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The Role of Chloro Substituents in Solid Inclusion Formation. Crystal Structures Formed by a Bulky Hydroxy Host with Ethyl Acetate (2:1) and Cyclohexylamine (1:2) as Guest

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Two inclusion compounds of the 11-[bis(*p*-chlorophenyl)hydroxymethyl]-9,10-dihydro-9,10-ethanoanthracene host (1) have been studied by X-ray diffraction in order to find an explanation of the exceptional clathrate formation ability of the present chloro-containing host as compared with that of closely related chlorine-free host analogues. Crystal data: 1·ethyl acetate (2:1), $C_{29}H_{22}OCl_2 \cdot 1/2(C_4H_8O_2)$, $M_w = 501.45$, $P2_1/c$, $a = 8.9060(5)$, $b = 11.1109(6)$, $c = 25.642(1)$ Å, $\beta = 99.03(1)°$, $Z = 4$, $R = 0.047$ for 2029 F values with $I > 2\sigma(I)$; 1·cyclohexylamine (1:2), $2[C_{29}H_{22}OCl_2 \cdot 2(C_6H_{13}N)]$, $M_w = 1311.50$, Pc, $a = 12.144(2)$, $b = 12.689(3)$, $c = 23.119(8)$ Å, $\beta = 91.68(1)°$, $Z = 2$, $R = 0.054$ for 3073 F values with $I > 2\sigma(I)$. Although the two solid inclusion compounds differ in host–guest stoichiometry, space group symmetry and also in host–guest recognition mode, both co-crystals are held together by numerous C—H···X (X = O, N or Cl) interactions, in which the chloro-substituents of 1 play a very active role. The observed frequent participation of chlorine in intermolecular interactions in these compounds suggests an ability of the (C—)Cl substituents to effectively enhance the crystal formation in the absence of more dominant forces.

Keywords: Crystalline host–guest complexes, hydroxy host, ethyl acetate and cyclohexylamine guests, C—H···Cl interaction, X-ray diffraction

INTRODUCTION

Non-covalent interactions are the central theme of supramolecular chemistry [1], with hydrogen bonding being the most important intermolecular force [2]. Conventional O—H···O and N—H···O hydrogen bonds have widely been used to create supramolecular assemblies [3–5]. On the other hand, unconventional, weak hydrogen bonds like C—H···O have also been recognized as significant secondary interactions [6]. Moreover, halogen atoms covalently bonded to carbon are also known to form weak contacts to hydrogen, nitrogen, oxygen, sulfur and also to other halogens [7]. Although weak in nature, all these contacts may play dominant roles in

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determining the crystal packing [7, 8] and in stabilization of inclusion crystals [9], thus being valuable tools in the engineering and formation of crystalline supramolecular complexes [10, 11].

Related to this work, we recently reported on remarkable Cl $\cdots \pi$ interactions formed by *trans*-11,12-bis[bis-*p*-chlorophenyl)hydroxymethyl]-9,10-dihydro-9,10-ethanoanthracene in its inclusion complexes with guests of varying polarity and proton acceptor ability [12]. Lowering both the number of hydroxy groups and chloro sites, such as verified in compound **1**, invites comparison with both the mentioned higher derivative of compound **1** and, even more, with its chlorine-free analogue, 11-(diphenylhydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene which show only modest inclusion ability [13].

Here we report the structures of two crystalline complexes of host compound **1**, namely **1**·ethyl acetate (2:1) and **1**·cyclohexylamine (1:2), elucidating the raised questions.

EXPERIMENTAL

Sample Preparation

The host compound **1**, synthesized as described earlier [13], was dissolved in a minimum amount of the respective guest solvent under heating. The crystals were formed when the solutions were allowed to cool slowly. The selected single crystals were coated with epoxy glue in order to prevent solvent evaporation during the X-ray diffraction studies.

X-ray Data Collection, Structure Analysis and Refinement

The net intensities, collected using a STOE/AED2 diffractometer (equipped with a graphite monochromator) and the $\omega-2\theta$ scan method, were corrected for background, crystal deterioration, Lorentz and polarization effects, and in case of the **1**·ethyl acetate (2:1) complex also

