactions, analogous to those reported in the present paper.

No intermolecular interactions other than van der Waals forces (Tables 2 and 3) were observed between host and guest, so that this fact and the large voids left in the host matrix could be responsible for disorder (Figure 2) and for the large thermal displacement parameters displayed by the guest. The local packing coefficients ($C_p^l = V_{guest}/V_{hole}$) for all complexes are 0·42 on average. Both ends of the range in C_p^l (0·35–0·53) correspond to the guest molecules in **2a**·3-methylcyclohexanone. The fenchone complex also lies in the lowest end of the range ($C_p^l = 0{\cdot}36$). The lower the C_p^l value, the greater is the disorder presented by the guest.

The structures of some compounds are illustrated in Figures 3–5. In the host **2a**, the replacement of the H atoms at the *para*-position in the phenyl rings of **1a** by Me groups seems to significantly affect the crystal packing. In

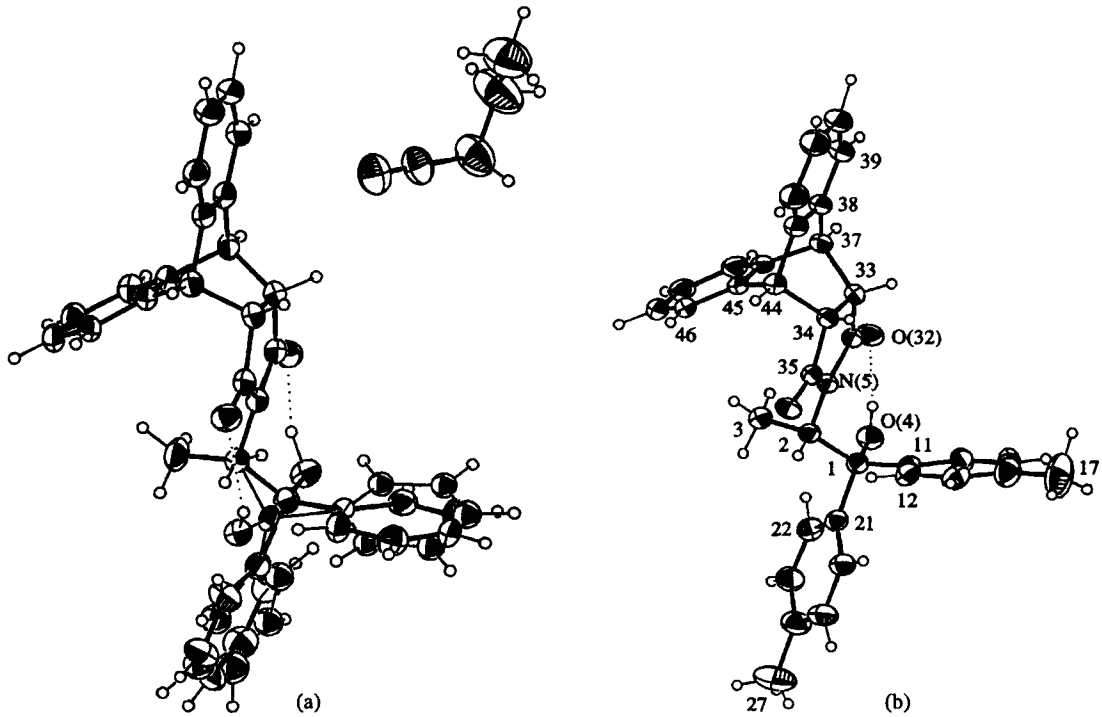


Figure 1. (a) An Ortep[37] view of the molecular structure of the **1b**-butyronitrile complex showing the configurational disorder. The dotted line represents the intramolecular hydrogen bond. Ellipsoids are drawn at the 30% probability level. (b) Same for the optically resolved free host **2a**

