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Separation by Inclusion: Selectivity by Tetraphenylethanediol of Toluene and Mono-halo Substituted Benzenes

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The host 1,1,2,2-tetraphenyl-1,2-ethane diol was found to form inclusion compounds with the guest toluene and three mono-halo substituted benzenes; chloro-, bromo-, and iodo-benzene. These compounds were characterised by thermal analysis, which showed host:guest ratios of 1:1/2, and their structures were elucidated and compared. Two-, three- and four-component competition experiments were conducted to investigate the selectivity of the host for the respective guests and to determine the separation capabilities of this system.

Keywords: Selectivity; Tetraphenyldiol host; Monosubstitued benzenes

INTRODUCTION

The process of inclusion, whereby a given host compound captures a guest molecule and forms a crystalline host–guest compound, depends on the phenomenon of molecular recognition. When the host is presented with two or more guests, then the selectivity for a particular guest depends on the extent of the non-bonded interactions which occur between the various molecules in the crystal structure [1].

Many types of organic host compounds have been developed in the last thirty years, some of which were targeted at specific guests by optimizing the complementarity of the host–guest system and thus lowering the lattice energy of the targeted inclusion compound. Particularly successful hosts which form lattice inclusion compounds are the derivatives of tartaric acid, deoxycholic acid, binapthols and wheel-and-axle diols [2]. The host 1,1,2,2-tetraphenyl-1,2-ethane diol is an example of the latter, and its ability to form inclusion compounds and to react selectivity with picolines was studied by Toda [3,4].

The crystal structures of its inclusion compounds formed with dioxane [5] and three isomers of lutidine [6] have been elucidated. More recently we have studied the selectivity of this diol host towards the isomers of picoline and have elucidated the relevant crystal structures as well as analysed the effects of the addition of benzene to the picoline mixtures [7].

In this work we present the results of the competition carried out with this host and the guests; toluene, chloro-, bromo- and iodo-benzenes, shown in Scheme 1.

RESULTS AND DISCUSSION

The crystal data for all four inclusion compounds are shown in Table I. Thermal Gravimetry, TG, yielded satisfactory results which fixed the H:G ratio at 1:1/2 for all four compounds.

The structure of $\mathrm{H}\cdot\frac{1}{2}\mathrm{MePh}$ crystallizes in the space group $P2_1/c$ with $Z = 4$. The host is in a general position while the toluene guest is located on a centre of inversion at Wyckoff position *d*. The centre of the phenyl ring is coincident with the crystallographic centre of symmetry and therefore the methyl moiety is disordered. The two central carbon atoms of the host are disordered each over two positions, and were each refined with fractional site occupancy. The disorder reoccurred in the $\mathrm{H}\cdot\frac{1}{2}\mathrm{ClPh}$ and $\mathrm{H}\cdot\frac{1}{2}\mathrm{IPh}$ structures. This is shown in Fig. 1. The host molecules are stabilized by Host–O–H$\cdots$O(H)Host hydrogen bonding with an O$\cdots$O distance of 2.685(4) Å. Similar H-bonding occurs in the remaining structures as given in Table II. The toluene guest

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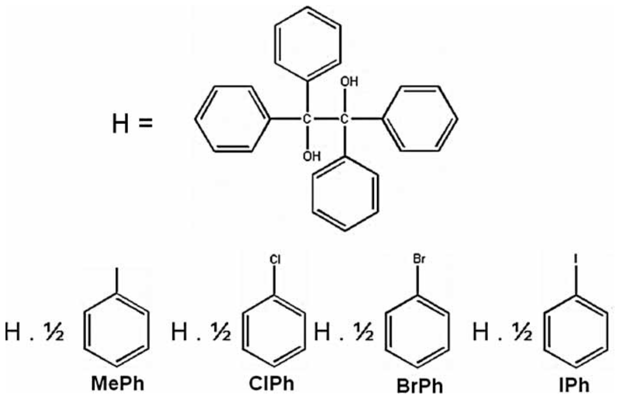

SCHEME 1

is located in channels running in the [100] direction, which have cross sections ranging from 4.1 × 5.5 Å at the narrowest to 4.1 × 9.6 Å at their widest, the latter corresponding to the centres of inversion. This is shown in Fig. 2, in which the guest molecules have been omitted and the host atoms are represented with van der Waals radii.