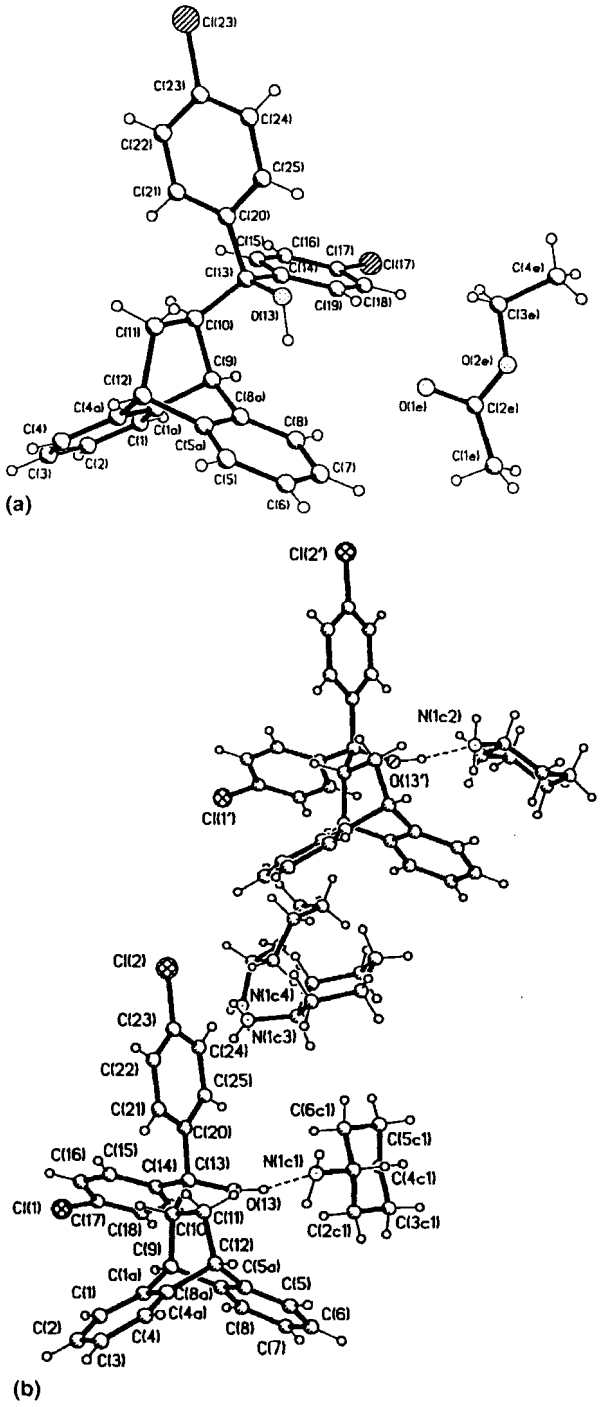

FIGURE 1 Perspective view of the stoichiometric units of (a) **1**·ethyl acetate (2:1) and (b) **1**·cyclohexylamine (1:2) inclusion compounds, showing the crystallographic labeling of the non-hydrogen atoms. Only one of the two disorder positions of the ethyl acetate guest is depicted in (a). Dashed lines represent 'ordinary' (O)H $\cdots$ N hydrogen bond interactions.

for absorption effects. The applied empirical absorption corrections were based on ψ scans of five reflections with high χ values ($72 < \chi < 80°$) and various 2θ angles ($11 < 2\theta < 64°$). The transmission factors ranged between 0.46 and 0.61. Furthermore, it was noted that crystals of the 1·cyclohexylamine (1:2) complex were rather unstable in air despite the protecting film of epoxy glue. Interestingly enough, lowering the temperature from 293 to 173 K accelerated the decrease of the reflection intensities over time. Following some simple tests, a temperature somewhat below room temperature (253 K) was chosen for the data collection. Despite these efforts, significant intensity decrease was indicated by the repeatedly measured test reflections during the data collection for the 1·cyclohexylamine (1:2) compound (Tab. I).

TABLE I Crystal data, experimental parameters and selected details of the refinement calculations of compounds 1·ethyl acetate (2:1) and 1·cyclohexylamine (1:2). (Esd's, where given, are in parentheses)

