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Synthesis and Crystalline Inclusion Behavior of New Dumb-Bell-Shaped Hosts

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New host molecules, 1(a, b) and 2(a, b), each containing two bulky borneol or fenchol terminal groups attached to ethynylene central units of different lengths, have been synthesized. Their properties of crystalline inclusion with a variety of organic guests, including alcohols, amines and dipolar aprotic compounds, are reported (26 examples of inclusion compounds). The crystal structures of four selected inclusion compounds have been determined by X-ray diffraction, showing varied modes of supramolecular interaction dependent on the host and guest constitutions. Varying stoichiometries, host–guest compositions and appearance of disorder all indicate match/mismatch phenomena in the molecular recognition process under the build-up of macroscopic crystals. All these crystalline associations are organized through the hydrogen bonding capability of the host hydroxyl groups, thus corresponding to coordinato-clathrate scenery.

Keywords: Inclusion hosts; Organic guests; Crystalline inclusion compounds; H-bonding; X-ray crystal structure determinations

INTRODUCTION

Molecules having a structure that prevents close packing in the crystal are interesting targets in the formation of crystalline inclusion compounds [1–3]. This idea has given rise to a variety of molecular constructions all suited to act as crystalline hosts [4]. Representative examples feature a wheel-and-axle [5], a scissor-type [6] or a roof-shaped design [7]. Recently, we have shown that certain dumb-bell-shaped molecules (cf. sketch in Scheme 1), produced from a linear oligoalkyne central spacer with bulky and quasi spherical adamantyl moieties attached to the termini, may give rise to a promising new class of crystalline inclusion hosts, e.g. capable of building up crystalline channels wherein guest molecules are aligned [8]. Being pure hydrocarbons, these prototypical compounds of the dumb-bell-shaped host type are non-polar and highly symmetric in structure. On the other hand, the presence of hydroxyl groups in the framework of host molecules has proven a general advantage [9,10]. Thus, hydroxyl group-containing models of host compounds amalgamating the two design concepts appear an auspicious challenge. The first examples have been realized in compounds **1**(**a**, **b**) and **2**(**a**, **b**) (Scheme 1) reported in this paper.

Herein we report the synthesis of the new compounds, discuss their crystalline inclusion properties and describe the crystal structures of four inclusion compounds formed of **1a** [**1a**·H_2O (3:2), **1a**·DMF·H_2O (1:1:1)] and **2a** [**2a**·DMSO (2:3), **2a**·Et_2NH (1:2)] in detail.

RESULTS AND DISCUSSION

Synthesis

The host compounds **1a** and **1b** (Scheme 1) were prepared from camphor (**3a**) or fenchone (**3b**) with the lithium acetylide–ethylenediamine complex [11,12] in benzene in 36 and 12% yields, respectively (Scheme 2). The host compounds **2a** and **2b** (Scheme 1) were synthesized in 93 or 83% yield from ethynylated borneol and fenchol derivatives **4a** and **4b**, respectively, by using an Eglinton coupling

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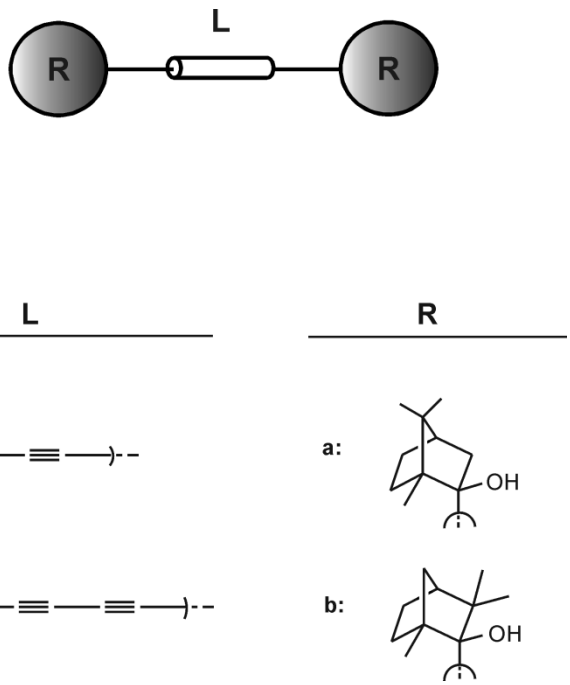
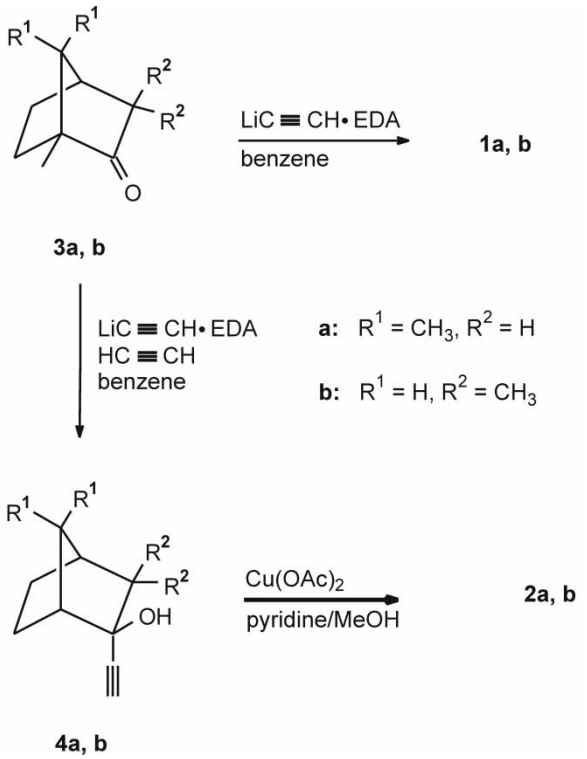


SCHEME 1 Host compounds studied in this paper.

reaction [13] with copper(II) acetate in pyridine/methanol. The ethynylated borneol and fenchol intermediates **4a** and **4b** were obtained from **3a** or **3b** with the lithium acetylide–ethylenediamine complex and ethyne in benzene in 90 or 85% yields [14], as shown in Scheme 2.