The structure of $H \cdot \frac{1}{2}ClPh$ is isomorphous with that of $H \cdot \frac{1}{2}MePh$, while $H \cdot \frac{1}{2}BrPh$ is isomorphous with respect to the positions of the host atoms, but the disorder of the bromobenzene guest is slightly different in that the crystallographic centre of inversion does not coincide with the centre of the benzene ring but is close to it. This also occurs in the $H \cdot IPh$ structure, shown in Fig. 4a.

The packing of the three isomorphous structures is characterised by layers of host molecules lying with their molecular planes perpendicular to [100] and with the guests located between the layers (Fig. 3). The channels are approximately 14 Å apart.

The $H \cdot \frac{1}{2}IPh$ structure exhibits somewhat different packing in that the hosts stack in two layers perpendicular to [100], but the guest iodobenzenes are now located in channels separated by double layers of host molecules which are much further apart [d(IPh...IPh) channels are at 9.0 and 20.8 Å, which correspond to the length of the *b* and *c* cell parameters]. This packing is illustrated in Fig. 4.

Thermal Analyses

The TG curves for each compound show an initial mass loss due to the desorption of the guest, which is signalled by a concomitant endotherm of the DTA.

There follows a sharp mass loss of the host at the latter's melting point. This is shown by a large endotherm in the DTA, which sometimes has evidence of a pre-melt, which may be due to a phase transformation. A typical example, that of the $H \cdot \frac{1}{2}ClPh$ compound, is shown in Fig. 5 and the salient results of the thermal analyses are given in Table III.

Competition Experiments

The selectivity of the host for the guests was established by carrying out competition experiments

TABLE I Crystal data, experimental and refinement parameters

	$H \cdot \frac{1}{2}MePh$	$H \cdot \frac{1}{2}ClPh$	$H \cdot \frac{1}{2}BrPh$	$H \cdot \frac{1}{2}IPh$
Molecular formula	$C_{26}H_{22}O_2 \cdot \frac{1}{2}(C_7H_8)$	$C_{26}H_{22}O_2 \cdot \frac{1}{2}(C_6H_5Cl)$	$C_{26}H_{22}O_2 \cdot \frac{1}{2}(C_6H_5Br)$	$C_{26}H_{22}O_2 \cdot \frac{1}{2}(C_6H_5I)$
Guest	Toluene	Chlorobenzene	Bromobenzene	Iodobenzene
Host:guest ratio	$1:\frac{1}{2}$	$1:\frac{1}{2}$	$1:\frac{1}{2}$	$1:\frac{1}{2}$
$M/g.mol^{-1}$	412.51	422.71	444.94	468.44
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1
a/Å	6.0309(1)	6.0302(1)	6.0444(12)	6.1068(1)
b/Å	16.0435(3)	16.0507(2)	16.035(3)	9.0137(2)
c/Å	22.7674(5)	22.7469(4)	22.850(5)	20.8475(3)
α/°	90	90	90	94.576(1)
β/°	90.558(1)	91.3450(10)	90.88(3)	93.379(1)
γ/°	90	90	90	103.254(1)
Z	4	4	4	2
$V/Å^3$	2202.80(7)	2201.04(6)	2214.4(8)	1109.89(3)
μ(Mo-Kα)/mm^{-1}	0.076	0.137	0.978	0.771
Temperature/K	113	113	113	113
Range scanned, θ/°	4.9–26.8	3.4–27.1	2.5–26.8	2.3–27.1
Index range	$7 \geq h \geq -7$, $20 \geq k \geq -20$, $28 \geq l \geq -28$	$7 \geq h \geq -7$, $20 \geq k \geq -20$, $29 \geq l \geq -29$	$6 \geq h \geq -7$, $18 \geq k \geq -19$, $27 \geq l \geq -27$	$7 \geq h \geq -7$, $11 \geq k \geq -11$, $26 \geq l \geq -26$
No. reflections collected	8402	9418	7765	9095
No. unique reflections	4596 ($R_{int} = 0.028$)	4807 ($R_{int} = 0.028$)	4207 ($R_{int} = 0.069$)	4895 ($R_{int} = 0.016$)
No. reflections with $I > 2\sigma I$	3396	3272	2171	3632
Data/restraints/parameters	4596 / 0 / 310	4807 / 0 / 302	4207 / 0 / 305	4895 / 0 / 319
Final R indices ($I > 2\sigma I$)	$R_1 = 0.1000$ $wR_2 = 0.1965$	$R_1 = 0.0801$ $wR_2 = 0.1943$	$R_1 = 0.0934$ $wR_2 = 0.1902$	$R_1 = 0.0943$ $wR_2 = 0.1814$
R indices (all data)	$R_1 = 0.1296$ $wR_2 = 0.2087$	$R_1 = 0.1169$ $wR_2 = 0.2155$	$R_1 = 0.1919$ $wR_2 = 0.2232$	$R_1 = 0.1245$ $wR_2 = 0.1979$
Largest diff. peak and hole /e. $Å^{-3}$	0.47; −0.40	0.65; −0.49	0.63; −0.52	2.37; −1.58