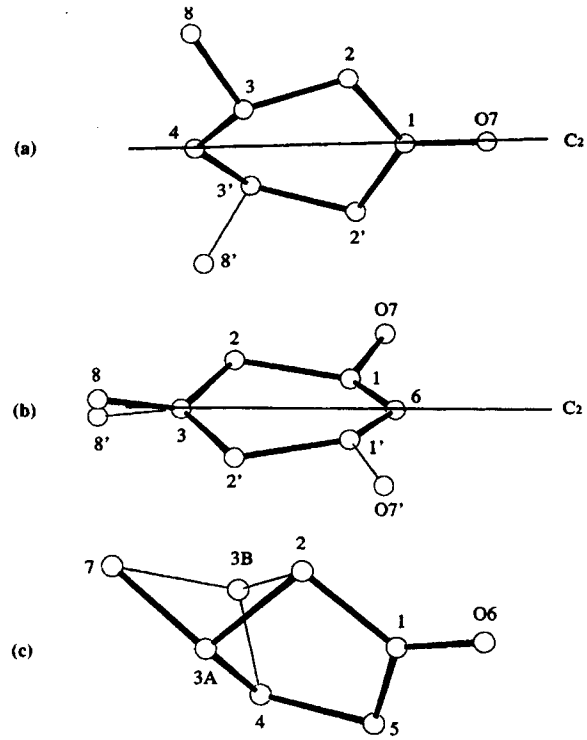


Figure 2. (a) Guest 1 and (b) guest 2 in **2a**·3-methylcyclohexanone, showing the disorder around the twofold axis. (c) Guest 1 in **1a**·3-methylcyclopentanone, displaying the configurational disorder

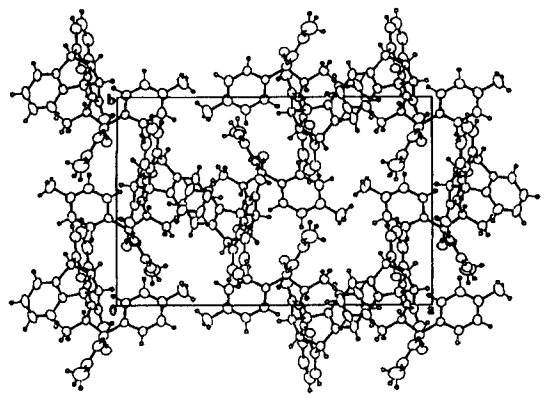


Figure 3. Crystal packing of compound **2a** as projected along the *c*-axis

1a,[11] the crystallographic unit cell ($P2_1$ symmetry) contains two independent hosts almost related by an inversion centre, whereas in **2a** the four molecules in the unit cell ($P2_12_12_1$ symmetry) are related to each other by a twofold screw axis (Figure 3). It is worth noting that **1a** always crystallizes with two independent formula units, be it host or host–guest complexes, in the asymmetry unit. The **1a** complexes have the same host matrix which includes the cyclohexanone guests without distinction between enantiomers or where the substitution of the Me group took place, i.e. 3-methyl or 2-methylcyclohexanone [Figures 4(a) and (b), respectively]. The corresponding volumes and surface areas of these guest molecules are similar on average, 110·4 Å^3, 135·6 Å^2 and 109·6 Å^3, 136·1 Å^2, respectively; those for the pentanone are 97·3 Å^3, 133·3 Å^2. The relative dispositions of both cyclohexanones in their pseudo-isomorphic structures (**1a** host matrix) has been obtained with reference to their eigensystem[20] computed without the Me groups in order to make both molecules alike. Their centroids are almost coincident but guests 1 and 2 are twisted by approximately 52° and 62° around the eigenvector that gives the minimum eigenvalue, that is, the shortest molecular dimension. The shapes of these guest molecules have been analysed by means of the