SCHEME 2 Synthesis of host compounds.

The inclusion compounds were prepared by recrystallization of the host compound from the respective guest solvent. The drying conditions specified in the experimental section (1 h, 15 Torr, room temperature) refer to what we consider a "stable clathrate" [15].

Inclusion Properties

In order to study the inclusion behavior of the potential host compounds **1**(**a**, **b**) and **2**(**a**, **b**), a rather broad variety of solvents including alcohols, amines, ketones, nitriles, nitro compounds and heterocycles of different constitutions (cf. Table I) were used for

TABLE I Crystalline inclusion compounds (host:guest stoichiometric ratios)

	Host			
Guest*	**1a**	**1b**	**2a**	**2b**
MeOH	–	–	2:1	1:1
EtOH	–	2:1	–	1:1
n-$PrNH_2$	–	–	1:2	1:2
Et_2NH	–	1:1	1:2	1:2
DMF	1:1 (H_2O)	1:1	2:1	1:1
DMSO	1:2	1:1	2:3	1:2
Acetone	–	2:1	–	†
THF	–	2:1	–	–
1,4-Dioxane	–	2:1	–	†

*Crystalline inclusion compounds were also obtained between **1a** and tetrahydropyran (1:1); **1b** and methyloxirane (1:1); **2a** and cyclohexylamine (1:2), 2-ethylpiperidine (1:1), cyclohexanone (1:1), γ-valerolactone (1:1), while 2-PrOH, 2-BuOH, *t*-BuOH, *c*-PentOH, *c*-HexOH, nitromethane, nitrobenzene, acetonitrile and benzonitrile, which were also tested as guest solvents, yielded no inclusion compounds with any of these hosts.
†Difficult to crystallize.

the recrystallization (clathration) experiments. Altogether 26 different crystalline inclusion compounds are specified, showing the general efficiency of the host design. Nevertheless, as can be seen from the table, the individual compounds **1**(**a**, **b**) and **2**(**a**, **b**) are rather different in their inclusion ability and demonstrate characteristic individual levels of selectivity.

Considering the number of crystalline inclusions formed by the individual host compounds, **1a** (three species) compares badly with **1b**, **2a** and **2b**, which form about the same number (six to nine species) of inclusions. This suggests that in **1a** the length of the central axis of the molecule is perhaps too short and thus a disadvantage to the creation of crystalline voids, while this seems not to be the case for the constitutional isomer **1b** having two geminal methyl groups displaced from position 7 to position 3 (cf. Scheme 1). Moreover, there are entrapment preferences induced by the nature and constitution of the solvents. Only DMF and DMSO yield crystalline inclusion compounds with all of the hosts. In contrast, acetone, THF and 1,4-dioxane are special cases, since they are only efficient guests with compound **1b**. A further remarkable point which emerges form Table I is that proton donor guests such as alcohols and amines are mostly included by **2a** and **2b** but only rarely by **1b**, and not at all by **1a**, indicating another potential effect of the host molecular geometry since all host molecules are equipped with two hydroxyl groups. However, dependent on the distance and constitutional vicinity, these functional groups may have different capabilities in guest binding. This is perhaps also a reason for the incorporation of auxiliary water molecules into the crystals of **1a** and **1a**·DMF yielding the hydrated species **1a**·H_2O (3:2) and **1a**·DMF·H_2O (1:1:1) while the inclusions of the elongated host analogue **2a**·DMSO (2:3) and **2a**·Et_2NH (1:2) are free of water.

Structural Study

As shown above, the inclusion abilities of the new type of host compounds are intimately related to their molecular shapes, in particular the length of the central axis, e.g. **1a** versus **2a**. In order to corroborate this behavior by a detailed structural study, we determined the crystal structures of four exemplary inclusion compounds: **1a**·H_2O (3:2), **1a**·DMF·H_2O (1:1:1), **2a**·DMSO (2:3) and **2a**·Et_2NH (1:2).

Basic crystallographic information for the four crystal structures is listed in Table II. Figures 1–8

TABLE II Crystallographic and structure refinement data for the inclusion compounds of **1a** and **2a**

Compound	**1a**·H_2O (3:2)	**1a**·DMF·H_2O (1:1:1)	**2a**·DMSO (2:3)	**2a**·Et_2NH (1:2)
Empirical formula	$3(C_{22}H_{34}O_2)\cdot 2(H_2O)$	$C_{22}H_{34}O_2\cdot C_3H_7NO\cdot H_2O$	$C_{24}H_{34}O_2\cdot 1.5(C_2H_6OS)$	$C_{24}H_{34}O_2\cdot 2(C_4H_{11}N)$
Formula weight	1027.57	421.63	471.74	516.81
Temperature (K)	294(2)	295(2)	294(2)	294(2)
Crystal system	Hexagonal	Orthorhombic	Monoclinic	Monoclinic
Space group	*R*32	$P2_12_12_1$	*C*2	$P2_1$
a (Å)	21.612(1)	7.143(1)	26.912(3)	10.689(1)
b (Å)	21.612(1)	12.208(1)	6.942(1)	11.740(1)
c (Å)	36.060(1)	29.153(1)	15.838(6)	13.886(2)
β (°)			113.30(2)	110.13(1)
Volume (Å^3)	14586.3(10)	2542.2(4)	2717.6(11)	1636.1(3)
Z	6	4	4	2
D_c (Mg m^{-3})	1.053	1.102	1.153	1.016
μ (mm^{-1})	0.520	0.577	1.615	0.473
F(000)	5094	928	1028	556
Crystal size (mm)	$0.40\times0.30\times0.30$	$0.30\times0.30\times0.20$	$0.40\times0.30\times0.20$	$0.33\times0.30\times0.22$
θ-range (deg)	$3.40 \le \theta \le 75.85$	$3.03 \le \theta \le 75.34$	$3.66 \le \theta \le 73.17$	$3.39 \le \theta \le 72.94$
Index ranges	$-13 \le h \le 25$; $-25 \le k \le 0$; $-q16 \le l \le 42$	$0 \le h \le 8$; $-15 \le k \le 0$; $-36 \le l \le 0$	$0 \le h \le 33$; $0 \le k \le 8$; $-19 \le l \le 18$	$0 \le h \le 13$; $-14 \le k \le 0$; $-17 \le l \le 16$
Reflections collected	7834	3156	2982	3469
Independent reflections, $R_{(int)}$	5801, 0.014	3004, 0.0045	2908, 0.0191	3353, 0.0076
Reflections $I > 2\sigma(I)$	5134	2377	2745	2102
Data/restraints/parameters	5801/0/351	3004/0/280	2908/193/314	3353/444/335
Goodness-of-fit on F^2	1.07	1.05	1.04	0.95
Extinction coefficient	0.00043(3)	0.0025(5)	–	0.0052(12)
Absolute structure parameter	−0.07(15)	0.3(3)	0.01(3)	0
Final *R* indices $[I > 2\sigma(I)]R_1$, wR^2	0.036, 0.101	0.046, 0.132	0.055, 0.154	0.059, 0.169
R indices (all data) R_1, wR^2	0.043, 0.105	0.063, 0.142	0.057, 0.157	0.087, 0.184
Largest diff. peak and hole (eÅ^{-3})	0.15 and −0.15	0.23 and −0.21	0.32 and −0.38	0.32 and −0.17