Compound	1·ethyl acetate(2:1)	1·cyclohexylamine(1:2)
Formula unit	$C_{29}H_{22}OCl_2 \cdot 1/2(C_4H_8O_2)$	$2[C_{29}H_{22}OCl_2 \cdot 2(C_6H_{13}N)]$
Formula weight	501.45	1311.50
Crystal shape/colour	long-shaped/colourless	long-shaped/colourless
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	Pc (No. 7)
Unit cell dimensions		
a, Å	8.906(1)	12.144(2)
b, Å	11.111(1)	12.689(3)
c, Å	25.642(1)	23.119(8)
β,deg	99.03(1)	91.68(1)
V_c, Å^3	2505.9(2)	3561(2)
No. of θ values used in the refinement of the cell dimensions within the 2θ limits,deg	55 20–50	44 10–42
Z	4	2
F(000)	1048	1400
D_c, Mg m^{-3}	1.329	1.223
μ, cm^{-1}	25.4	2.17
Data collection:		
Radiation/λ,Å	Cu$K\alpha$/1.54183	Mo$K\alpha$/0.71073
Temperature,K	293 ± 1	253 ± 1
Approximate crystal size,mm	0.47·0.13·0.28	0.56·0.26·0.41
No. of collected reflections within the θ limit,deg	4381 1–70	6672 1–26
Index ranges	$-9 \le h \le 9, 0 \le k \le 13, 0 \le l \le 31$	$-12 \le h \le 14, 0 \le k \le 15, 0 \le l \le 27$
No. of unique reflections	4381	6117
R_{int}	–	0.1040
No. of standard reflections	5	5
Time interval between the standards,min	90	90
Intensity instability	<2%	<20%
Refinement calculations:full-matrix least-squares based on all F^2 values [a]		
No. of refined parameters	333	833
Final R indices		
$R(=\Sigma\|\Delta F\|/\Sigma\|F_o\|)$	0.047	0.054
No. of F values used $[I > 2\sigma(I)]$	2029	3073
wR^a on F^2	0.152	0.181
S(=Goodness of fit on F^2)	1.032	1.035
Final $\Delta\rho_{max}/\Delta\rho_{min}$, e$^-$ Å^{-3}	0.24/ −0.30	0.26/ −0.26

[a] Using the SHELXL-93 program [15]. The weights of the structure factors were assumed as $w = [\sigma^2(F_o^2) + (0.065 \cdot P)^2 + 0.53 \cdot P]^{-1}$ for 1·ethyl acetate (2:1) and $w = [\sigma^2(F_o^2) + (0.10 \cdot P)^2 + 0.55 \cdot P]^{-1}$ for 1·cyclohexylamine (1:2), where $P = (F_o^2 + 2F_c^2)/3$ in both cases.

Direct methods (SHELXS [14]) yielded reasonable starting models comprising the Cl, C and O atoms of the host molecules and fragments of the guests. Difference electron density ($\Delta\rho$) calculations [15] were used to discern the skeleton of the disordered ethyl acetate molecule and to find some missing C positions of the cyclohexylamine guests. The hydroxy H atoms of the hosts in both compounds and the amine hydrogens linked to N(1C1) and N(1C2) in the cyclohexylamine complex [Fig. 1(b)] were also derived from $\Delta\rho$ maps, and were then held riding on their parent O and N atoms during the subsequent calculations. All the other H atoms [the carbon bonded ones in both compounds as well as the amine hydrogens of N(1C3) and N(1C4)] were assumed to be in idealized positions, which were recalculated after each refinement cycle using geometric evidence, and by taking into account the effects of the crystallographic environment and the temperature [15].

The ethyl acetate guest in the **1**·ethyl acetate (2:1) complex occurs in two partly overlapping positions, each with 50% occupancy due to the space group symmetry requirements. The disorder models, having the O(2E) atom (at 1/2,0,0) in common, are centrosymmetrically related. Proximity of the disorder positions belonging to different molecular sites complicated the refinement.

The systematic absences in the diffraction pattern of the **1**·cyclohexylamine (2:1) compound suggested $P2/c$ or Pc as possible space group symmetries for the monoclinic unit cell, which contained four host and eight guest molecules. The solution and refinement of the structure proved the non-centric space group (Pc), indicated also by the intensity statistics. Hence, the crystallographic asymmetric unit of the cyclohexylamine complex contains two host and four guest molecules, yielding 184 independent atom positions (108 non-H and 76 H positions) for that structure. The Flack x parameter, estimated and refined using the SHELXL-93 program [15], yielded the value −0.11(10), thus indicating that the handedness of the studied crystal (*cf.* Fig. 1) was most likely correctly assigned.

In the last stage of the refinement, the non-hydrogen atoms with full site occupancy were allowed to vibrate anisotropically, whereas the C and O disorder sites of the ethyl acetate guest were refined with isotropic displacement parameters. Isotropic vibrational parameters were used also for the hydrogen atoms: individual ones were refined for the host H positions in the **1**·ethyl acetate (2:1) complex and for those derived from $\Delta\rho$ maps in the **1**·cyclohexylamine (1:2) compound; one common parameter was refined for the H disorder sites in the ethyl acetate guest; whereas fixed isotropic displacement parameters (1.2 times the U_{eq} of the parent atom) were given to the calculated positions in the **1**·cyclohexylamine (1:2) complex, in order to restrict the number of parameters to be refined for this latter structure.

Crystal data, details of the diffraction experiments and the refinement calculations are shown in Table I. The final atomic coordinates of the non-hydrogen atoms together with their equivalent isotropic/isotropic displacement parameters (U_{eq}/U_{iso}) are available from the author.