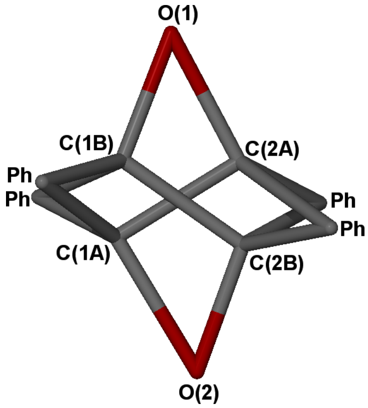

FIGURE 1 Disorder in two central carbon atoms of the host.

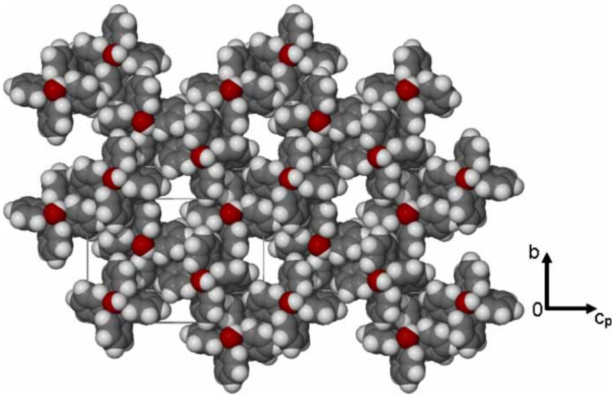

FIGURE 2 Packing diagram of $H \cdot \frac{1}{2}MePh$ viewed along [100], the guest molecules are omitted and the host is represented with van der Waals radii.

between pairs of guests. The method employed a series of vials containing mixtures of guests of varying mole fraction in which the total guest:host ratio in the initial solutions was 145:1. The inclusion compounds were allowed to crystallize and the crystals, as well as the mother liquor, were analysed by gas chromatography. The results are plotted on a graph of the mole fraction, X, of a given guest in the liquid versus Z, the mole fraction in the crystal.

Following Ward [8], for each pair of guests, A and B, a selectivity coefficient may be determined such that

$$K_{A:B} = Z_A/Z_B{*}X_B/X_A, \quad \text{where} \quad (X_A + X_B = 1)$$

and we found $K_{ClPh:MePh} = 1.7$; $K_{BrPh:MePh} = 4.9$ and $K_{BrPh:ClPh} = 2.0$.

We extended the experiment to a 3-component competition, and the results are shown in Fig. 6. The results are plotted on an equilateral triangle, the apices of which represent the pure components. The starting mixtures are represented by the dots located in the inner grey triangle, and the result of the enclathration is given by the outer triangle of dots. The host shows a preference for bromobenzene and is entirely consistent with the results of the two-component competition experiments.