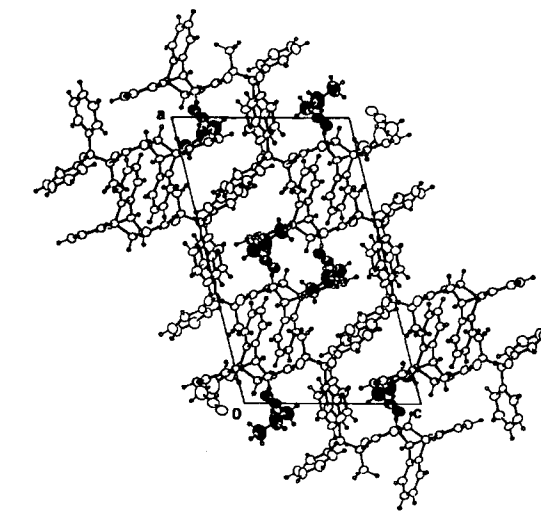
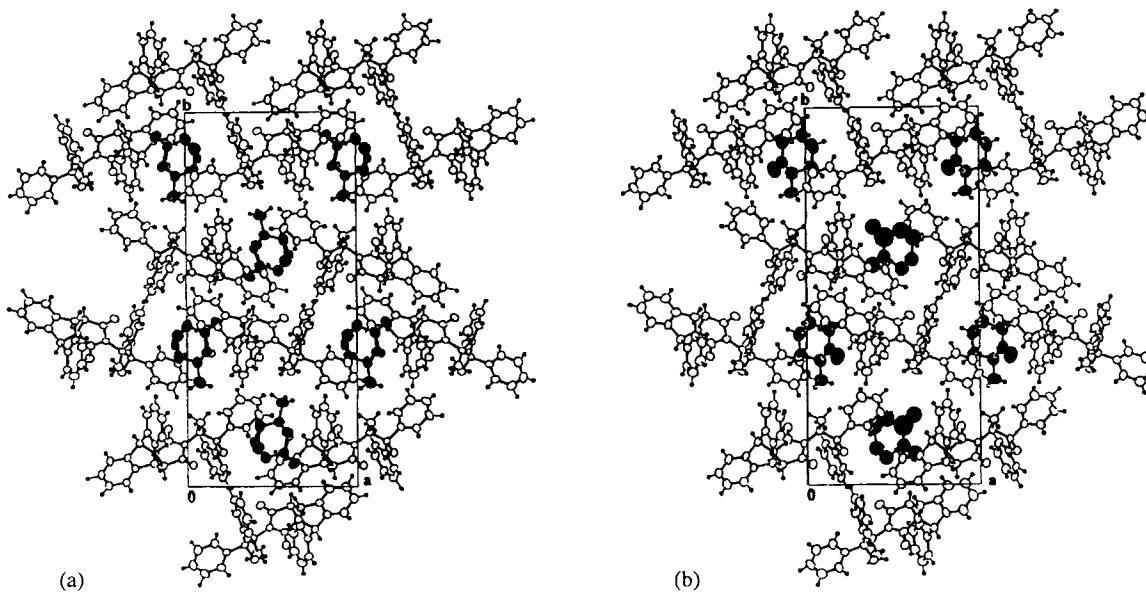


Figure 5. Crystal packing of **1b**·butyronitrile down the *b*-axis



(a) (b)

Figure 4. Crystal packing of compounds (a) **1a**·3-methylcyclohexanone[11] (for comparison purposes, see text) and (b) **1a**·2-methylcyclohexanone down the *c*-axis

ratios of the specific inertial moments of volume to those of surface area.[20] Although the 3-methylcyclohexanone and 3-methylcyclopentanone molecules depart somewhat from rotational symmetry, they seem to be similar and appear to have oblate shapes. The guest molecules are included in cavities (**1a**·3-methylcyclopentanone, **1b**·butyronitrile and **2a**·3-methylcyclohexanone) and channels [**1a**·2-methylcyclohexanone, **1b**·propan-1-ol and **1b**·(−)-fenchone].

EXPERIMENTAL

Synthesis. *cis*-9,10-Dihydro-9,10-ethanoantracene-11,12-dicarbocylic acid anhydride (**16**) was obtained according to the literature.[12]

Amino acid ethyl ester hydrochlorides **7–9** were prepared from the respective amino acids by a modified literature procedure[22] as described previously.[11] **7a**: Colourless crystals (93%), m.p. 78 °C (lit.,[23] 76 °C); $[\alpha]_D^{20}$ +2·8° (*c* 7·37 in H_2O) [lit.,[23] +3·1° (*c* 2·5 in H_2O]. **7b**: Colourless crystals (97%), m.p. 84–85 °C (lit.,[24] 86·5–87 °C). **8a**: Colourless crystals (98%), m.p. 196–199 °C (lit.,[25] 197–198 °C); $[\alpha]_D^{20}$ +91·0° (*c* 1·93 in H_2O) [lit.,[26] +90·7 (*c* 5·07 in H_2O)]. **9a**: Colourless crystals (65%), m.p. 153–154 °C (lit.,[27] 154 °C); $[\alpha]_D^{20}$ −7·5° (*c* 1·71 in H_2O) [lit.,[27] −7·7 (*c* 4 in H_2O)].