RESULTS AND DISCUSSION

Perspective views of the unique structural units of the inclusion compounds **1**·ethyl acetate (2:1) and **1**·cyclohexylamine (1:2) are depicted in Figures 1(a) and (b), respectively. Packing relations are illustrated in Figures 2 and 3. Selected conformation features of host **1** and geometric parameters of possible intermolecular interactions are listed in Tables II and III, respectively.

Molecular Structures

Despite the different guest recognition modes and the potential rotational freedom of the bulky diarylmethanol substituent, the observed host geometries in the ethyl acetate and cyclohexyla-

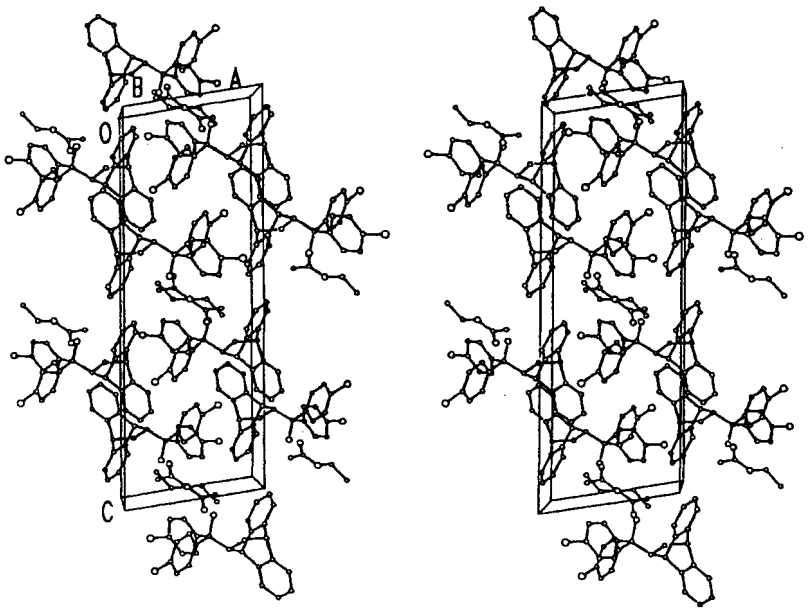

FIGURE 2 Stereo illustration of the crystal structure of 1·ethyl acetate (2:1), showing both disorder positions of the guest molecule. The hydrogens are omitted for clarity.

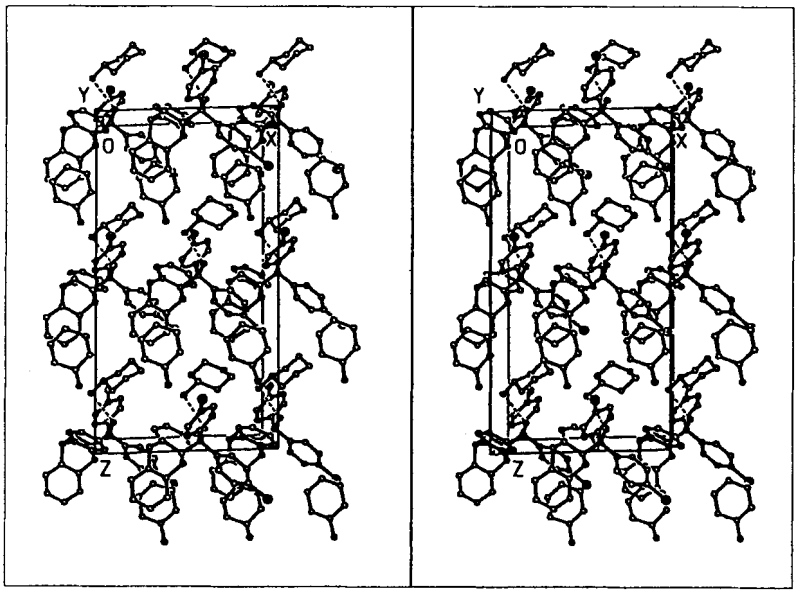

FIGURE 3 Stereo packing diagram of 1·cyclohexylamine (1:2). The hydrogens are omitted for clarity; the chloro substituents are hatched; dashed lines represent the O(H)···N hydrogen bond connections within the 1:1 host–guest associates.

mine inclusion compounds (three independent molecules) indicate limited flexibility for the host molecule (Tab. II). The conformation of 1 resembles also that of the related chlorine-free host [16] and may be compared with the structure of the analogous fluorine-containing molecule [16] and the corresponding tetrachloro-substituted diol host [12] as well. Thus, the

TABLE II Selected conformation parameters of host **1** in its inclusion compounds with ethyl acetate (2:1) and cyclohexylamine (1:2) as guests