We further extended the competition to all four components, and we plotted the results with the starting and final mole fractions of the guests represented in a regular tetrahedron, the apices of which correspond to the pure components. This same technique was employed in the study of the selectivity of aliphatic alcohols by the host 1,1-bis(4-hydroxyphenyl)cyclohexane [9].

The result is shown in Fig. 7, in which the initial mixtures, shown by the inner tetrahedron, drift sharply away from the toluene and towards the iodobenzene (outer tetrahedron).

TABLE II Hydrogen bonding details

Compound	D–H…A	D–H (Å)	D…A (Å)	D–H…A (°)
$H \cdot \frac{1}{2}MePh$	O1–H1O…O2	0.85(5)	2.685(4)	131(4)
$H \cdot \frac{1}{2}ClPh$	O1–H1O…O2	0.84	2.698(3)	122
	O2–H2O…O1	0.84	2.698(3)	128
$H \cdot \frac{1}{2}BrPh$	O1–H1O…O2	0.85(9)	2.681(2)	118(8)
$H \cdot \frac{1}{2}IPh$	O1–H1O…O2	0.7(1)	2.655(6)	137(11)

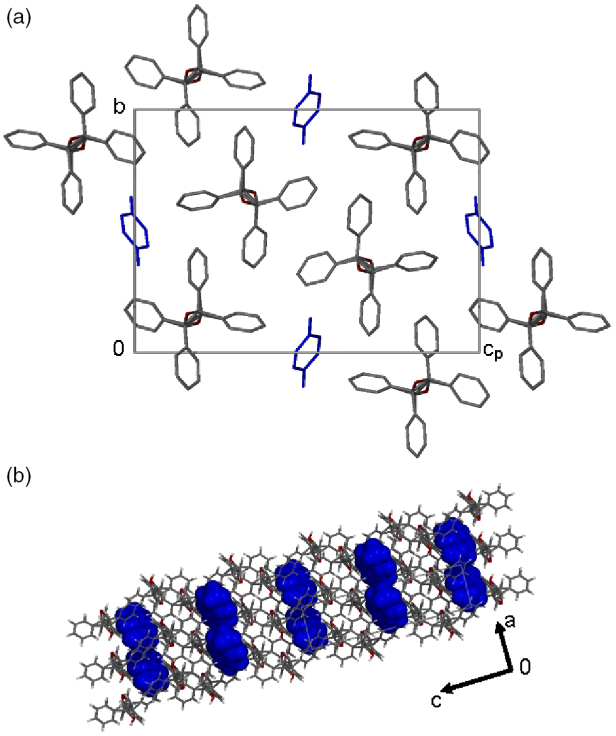

FIGURE 3 Packing diagrams of $H \cdot \frac{1}{2}MePh$, where (a) a single unit cell is viewed along [100] and (b) four unit cells are viewed along [010], the guest molecules are represented with van der Waals radii. (Structures of $H \cdot \frac{1}{2}ClPh$ and $H \cdot \frac{1}{2}BrPh$ are isomorphous with $H \cdot \frac{1}{2}MePh$.)