2-Amino alcohols **10–15** were synthesized via Grignard reactions as described for **10a** and **15a**.[28] However, in all cases, only a fivefold excess of Grignard reagent was used instead of an eightfold excess, and **13a** was prepared in Et_2O instead of THF to prevent the formation of phenylmagnesium chloride.

10a: From **7a** and bromobenzene; colourless powder (57%), m.p. 100–102 °C (lit.,[29] 101·5–102·5 °C); $[\alpha]_D^{20}$ −85·9° (*c* 2·77 in $CHCl_3$) [lit.,[28] −82·4° (*c* 0·814 in $CHCl_3$)].

11a·HCl: from **7a** and 4-methylbromobenzene; synthesis yielded the corresponding hydrochloride;[30] colourless powder (36%), m.p. 235–238 °C; $[\alpha]_D^{20}$ +47·8 °C (*c* 4·28 in MeOH) [lit.,[30] +40·7° (*c* 2·02 in EtOH)].

12a: From **7a** and 4-*tert*-butylbromobenzene; colourless crystals (36%), m.p. 217–218 °C (from EtOH) (found, C 81·10, H 9·90, N 4·23; $C_{23}H_{33}NO$ requires C 81·37, H 9·80, N 4·13%); $[\alpha]_D^{20}$ −47·1° (*c* 3·03 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 0·92 (3H, d, *J* 6·3 Hz, Me), 1·25 (9H, s, *t*-Bu), 1·27 (9H, s, *t*-Bu), 4·06 (1H, q, *J* 6·3 Hz, NCH), 7·22–7·57 (8H, m, ArH); *m/z* (FAB; *m*-NBA) 340·5 (M + H).

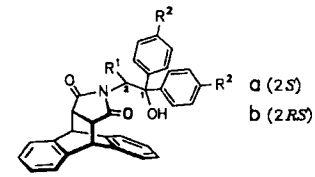
12b: From **7b** and 4-*tert*-butylbromobenzene; colourless powder (43%), m.p. 208–212 °C; spectroscopic data correspond to **12a**.

13a: From **7a** and 4-chlorobromobenzene; colourless powder (37%), m.p. 106–109 °C (found, C 60·53, H 5·15, N 4·87; $C_{15}H_{15}Cl_2NO$ requires C 60·83, H 5·10, N 4·73%); $[\alpha]_D^{20}$ −81·9° (*c* 3·01 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 0·92 (3H, d, *J* 6·3 Hz, Me), 1·22 (2H, br, s, NH_2), 4·04 (1H, q, *J* 6·3 Hz, NCH), 4·36 (1H, br, s, OH), 7·16–7·42 (6H, m, ArH), 7·46–7·57 (2H, m, ArH); *m/z* (FAB, *m*-NBA) 296·2 (M + H).

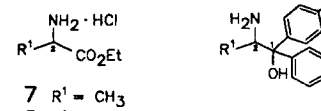
14a: From **8a** and bromobenzene; colourless powder (22%), m.p. 128–130 °C (found, C 82·87, H 6·29, N 5·00; $C_{20}H_{19}NO$ requires C 83·01, H 6·62, N 4·84%); $[\alpha]_D^{20}$ −241·3° (*c* 2·42 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 1·59 (2H, br, s, NH_2), 4·66 (1H, br, s, OH), 5·00 (1H, s, NCH), 6·97–7·20 (9H, m, ArH), 7·26 (2H, m, ArH), 7·41 (2H, m, ArH), 7·74 (2H, m, ArH); *m/z* (FAB, *m*-NBA) 290·2 (M + H).

15a: From **9a** and bromobenzene; colourless powder (26%), m.p. 140–143 °C (lit.,[28] 144–145 °C); $[\alpha]_D^{20}$ −82·9° (*c* 3·07 in $CHCl_3$) [lit.,[28] −88·50° (*c* 0·604 in $CHCl_3$)].

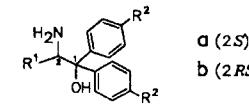
Dicarboximido alcohols **1–6** were prepared by the procedure described for **1a**.[11] For **2a**, the hydrochloride **11a**·HCl was used instead of free **11a**. The synthesis of **6a** gave rise to two atropodiastereomers (**6a** and **6a***).