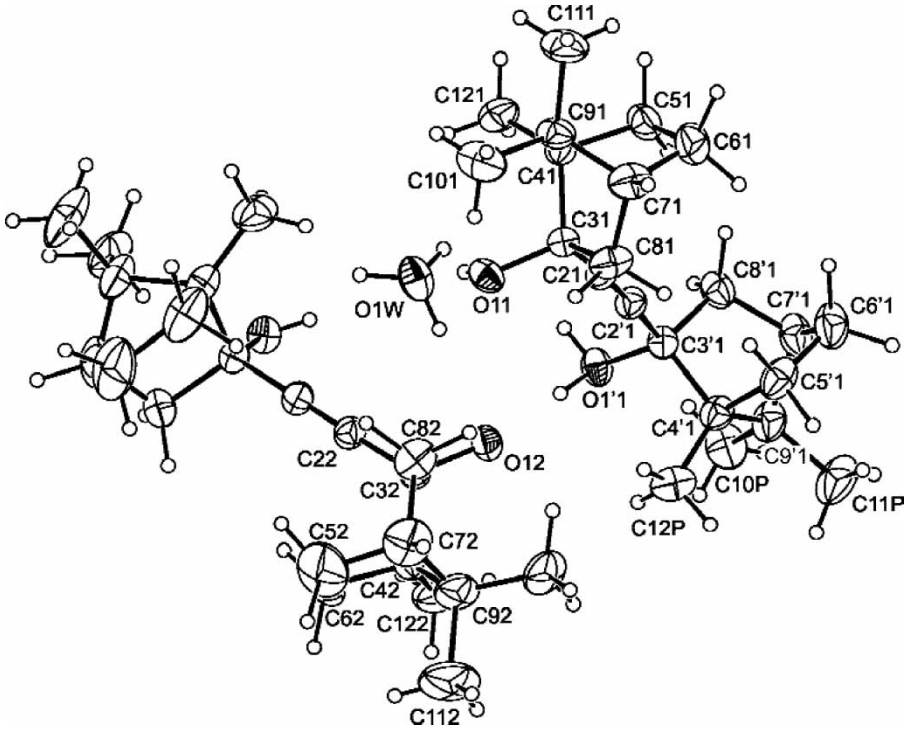


FIGURE 1 Structure model of the **1a**·H_2O (3:2) crystal showing 30% probability atomic displacement parameters for non-hydrogen atoms. Only atoms of the asymmetric unit are numbered; unnamed atoms stem from ideal twofold symmetry generation.

show the four host–guest ensembles (crystallographic models/asymmetric units) and the packing of these molecules in their respective associate crystals. Molecular conformation and relevant intermolecular contacts are listed in Tables III and IV.

Intramolecular/Intra Associate Features. The crystal structure of **1a**·H_2O (3:2) (Fig. 1) has the highest symmetry among these compounds (hexagonal space group *R*32). One of the host molecules lies on a twofold crystallographic symmetry axis while the other one is slightly twisted off of an ideal twofold molecular symmetry as reflected by the torsion angles (Table III). The disordered water molecule itself appears to lie on a threefold symmetry axis thus yielding to three equally 2/3 populated disordered hydrogen atomic sites. Obviously a water molecule cannot adopt threefold symmetry. Thus disorder stems from two water molecules occupying randomly three crystallographic positions dictated by the threefold

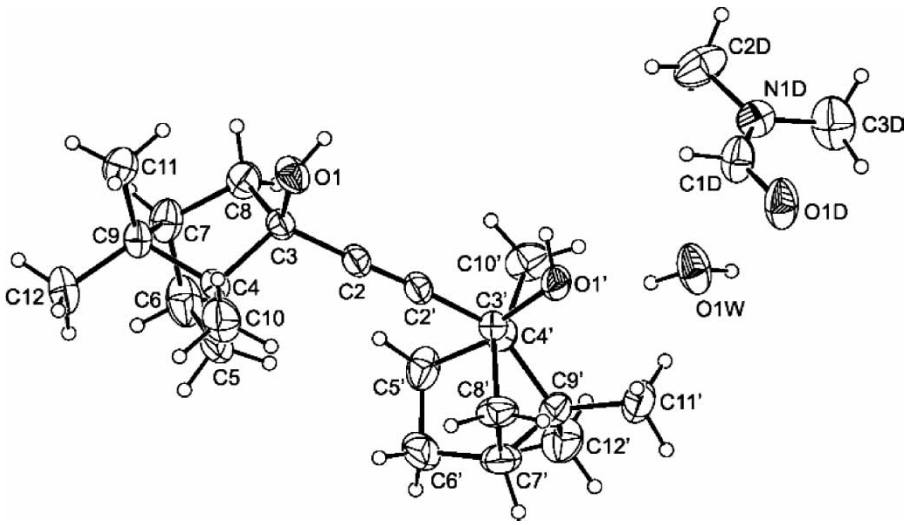


FIGURE 2 Structure model of the **1a**·DMF·H_2O (1:1:1) crystal showing 30% probability atomic displacement representation for non-hydrogen atoms.