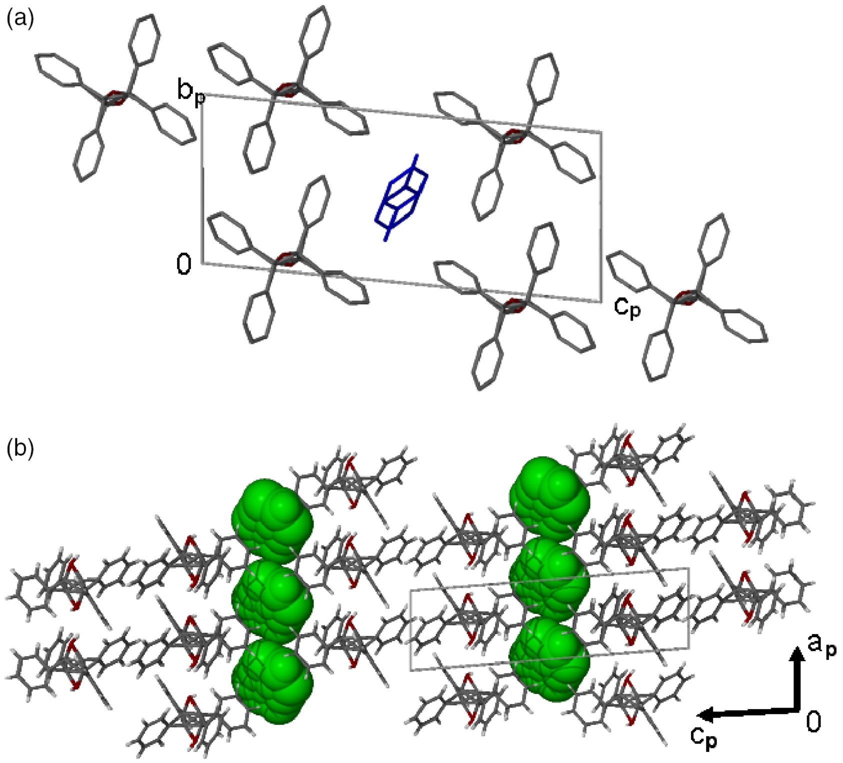

FIGURE 4 Packing diagrams of $H\cdot\frac{1}{2}IPh$, where (a) a single unit cell is viewed along [100] and (b) four unit cells are viewed along [010], the guest molecules are represented with van der Waals radii.

We may extend the definition of the selectivity coefficient for three and four component systems as follows,

$$K_{A:(B+C)} = Z_A/Z_{(B+C)}{}^{*}X_{(B+C)}/X_A,$$

$$\text{where} \quad (X_A + X_B + X_C = 1)$$

$$K_{A:(B+C+D)} = Z_A/Z_{(B+C+D)}{}^{*}X_{(B+C+D)}/X_A,$$

$$\text{where} \quad (X_A + X_B + X_C + X_D = 1)$$

Our results show $K_{BrPh:(ClPh+MePh)} = 2.6$ and $K_{IPh:(BrPh+ClPh\,+\,MePh)} = 3.1$

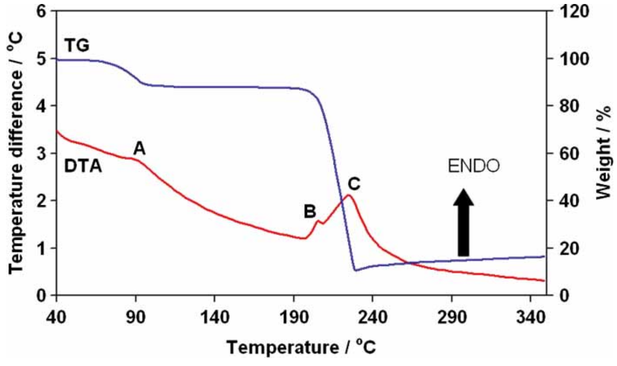

FIGURE 5 TG and DSC trace of $H\cdot\frac{1}{2}ClPh$.

CONCLUSIONS

The structures of the host–guest complexes formed between the host and the four guests were elucidated and compared. The structures of $H\cdot\frac{1}{2}MePh$, $H\cdot\frac{1}{2}ClPh$ and $H\cdot\frac{1}{2}BrPh$ were found to be isomorphous, while that of $H\cdot\frac{1}{2}IPh$ packed differently. In all cases the guest molecules are located in channels formed by the host, running in the [100] direction. Competition experiments showed that the host selectivity occurs in the order iodobenzene > bromobenzene > chlorobenzene > toluene, which correlate with the peak temperatures of the guest release endotherms.

EXPERIMENTAL

General

Suitable crystals of the inclusion compounds were formed by stirring a solution of 50 mg of host in a minimum amount of solvent at approximately 70°C. Once dissolution had occurred, the solution was filtered through a 0.5 μm syringe filter and then left to evaporate slowly at room temperature.

