Exploring the Inclusion Properties of New Clathrate Hosts Derived from Tartaric Acid. X-Ray Structural Characterization of the Free Ligands and their Selective Interaction Modes with Alkylamine Guests

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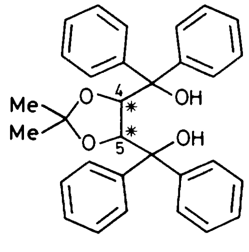
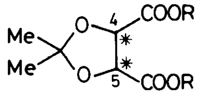
A new host 4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxolane (**1**) was found to form very selectively crystalline complexes with simple alkylamines. Crystals of the three different stereochemical species of this host, optically resolved (**1a**), racemic (**1b**), and *meso* (**1c**), as well as of the inclusion complexes formed by (**1a**) and (**1b**) with $\mathrm{Pr^nNH_2}$, $\mathrm{Pr^n_2NH}$, and $\mathrm{Pr^n_3N}$ have been studied by X-ray diffraction. The clathrate inclusion behaviour of (**1**) is related to structure, and patterns of molecular recognition between this host and the amine guests are characterized. The three different hosts (**1a**), (**1b**), and (**1c**) contain an intramolecular hydrogen bond and are rather rigid; they dimerize in the solid by hydrogen bonding through their hydroxy groups, forming eight-membered $\mathrm{(OH)_4}$ rings. Circular motifs of 2:1 (which involve ten-membered rings of H-bonded –OH and –NH moieties) and 2:2 (involving 12-membered circles) co-ordination between host and guest have also been observed in the inclusion complexes of (**1a**) with $\mathrm{Pr^n_2NH}$ and of (**1b**) with $\mathrm{Pr^nNH_2}$, respectively. Crystals of the other inclusion complexes between (**1a**) and the primary and tertiary amines, and between (**1b**) and the secondary and tertiary amines are characterized by localized 1:1 co-ordination between the complexing partners. It appears that preferential co-ordination of a given host with an amine guest is associated mainly with the formation of larger clusters of H-bonded molecules. The host–guest binding patterns are discussed in detail, in relation to those found in related systems of co-ordination-assisted clathrates.

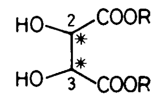
Clathrate inclusion chemistry has successfully been applied in recent years to problems involving molecular separation between close structural isomers and optical resolution of chiral materials.[1,2] In order to extend and refine the scope of applications provided by naturally occurring resolving agents (*e.g.*, tartaric acid, brucine, and other alkaloids) a considerable effort has been made to design new synthetic alternatives. Most consistent results in this area refer to experiments which are based on co-ordination-assisted clathrate formation between functionalized hosts and polar guest components.[3–5] The formation and stability of such lattice-type complexes are affected by functional as well as by topological complementarity, and consequently are sensitive to small structural variations. In this respect it has already been shown that highly selective enclathration of chiral as well as achiral guest moieties can be obtained even with very simple host compounds. Suitable examples previously studied by the present authors include triphenylmethanol,[6] 1,1-di(*p*-hydroxyphenyl)cyclohexane,[7] 2,2′-dihydroxy-1,1′-binaphthyl,[8] 1,1′-binaphthyl-2,2′-dicarboxylic acid,[4a,9] and 9,10-ethano-9,10-dihydroanthracene-11,12-dicarboxylic acid[4b] host frameworks and a variety of mostly alcoholic and oxide-type smaller guest constituents.



(**1**)**a**; (4*R*,5*R*)
b; (4*RS*,5*RS*)
c; (4*R*,5*S*)
(**2**) = (**1a**)•$\mathrm{Pr^nNH_2}$ (1:1)
(**3**) = (**1a**)•$\mathrm{Pr^n_2NH}$ (1:1)
(**4**) = (**1a**)•$\mathrm{Pr^n_3N}$ (1:1)
(**5**) = (**1b**)•$\mathrm{Pr^nNH_2}$ (1:1)
(**6**) = (**1b**)•$\mathrm{Pr^n_2NH}$ (1:1.5)
(**7**) = (**1b**)•$\mathrm{Pr^n_3N}$ (1:1)



(**8**)**a**; (4*R*,5*R*), R = Me
b; (4*RS*,5*RS*), R = Me
c; (4*R*,5*S*), R = Et



(**9**)**a**; (2*R*,3*R*), R = Me
b; (2*RS*,3*RS*), R = Me
c; (2*R*,3*S*), R = Et

More recently, useful inclusion properties have been demonstrated by a new series of host compounds based on the 4,5-bis(hydroxydiphenylmethyl)-1,3-dioxolane framework.[10,11] The 2,2-dimethyl derivative of this host (**1**) is of a particular interest. The optically resolved form (**1a**) was found to be effective in the optical resolution of racemic bicyclic enones.[10] On the other hand, both the optically resolved (**1a**) and the racemic (**1b**) stereoisomers exhibited preferential enclathration of primary and secondary amines over a series of other solvents.[11] In the latter case, selectivity studies of clathrate formation from equimolar two component guest mixtures showed further differentiation between the amine guests. Thus, host (**1a**) was found to be distinctly selective towards secondary amines in competition with the corresponding primary and tertiary derivatives. Host (**1b**), in turn, exhibits under similar conditions, higher preference for the primary analogue. The inclusion of tertiary amines is, in general, considerably less effective. The selectivity features of hosts (**1a**) and (**1b**) toward amines are summarized in Tables 1 and 2 of ref. 11. Their relation to structure was carried out on the propylamine series of guest compounds, and some results of the corresponding structural interpretations have been included in the preliminary publication.[11] A more comprehensive evaluation of the observed structural patterns is presented below. The crystal and molecular structures of the free hosts (**1a–c**) and the inclusion compounds of the optically resolved host (**1a**) with primary, secondary, and tertiary n-propylamine guests (**2**)–(**4**) are described in detail in this report. Crystal data related to the corresponding clathrates of the racemic host (**1b**) with the primary, secondary, and tertiary n-propylamine, reported earlier,[11] will be referred to in the discussion as compounds (**5**)–(**7**), respectively. Suitable crystals of the related less-favoured clathrates involving (**1c**) could not be obtained.

Experimental

General Methods and Materials.—M.p.s were determined with a Reichert hot-stage apparatus. High-resolution mass spectra were obtained from an AEI MS 50 instrument. IR spectra were recorded on a Unicam SP-1100 infrared spectrometer. ^{1}H NMR spectra were measured (Me$_4$Si as internal standard) with a Varian EM-360; ^{13}C NMR with a Bruker WH-90 spectrometer. Dry Et$_2$O was obtained by fresh distillation from Na wire under N$_2$.

Starting compounds [(2*RS*,3*RS*)-tartaric acid, (2*R*,3*R*)-dimethyl tartrate (**9a**), 2,2-dimethoxypropane, and bromobenzene] were purchased from Janssen. (2*R*,3*S*)-Tartaric acid,[12] (**9b**),[13] and (**9c**)[14] were synthesized as described. Diesters (**8a–c**) were obtained by *trans*-ketalization of the corresponding tartaric acid diesters (**9a–c**) with 2,2-dimethoxypropane and toluene-*p*-sulphonic acid according to literature procedures.[15]

Host compounds (**1a–c**) were prepared *via* a Grignard reaction as described for (**1a**).[16] Specific details are given for each compound.

(4R,5R)-*Bis*(*hydroxydiphenylmethyl*)-2,2-*dimethyl*-1,3-*dioxolane* (**1a**). From diester (**8a**) with phenylmagnesium bromide in dry Et$_2$O; 74% colourless powder; m.p. 192–193 °C (lit.,[16] 190–192 °C); $[\alpha]_D^{20}$ −62.6° (*c* 1, in CHCl$_3$); {lit., $[\alpha]_D^{20}$ −59.2°,[16a] $[\alpha]_D^{20}$ −68.5°[16b] (*c* 1, in CHCl$_3$)}.

(4RS,5RS)-*Bis*(*hydroxydiphenylmethyl*)-2,2-*dimethyl*-1,3-*dioxolane* (**1b**). From diester (**8b**) with phenylmagnesium bromide in dry Et$_2$O; 66% colourless powder; m.p. 202–207 °C, 210–213 °C* (Found: C, 79.7; H, 6.55; M^+ − Me, 451.1917. C$_{31}$H$_{30}$O$_4$ requires C, 79.80; H, 6.48%; M − Me, 451.1902); ν_{max}(KBr) 3 470, 3 280 (OH), 1 600, 1 500 (Ar), 1 250 (CO), 1 185, 1 100, 1 060, and 1 035 cm^{-1} (ketal); δ_H(60 MHz; CDCl$_3$) 1.00 (6 H, s, Me), 3.80 (2 H, s, OH), 4.55 (2 H, s, CH), and 7.10–7.60 (20 H, m, Ar); δ_C(90 MHz; CDCl$_3$) 27.06, 73.03, 80.88, 109.33, 127.20, 127.46, 127.75, 128.04, 128.79, 142.64, and 146.04.