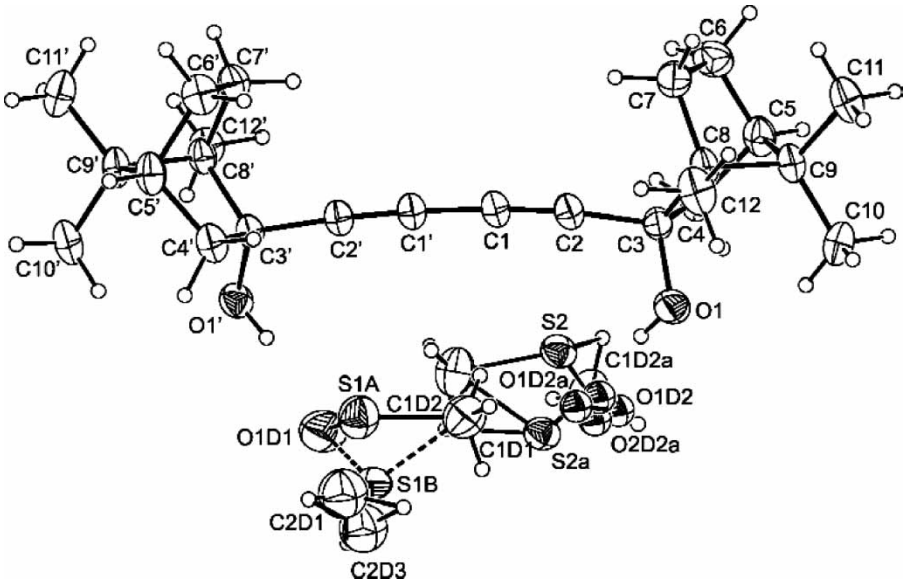


FIGURE 3 Structure model of the **2a**·DMSO (2:3) crystal showing 30% probability atomic displacement representation for non-hydrogen atoms. Minor population disorder sites are shown with broken "bonds", symmetry generated sites by letters "a".

symmetry, hence follows the odd 3:2 stoichiometry. The disorder manifested in the water hydrogen positions is followed by one of the host −OH hydrogen atoms, which has two positions. All these hydrogen positions, including the disordered ones, maintain fair H-bridge geometry (Table IV).

The crystal structure of **1a**·DMF·H_2O (1:1:1) (Fig. 2) also has relatively high (orthorhombic) symmetry. The host molecule deviates from twofold symmetry somewhat more than in the related crystal. The value (−18.0°) of the O1−C3···C3′−O1′ pseudo torsion angle indicates *syn-periplanar* (*sp*) configuration similar to that found in the **1a**·H_2O (3:2) inclusion (values of 23° and 27°, respectively; Table III). The water molecule plays a mediator role here by linking DMF to the host −OH group by hydrogen bridges (Fig. 2, Table IV) and is held tight by three-dimensional (*3-D*) productive interactions. DMF is also firmly held by two strong donated H-bonds (productive *2-D* fixation) and by close approach of O1 to one of the methyl groups in the tight host matrix.

The crystal structures of **2a** inclusions are both of lower monoclinic symmetry. The **2a**·DMSO (2:3) (Fig. 3) inclusion has severe disorder of the guest molecule sites. This conspicuous feature originates from a mismatch in the molecular recognition. Obviously, host **2a** is more elongated than **1a** and

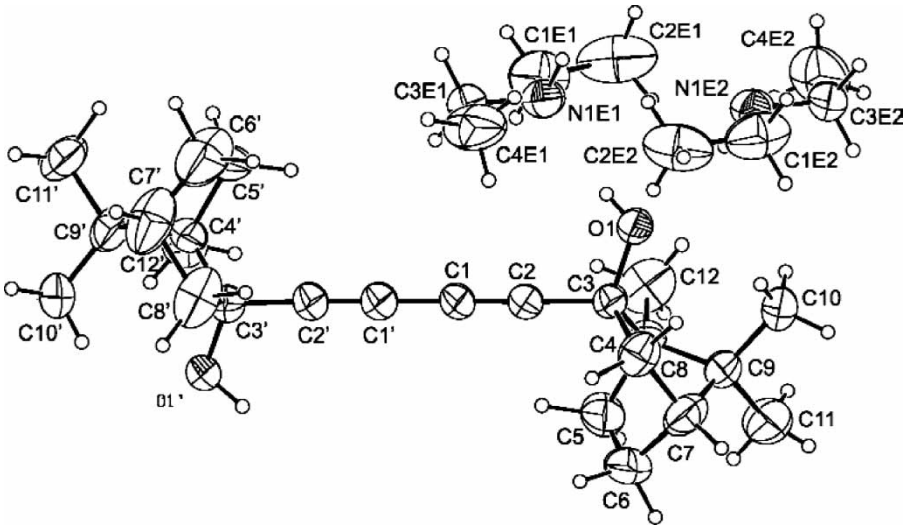


FIGURE 4 Structure model of the **2a**·Et_2NH (1:2) crystal showing 30% probability atomic displacement representation for non-hydrogen atoms.