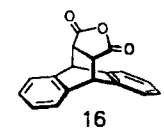
1 R^1 = CH_3, R^2 = H
2 R^1 = CH_3, R^2 = CH_3
3 R^1 = CH_3, R^2 = *t*-Bu
4 R^1 = CH_3, R^2 = Cl
5 R^1 = Ph, R^2 = H
6 R^1 = CH_2Ph, R^2 = H



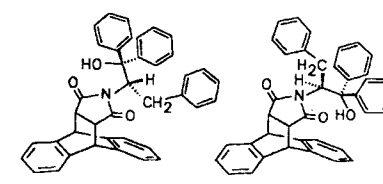
7 R^1 = CH_3
8 R^1 = Ph
9 R^1 = CH_2Ph



10 R^1 = CH_3, R^2 = H
11 R^1 = CH_3, R^2 = CH_3
12 R^1 = CH_3, R^2 = *t*-Bu
13 R^1 = CH_3, R^2 = Cl
14 R^1 = Ph, R^2 = H
15 R^1 = CH_2Ph, R^2 = H



16



6a **6a***

1a: From **10a** and **16**; colourless crystals (61%), m.p. 206–208 °C (from EtOH).[11]

2a: From **11a** and **16**; colourless crystals (57%), m.p. 178–182 °C (from MeOH) (found, C 81·88, H 6·27, N 2·91; $C_{35}H_{31}NO_3$ requires C 81·85, H 6·08, N 2·73%); $[\alpha]_D^{20}$ −44·9° (*c* 4·02 in $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 0·41 (3H, d, *J* 6·9 Hz, Me), 2·19 (3H, s, Me), 2·27 (3H, s, Me), 2·86, 3·06 (2H, dd, *J* 8·3 and 3·5 Hz, CH), 4·71, 4·79 (2H, d, *J* 3·5 Hz, CH), 4·98 (1H, q, *J* 6·9 Hz, NCH), 5·85 (1H, s, OH), 6·95–7·43 (16H, m, ArH); *m/z* (FAB; *m*-NBA) 514·2 (M + H).

3a: From **12a** and **16**; colourless powder (64%), m.p. 322–323 °C (from acetone) (found, C 82·17, H 7·27, N 2·14; $C_{41}H_{43}NO_3$ requires C 82·38, H 7·25, N 2·34%); $[\alpha]_D^{20}$ −44·4° (*c* 2·51 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 0·33 (3H, d, *J* 7·1 Hz, Me), 1·17 (9H, s, *t*-Bu), 1·22 (9H, s, *t*-Bu), 2·77, 2·98 (2H, dd, *J* 8·1 and 3·2 Hz, CH), 4·65, 4·74 (2H, d, *J* 3·2 Hz, CH), 4·92 (1H, q, *J* 7·1 Hz, NCH), 5·77 (1H, s, OH), 7·08–7·45 (16H, m, ArH); *m/z* (FAB; *m*-NBA + NaOAc) 580·3 (M − OH), 620·3 (M + Na).

3b: From **12b** and **16**; colourless powder (86%), m.p. 298–300 °C (from EtOH) (found, C 82·23, H 7·24, N 2·07; $C_{41}H_{43}NO_3$ requires C 82·38, H 7·25, N 2·34%); spectroscopic data correspond to **3a**.

4a: From **13a** and **16**; colourless powder (66%), m.p. 172–176 °C (from EtOH) (found, C 71·67, H 4·45, N 2·70; $C_{33}H_{25}Cl_2NO_3$ requires C 71·49, H 4·54, N 2·52%); $[\alpha]_D^{20}$ −53·1° (*c* 5·485 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 0·30 (3H, d, *J* 6·8 Hz, Me), 2·84, 3·06 (2H, dd, *J* 8·3 and 3·4 Hz, CH), 4·66, 4·75 (2H, d, *J* 3·4 Hz, CH), 4·86 (1H, q, *J* 6·8 Hz, NCH), 5·98 (1H, s, OH), 7·02–7·51 (16H, m, ArH); *m/z* (FAB; *m*-NBA) 554·2 (M + H).