(4R,5S)-*Bis*(*hydroxydiphenylmethyl*)-2,2-*dimethyl*-1,3-*dioxolane* (**1c**). From diester (**8c**) with phenylmagnesium bromide in dry Et$_2$O using an activation method[17] for the Grignard reagent; 59% colourless powder; m.p. 190–194 °C, 214–216 °C* (Found: C, 79.75; H, 6.75; M^+ − Me, 451.1908. C$_{31}$H$_{30}$O$_4$ requires C, 79.80; H, 6.48%; M − Me, 451.1902); ν_{max}(KBr) 3 450, 3 320 (OH), 1 600, 1 500 (Ar), 1 250 (CO), 1 170, 1 085, 1 060, and 1 030 cm^{-1} (ketal); δ_H(60 MHz; CDCl$_3$) 1.40 (3 H, s, Me), 1.60 (3 H, s, Me), 4.30 (2 H, s, OH), 5.50 (2 H, s, CH), and 6.60–7.60 (20 H, m Ar); δ_C(90 MHz; CDCl$_3$) 25.40, 26.44, 77.84, 81.44, 107.41, 124.36, 125.29, 126.27, 126.44, 127.33, 127.68, 127.99, 128.17, 128.41, 128.69, 144.01, and 146.56.

Inclusion Compounds (**2**)–(**7**).—*Sample preparation.* Inclusion compounds were obtained by recrystallization of the corresponding host from a minimum amount of the respective amine solvent (Pr^{n}NH$_2$, Pr$^n_2$NH, Pr$^n_3$N). Suitable crystals for X-ray diffraction were prepared by slow cooling of the solutions. Single crystals of (**1a–c**) were obtained by slow crystallization from mesitylene, EtCN, and MeOH, respectively.

Crystal-structure determination: data collection and processing.—X-ray diffraction data were measured on CAD4 diffractometers equipped with a graphite monochromator, using Mo-K_α (λ = 0.7107 Å) radiation and the ω–$p\theta$ scan technique (*p* varying between 0 and 2 for the different crystals, according to the shape of the diffraction peaks). Measurements for compounds (**1a–c**), (**2**), and (**4**) were carried out at room temperature (*ca.* 297 K); due to the relatively large unit cell in (**3**), low-temperature measurements (*ca.* 193 K) with a higher resolution were preferred in order to increase the data-to-parameters ratio, in this case. The cell constants and pertinent details of the experimental conditions are summarized in Table 1. Possible deterioration of the analysed crystals was tested by detecting frequently the intensities of either two or three standard reflections from different zones of the reciprocal space; for compounds (**1a–c**), (**3**), and (**4**) it was negligible during the measurements. The standard intensities of (**2**), however, exhibited a linear decrease as a function of time (of about 10% over the entire experiment), which required an appropriate correction of this set of data. All intensities were converted to structure factors in a conventional manner, but they were not corrected for absorption or secondary extinction. Final refinements were based only on those observations that satisfied the conditions $I > 3\sigma(I)$ for (**1a–c**), (**2**), and (**4**), and $I > 1.5\sigma(I)$ for (**3**).

Structure analysis and refinement.—The crystal structures were solved by a combination of direct methods and Fourier techniques (MULTAN 80 and SHELXS 86).[18,19] Their refinements were carried out by large-block least squares (SHELX 76),[20] including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The guest constituents in complexes (**2**) and (**3**) were found to exhibit large amplitude 'wagging' motions or possible disorder, and were included in the refinement with isotropic thermal parameters only. Most hydrogen atoms were introduced into the structure factor computations in calculated positions, the methyl substituents being treated as rigid groups. Approximate positions of the hydroxy H atoms were found directly in difference-Fourier maps; however, the amine H atoms in (**2**) and (**3**) could not be located reliably. Structures (**1a–c**) and (**4**) turned out to be perfectly ordered and well defined. Less precise was the determination of complexes (**2**) and (**3**) due to a partial disorder exhibited by the guest species [in (**3**) this refers mainly to the unco-ordinated molecule of the solvent]. In the loosely packed (**2**), the peripheral atoms of the phenyl rings are also characterized by large parameters of thermal motion; consequently, the observed data-to-parameters ratio in this structure is rather low. In order to avoid unreasonable distortions of bond lengths and bond angles, the phenyl rings in (**2**) and the corresponding amine molecules in (**2**) and (**3**) were refined with a constrained geometry. The final difference Fourier maps of the six structures showed no indication of incorrectly placed or missing atoms.

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* Polymorphous behaviour (*cf.* C. Weygand, A. Weissberger, and H. Baumgartel, *Ber. Dtsch. Chem. Ges.*, 1932, **65**, 696; L. Kofler, A. Kofler, and M. Brandstatter, 'Thermo-Mikro-Methoden,' Verlag Chemie, Weinheim, 1954, p. 113).

Table 1. Summary of crystal data and experimental parameters.

Compound	(**1a**)	(**1b**)	(**1c**)	(**2**)	(**3**)	(**4**)
M^a	466.6	466.6	466.6	525.7	567.8	609.8
Space group	$P1$	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1$	$P2_1$
Z	2	2	4	4	4	2
a/Å	9.341(9)	9.659(3)	10.514(2)	10.915(3)	11.715(3)	9.155(2)
b/Å	11.841(5)	11.320(9)	21.201(5)	11.184(8)	14.038(7)	17.180(7)
c/Å	12.824(3)	12.063(3)	11.646(2)	24.117(6)	20.490(4)	11.643(3)
α/°	109.12(3)	103.12(3)	90.0	90.0	90.0	90.0
β/°	97.36(4)	93.46(2)	103.24(1)	90.0	105.69(2)	91.76(2)
γ/°	102.50(5)	105.04(5)	90.0	90.0	90.0	90.0
V/Å^3	1 277.6	1 230.5	2 527.0	2 944.0	3 244.1	1 830.4
D_x/Mg m^{-3}	1.213	1.259	1.226	1.186	1.163	1.107
F(000)	496	496	992	1 128	1 224	660
μ/m^{-1}	0.074	0.077	0.075	0.072	0.069	0.065
2θ limits/°	50	50	46	46	54	50
N(unique)	4 076	3 823	3 145	2 013	8 970	2 800
N(obs)^b	2 587	2 330	1 973	1 054	7 025	1 254
R_F	0.047	0.052	0.051	0.076	0.083	0.055
$\lvert\Delta\rho\rvert_{max}$	0.20	0.29	0.24	0.37	0.65	0.23

^{a}Molecular weights are given for one host molecule or 1 : 1 host–guest unit. The asymmetric unit in (**1a**) contains, however, two hosts, and that in (**3**) two hosts and two guests. ^{b} For compounds (**1a–c**), (**2**) and (**4**) $I > 3\sigma(I)$; for compound (**3**) $I > 1.5\sigma(I)$.

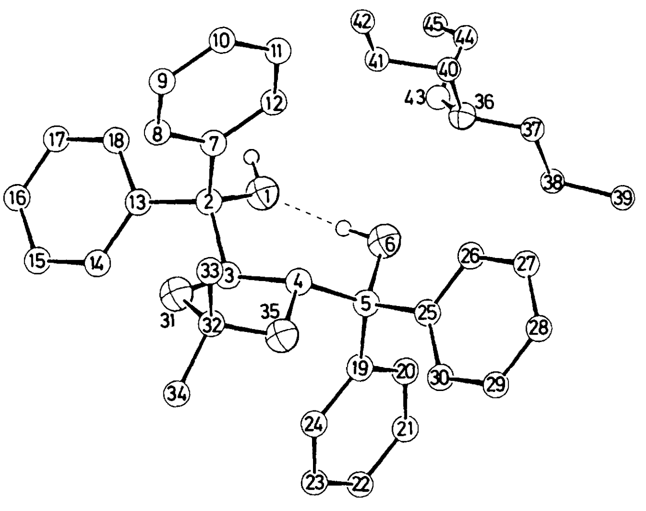

Figure 1. Representative molecular structure of an enantiomer of host (**1**), and the crystallographic numbering used for the host and guest species (the O and N atoms are marked by crossed circles). For Pr^{n}NH$_2$ guest the atomic labels are N(36) through C(39), while for Pr$^n_2$NH guest they include N(36) through C(42).