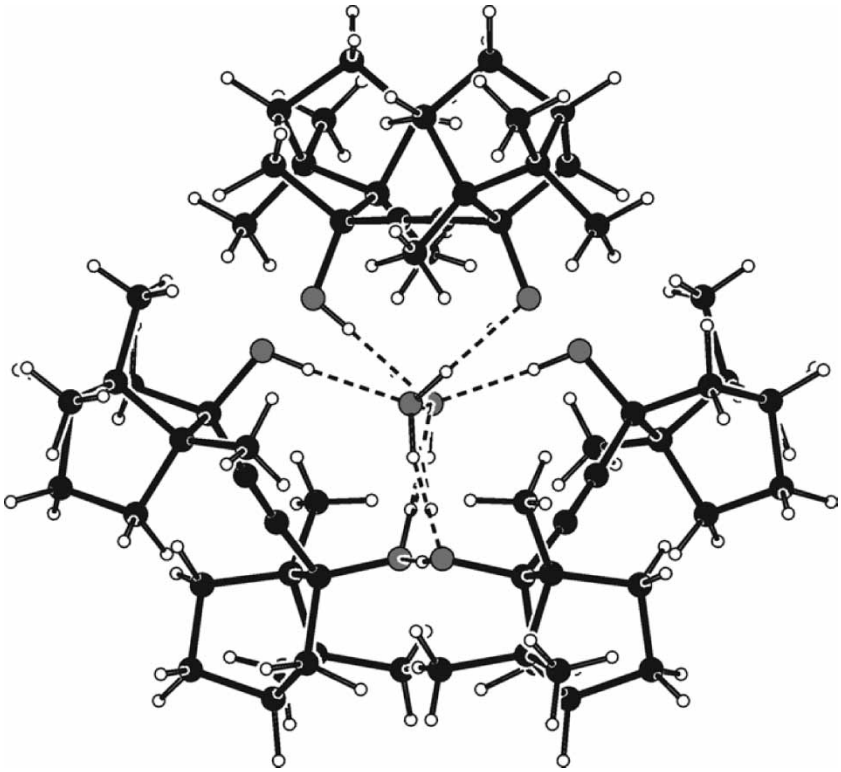


FIGURE 5 Basic packing motif of **1a**·H_2O (3:2), viewed near to the crystallographic *c* axis. H-bond contacts are shown in broken lines.

does not possess enough *3-D* fixing power to keep pyramid-like DMSO molecules firmly in place in the crystal. The only productive interaction to the guest molecules is a one-dimensional (*1-D*) fixing through a donated H-bridge to each guest O atom. The overall host molecule shape changes here to *syn-clinal* (*sc*) conformation as shown by the $-51.6°$ value of the O1–C3···C3′–O1′ pseudo torsion angle (*-sc*; Table III).

The host shape is characterized by an *anti-periplanar* (*ap*) displacement of the borneol groups ($+ap$, O1–C3···C3′–O1′ = 160.5°; Table III) in the crystal structure of **2a**·Et_2NH (1:2) (Fig. 4). This crystal structure is impaired by probable

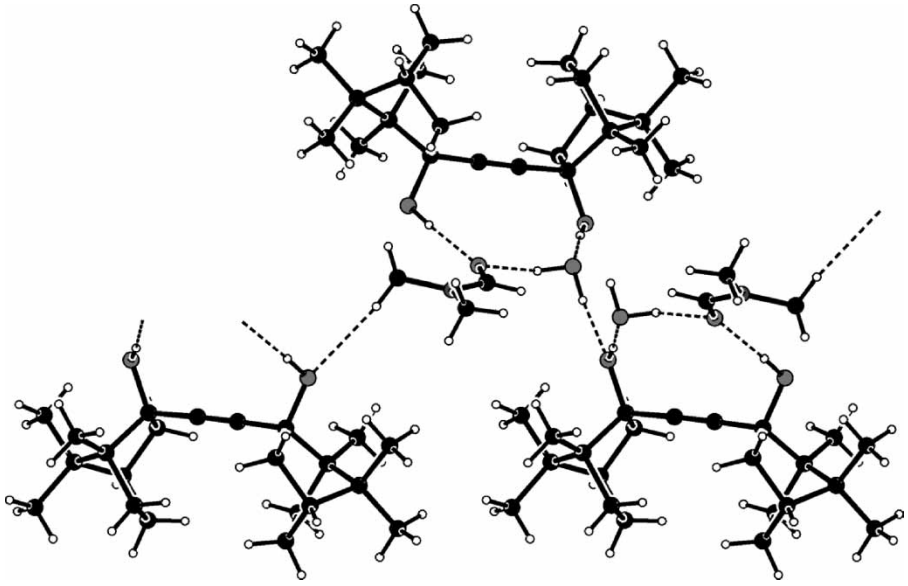


FIGURE 6 Packing in the crystal structure of **1a**·DMF·H_2O (1:1:1), with H-bond contacts in broken lines.

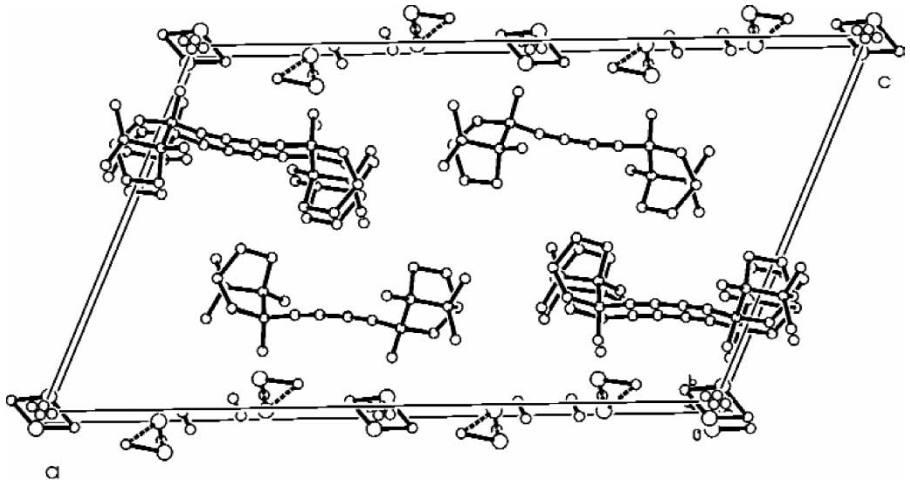


FIGURE 7 Packing of **2a**·DMSO (2:3) as viewed down the crystallographic screw axis. H-atoms are omitted for clarity.