TG/DTA experiments were performed on a Mettler Toledo TGA/SDTA 851e under N_2 gas purge (flow rate 30 mL/min). The samples were crushed and blotted dry and the experiments were performed at a heating rate of 20 K/min over the temperature range 30–350°C.

TABLE III Thermal analyses

		H·$\frac{1}{2}$MePh	H·$\frac{1}{2}$ClPh	H·$\frac{1}{2}$BrPh	H·$\frac{1}{2}$IPh
H:G ratio		1:1/2	1:1/2	1:1/2	1:1/2
TG results	Calc. % mass loss	11.2	13.3	17.7	21.8
	Exp. % mass loss	10.8	11.7	17.7	17.4
DSC results	T_{peak} (K):A	355	365	375	385
	B	475	478	471	471
	C	508	498	485	528

Competition experiments were carried out with pairs of guests as follows: A series of mixtures of two guests was prepared such that the mole fraction of a given guest varied from 0 to 1. The host compound was then added to these mixtures, with a total guest:host ratio of 145:1, and dissolved by heating and stirring the solutions. The solutions were then filtered through a 0.5 μm syringe filter and left to evaporate slowly at room temperature, resulting in the formation of crystals. These crystals were then filtered, dried and dissolved in acetone and analysed by gas chromatography using a Varian 3400 gas chromatograph equipped with a polar, carbowax column (25 m length, 0.25 mm diameter).

Single Crystal X-ray Analyses

Cell dimensions were established from the intensity data measurements on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo *Kα* radiation for each of the inclusion compounds. The strategy for the data collections was evaluated using the COLLECT [10] software. For all structures, data were collected by the standard phi- and omega-scan techniques, and were scaled and reduced using DENZO-SMN [11] software. Crystallographic data, experimental and refinement parameters are given in Table I. The structures were solved by direct methods using SHELX-86 [12] and refined by least-squares with SHELX-97 [13], refining on F^2. The program X-Seed [14,15] was used as a graphical interface for structure solution and refinement using SHELX, as well as to produce the packing diagrams.

In each of the structures the positions of all non-hydrogen host atoms were obtained by direct methods and the non-hydrogen guest atoms were located in difference electron density maps. The hydroxyl hydrogens on the host molecule for H·$\frac{1}{2}$MePh, H·$\frac{1}{2}$BrPh and H·$\frac{1}{2}$IPh were located in the difference electron density maps and were refined without bond length constraints. The rest of the hydrogen atoms and the host hydroxyl hydrogens for H·$\frac{1}{2}$ClPh were placed in geometrically