The crystallographic atom labelling scheme used for the host and guest molecules is shown in Figure 1. The second independent molecule of the host in the asymmetric unit of (**1a**) and (**3**), as well as the unco-ordinated solvent in (**3**), are marked by primed labels. The final atomic co-ordinates of the six compounds are given in Table 4 (see later). Lists of the anisotropic thermal parameters, as well as bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.* All the covalent parameters are within the normal range; marked deviations were observed only in the disordered fragments of compounds (**2**) and (**3**) (see above).

Results and Discussion

The observed molecular structures of hosts (**1a–c**) in all the crystals [including (**2**)–(**7**)] beautifully reflect on the conformational rigidity of these species. Incorporation of the inner oxygens [O(31) and O(35)] (see Figure 1) into a five-membered ring forces the outer OH groups [O(1) and O(6)] to lie on the same side of the tartaric acid framework and within a hydrogen bonding distance from one another. Formation of the H-bonds is inherent to the molecular structure as it occurs irrespective of the presence or absence of a guest component, providing an additional contribution to the rigidity of the host framework. Geometric details on the intramolecular hydrogen bonds and the torsions around the central C–C bonds are included in Table 2. As can clearly be seen, all the chiral [either *RR* or *SS*] host isomers in the resolved as well as unresolved compounds are characterized by consistent conformational features, the relevant torsion angles being confined to narrow ranges. Other closely related derivatives of (**1**), which are substituted at the *para* positions of the phenyl rings, are characterized by similar geometries.[21] The only outstanding example is the *meso* compound (**1c**) which has a significantly different conformation, due to the opposite chiralities (*R* and *S*) of the two central C atoms [C(3) and C(4)]; it still maintains, however, the intramolecular H-bonding interaction.†

Another feature common to all the host species relates to the nature of their molecular surface. One face of each molecule contains the O–H•••OH moieties, and is polar. Since organic hydroxy groups are most commonly involved in two-hydrogen bonds, this polar site is still capable of forming additional bonds by donating one proton to and/or accepting another proton from adjacent moieties. The remaining surface of the molecules consists mainly of C–H bonds (from the peripheral phenyl and methyl substituents), and is hydrophobic. The above characteristics play a dominant role in determining possible patterns of intermolecular interactions in the solid and possibly also in the liquid phase.

A suitable example is provided by the crystal structures of the free ligands (**1a–c**) (Figure 2). Invariably, the molecular entities in these crystals form dimers through their hydroxyl groups. Within each dimer there are 8-membered hydrogen bonded (OH)$_4$ rings which consist of two intra- and two inter-molecular interactions, reflecting on the strong tendency of the OH groups to act as proton donors and proton acceptors at the same time.

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* For details of the CCDC deposition scheme see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, 1990, issue 1. See also, *ibid.*, 1990, p. v and vi.

† Intramolecular H-bonding is also in solution (CCl$_4$) as manifested by IR studies under different concentration (see, H. Gunzler and H Bock, 'IR-Spektroskopie,' Verlag Chemie, Weinheim, 1975; solid state IR data are given in the Experimental section).

Table 2. Intramolecular conformation and hydrogen bonding in the host species.

	Torsional angle/°						Bond length/Å			Bond angle/°
Compound	O(1)–C(2)–C(3)–C(4)	C(2)–C(3)–C(4)–C(5)	O(31)–C(3)–C(4)–O(35)	C(3)–C(4)–C(5)–O(6)	Donor[a]	Acceptor[a]	O–H	O···O	H···O	O–H···H
(1a)	69.6(6)	−93.6(6)	27.6(5)	61.8(6)	OH(1)	O(6)	1.05	2.604(4)	1.56	171
	68.3(6)	−91.8(7)	28.8(5)	61.7(7)	OH(6)	O(1′)	1.05	2.602(5)	1.55	177
(1b)	66.2(4)	−89.9(4)	29.9(3)	72.1(4)	OH(6)	O(1)	0.93	2.616(3)	1.71	162
(1c)	−38.4(4)	−38.9(5)	35.3(3)	64.7(4)	OH(1)	O(6)	1.00	2.680(3)	1.68	180
(2)	61.9(12)	−89.9(13)	30.2(10)	73.6(12)	OH(6)	O(1)	1.03	2.635(11)	1.63	162
(3)	73.4(6)	−89.5(7)	31.6(5)	66.7(6)	OH(1)	O(6)	1.02	2.637(6)	1.62	175
	63.4(6)	−88.3(7)	33.8(6)	77.0(7)	OH(6′)	O(1′)	0.96	2.644(6)	1.74	158
(4)	71.0(9)	−86.3(10)	31.9(8)	70.5(9)	OH(1)	O(6)	0.93	2.663(8)	1.75	168
(5)	77.1(6)	−88.2(6)	30.2(5)	63.6(6)	OH(1)	O(6)	1.11	2.685(6)	1.62	157
(6)	77.1(12)	−90.0(13)	28.6(11)	60.9(12)	OH(1)	O(6)	1.11	2.655(11)	1.74	136
(7)	67.9(5)	−90.1(5)	29.8(5)	72.7(5)	OH(1)	O(6)	0.96	2.646(5)	1.74	157

[a] Primed atoms relate to the second independent molecule of the asymmetric unit.

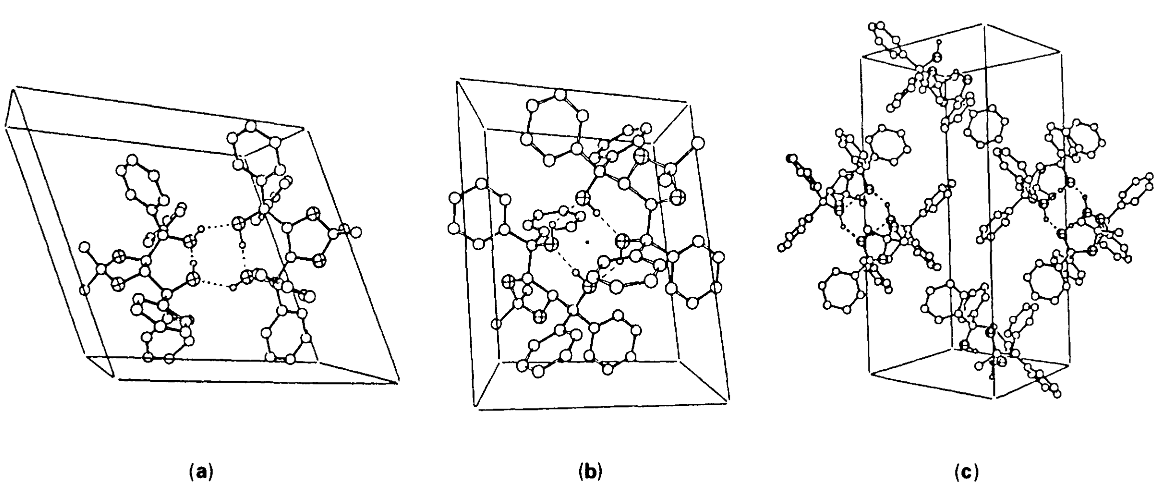

Figure 2. Crystal structures of the free hosts, showing the hydrogen-bonding dimerization: (*a*) (**1a**); (*b*) (**1b**); (*c*) (**1c**).

Table 3. Intermolecular co-ordinative interactions.

Compound	Donor (at *x,y,z*)	Acceptor	At site	DH ••• A (*d*/Å)
(**1a**)	OH(6)	O(6′)	*x,y,z* − 1	2.724(5)
	OH(1′)	O(1)	*x,y,z* + 1	2.718(4)
(**1b**)	OH(1)	O(6)	1 − *x*,1 − *y*,1 − *z*	2.712(3)
(**1c**)	OH(6)	O(1)	−*x*,1 − *y*,−*z*	2.734(3)
(**2**)	OH(1)	N(36)	*x,y,z*	2.600(19)
(**3**)	OH(1′)	O(1)	*x,y,z*	2.729(5)
	OH(6)	N(36)	*x,y,z*	2.669(7)
	NH(36)	O(6′)	*x,y,z*	3.176(7)
(**4**)	OH(6)	N(36)	*x,y,z* − 1	2.712(10)
(**5**)	OH(6)	N(36)	*x,y,z*	2.745(8)
	$NH_2(36)$	O(1)	1 − *x*,1 − *y*,1 − *z*	3.398(8)
(**6**)	OH(6)	N(36)	*x,y,z*	2.761(14)
(**7**)	OH(6)	N(36)	*x,y,z*	2.710(5)

Correspondingly, the circular arrangement of the hydroxy groups is preserved not only in structures of (**1b**) [Figure 2(*b*)] and (**1c**) [Figure 2(*c*)], where the dimers are located on crystallographic centres of inversion, but also in the non-centrosymmetric structure of (**1a**) [Figure 2(*a*)] in which there are two molecules of (**1a**) in the asymmetric unit. The crystal packing of the dimers is stabilized by ordinary van der Waals interactions between their lipophilic surfaces. Details on the intermolecular hydrogen bonds are included in Table 3. Evidently, formation of the dimeric arrangement is disrupted in the clathrates where the intermolecular packing is optimized in a different manner. The crystal structures of the chiral complexes of host (**1a**) with Pr^nNH_2 (1:1), Pr^n_2NH (1:1), and Pr^n_3N (1:1) [(**2**)–(**4**), respectively] are shown in Figure 3. The interaction mode in (**3**) [Figure 3(*b*)] can be described as incorporation of the Pr^n_2NH guest into the dimeric arrangement of the host species, leaving one intermolecular OH(host) ••• O(host) bond intact while replacing the other one by an OH(host) ••• NH(guest) ••• O(host) co-ordination. Consequently, a 10-membered ring of H-bonded species is formed with four strong and one weaker interaction (Tables 2 and 3). The crystal structure of (**3**) contains two additional loosely packed molecules of Pr^n_2NH per unit cell. They fill the space between the complexed entities but are not co-ordinated to the surrounding moieties.