Compounds	**1**·ethyl acetate (2:1)	**1**·cyclohexylamine (1:2)	
		Unprimed molecules	Primed molecules
Selected torsion angles/deg			
C(1a)–C(9)–C(10)–C(13)	−172.4(3)	−167.2(6)	−165.1(7)
C(8a)–C(9)–C(10)–C(13)	72.4(3)	78.7(7)	81.5(7)
C(13)–C(10)–C(11)–C(12)	−131.5(3)	−136.3(6)	−138.2(6)
C(9)–C(10)–C(13)–C(14)	53.6(4)	57.0(7)	59.0(8)
C(9)–C(10)–C(13)–C(20)	173.4(3)	173.3(6)	178.2(6)
C(9)–C(10)–C(13)–C(13)	−69.2(4)	−60.7(8)	−58.0(8)
C(11)–C(10)–C(13)–C(14)	178.2(3)	−178.8(6)	−175.2(6)
C(11)–C(10)–C(13)–C(20)	−61.9(4)	−62.4(8)	−56.1(8)
C(11)–C(10)–C(13)–O(13)	55.4(4)	63.6(8)	67.7(8)
O(13)–C(13)–C(14)–C(15)	−177.8(3)	−172.6(6)	−172.3(6)
O(13)–C(13)–C(20)–C(21)	−154.7(3)	−142.2(7)	−146.5(7)
Dihedral angles between the phenyl ring planes/deg			
ring C(1a)···C(4a)/ring C(5a)···C(8a)	127.0(1)	119.4(2)	120.0(2)
ring C(1a)···C(4a)/ring C(14)···C(19)	136.3(1)	126.8(2)	126.2(2)
ring C(1a)···C(4a)/ring C(20)···C(25)	79.3(1)	74.0(2)	68.9(2)
ring C(5a)···C(8a)/ring C(14)···C(19)	9.4(1)	13.2(2)	11.5(2)
ring C(5a)···C(8a)/ring C(20)···C(25)	97.9(1)	102.1(2)	95.2(2)
ring C(14)···C(19)/ring C(20)···C(25)	99.1(1)	90.9(2)	96.2(2)

dihydroethanoanthracene moiety has the usual roof shape with an average dihedral angle of 122[3]° between the two phenyl rings (calculated for the three independent molecules of **1**, with the r.m.s. deviation given in angular brackets). The C—C bonds forming the ethano bridge together with the C(9)—C(13) bond, which links the bulky diarylmethanol group to the bridge, are slightly elongated. The distances, ranging from 1.536(4) to 1.576(10) with a mean value of 1.56[1] Å, indicate, however, less strain in the monomethanol than in the corresponding diol analogue [12]. The C—Cl bond lengths vary from 1.723(9) to 1.746(5), the average value is 1.736[8] Å. The Cl(17) and Cl(23) atoms in the ethyl acetate complex are 0.045(1) and 0.150(1) Å out of the plane of the phenyl ring they are linked to, respectively, possibly due to the weak but directional $Cl(17)\cdots Cl(23)_{x,y-1,z}$ interaction [$Cl\cdots Cl = 3.861(2)$ Å, $< C—Cl(17)\cdots Cl = 99.0(2)$ and $< Cl\cdots Cl(23)—C = 107.7(2)°$]. No similar halogen–halogen connection was observed in the **1**·cyclohexylamine (1:2) compound, where the corresponding chloro substituents are all coplanar within 0.025 Å with the respective aryl ring planes.

Host **1** establishes hydrogen bond interaction to the cyclohexylamine guest, but not to the ethyl acetate. Instead, in the **1**·ethyl acetate (2:1) compound the host alcoholic function is directed toward the ethanoanthracene moiety within the same molecule, indicating a possible weak $O(H)\cdots\pi$ interaction with the nearest aryl π electrons (Tab. III). The OH group lies above the periphery of the π-cloud [$O(13)\cdots C(8a) = 2.970(4)$, $H(13)\cdots C(8a) = 2.16$ Å, $< O(13)—H(13)\cdots C(8a) = 137°$], with a distance of 2.968(2) Å between the O(13) atom and the least-squares (LS) plane of the ring, in agreement with our earlier observations in related hydroxy hosts exhibiting the so called 'inactive' conformation [12]. We noted, however, that despite the different engagement of the host alcoholic functions, the oxygens in the cyclohexylamine complex have similar locations relative to the respective anthracene moieties [$O(13)\cdots C(8a) =$

TABLE III Distances (Å) and angles (°) in possible hydrogen bond interactions and selected[a] intermolecular contact distances (Å)