twinning. The fixing of the more extended guest molecules seems to be somewhat better, since both secondary N atoms act simultaneously both as H-bond donors and as H-bond acceptors (two productive interactions, *2-D* fixation; Table IV). Still, the magnitude of the atomic displacement parameters indicates that this fastening, albeit better than in the DMSO inclusion, leaves ample room for either dynamic movements of the ethyl substituent wings or of their statistical disorder, indiscernible from the effects of twinning in the X-ray scattering pattern.

Intermolecular Features. The crystal structure of **1a**·H_2O (3:2) (Fig. 5) is determined by the threefold symmetry of the space group. Two water molecules effectively glue together three hosts in the average structure model (cf. Table IV). Host and guest molecules in the crystal structure of **1a**·DMF·H_2O (1:1:1) (Fig. 6) are essentially arranged in such a way that a strip of guest molecules is formed

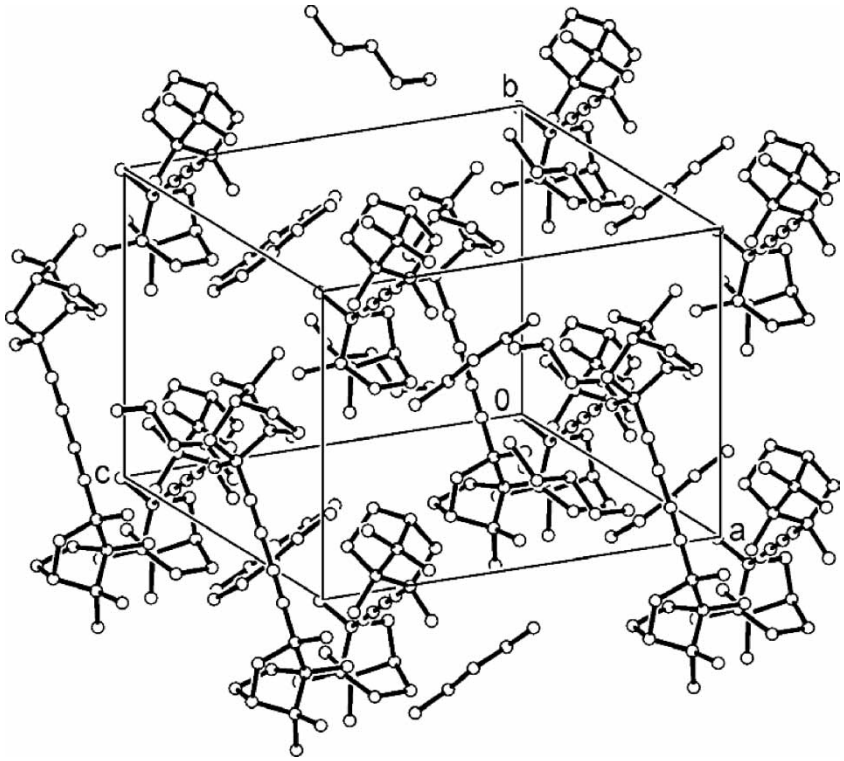


FIGURE 8 Packing in **2a**·Et_2NH (1:2) as viewed down the crystallographic *a* face.

TABLE III Some shape descriptors (torsion and pseudo torsion angles) for the inclusion compounds of **1a** and **2a** with their standard deviations

1a·H_2O (3:2)		**1a**·DMF·H_2O (1:1:1)		**2a**·DMSO (2:3)		**2a**·Et_2NH (1:2)	
Atoms involved	Angle (°)	Atoms involved	Angle (°)	Atoms involved	Angle (°)	Atoms involved	Angle (°)
O11–C31···C3′1–O1′1	23(3)	O1–C3···C3′–O1′	−18(5)	O1–C3···C3′–O1′	−52(3)	O1–C3···C3′–O1′	161(5)
C21–C2′1–C3′1–O1′1	34(3)	C2′–C2–C3–O1	−108(5)	C1–C2–C3–O1	−29(3)	C1–C2–C3–O1	−54(12)
C21–C2′1–C3′1–C8′1	154(3)	C2′–C2–C3–C8	17(5)	C1–C2–C3–C8	−150(3)	C1–C2–C3–C8	68(12)
C2′1–C21–C31–O11	−43(2)	C2–C2′–C3′–O1′	−142(5)	C1′–C2′–C3′–O1′	−29(5)	C1′–C2′–C3′–O1′	−77(9)
C2′1–C21–C31–C81	78(2)	C2–C2′–C3′–C8′	−22(5)	C1′–C2′–C3′–C8′	−151(5)	C1′–C2′–C3′–C8′	47(9)
O12–C33···C32*–O12*	27(5)						
C22*–C22–C32–O12	−44(5)						
C22*–C22–C32–C82	77(5)						

*Symmetry codes to generate equivalent atoms: $-x+1/3-1$, $-x+y+2/3-1$, $-z+2/3-1$.

propagated by a twofold axis. Host molecules form such a matrix that they turn with their hydrophilic faces towards this guest strip from both sides, concurrently facing each other laterally through their hydrophobic sides. The layering is even more apparent in the crystal structure of **2a**·DMSO (2:3) (Fig. 7). Here, the poorly recognized DMSO molecules sit in a channel along a crystallographic direction at $\{x, 0, 0\}$ coordinates while a double layer of hosts delineates this hydrophilic region. The crystal structure of **2a**·Et_2NH (1:2) (Fig. 8) has no such clear-cut distinction between hydrophilic and hydrophobic faces. The crystal build-up is possibly governed by the combination of two guests and two host molecules, fused in a single loop of a quasi-quadratic [a rhomb-like D_2^2 (*4*) motif] ring of H-bonds and by the herring-bone-like host arrangements.