A different binding scheme characterizes clathrates (**2**) and (**4**) including the primary and tertiary amine guests [Figures 3(*a*) and 3(*c*), respectively]. These two structures consist of discrete 1:1 units of the complex, within which there is only one direct hydrogen bond between the host and the guest (see Table 3). In case of the least favoured tertiary amine guest, the alkyl residues extend in three dimensions, effectively shielding the hydrophilic zone from, and thus preventing additional coordination to, the surrounding molecules. The complexed units are held together in the solid state mainly by weak dispersion forces. As has previously been illustrated, a similar variety of binding schemes occurs in the racemic clathrates of (**1b**) with the n-propylamine series of guests [(**5**)–(**7**)].[11] However, in this case, associations between host and guest through a single H-bond were found in the complexes of (**1b**) with the secondary and the tertiary amine derivatives [(**6**), which also contains additional molecules of disordered solvent, and (**7**)]. On the other hand, the host and the Pr^nNH_2 guest species in (**5**) form a centrosymmetric arrangement which involves the hydrophilic sites of two hosts and two guests. This results in a 12-membered ring of hydrogen bonded moieties around centres of inversion with two strong OH ••• N and two weak NH ••• O intermolecular interactions (Table 3). A schematic representation of the various binding modes is shown in Figure 4.

Relation of the structural data to the inclusion behaviour and selectivity properties of host (**1**) provides some interesting indications. It appears that the bulkiness and rigidity of the host's molecular framework limits the capability to optimize simultaneously the H-bonding requirements and to close pack efficiently in the solid state, thus providing an important driving force for the formation of clathrates. Although stable and well organized crystals of the free hosts (**1a–c**) can be formed, they co-crystallize preferentially with an amine guest component. In some of the clathrates [*e.g.*, (**2**), (**4**), (**6**), and (**7**)] the hydrogen bonding pattern is, however, less extensive, the guest amine and one of the host-OH moieties being involved only in a single interaction (as a proton donor and a proton acceptor, respectively).* It can reasonably be assumed that more effective van der Waals forces as well as an increased entropy provide a compensating contribution to the stability (free energy) of these crystals, as the inclusion of conformationally flexible guest species should allow for a better optimization of the dispersive interactions. This argument needs to be confirmed, however, by quantitative estimates of the corresponding thermodynamic variables.

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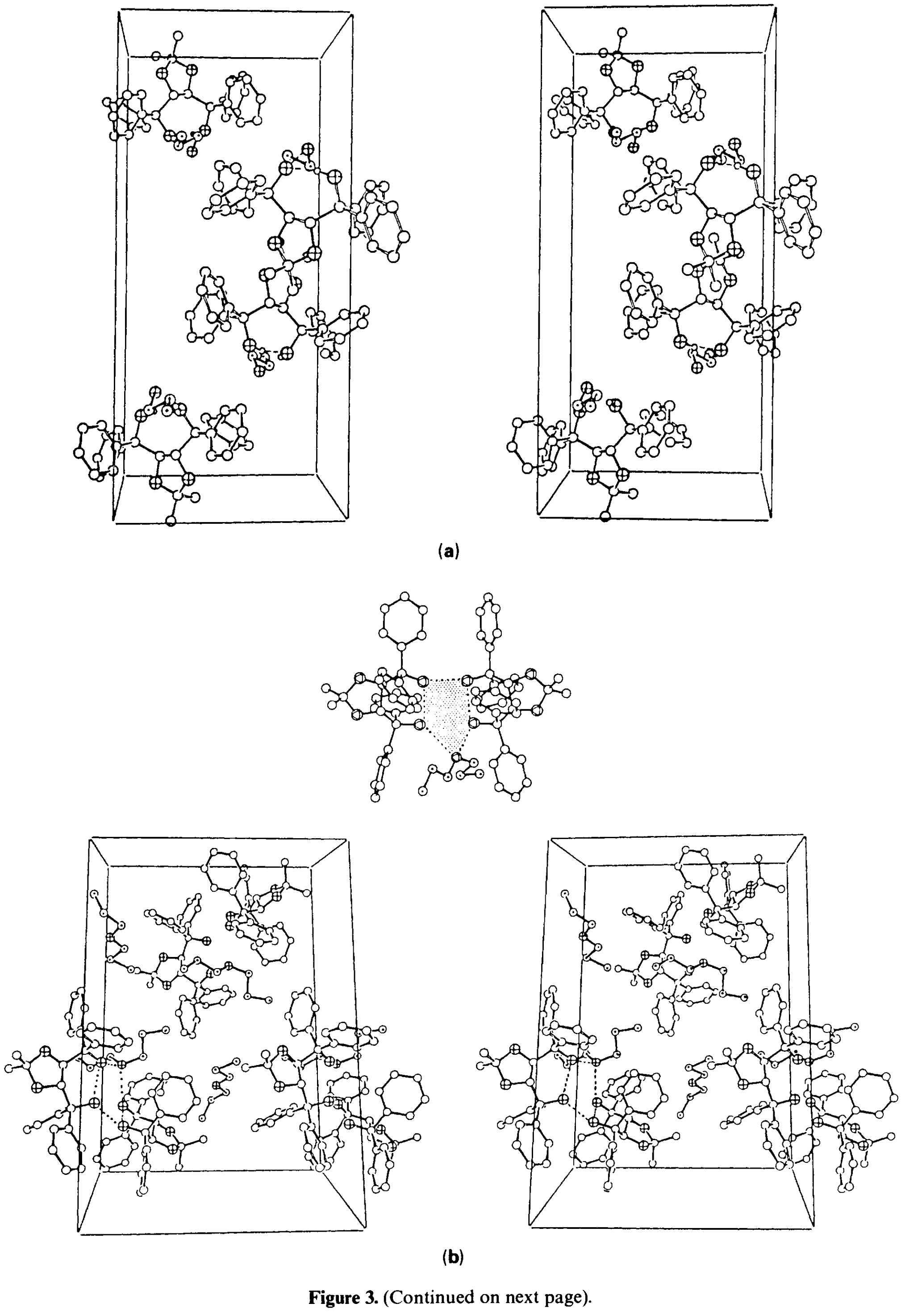
* The nitrogen sites in the guest species are more basic than the hydroxy groups in (**1**). However, primary and secondary amines are known to be better donors than acceptors of hydrogen bonds: M. C. Etter, Annual Meeting of the American Crystallographic Association, Seattle, 1989.