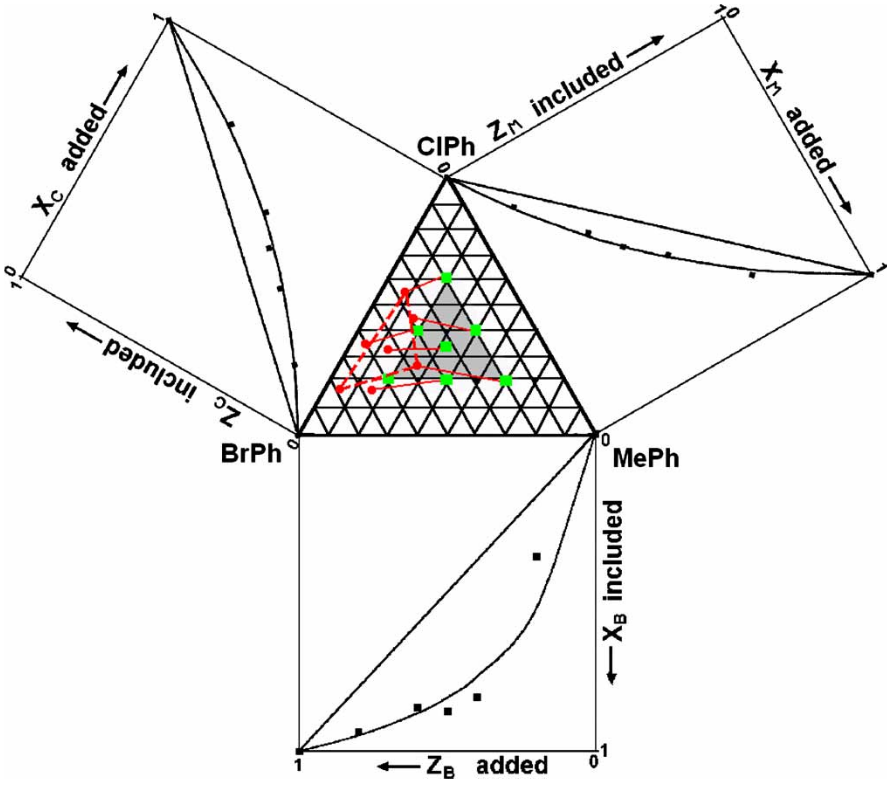

FIGURE 6 Results of the three-component competition experiments of the host with toluene, chloro- and bromo-benzene.

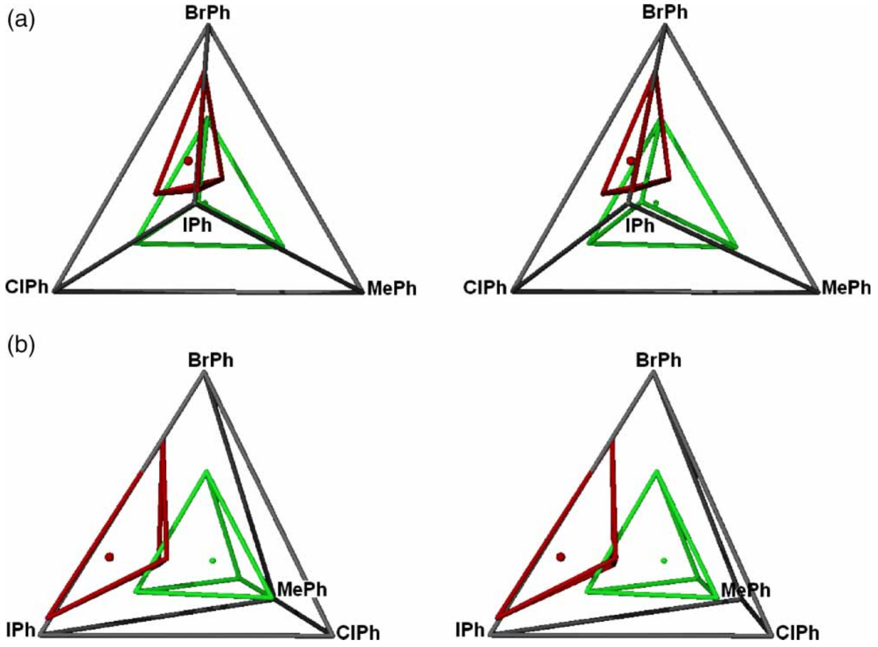

FIGURE 7 Results of the four-component competition experiments, presented in stereo. The inner green tetrahedron represents the starting concentrations, while the red tetrahedron represents the concentrations of the four components included by the host. (a) View of the tetrahedron perpendicular to the toluene / chlorobenzene / bromobenzene plane; (b) side view of the tetrahedron.

constrained positions and refined with isotropic temperature factors.

The ethane C atoms of the host molecule are disordered in the $H\cdot\frac{1}{2}$MePh, $H\cdot\frac{1}{2}$ClPh and $H\cdot\frac{1}{2}$IPh structures. The final site occupancies for these structures refined to 0.30/0.70 in $H\cdot\frac{1}{2}$MePh; 0.20/0.80 in $H\cdot\frac{1}{2}$ClPh and 0.50/0.50 in $H\cdot\frac{1}{2}$IPh. Owing to the high disorder in the guest molecules for the $H\cdot\frac{1}{2}$BrPh and $H\cdot\frac{1}{2}$IPh structures, no hydrogen atoms were located or placed.

CCDC 607712–607715 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing E-mail: data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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