Atoms involved	Symmetry	Distances			Angle
		Donor···Acceptor	D-H	H···A	<D-H···A
1·ethyl acetate (2:1)					
O(13)–H(13)···*centroid*$_{(2)}$[b]	x, y, z	3.403(3)	1.00	2.47	156
C(8)–H(8)···O(1E)	x, y, z	3.557(8)	0.93	2.86	133
C(18)–H(18)···O(1E)	x, y, z	3.208(9)	0.93	2.76	111
C(19)–H(19)···O(1E)	x, y, z	3.161(9)	0.93	2.66	114
C(7)–H(7)···Cl(23)	$-x+1, y-1, z$	3.968(5)	0.93	3.33	128
C(10)–H(10)···Cl(17)	$-x+1, y+0.5, -z+0.5$	3.844(4)	0.98	2.90	162
C(15)–H(15)···Cl(17)	$-x+1, y+0.5, -z+0.5$	4.087(5)	0.93	3.27	147
C(18)–H(18)···Cl(23)	$x, y-1, z$	4.017(6)	0.93	3.16	154
C(25)–H(25)···O(13)	$-x+1, -y+1, -z$	3.426(5)	0.93	2.65	142
C(1E)–H(E1A)···Cl(23)	$-x+1, -y+1, -z$	3.89(1)	0.96	3.25	126
C(3E)–H(E3B)···Cl(23)	$x, y-1, z$	3.57(1)	0.97	2.84	132
C(4E)–H(E4B)···Cl(23)	$x, y-1, z$	3.92(1)	0.96	3.29	125
C(4E)–H(E4A)···Cl(23)	$-x, -y+1, -z$	3.98(1)	0.96	3.45	117
1·cyclohexylamine (1:2)					
O(13)–H(13)···N(1C1)	x, y, z	2.80(2)	0.94	1.89	163
O(13′)–H(13′)···N(1C2)	x, y, z	2.76(1)	0.95	1.82	171
C(24)–H(24)···N(1C3)	x, y, z	3.55(1)	0.93	2.74	146
C(3)–H(3)···Cl(1)	$x-1, y, z$	3.555(9)	0.93	3.02	118
C(4)–H(4)···Cl(1)	$x-1, y, z$	3.734(8)	0.93	3.34	108
C(15′)–H(15′)···Cl(1)	$x, -y+1, z-0.5$	3.762(8)	0.93	3.07	133
C(4C1)–H(421)···Cl(1)	$x, -y+2, z-(0.5)$	3.91(1)	0.93	3.34	108
C(5C1)–H(511)···Cl(1)	$x, -y+2, z-0.5$	3.96(1)	0.97	3.45	115
C(3C2)–H(322)···Cl(1)	$x, y, z-1$	3.54(1)	0.97	2.93	122
C(6)–H(6)···Cl(2)	$x, y+1, z$	3.942(9)	0.93	3.39	120
C(7)–H(7)···Cl(2)	$x, y+1, z$	3.988(8)	0.93	3.46	118
C(2C1)–H(222)···Cl(2)	$x, y+1, z$	3.806(9)	0.97	3.21	121
C(3C1)–H(321)···Cl(2)	$x, y+1, z$	3.50(1)	0.97	2.91	120
C(5C2)–H(512)···Cl(2)	$x+1, y+1, z-0.5$	4.05(1)	0.97	3.21	145
C(15)–H(15)···Cl(1′)	$x-1, -y+1, z+0.5$	3.812(8)	0.93	3.15	130
C(3C1)–H(311)···Cl(1′)	$x+1, y+1, z$	4.11(1)	0.97	3.17	162
C(3′)–H(3′)···Cl(1′)	$x-1, y, z$	3.607(9)	0.93	3.00	125
C(4′)–H(4′)···Cl(1′)	$x-1, y, z$	3.884(9)	0.93	3.54	105
C(4C2)–H(422)···Cl(1′)	$x, -y+1, z-0.5$	3.97(1)	0.97	3.16	142
C(2C2)–H(212)···Cl(2′)	$x, y+1, z$	3.88(1)	0.97	3.20	129
C(3C2)–H(322)···Cl(2′)	$x, y+1, z$	3.69(1)	0.97	3.07	123
C(4C2)–H(412)···Cl(2′)	$x, y+1, z$	3.86(1)	0.97	3.17	129
N(1C2)–H(122)···N(1C3)	$x, -y+1, z-0.5$	3.58(2)	0.90	2.72	159
N(1C1)–H(121)···N(1C4)	$x+1, y, z$	3.61(2)	0.88	2.94	135