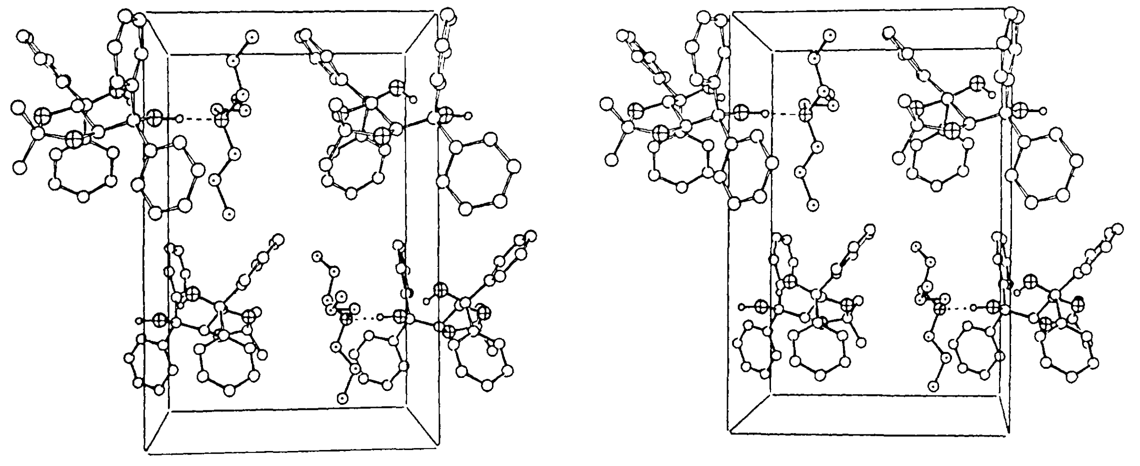
The crystallographic results indicate clearly that the observed selectivity among the amine guests[11] can be attributed mainly to the formation of a cyclic arrangement of hydrogen bonds between the interacting constituents in the polar regions of the preferred structures. In the optically resolved series of clathrates involving (**1a**) as host, the circular pattern occurs only in the complex of (**1a**) with Pr$^{n}{}_{2}$NH (**3**); indeed, this host was found to be distinctly selective towards secondary amine derivatives.[11] On the other hand, host (**1b**) preferentially enclathrates the primary alkylamines,[11] in agreement with the more extensive H-bonding observed in (**5**), but not in the less-favoured clathrates (**6**) and (**7**) (Figures 3 and 4). The apparent tendency of Pr$^{n}{}_{2}$NH to co-ordinate better with a pure enantiomer of the host (**1a**) rather than with its racemic mixture (**1b**) in the solid phase has not led, however, to a spontaneous resolution of the latter in the crystallization process from Pr$^{n}{}_{2}$NH. This can possibly be explained by the general (though not exclusive) observation that racemic compounds are often less soluble in a given solvent than their optically pure stereoisomers.[22] It has further been shown that clathrates of (**1a**) and (**1b**) with the secondary amine [(**3**) and (**6**)] contain unco-ordinated as well as host-co-ordinated guest moieties. The 'free' guests, of a roughly linear shape, are accommodated between the dimethyl ends of adjacent host molecules without any specific association with



(a)

(b)

Figure 3. (Continued on next page).



(c)

Figure 3. Stereoviews of the inclusion complexes between (**1a**) and the propylamine guests. The heteroatoms are indicated by crossed circles, and the amine moieties by darker bonds and 'dotted' C-atoms: (*a*) (**2**) [(**1a**)·$\mathrm{Pr^nNH_2}$ (1:1)], viewed approximately down the **a** axis of the unit-cell; (*b*) (**3**) [(**1a**)·$\mathrm{Pr^n_2NH}$ (1:1)], viewed approximately down **a**. An additional entity of the 2:1 host–guest co-ordinated complex was included in order to illustrate better the crystal packing arrangement. The co-ordination scheme between host and guest is indicated in the lower-left-hand corner of the unit-cell, and also in an enlarged form above it; (*c*) [(**1a**)·$\mathrm{Pr^n_3N}$ (1:1)] viewed down **a**, showing localized host–guest co-ordination. Two additional molecules of the host are included for a better illustration of the intermolecular packing.

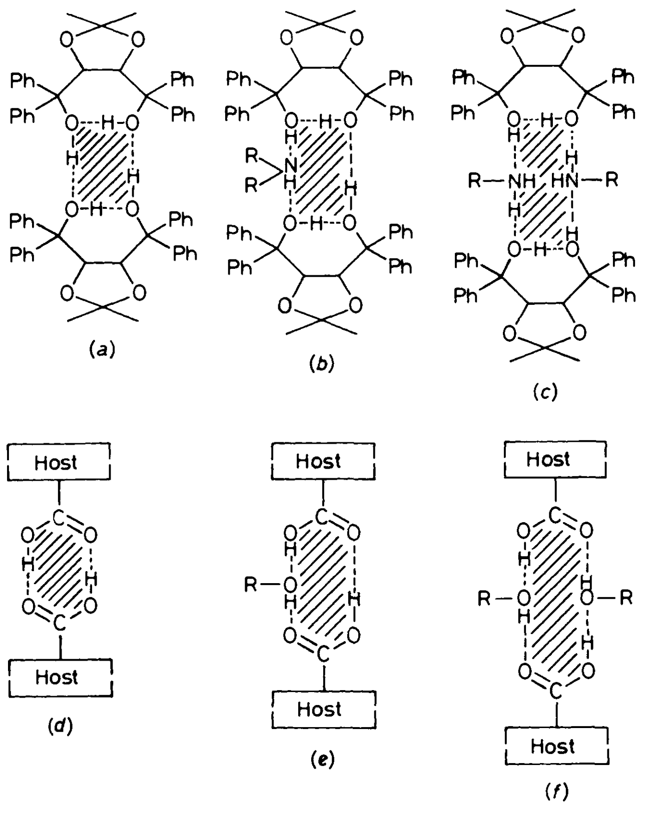


Figure 4. Schematic summary of host–guest hydrogen bonding in compounds (**1a–c**) and (**2**)–(**7**) [(*a*)–(*c*)], in relation to the molecular recognition patterns observed between carboxylic acid hosts and alcoholic guests [(*d*)–(*f*)].[4,23] Square brackets symbolize the hydrocarbon molecular frameworks of the carboxylic hosts: 9,10-ethano-9,10-dihydroanthracene and 1,1′-binaphthyl, while R represents a short alkyl residue (Me, Pr, or Bu). Dimerization of the host and formation of eight-membered rings is shown in (*a*) [as in (**1a–c**)] and (*d*). Incorporation of one guest moiety into the circular pattern, and formation of ten-membered rings is shown in (*b*) [as in (**3**)] and (*e*). Inclusion of two guests in a 12-membered circles is shown in (*c*) [as in (**5**)] and (*f*).

the surrounding species. The lipophilic environments between the alkyl and the aryl substituents on the hosts provide indeed the most probable sites for nonspecific inclusion of aprotic and non-polar guests such as various heterocycles, amides, and aromatic hydrocarbons (*cf.* refs. 10 and 11). The different interaction modes of (**1a**) and (**1b**) with the primary and the secondary amines relate to variations in van der Waals packing forces and the crystallographic symmetry, and could not be fully explained.

An interesting correlation can be made between the current results and previous observations for other clathrate systems based on similar principles of host design.[23] While the present diol hosts turned out to be useful for preferred amine inclusion, dicarboxylic acid hosts proved to be very effective for selective inclusions of alcoholic guests.[4] In fact, clathrates of 1,1′-binaphthyl-2,2′-dicarboxylic acid[4a] and 9,10-ethano-9,10-dihydroanthracene-11,12-dicarboxylic acid[4b] exhibit binding patterns between host and guest which are very similar to those described above [Figures 4(*a*)–(*d*)]. Thus, eight-membered cycles of hydrogen bonds are formed between two carboxylic hosts in the solvent-free state.[4b] Insertion of one guest species between the two hosts produces a 10-membered ring of H-bonded moieties, while the complexation with two alcoholic guests results in a centrosymmetric 12-membered arrangement [Figures 4(*e*)–(*g*)].[4,23] Formation of circular patterns of H-bonds is also common in the clathrates of various mono- and poly-functional hydroxyphenyl hosts with other alcohols, in some cases giving rise to effective discrimination between potential guests in the clathrate formation.[6,24]

Conclusions

In conclusion, the molecular design of host (**1**) was found particularly suitable to provide specific inclusion selectivity toward aliphatic amines. The structural basis for the distinct differentiation between primary and secondary amines by clathrate formation with this host lies in the variation of the primary (H-bonding) as well as secondary (dispersion) interaction schemes in the individual crystals, and the high sensitivity of the condensed solid phase to such differences. Similar interplays between strong and weak intermolecular forces were found to have an important effect on molecular