5a: From **14a** and **16**; colourless powder (72%), m.p. 276–278 °C (found, C 83·33, H 5·28, N 2·69; $C_{38}H_{29}NO_3$ requires C 83·34, H 5·34, N 2·56%); $[\alpha]_D^{20}$ −108·7° (*c* 2·275 in $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 2·74, 3·00 (2H, dd, *J* 8·8 and 3·4 Hz, CH), 4·63, 4·66 (2H, d, *J* 3·4 Hz, CH), 5·92 (1H, s, NCH), 6·09 (1H, s, OH), 6·31 (2H, d, ArH), 6·75–7·35 (19H, m, ArH), 7·44 (2H, d, ArH); *m/z* (FAB, *m*-NBA + NaOAc) 548·2 (M + H), 507·2 (M + Na).

6a and **6a***: From **15a** and **16**; colourless crystals (61%) (found, C 83·43, H 5·73, N 2·75; $C_{39}H_{31}NO_3$ requires C 83·40, H 5·56, N 2·49%); *m/z* (FAB; *m*-NBA + NaOAc) 562·2 (M + H), 584·1 (M + Na). **6a**: δ_H (400 MHz; $CDCl_3$) 2·03 (1H, dd, CH_2), 2·64, 2·80 (2H, dd, CH), 3·06 (1H, dd, CH_2), 4·65, 4·68 (2H, dd, CH), 5·31 (1H, dd, NCH), 5·86 (1H, s, OH), 6·41–7·62 (23H, m, ArH). **6a***: δ_H (400 MHz; $CDCl_3$) 2·43 (1H, dd, CH), 2·60 (1H, dd, CH_2), 2·88 (1H, dd, CH), 3·17 (1H, dd, CH_2), 4·44, 4·54 (2H, dd, CH), 5·34 (1H, dd, NCH), 6·04 (1H, s, OH), 6·41–7·62 (23H, m, ArH).

Crystalline inclusion compounds. These were obtained by recrystallization of the corresponding host compound from a minimum amount of the respective guest solvent. The crystals formed were collected by suction filtration, washed with an inert solvent (MeOH) and dried [1 h, 15 Torr (1 Torr = 133·3 Pa), room temperature]. Host–guest stoichiometry was determined by ^1H NMR integration. Data for each compound are given in Table 1.

Sample preparation. Host–guest crystals of **1a** and **2a** suitable for x-ray analysis were obtained by slow cooling of a solution of the corresponding host compound in the guest solvent (3-methylcyclopentanone, 2- or 3-methylcyclohexanone, propan-1-ol, butyronitrile and (−)-fenchone). Single crystals of the free host **2a** were grown from MeOH solution.

X-ray structure determination. Single crystals were sealed in Lindemann glass capillaries. Crystal data and refinement parameters are given in Table 4 and 5. The structures were solved by direct methods[31,32] and refined by least-squares procedures.[33] When solving the structure of the **1b**·butyronitrile complex, disorder of the host molecule around the asymmetric C(2) carbon atom was observed and in this case a new set of data at 225 K was collected and a disorder model established. The population parameter refined to 0·68(2), 0·38(2) for the thick and thin lines in Figure 1(a). Hydrogen atoms were located in Fourier difference maps except some of the guest molecules. In spite of the high atomic displacement parameters displayed by the guest molecules, and the lack of interactions between host and guest (see Discussion), we were not able to collect new sets of data at low temperature. However, a disorder model could be obtained for the complexes mentioned below and their population parameters refined. For **2a**·3-methylcyclohexanone, the Me group of two out of four guest molecules in the unit cell was modelled by two sites related by a crystallographic twofold axis at (0, 0, ½) [atoms C(1), C(4) and O(7) lie on the axis, Figure 2(a)]. The same happens to the other two guest molecules, but now the oxygen atom is also disordered around a twofold axis at (0, 0, 0) [C(3) and C(6) on the twofold axis, Figure 2(b)]. In **1a**·3-methylcyclopentanone, the two independent guests are disordered in such a way that both enantiomers are present in the same host-lattice void sharing all atoms except the asymmetric carbon [Figure 2(c)]. The site occupancies refined to 0·49(3), 0·51(3) for guest 1 and 0·53(2), 0·47(2) for guest 2 correspond to *S*/*R* and *R*/*S* enantiomers, respectively. Nevertheless, in **1a**·2-methylcyclohexanone, in spite of the high thermal displacement parameters displayed by guest 1 (two independent guests in the asymmetric unit), no disorder model could be obtained. The crystal structure of the complex **1a**·2-methylcyclohexanone is pseudo-isomorphous with that of **1a**·3-methylcyclohexanone reported previously.[11] The pseudocisomorphism was checked by half normal