Atoms	Symmetry	Distance	Atoms	Symmetry	Distance
1·ethyl acetate (2:1)					
C(1a)···C1(17)	$-x+1, y+0.5, -z+0.5$	3.793(4)	C(4)···C(15)	$x+1, y, z$	3.553(6)
C(1)···Cl(17)	$-x+1, y+0.5, -z+0.5$	3.525(4)	C(4a)···C(16)	$x+1, y, z$	3.577(5)
C(2)···Cl(17)	$-x+1, y+0.5, -z+0.5$	3.868(5)	C(4)···C(16)	$x+1, y, z$	3.519(6)
C(8)···Cl(17)	$x+1, y, z$	3.772(4)	C(6)···C(18)	$x+1, y, z$	3.595(6)
C(7)···Cl(23)	$x+1, y-1, z$	3.968(5)	C(24)···C(3E)	$-x+1, -y+1, -z$	3.58(1)
C(2E)···Cl(23)	$-x+1, -y+1-z$	3.83(1)			
C(2E)···Cl(23)	$x, y-1, z$	3.85(1)			
1·cyclohexylamine (1:2)					
C(4)···C(16′)	$x-1, -y+1, z+0.5$	3.58(1)	C(4′)···C(16)	$x, -y+1, z-0.5$	3.60(1)
C(18)···C(21′)	$x, -y+1, z+0.5$	3.57(1)	C(18′)···C(21)	$x+1, -y+1, z-0.5$	3.53(1)
C(23)···N(1C4)	$x-1, y, z$	3.52(1)	C(24′)···N(1C4)	$x, -y+1, z-0.5$	3.58(1)
C(24)···N(1C4)	$x-1, y, z$	3.59(1)			

[a] Distances with C/N/O···C < 3.6 Å and C/N/O···Cl < 4 Å are listed.
[b] *Centroid*$_{(2)}$′ means the center of the C(5a)···C(8a) phenyl ring.

2.991(9)/2.983(9) Å, and the distances between the O(H) atom and the corresponding LS ring plane are 2.850(6)/2.795(6) Å in the unprimed/primed molecules, respectively]. It is worth mentioning that in the dioxane inclusion compound of the *trans*-11,12-bis[bis(*p*-chlorophenyl)methyl]-substituted diol host [12] one of the OH groups [O(13)H] is H-bonded to one guest, but not the other [O(26)H]. Despite the different orientations of the O—H bonds, the two oxygens are located similarly above the periphery of the nearest phenyl ring of the dihydroanthracene skeleton [the shortest $O\cdots C_{aryl}$ distances are 2.895(4)/2.990(4) Å, and the O(13)/O(26) atoms are 2.892(2)/2.959(2) Å above the corresponding nearest aryl ring plane, respectively]. It seems likely that the observed shorter $O\cdots C_{aryl}$ or $O\cdots\pi_{aryl}$ distances are just connections and not bonds, and the molecular conformation as well as the alcoholic O position(s) within these roof-shaped mono- or diol-hosts are determined by other than the possible $O(H)\cdots\pi$ interaction forces.

The guest molecules show the expected geometries. Accordingly, each cyclohexyl ring exhibits a more or less distorted 'chair' shape with the amine group in equatorial position. The mean values of the puckering parameters (following Cremer and Pople [17]), calculated for the four crystallographically independent guest molecules using the PARST program [18], are $q_2 = 0.02[1]$ Å, $\phi_2 = 16[6]°$, $q_3 = 0.53[3]$ Å, $Q_T = 0.53[3]$ Å, and $\theta_2 = 2[2]°$. For an ideal chair conformation one should observe: $\theta_2 = 0$ or 180°, $q_2 = 0$ Å, $\phi_2 = 0°$ and $q_3 = Q_T$. The mean value of the N—C—C—C torsion angles (τ), calculated [18, 19], for all four molecules, is 173[4]°. We noted, however, that τ has somewhat higher values for the amine groups involved in H-bonds with the host (average for N(1) and N(2) is 177[2]°) than for the other ones (average τ for N(3) and N(4) is 170[3]°).

The ethyl acetate guest, on the other hand, occupies two partly overlapping, centrosymmetrically related disorder positions. The displacement parameters of this latter guest (the mean U_{iso} value of the O and C disorder sites is 0.096[2] Å[2]) indicate rather high mobility, and the observed host–guest contact distances suggest modest fixation. Hence, the refinement calculations yielded a geometry with rather high uncertainty for the ethyl molecule.

Packing Relations

Although host **1** is equipped with an OH group, known to be a good proton donor and an acceptor as well [2], recent X-ray studies of inclusion compounds of mono-substituted diarylmethanol-containing roof-shaped hosts [16] suggest that these hosts rarely function as proton donors in 'ordinary' (O—H···O/N) hydrogen bonds to the guest or to other host molecules. Instead, the guests are frequently included in the crystals by weaker intermolecular bonds or by lattice forces only. Such is the case in the present **1**·ethyl acetate (2:1) complex (Tab. III and Fig. 2), and also in those of closely related chlorine-free or fluorine-containing hosts formed with acetone (2:1) and toluene (1:1) as guest, respectively [16]. Nevertheless, in the case of the **1**·cyclohexylamine (1:2) compound, each host establishes an O—H···N bond to a guest, but the crystal contains also additional guests, which are trapped by weaker bonds and/or by lattice forces (Tab. III and Fig. 3).