Table 4. Atomic position parameters.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
(1a)							
O(1)	0.2010	0.1296	−0.0011	O(1′)	0.161 1(4)	0.106 3(3)	0.778 4(3)
C(2)	0.268 9(5)	0.201 7(4)	0.115 9(4)	C(2′)	0.067 1(6)	0.123 3(5)	0.689 8(4)
C(3)	0.320 3(5)	0.110 3(5)	0.163 8(4)	C(3′)	0.052 1(6)	0.005 9(5)	0.584 9(4)
C(4)	0.451 3(6)	0.060 8(5)	0.124 1(4)	C(4′)	−0.037 8(6)	−0.120 2(4)	0.583 6(4)
C(5)	0.414 0(5)	−0.064 6(4)	0.022 6(4)	C(5′)	0.041 6(6)	−0.201 1(5)	0.629 0(4)
O(6)	0.338 2(4)	−0.041 9(3)	−0.069 2(3)	O(6′)	0.106 9(4)	−0.128 8(3)	0.747 1(3)
C(7)	0.398 4(6)	0.310 6(5)	0.127 0(4)	C(7′)	0.149 5(6)	0.244 6(5)	0.680 6(5)
C(8)	0.453 1(7)	0.318 7(6)	0.033 3(5)	C(8′)	0.192 3(7)	0.254 5(6)	0.583 9(5)
C(9)	0.569 4(8)	0.418 2(7)	0.043 2(6)	C(9′)	0.270 7(7)	0.368 9(6)	0.584 2(6)
C(10)	0.639 8(7)	0.508 8(6)	0.146 6(7)	C(10′)	0.307 4(7)	0.472 6(6)	0.681 1(6)
C(11)	0.586 5(7)	0.502 1(5)	0.240 6(6)	C(11′)	0.267 7(8)	0.463 4(6)	0.776 6(5)
C(12)	0.467 5(6)	0.404 3(5)	0.231 7(5)	C(12′)	0.186 4(7)	0.350 4(5)	0.776 0(5)
C(13)	0.142 3(6)	0.248 1(5)	0.166 3(5)	C(13′)	−0.086 0(6)	0.130 3(4)	0.718 3(4)
C(14)	0.068 7(7)	0.309 8(6)	0.112 8(6)	C(14′)	−0.183 1(6)	0.170 7(5)	0.657 7(4)
C(15)	−0.053 9(7)	0.347 2(7)	0.148 9(7)	C(15′)	−0.322 7(7)	0.175 0(5)	0.680 4(5)
C(16)	−0.098 1(7)	0.326 6(6)	0.240 7(6)	C(16′)	−0.365 9(7)	0.141 2(6)	0.767 7(5)
C(17)	−0.025 2(8)	0.268 3(7)	0.294 2(6)	C(17′)	−0.272 4(8)	0.101 3(6)	0.828 2(5)
C(18)	0.093 6(7)	0.228 2(6)	0.257 9(5)	C(18′)	−0.132 1(7)	0.096 2(6)	0.804 9(5)
C(19)	0.555 8(6)	−0.096 4(4)	−0.011 7(4)	C(19′)	0.165 4(7)	−0.234 1(5)	0.568 9(4)
C(20)	0.535 4(6)	−0.192 6(6)	−0.114 4(5)	C(20′)	0.129 8(6)	−0.337 9(5)	0.468 5(5)
C(21)	0.654 4(7)	−0.224 5(6)	−0.154 3(5)	C(21′)	0.241 5(7)	−0.368 3(6)	0.412 3(5)
C(22)	0.798 3(7)	−0.162 7(7)	−0.093 9(6)	C(22′)	0.386 1(8)	−0.298 4(7)	0.454 0(6)
C(23)	0.820 7(7)	−0.068 6(6)	0.008 3(5)	C(23′)	0.424 6(7)	−0.197 0(7)	0.553 6(6)
C(24)	0.699 7(6)	−0.035 6(5)	0.049 4(4)	C(24′)	0.312 8(6)	−0.165 5(6)	0.609 2(5)
C(25)	0.316 6(6)	−0.171 5(5)	0.044 9(4)	C(25′)	−0.068 5(6)	−0.316 1(5)	0.628 5(4)
C(26)	0.162 8(6)	−0.207 0(6)	0.010 0(5)	C(26′)	−0.218 6(7)	−0.354 2(5)	0.578 2(5)
C(27)	0.076 0(7)	−0.303 1(6)	0.030 0(7)	C(27′)	−0.315 7(7)	−0.454 6(6)	0.588 5(5)
C(28)	0.141 4(8)	−0.367 6(6)	0.082 8(7)	C(28′)	−0.261 5(8)	−0.517 7(6)	0.648 8(6)
C(29)	0.294 1(8)	−0.335 0(6)	0.117 7(6)	C(29′)	−0.111 8(9)	−0.482 9(6)	0.698 8(6)
C(30)	0.381 0(6)	−0.236 9(5)	0.100 5(5)	C(30′)	−0.016 3(7)	−0.383 2(5)	0.687 9(5)
O(31)	0.379 5(4)	0.173 4(3)	0.282 3(3)	O(31′)	−0.030 4(4)	0.015 5(3)	0.489 8(3)
C(32)	0.477 6(6)	0.111 5(5)	0.318 1(4)	C(32′)	−0.102 3(6)	−0.105 6(5)	0.408 8(4)
C(33)	0.609 9(7)	0.209 1(6)	0.403 2(5)	C(33′)	−0.013 6(7)	−0.139 1(6)	0.318 5(5)
C(34)	0.397 3(6)	0.020 1(6)	0.364 0(5)	C(34′)	−0.256 6(7)	−0.109 3(6)	0.362 8(5)
O(35)	0.526 0(4)	0.047 2(3)	0.220 5(3)	O(35′)	−0.102 5(4)	−0.187 7(3)	0.466 9(3)
H(1)	0.2537	0.0602	−0.0364	H(1′)	0.1621	0.1568	0.8534
H(6)	0.2491	−0.0994	−0.1192	H(6′)	0.1316	−0.0342	0.7580
(1b)							
O(1)	0.327 4(2)	0.417 3(2)	0.490 7(2)	C(20)	0.648 0(4)	0.253 6(4)	0.215 8(3)
C(2)	0.225 8(3)	0.296 1(3)	0.484 4(3)	C(21)	0.742 6(5)	0.202 2(5)	0.152 6(4)
C(3)	0.191 4(3)	0.237 8(3)	0.352 9(3)	C(22)	0.705 4(5)	0.145 5(4)	0.038 8(4)
C(4)	0.314 1(3)	0.204 8(3)	0.286 8(2)	C(23)	0.573 8(5)	0.140 2(4)	−0.012 0(3)
C(5)	0.412 7(3)	0.306 9(3)	0.236 7(3)	C(24)	0.478 7(4)	0.191 7(3)	0.050 0(3)
O(6)	0.501 6(2)	0.397 9(2)	0.333 9(2)	C(25)	0.337 1(4)	0.374 4(3)	0.167 0(3)
C(7)	0.097 4(3)	0.325 2(3)	0.540 6(3)	C(26)	0.412 3(4)	0.494 9(3)	0.161 4(3)
C(8)	−0.034 2(4)	0.312 9(3)	0.479 8(3)	C(27)	0.354 5(6)	0.558 7(4)	0.095 7(4)
C(9)	−0.141 0(4)	0.352 8(4)	0.536 1(3)	C(28)	0.220 2(7)	0.505 1(5)	0.034 2(4)
C(10)	−0.119 9(4)	0.405 2(4)	0.651 6(3)	C(29)	0.143 4(5)	0.386 4(4)	0.038 5(4)
C(11)	0.009 5(4)	0.417 7(4)	0.711 9(3)	C(30)	0.201 9(4)	0.321 7(3)	0.104 7(3)
C(12)	0.116 6(4)	0.377 0(4)	0.657 6(3)	O(31)	0.085 2(2)	0.118 4(2)	0.332 1(2)
C(13)	0.294 1(3)	0.216 4(3)	0.544 3(2)	C(32)	0.121 9(3)	0.027 3(3)	0.243 1(3)
C(14)	0.207 2(4)	0.111 3(3)	0.572 6(3)	C(33)	0.172 0(4)	−0.067 2(3)	0.293 2(3)
C(15)	0.267 0(4)	0.035 4(3)	0.622 9(3)	C(34)	−0.005 9(4)	−0.032 5(4)	0.152 3(3)
C(16)	0.414 4(4)	0.062 4(4)	0.647 2(3)	O(35)	0.235 3(2)	0.099 8(2)	0.195 6(2)
C(17)	0.501 8(4)	0.167 4(4)	0.620 4(3)	H(1)	0.3413	0.4749	0.5653
C(18)	0.441 9(4)	0.243 4(3)	0.569 3(3)	H(6)	0.4386	0.4195	0.3855
C(19)	0.515 2(3)	0.248 6(3)	0.165 3(3)				
(1c)							
O(1)	−0.023 5(2)	0.418 8(1)	−0.026 1(2)	C(20)	0.403 7(4)	0.409 1(2)	0.065 7(3)
C(2)	0.013 9(3)	0.358 0(2)	0.022 3(3)	C(21)	0.504 8(4)	0.369 6(2)	0.055 9(4)
C(3)	0.056 5(3)	0.362 1(2)	0.158 7(3)	C(22)	0.553 6(4)	0.326 6(2)	0.142 9(4)
C(4)	0.135 9(3)	0.418 7(2)	0.222 8(3)	C(23)	0.500 2(4)	0.321 8(2)	0.239 6(4)
C(5)	0.246 3(4)	0.452 3(2)	0.180 8(3)	C(24)	0.399 6(4)	0.361 6(2)	0.249 8(3)
O(6)	0.195 2(2)	0.482 5(1)	0.069 9(2)	C(25)	0.314 9(4)	0.502 2(2)	0.269 9(3)
C(7)	0.118 6(4)	0.329 7(2)	−0.033 6(3)	C(26)	0.285 3(4)	0.513 5(2)	0.376 6(4)
C(8)	0.129 3(4)	0.351 0(2)	−0.143 1(4)	C(27)	0.353 8(5)	0.557 7(3)	0.453 4(4)
C(9)	0.213 7(5)	0.324 0(3)	−0.201 7(4)	C(28)	0.452 1(5)	0.591 7(2)	0.423 3(5)
C(10)	0.290 8(5)	0.275 1(3)	−0.153 2(5)	C(29)	0.483 1(5)	0.580 5(2)	0.317 7(5)