Table 4. Crystal analysis parameters for **I–IV**[a]

	I	**II**	**III**	**IV**
Crystal data				
Formula	$C_{35}H_{31}NO_3$	$C_{35}H_{31}NO_3 \cdot C_7H_{12}O$	$C_{33}H_{27}NO_3 \cdot C_6H_{10}O$	$C_{33}H_{27}NO_3 \cdot C_7H_{12}O$
Crystal habit	Colourless prism	Colourless prism	Colourless prism	
Crystal size (mm)	0·33 × 0·50 × 0·50	0.33 × 0·50 × 0·10	0.43 × 0·33 × 0·27	0·50 × 0·50 × 0·66
Symmetry	Orthorhombic, $P2_12_12_1$	Monoclinic, $C2$	Triclinic, $P1$	Monoclinic, $P2_1$
Unit cell determination	Least-squares fit from 97 reflections ($\Theta < 45°$)	Least-squares fit from 87 reflections ($\Theta < 45°$)	Least-squares fit from 81 reflections ($\Theta < 45°$)	Least-squares fit from 81 reflections ($\Theta < 45°$)
Unit cell dimensions (Å, °)	a = 20·4260(10)	a = 14·7859(8)	a = 15·2279(16)	a = 13·1181(6)
	b = 13·7014(6)	b = 11·5649(4)	b = 12·5931(13)	b = 27·9193(22)
	c = 10·2553(3)	c = 21·0002(14)	c = 8·9089(3)	c = 8·8624(3)
	90	90	92·271(6)	90
	90	104·598(5)	99·434(5)	92·954(3)
	90	90	108·163(9)	90
Packing: V (Å^3), Z	2870·1(2), 4	3475·1(3), 4	1593·8(3), 2	3241·5(3), 4
D_c (g cm^{-3}), M, F(000)	1·189, 513·64, 1088	1·196, 625·81, 1336	1·216, 583·73, 620	1·225, 597·75, 1272
μ (cm^{-1})	5·59	5·64	5·83	5·84
T (K)	295	295	295	295
Experimental data				
Technique	Four-circle diffractometer: Philips PW1100. Bisecting geometry, $\omega/2\Theta$ scans. Graphite oriented monochromator: Cu Kα. Detector apertures 1 × 1°			
Θ_{max}	65°	65°	65°	65°
Scan width	1·4°	1·6°	1·6°	1·4°
	1 min/reflection	½ min/reflection	½ min/reflection	½ min/reflection
	Two standard reflections monitored every 90 min			
Decay	1·1%	2·0%	15·0%	18·0%
No. of reflections:				
Independent	2755	3118	5438	5645
Observed	2503 [3$\sigma(I)$ criterion]	2305 [3$\sigma(I)$ criterion]	4444 [3$\sigma(I)$ criterion]	4090 [3$\sigma(I)$ criterion]
Solution and refinement				
Solution	Direct methods	Direct methods	Direct methods	Direct methods
Least-squares on F_o	2 blocks	2 blocks	7 blocks	6 blocks
Final shift/error	0·18	0·15	0·11	0·64
Weighting scheme	Empirical as to give no trends in $\langle \omega \Delta^2 F \rangle$ vs $\langle \lvert F_{obs} \rvert \rangle$ and $\langle \sin \Theta/\lambda \rangle$			
Final ΔF peaks	0·17 e^{-3}	0·57 e^{-3}	0·33 e^{-3}	0·44 e^{-3}
Final R and R_w	0·046, 0·046	0·096, 0·106	0·086, 0·103	0·084, 0·102

[a] **I** = **2a**; **II** = **2a**·3-methylcyclohexanone (1 : 1); **III** = **1a**·3-methylcyclopentanone (1 : 1); **IV** = **1a**·2-methylcyclohexanone (1 : 1).