The packing arrangements in the four crystals of monomethanol hosts (*cf.* above), studied by X-ray diffraction, resemble each other by containing layer-like arrangements of the bulky host molecules, with the alcoholic oxygens directed toward the surface of the layers. In the case of the cyclohexylamine complex, however, the layers consist of hydrogen bonded host–guest (1:1) units. The weakly bonded guests, on the other hand, are usually trapped in the voids between the host (or host–guest) layers.

required in the solution equilibrium models [10], but were not detected in the ESI-MS spectra at any level of protonation. The cation complexes observed previously are relatively weak, and the solutions are dilute, so the extent of complex formation is very low. Using the known formation constants, it can be calculated [17] that less than 1% of any cation is bound, and less than 10% of the total ligand is involved in cation complexes. The *ratios* of the concentrations of complexes of $\{A+M\}^-$ stoichiometry, normalised to the K^+ complex, are given in the final column of Table I. If ESI-MS probes solution speciation then these ratios should directly relate to the observed intensities of the individual ions (not corrected for solution composition) on the assumption that complex protonation affects complex stability in a linear way across the series of cations. The agreement is poor. This may simply reflect the accumulated errors of comparing different ions under different solvent conditions. As developed below, it more probably indicates an inherent difference between ESI-MS ion intensities and solution chemistry.

A similar experiment using mixed alkaline earth chlorides and H_2A is illustrated in Figure 2 and summarised in Table II. Although the spectrum is substantially more complex, all observed ions can be assigned. The charge of the ion can be deduced from the mass separations of the isotope peaks: monocations ions give unit mass isotope sequences, dications give half integral spacing, and so on. The insets to Figure 2 illustrate this point. Thereafter, calculated masses for various stoichiometries can be compared with the observed masses, and ion charge states can be confirmed *via* comparison of calculated and observed isotope distribution patterns. The dominant solution species calculated using only known stability constants [10] and the concentration and pH of the experiment are the neutral (unobservable by MS) mononuclear complexes $\{A+Sr\}^0$ and $\{A+Ba\}^0$. The deprotonated 1:2 complexes $\{A+2Ba\}^{2+}$ and

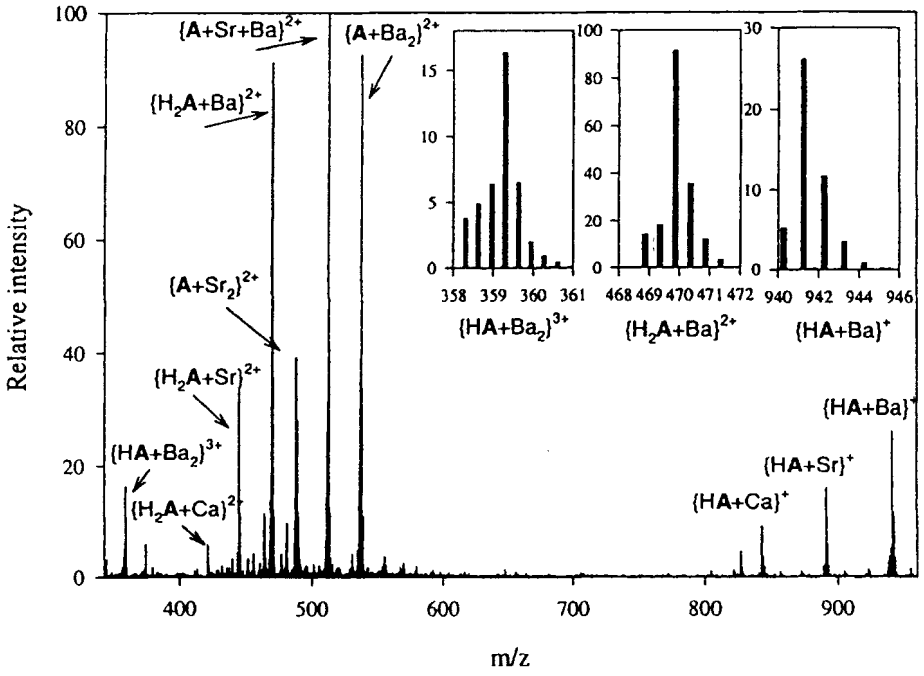

FIGURE 2 ESI-MS spectrum of H_2A and mixed alkaline earth cations. Inset: expansion showing mass separation of isotope peaks for various charge states. Concentrations are given in the footnote to Table II.

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