Table 4 (*continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
(**1c**) – *continued*							
C(11)	0.283 6(4)	0.252 3(2)	−0.044 8(5)	C(30)	0.415 4(4)	0.536 2(2)	0.242 6(4)
C(12)	0.197 1(4)	0.279 8(2)	0.014 4(4)	O(31)	−0.055 9(2)	0.366 2(1)	0.207 5(2)
C(13)	−0.104 8(4)	0.314 7(2)	−0.012 9(3)	C(32)	−0.066 8(4)	0.427 5(2)	0.256 4(3)
C(14)	−0.110 9(4)	0.257 0(2)	0.040 8(3)	C(33)	−0.194 7(4)	0.457 4(2)	0.197 2(5)
C(15)	−0.216 9(4)	0.217 8(2)	0.005 0(4)	C(34)	−0.051 3(5)	0.420 1(2)	0.388 1(3)
C(16)	−0.319 6(4)	0.235 1(2)	−0.086 0(4)	O(35)	0.037 0(2)	0.462 7(1)	0.229 6(2)
C(17)	−0.314 1(4)	0.290 8(2)	−0.141 2(4)	H(1)	0.0581	0.4426	0.0097
C(18)	−0.207 6(4)	0.330 3(2)	−0.105 3(4)	H(6)	0.1638	0.5328	0.0686
C(19)	0.350 3(3)	0.405 7(2)	0.163 5(3)				
(**2**)							
O(1)	−0.014 8(8)	0.783 2(7)	0.189 6(3)	C(22)	0.188 3(8)	0.326 5(7)	0.112 7(3)
C(2)	0.008 0(12)	0.856 1(10)	0.140 8(4)	C(23)	0.166 1(8)	0.395 3(7)	0.065 5(3)
C(3)	0.010 6(12)	0.764 2(10)	0.092 4(5)	C(24)	0.066 8(8)	0.473 7(7)	0.064 2(3)
C(4)	−0.108 1(12)	0.689 0(11)	0.079 8(4)	C(25)	−0.231 0(8)	0.494 0(7)	0.088 3(3)
C(5)	−0.121 5(12)	0.567 1(10)	0.110 7(5)	C(26)	−0.230 4(8)	0.448 2(7)	0.034 5(3)
O(6)	−0.151 5(8)	0.595 0(6)	0.167 5(3)	C(27)	−0.331 3(8)	0.384 3(7)	0.014 9(3)
C(7)	0.124 9(6)	0.923 5(6)	0.146 8(3)	C(28)	−0.432 7(8)	0.366 3(7)	0.049 1(3)
C(8)	0.138 3(6)	0.988 0(6)	0.196 0(3)	C(29)	−0.433 3(8)	0.412 2(7)	0.102 9(3)
C(9)	0.245 1(6)	1.053 2(6)	0.205 6(3)	C(30)	−0.332 4(8)	0.476 0(7)	0.122 5(3)
C(10)	0.338 6(6)	1.053 9(6)	0.166 2(3)	O(31)	0.025 5(8)	0.824 8(6)	0.041 3(3)
C(11)	0.325 2(6)	0.989 4(6)	0.117 1(3)	C(32)	−0.051 1(11)	0.775 0(12)	−0.001 4(5)
C(12)	0.218 4(6)	0.924 2(6)	0.107 4(3)	C(33)	0.027 4(12)	0.744 1(11)	−0.048 5(4)
C(13)	−0.102 9(7)	0.938 4(7)	0.135 4(3)	C(34)	−0.149 2(12)	0.859 9(10)	−0.016 2(5)
C(14)	−0.087 9(7)	1.043 1(7)	0.104 7(3)	O(35)	−0.098 3(7)	0.669 5(6)	0.022 0(3)
C(15)	−0.187 3(7)	1.119 2(7)	0.096 1(3)	N(36)	0.164 4(15)	0.667 3(16)	0.236 0(7)
C(16)	−0.301 8(7)	1.090 7(7)	0.118 2(3)	C(37)	0.284 1(17)	0.642 9(16)	0.207 8(7)
C(17)	−0.316 8(7)	0.985 9(7)	0.148 9(3)	C(38)	0.364 9(17)	0.735 8(19)	0.232 7(9)
C(18)	−0.217 4(7)	0.909 8(7)	0.157 5(3)	C(39)	0.488 7(15)	0.723 7(17)	0.218 9(7)
C(19)	−0.010 3(8)	0.483 4(7)	0.110 1(3)	H(1)	0.0704	0.7632	0.2010
C(20)	0.011 9(8)	0.414 7(7)	0.157 3(3)	H(6)	−0.0895	0.6580	0.1814
C(21)	0.111 2(8)	0.336 2(7)	0.158 6(3)				
(**3**)							
O(1)	0.172 2(3)	0.1071	0.162 7(2)	O(1′)	0.334 5(3)	−0.007 0(3)	0.248 2(2)
C(2)	0.173 8(5)	0.204 7(4)	0.142 6(3)	C(2′)	0.364 5(5)	−0.102 3(4)	0.235 8(3)
C(3)	0.043 1(5)	0.230 4(4)	0.105 7(3)	C(3′)	0.436 8(5)	−0.136 0(4)	0.308 9(3)
C(4)	−0.043 4(5)	0.243 3(4)	0.148 5(3)	C(4′)	0.369 3(6)	−0.139 9(4)	0.363 4(3)
C(5)	−0.110 9(5)	0.154 9(4)	0.162 1(3)	C(5′)	0.364 2(6)	−0.049 5(4)	0.406 0(3)
O(6)	−0.022 0(3)	0.094 1(3)	0.203 8(2)	O(6′)	0.279 2(4)	0.013 2(3)	0.364 3(2)
C(7)	0.251 4(5)	0.207 5(4)	0.093 8(3)	C(7′)	0.441 3(5)	−0.101 3(4)	0.186 7(3)
C(8)	0.204 6(6)	0.193 9(5)	0.023 3(3)	C(8′)	0.396 1(6)	−0.050 4(5)	0.126 5(3)
C(9)	0.279 9(7)	0.191 4(6)	−0.018 3(4)	C(9′)	0.463 1(7)	−0.044 8(5)	0.078 6(3)
C(10)	0.401 0(7)	0.207 1(6)	0.007 3(5)	C(10′)	0.571 6(7)	−0.090 4(5)	0.090 2(4)
C(11)	0.448 1(7)	0.219 2(8)	0.078 4(5)	C(11′)	0.614 3(6)	−0.141 1(5)	0.151 1(4)
C(12)	0.370 6(6)	0.217 0(8)	0.117 0(4)	C(12′)	0.551 4(6)	−0.145 9(5)	0.198 6(4)
C(13)	0.223 5(5)	0.269 5(5)	0.203 7(3)	C(13′)	0.254 5(5)	−0.164 3(4)	0.207 8(3)
C(14)	0.240 8(7)	0.367 5(5)	0.193 3(4)	C(14′)	0.143 8(5)	−0.134 7(5)	0.212 2(3)
C(15)	0.287 0(8)	0.426 7(6)	0.246 9(4)	C(15′)	0.043 2(6)	−0.191 9(6)	0.187 4(4)
C(16)	0.317 6(8)	0.391 6(6)	0.314 2(4)	C(16′)	0.056 4(7)	−0.280 9(6)	0.157 4(4)
C(17)	0.303 8(7)	0.293 4(6)	0.324 2(4)	C(17′)	0.169 4(6)	−0.311 0(5)	0.154 0(4)
C(18)	0.254 4(7)	0.233 8(5)	0.268 8(3)	C(18′)	0.267 3(6)	−0.253 3(4)	0.178 9(3)
C(19)	−0.206 5(5)	0.176 3(4)	0.198 1(3)	C(19′)	0.310 7(7)	−0.077 0(5)	0.463 8(3)
C(20)	−0.215 8(6)	0.265 2(5)	0.227 4(3)	C(20′)	0.373 0(10)	−0.057 0(7)	0.532 0(4)
C(21)	−0.300 2(6)	0.279 5(5)	0.261 8(3)	C(21′)	0.315 2(12)	−0.079 9(8)	0.583 2(4)
C(22)	−0.376 2(6)	0.205 3(6)	0.268 8(3)	C(22′)	0.205 0(10)	−0.122 0(7)	0.567 9(5)
C(23)	−0.365 1(6)	0.118 3(5)	0.241 3(3)	C(23′)	0.150 4(9)	−0.149 1(9)	0.500 0(5)
C(24)	−0.280 7(5)	0.103 2(5)	0.206 3(3)	C(24′)	0.204 5(7)	−0.129 9(8)	0.450 4(4)
C(25)	−0.165 2(5)	0.100 3(4)	0.095 3(3)	C(25′)	0.484 0(6)	0.000 1(5)	0.431 0(3)
C(26)	−0.117 8(6)	0.014 7(5)	0.080 4(3)	C(26′)	0.490 9(9)	0.097 0(7)	0.419 4(4)
C(27)	−0.169 5(7)	−0.032 2(5)	0.019 2(4)	C(27′)	0.602 3(12)	0.145 1(10)	0.443 2(5)
C(28)	−0.264 4(6)	0.007 4(6)	−0.028 5(4)	C(28′)	0.701 3(12)	0.097 2(14)	0.477 2(6)
C(29)	−0.312 0(6)	0.095 5(6)	−0.014 4(3)	C(29′)	0.693 0(11)	0.002 8(11)	0.488 9(7)
C(30)	−0.263 5(5)	0.141 5(5)	0.046 6(3)	C(30′)	0.585 7(8)	−0.049 3(8)	0.467 1(5)
O(31)	0.042 4(3)	0.322 9(3)	0.075 5(2)	O(31′)	0.471 2(4)	−0.232 9(3)	0.305 2(2)
C(32)	−0.069 9(5)	0.364 3(5)	0.069 1(3)	C(32′)	0.475 4(7)	−0.278 9(5)	0.369 4(3)
C(33)	−0.049 5(8)	0.466 9(5)	0.093 2(5)	C(33′)	0.395 3(9)	−0.365 4(6)	0.354 3(4)