Table 5. Crystal analysis parameters for V–VII[a]

	V	VI	VII
Crystal data			
Formula	$C_{33}H_{27}NO_3 \cdot C_4H_7N$	$2(C_{33}H_{27}NO_3 \cdot C_3H_8O$	$C_{33}H_{27}NO_3 \cdot C_{10}H_{16}O$
Crystal habit	Colourless prism	Colourless prism	
Crystal size (mm)	0·33 × 0·17 × 0·17	0.47 × 0·30 × 0·20	0.40 × 0·33 × 0·33
Symmetry	Monoclinic, $P2_1/n$	Triclinic, $P1$	Monoclinic, $P2_1/c$
Unit cell determination	Least-squares fit from 58 reflections ($\Theta < 45°$)	Least-squares fit from 81 reflections ($\Theta < 45°$)	Least-squares fit from 81 reflections ($\Theta < 45°$)
Unit cell dimensions (Å, °)	a = 20·5022(24)	a = 14·4623(15)	a = 11·5238(5)
	b = 12·1211(13)	b = 19·1712(34)	b = 12·4498(5)
	c = 12·1110(14)	c = 10·5326(7)	c = 24·5534(16)
	90	104·797(9)	90
	104·463(11)	94·736(4)	92·060(4)
	90	102·150(11)	90
Packing: V (Å^3), Z	2914·3(6), 4	2371·3(6), 2	3520·4(3), 4
D_c (g cm^{-3}), M, F(000)	1·264, 554·69, 1076	1·196, 983·26, 1044	1·203, 637·82, 620
μ (cm^{-1})	5·97	5·38	5·66
T (K)	225	295	295
Experimental data			
Technique	Four-circle diffractometer: Philips PW1100. Bisecting geometry, $\omega/2\Theta$ scans Graphite oriented monochromator: Cu Kα. Detector apertures 1 × 1°		
Θ_{max}	65°	60°	60°
Scan width	1·4°	1·5°	1·6°
	1 min/reflection	1 min/reflection	¾ min/reflection
	Two standard reflections monitored every 90 min		
Decay	1·1%	1·0%	5·0%
No. of reflections:			
Independent	4879	8130	5161
Observed	3424 [3$\sigma(I)$ criterion]	6129 [3$\sigma(I)$ criterion]	3499 [3$\sigma(I)$ criterion]
Solution and refinement			
Solution	Direct methods	Direct methods	Direct methods
Least-squares on F_o	2 blocks	5 blocks	Full matrix
Final shift/error	0·14	0·13	0·24
Weighting scheme	Empirical as to give no trends in $\langle \omega\Delta^2 F \rangle$ vs $\langle \lvert F_{obs} \rvert \rangle$ and $\langle \sin \Theta/\lambda \rangle$		
Final ΔF peaks	0·27 e^{-3}	0·83 e^{-3}	0·46 e^{-3}
Final R and R_w	0·089, 0·092	0·082, 0·088	0·093, 0·111

[a] **V** = **1b**·butyronitrile (1 : 1); **VI** = **1b**·propan-1-ol (2 : 1); **VII** = **1b**·(−)-fenchone (1 : 1).

probability plots.[35] A fairly linear plot was obtained when the fractional coordinates of the non-hydrogen atoms of the host molecules were compared (correlation coefficient ρ = 0·996). The main differences are due to the orientation of the guest molecules (see Discussion). All the calculations were performed on a VAX6410 computer. Most of them were carried out using the XRAY80 system.[34] The atomic scattering factors were taken from the literature.[36]

CONCLUSIONS

All the crystalline inclusion compounds reported here can be considered of 'true clathrate type' since none presents any kind of interaction between host and guest other than derived from van der Waals forces. This lack of directional interaction seems to be responsible for crystallographic disorder of the guests. Besides, the host disorder observed in the **1b**·butyronitrile complex indicates that these molecules may give rise to problems when being used as chiral selectors since in this particular case they are unable to recognize their own chirality. On the other hand, the presence of a methyl group in the *para*-position on the phenyl rings as in **2** led to a drastic change in the crystal packing modes.

In summary, the present host molecules seem to be already in a satisfied bonding state with the hydroxyl group being involved in a fairly strong intramolecular

hydrogen bond. Breaking of this bond is therefore a critical point for obtaining new host molecules of this type that show chiral recognition properties.

SUPPLEMENTARY MATERIAL

Lists of the structure factors, atomic coordinates and thermal components for the non-hydrogen atoms, hydrogen atom parameters and bond distances and angles are available from C.F.-F. on request.

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