CONCLUSION

The attachment of two bulky borneol or fenchol groups to linear ethynylene spacer units of different lengths has produced new dumb-bell-shaped crystalline inclusion hosts with novel structures. They form crystalline inclusions with a considerable variety of uncharged molecules ranging from protic polar to rather apolar compounds (26 different species; Table I), but with a clear preference for DMF and DMSO, while pure hydrocarbons were found to be inefficient. X-ray diffraction analyses of four selected cocrystals indicated different involvement of the host alcoholic functions in the enclathration of guest molecules with H-bond capability. A more elongated host shape (a "more elongated grip") leads possibly to larger freedom as well as poorer fixing of the guests. Hence mismatch

TABLE IV Relevant intermolecular contacts for the inclusion compounds of **1a** and **2a***

	Atoms involved			Distance (Å)			Angle (°)
Compound	D	H	A	D–H	H···A	D···A	D–H···A
1a·H_2O (3:2)	O12	H12O	O1W[a]	0.82	1.95	2.766(2)	177
	O1′1	H1PO	O1W[a]	0.88	1.87	2.746(2)	168
	O1′1	H1PH	O1′1[a]	0.91	1.96	2.857(2)	168
	O11	H11O	O1W	0.88	1.89	2.766(2)	173
	O1W	H1W	O1W[a]	0.96	1.79	2.749(3)	173
	O1W	H2W	O1′1[a]	0.96	1.84	2.746(2)	155
	O1W	H3W	O12[a]	0.96	1.93	2.766(2)	144
1a·DMF·H_2O (1:1:1)	O1	H1A	O1D[b]	0.85	1.94	2.788(3)	177
	O1′	H1′A	O1W[b]	0.85	1.86	2.704(3)	175
	O1W	H2W	O1D	0.92	1.99	2.763(3)	141
	O1W	H3W	O1′	0.93	1.89	2.793(2)	165
	C3D	H3DC	O1[c]	0.96	2.53	3.449(5)	159
2a·DMSO (2:3)	O1′	H1′	O1D1	0.82	1.98	2.785(4)	169
	O1	H1	O1D2	0.82	2.18	2.91(2)	149
	O1	H1	O2D2	0.82	1.94	2.714(8)	158
	O1	H1	O1D2	0.82	2.03	2.84(2)	171
	O1	H1	O2D2	0.82	2.20	2.989(8)	160
	O1	H1	S2	0.82	2.96	3.639(3)	142
2a·Et_2NH (1:2)	O1	H1	N1E1	0.76	2.04	2.791(4)	172
	O1′	H1′	N1E2[d]	0.91	1.93	2.805(4)	160
	N1E1	H1N	O1′[e]	1.04	2.33	3.268(4)	150
	N1E2	H2N	O1	1.12	2.17	3.181(4)	149

*E.s.d's are given for parameters involving only non-H atoms. Symmetry codes to generate equivalent atoms: [a] $-x-2/3$, $-x+y-1/3$, $-z-1/3$; [b] $x+1/2$, $3/2-y$, $-z$; [c] x, $y-1$, z; [d] $x-1$, y, z; [e] $x+1$, y, z.

develops in molecular recognition. These structural findings are both in agreement with the host:guest stoichiometric ratios and the shape and size relationships between host and guest in the inclusion compounds. Thus, structural variation of the central axis of the host molecules using specific building blocks [8,16] would be a promising modification of this design concept.

Moreover, considering the chirality of the borneol and fenchol terminal groups, which have been derived from optically pure camphor or fenchone out of the natural chiral pool, these and related host compounds are highly potential candidates for operating as chiral selectors in optical separation of racemic guests, similar to a closely connected type of host compounds [14,17]. Studies along these lines are in progress.

EXPERIMENTAL

General

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Bruker MSL 300 at 25°C. Chemical shifts are reported in ppm with TMS as an internal standard ($\delta = 0$ ppm). IR spectra were obtained using a Perkin–Elmer 1600 FT–IR instrument. Mass spectra were determined on an A. E. I. (Manchester, England) MS 50 instrument. The elemental analyses were perfomed with a Heraeus CHN rapid analyzer.

Starting Compounds

2α-Ethynyl-2β-hydroxybornane (**4a**) and 2α-ethynyl-2β-hydroxyfenchane (**4b**) were prepared by ethynylation of (+)-camphor (**3a**) or (−)-fenchone (**3b**) with the lithium acetylide–ethylenediamine complex and ethyne in benzene according to the literature [14].

Synthesis of Host Compounds 1a and 1b. General Procedure

A solution of the ketone **3** (30.40 g, 200 mmol) in dry benzene (250 ml) was dropped to the lithium acetylide–ethylenediamine complex (20.05 g, 220 mmol) under an atmosphere of argon over 1 h. The mixture was stirred for 2 h at room temperature and then 24 h at 45°C. After cooling, the mixture was quenched with aqueous brine (5%, 250 ml) and extracted with diethyl ether. The extract was washed with water, dried (Na_2SO_4) and evaporated. Recrystallization and drying *in vacuo* at 70°C yielded the pure products. Specific details are given for each compound.