Table 4 (*continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
(3) – *continued*							
C(34)	−0.143 4(6)	0.352 4(8)	−0.006 0(4)	C(34′)	0.605 6(7)	−0.300 3(7)	0.407 3(4)
O(35)	−0.126 0(3)	0.312 3(3)	0.109 7(2)	O(35′)	0.431 5(4)	−0.211 0(3)	0.406 9(2)
N(36)	0.014 7(5)	0.087 9(4)	0.338 1(3)	N(36′)	0.231 0(11)	0.034 5(8)	−0.249 0(6)
C(37)	0.028 4(9)	0.186 2(7)	0.364 3(5)	C(37′)	0.348 1(14)	0.089 1(11)	−0.214 7(7)
C(38)	0.098 2(13)	0.182 7(11)	0.441 3(7)	C(38′)	0.446 3(13)	0.018 5(11)	−0.179 8(8)
C(39)	0.131 8(16)	0.289 9(13)	0.455 2(9)	C(39′)	0.411 5(11)	−0.028 9(9)	−0.120 6(6)
C(40)	−0.071 0(8)	0.028 1(6)	0.358 5(4)	C(40′)	0.141 1(15)	0.094 6(12)	−0.284 0(8)
C(41)	−0.089 2(8)	−0.066 0(7)	0.321 2(5)	C(41′)	0.017 8(19)	0.023 8(16)	−0.316 7(10)
C(42)	−0.177 4(11)	−0.128 5(8)	0.348 2(6)	C(42′)	−0.055 8(25)	0.117 5(21)	−0.349 9(14)
H(1)	0.1004	0.1009	0.1808	H(6′)	0.2813	0.0136	0.3177
(4)							
O(1)	0.228 3(6)	0.1601	0.117 0(5)	C(25)	−0.155 3(10)	0.320 7(6)	−0.037 8(9)
C(2)	0.195 1(10)	0.196 5(6)	0.222 4(7)	C(26)	−0.140 5(12)	0.394 6(7)	0.004 1(10)
C(3)	0.029 3(9)	0.210 3(6)	0.226 0(7)	C(27)	−0.213 4(14)	0.456 3(8)	−0.059 0(11)
C(4)	−0.034 9(9)	0.272 9(6)	0.146 7(7)	C(28)	−0.285 5(14)	0.441 7(8)	−0.158 6(11)
C(5)	−0.078 2(10)	0.250 6(5)	0.024 6(7)	C(29)	−0.299 8(14)	0.368 7(9)	−0.200 6(10)
O(6)	0.055 4(6)	0.237 3(4)	−0.031 7(5)	C(30)	−0.230 8(12)	0.307 7(7)	−0.138 6(9)
C(7)	0.248 5(11)	0.136 6(5)	0.314 1(8)	O(31)	−0.007 4(6)	0.235 2(4)	0.335 6(4)
C(8)	0.154 5(12)	0.089 0(6)	0.373 0(8)	C(32)	−0.137 4(11)	0.279 7(6)	0.326 2(9)
C(9)	0.209 3(13)	0.030 8(7)	0.444 0(8)	C(33)	−0.267 2(12)	0.233 5(8)	0.364 8(9)
C(10)	0.357 9(14)	0.019 5(7)	0.458 0(10)	C(34)	−0.116 9(13)	0.353 5(8)	0.389 7(10)
C(11)	0.451 8(11)	0.064 6(7)	0.401 1(9)	O(35)	−0.157 6(6)	0.295 5(4)	0.206 6(5)
C(12)	0.395 1(11)	0.122 0(6)	0.328 5(8)	N(36)	0.109 8(9)	0.240 2(6)	0.740 7(7)
C(13)	0.284 4(10)	0.270 5(6)	0.240 0(8)	C(37)	0.105 2(13)	0.318 9(8)	0.696 7(9)
C(14)	0.357 7(11)	0.302 2(7)	0.148 4(9)	C(38)	0.189 1(14)	0.375 7(8)	0.769 3(10)
C(15)	0.438 2(14)	0.368 3(8)	0.166 2(11)	C(39)	0.173 9(16)	0.456 8(9)	0.719 4(11)
C(16)	0.437 8(13)	0.406 3(7)	0.268 4(13)	C(40)	0.016 8(14)	0.190 3(8)	0.666 2(10)
C(17)	0.365 3(13)	0.375 7(8)	0.360 9(11)	C(41)	−0.003 7(16)	0.112 8(9)	0.697 1(10)
C(18)	0.289 3(11)	0.307 1(7)	0.343 3(9)	C(42)	−0.123 6(15)	0.071 3(9)	0.630 4(12)
C(19)	−0.178 5(10)	0.181 4(6)	0.019 8(7)	C(43)	0.260 8(13)	0.205 9(8)	0.764 2(10)
C(20)	−0.324 8(11)	0.185 7(7)	0.048 6(8)	C(44)	0.349 5(16)	0.203 2(8)	0.665 7(11)
C(21)	−0.413 1(11)	0.121 8(7)	0.043 9(9)	C(45)	0.496 9(17)	0.164 7(11)	0.697 0(15)
C(22)	−0.358 2(14)	0.051 9(8)	0.018 0(10)	H(1)	0.1785	0.1917	0.0642
C(23)	−0.216 3(14)	0.043 4(8)	−0.010 5(10)	H(6)	0.0755	0.2384	−0.1159
C(24)	−0.126 4(11)	0.107 7(6)	−0.006 3(8)				

recognition in other systems.[25,26] Since (**1**) is derived from a natural chiral source, it can also be used to resolve optically active enantiomers from a racemic guest mixture. The presence of an optically pure component (**1a**) in the clathrate will always generate a chiral lattice, thus providing an asymmetric environment for the complexing partner. The first example of an effective optical resolution of bicyclic enones through crystalline complexation with (**1a**) has already been reported.[10] More recently, (**1a**) has successfully been used to resolve enantiomers of tricyclic enone compounds as well.[27] The structural motifs in the solid phase and features of the intermolecular interaction have been characterized in this case and will be reported elsewhere. Other structural modifications of the tartaric acid derived host also exhibit inclusion behaviour, and can be suitable for molecular recognition of different guest species. The full potential of these ligands has not been fully exploited as yet, and efforts are under way to improve their molecular design for new and more sophisticated applications.[28]

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