2α,2′α-Ethynediyl-bis(1,7,7-trimethylbicyclo[2.2.1]-heptane-2β-ol) (1a)

(+)-Camphor (**3a**) was used; recrystallization from ethanol; 36% yield; mp 208°C; IR (KBr, cm^{-1}) 3423 (OH), 2952 (CH), 2365, 2290 (C≡C), 1064 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (s, 6 H, CH_3), 0.85 (s, 6 H, CH_3), 1.01 (s, 6 H, CH_3), 1.05–1.10 (m, 2 H, bornyl), 1.37–1.47 (m, 2 H, bornyl), 1.59–1.85 (m, 8 H, CH_2), 2.14–2.22 (m, 2 H, bornyl), 2.32 (s, 2 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.6, 21.1, 21.4 (CH_3), 27.0, 32.9 (CH_2), 45.2 (CH), 47.6 (*C*H_2CO), 53.7 (qC), 67.9 (CO), 82.9 (C≡C); MS *m/z* Calcd for $C_{22}H_{34}O_2$: 330.2550. Found: 330.2557. Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.68; H, 10.29.

2α, 2′α-Ethynediyl-bis(1,3,3-trimethylbicyclo[2.2.1]-heptane-2β-ol) (1b)

(−)-Fenchone (**3b**) was used; recrystallization from methanol; 12% yield; mp 119°C; IR (KBr, cm^{-1}) 3472 (OH), 2960 (CH), 2378 (C≡C), 1062 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 6 H, CH_3), 1.12 (s, 6 H, CH_3), 1.18 (s, 6 H, CH_3), 1.00–1.13 (m, 2 H, fenchyl), 1.36–1.42 (m, 4 H, fenchyl), 1.64–1.70 (m, 8 H, fenchyl), 1.88–1.92 (m, 2 H, fenchyl), 2.03 (s, 2 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.3 (CH_3), 21.8 (CH_2), 25.9 (CH_3), 27.4 (CH_3), 30.3 (CH_2), 41.2 (CH), 43.7 (qC), 48.6 (qC), 53.5 (CO), 80.9 (C≡C); MS *m/z* Calcd for $C_{22}H_{34}O_2$: 330.2550. Found: 330.2560. Anal. Calcd for $C_{22}H_{34}O_2$: Found: 330.2560. Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 80.06; H, 10.12.

Synthesis of Host Compounds 2a and 2b. General Procedure

To a suspension of powdered copper(II) acetate (11.0 g, 56 mmol) in pyridine/methanol (1:1, 40 ml) was added the respective compound **4** (7.0 g, 40 mmol). The mixture was heated for 4 h to reflux, then cooled and poured under cooling with ice into aqueous sulfuric acid (18 N, 200 ml). The white suspension was extracted with diethyl ether, washed with water, dried (Na_2SO_4) and evaporated. Recrystallization and drying *in vacuo* at 70°C yielded the pure products.

2α,2′α-(1,3-Butadiyne-1,4-diyl)bis(1,7,7-trimethyl-bicyclo[2.2.1]heptane-2β-ol) (2a)

Compound **4a** was used; recrystallization from acetone; 93% yield; mp 248°C; IR (KBr, cm^{-1}) 3457 (OH), 2953 (CH), 2310, 2100 (C≡C), 1060 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (s, 6 H, CH_3), 0.93 (s, 6 H, CH_3), 1.02 (s, 6 H, CH_3), 1.08–1.17 (m, 2 H, bornyl), 1.40–1.52 (m, 2 H, CH), 1.58–1.80 (m, 8 H, bornyl), 2.00 (s, 2 H, OH), 2.15–2.20 (m, 2 H, CH);

^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4, 20.9, 21.3 (CH_3), 26.9, 32.5 (CH_2), 45.3 (CH), 48.1 (*C*H_2CO), 54.15 (qC), 68.1 (CO), 78.5 (C≡C), 83.4 (C≡C); MS *m/z* Calcd for $C_{24}H_{34}O_2$: 354.2550. Found: 354.2569. Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.09; H, 9.65.

2α,2′α-(1,3-Butadiyne-1,4-diyl)bis(1,3,3-trimethylbicyclo[2.2.1]heptane-2β-ol) (2b)

Compound **4b** was used; recrystallization from methanol yielded the 1:1 clathrate with methanol which decomposed on heating *in vacuo*; 83% yield; mp 152–155°C; IR (KBr, cm^{-1}) 3426 (OH), 2966, 2875 (CH), 2249 (C≡C), 1061 (CO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 6 H, CH_3), 1.13 (s, 6 H, CH_3), 1,18 (s, 6 H, CH_3), 1.00–1.44 (m, 6 H, fenchyl), 1.63–1.74 (m, 8 H, fenchyl), 1.83–1.92 (m, 2 H, fenchyl), 2.10 (s, 2 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.0 (CH_3), 21.6 (CH_2), 25.8 (CH_3) 27.4 (CH_3), 29.8 (CH_2), 41.3 (CH), 44.1 (qC), 48.6 (*C*H_2CO), 54.0 (CO), 71.25 (C≡C), 81.5 (C≡C); MS *m/z* Calcd for $C_{24}H_{34}O_2$: 354.2550. Found: 354.2569. Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.16; H, 9.98.

Synthesis of Inclusion Compounds. General Procedure

The appropriate host compound was dissolved with heating in a minimum amount of the respective guest solvent. After the solution had stood for 12 h at room temperature, the crystals that had formed were collected, washed with diethyl ether, and dried (1 h, 15 Torr, room temperature). Host–guest stoichiometric ratios were determined by ^{1}H NMR integration. Data for each compound are given in Table I.

X-ray Crystallography

Single crystal data of **1a**·H_2O (3:2), **1a**·DMF·H_2O (1:1:1), **2a**·DMSO (2:3) and **2a**·Et_2NH (1:2) were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Cu–Kα radiation ($\lambda = 1.54184$ Å) at 294(2) K. The structures were solved by direct methods [18] (and subsequent difference syntheses), and refined by anisotropic full-matrix least squares refinement [19] on F^2 for all non-hydrogen atoms. All structures refined to proper Flack values except **2a**·DMSO (2:3) where twinning was assumed. Hydrogen atomic positions were calculated from assumed geometries except those of the water molecules, –OH groups of the host molecules and –NH of the secondary amine that were located in difference maps. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to. Details of data collection and refinement are reported in Table II. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-213909 to CCDC-213912. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk).

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