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Host behaviour of related compounds, TETROL and DMT, in the presence of two different classes of aromatic guest compounds

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ABSTRACT

The host potential of two closely-related compounds, TETROL [(+)-(2R,3R)-1,1–4,4-tetraphenylbutane-1,2,3,4-tetraol] and DMT [(−)-(2R,3R)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol], were compared when recrystallized from two different classes of guests, namely toluene, ethylbenzene, cumene and aniline, *N*-methylaniline, *N*,*N*-dimethylaniline. TETROL formed complexes with only aniline and *N*-methylaniline (host:guest ratios, 2:3 and 2:4), while DMT included all six guests with a consistent ratio (2:1). Aniline competition experiments showed that TETROL preferred aniline (67%), followed by *N*-methyl- (29%) and *N*,*N*-dimethyl- (4%) aniline; surprisingly, this order was exactly reversed for DMT [*N*,*N*-dimethylaniline (62%) > *N*-methylaniline (32%) > aniline (6%)]. Crystal diffraction analyses revealed that TETROL formed stabilizing hydrogen bonds with guests, behaving as both donor and, for the first time, acceptor (in 2TETROL·4N-methylaniline). DMT did not form bonds of this type with any guests. Furthermore, the host packing was isostructural for all DMT complexes but was guest-dependent for TETROL. Thermal analyses showed that complex stabilities correlated precisely with the host preferences.

1. Introduction

Host-guest chemistry is a burgeoning field within supramolecular chemistry, and considerations of host-guest methodologies and their applicability to the chemical industry are becoming increasingly pertinent [1]. One promising application of host-guest chemistry is the separation of mixtures of positional isomers which typically have similar physical properties and, therefore, frequently do not respond favourably to traditional separation methods [2]. Consequently, the selective inclusion by host materials of a particular guest species from such mixtures is an attractive attribute that may be exploited to potentially address this challenge. For example, industrial processes relying on single isomers of each of the cresols, xylenes and methylanisoles, amongst others, would benefit considerably if a simple method existed for their purification, since such isomers are widely used as precursors to an array of valuable end-products.

Kuhn et al. [3] have reviewed chiral separations by capillary zone electrophoresis and micellar electrokinetic capillary chromatography, which often involve host-guest chemistry principles, and have illustrated the potential of such methods. In particular are mentioned the host materials cyclodextrin and chiral crown ethers for these applications. Additionally, host materials may have the ability to enclathrate drug actives and, in so doing, improve the transport, activity, resistance, solubility, and overall drug delivery of these actives into the human body [4]. Other plausible applications include the removal of hazardous materials from the environment, improving the taste and stability of food products, asymmetric synthesis, and gas storage [5–9].

We have recently reported on the host behaviour of (−)-(2R,3R)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (DMT, Scheme 1) in the presence of various mixtures of xylenes [10] and anilines [11]. These investigations were prompted by the fact that each of the guests in both series are employed as building blocks for a wide variety of industrially-important products, and challenges have been encountered in their isolation and purification [12,13]. TETROL [(+)-(2R,3R)-1,1–4,4-tetraphenylbutane-1,2,3,4-tetraol, Scheme 1] is closely related to DMT in that its two secondary hydroxyl functionalities are further derivatized as methoxyl moieties. This subtle

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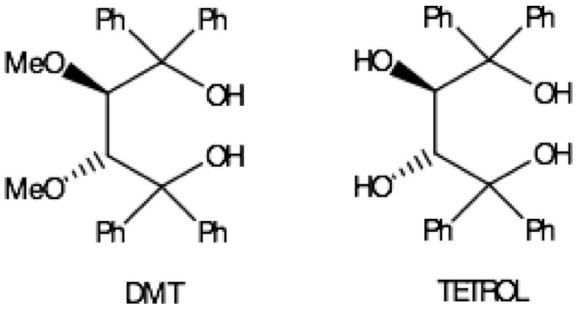

Scheme 1. Structures of related hosts DMT and TETROL.

change in host structure significantly changed the behaviour of the host when recrystallized under the same conditions in the presence of isomeric toluidine mixtures [14]: TETROL showed a marked increase in selectivity compared with DMT, but both host materials preferred the same guest (*p*-toluidine) in these competition experiments.

In the present work, we have investigated and compared the selective behaviour of TETROL and DMT when recrystallized from guest solvents comprising two different classes of aromatic compounds, namely the alkylated aromatics toluene, ethylbenzene and cumene, and the aminated aromatics aniline, *N*-methylaniline and *N*,*N*-dimethylaniline. Surprisingly, the preference order of DMT for the anilines [11] contrasted with that of TETROL; however, the extent of the selectivity for their preferred guests was comparable. These observations are distinctly different from the results obtained from the toluidine work, where TETROL was observed to be significantly more selective than DMT [14]. We employed single crystal diffraction analyses in order to ascertain the reasons for these differences, and thermal analyses to investigate the stabilities of all complexes formed, and report on these results here.

2. Results and discussion

2.1. Synthesis of DMT and TETROL

Both host materials were prepared from naturally-occurring (+)-diethyl L-tartrate using published methods [10,15].

2.2. Assessment of the inclusion ability of DMT and TETROL with the alkylated and aminated aromatic guests

2.2.1. Single-solvent recrystallizations

Single solvent experiments were performed by dissolving each host individually in an excess of the six aromatic guest solvents, and the vessels left open under ambient conditions until crystallization occurred. The resulting solids were collected by vacuum filtration, washed with petroleum ether (b.p. 40–60 °C), and analysed by means of ^{1}H NMR spectroscopy using $CDCl_3$ as the solvent. Where inclusion complex formation occurred, the H:G ratios were determined from appropriate host and guest compound resonance integrals. Table 1 summarises these results.

It is clear from this table that TETROL is significantly more discriminating than DMT, including only aniline and *N*-methylaniline from the list of six possible guests, and showed no affinity at all for the alkylated benzenes. DMT, on the other hand, formed complexes with all six solvents. Furthermore, H:G ratios in the case of complexes with TETROL were guest-dependent with aniline and *N*-methylaniline being included with 2:3 and 2:4 H:G ratios, respectively. In contrast, DMT favoured the 2:1 ratio in every instance.

Table 1
Host:guest (H:G) ratios of complexes obtained when TETROL and DMT were recrystallized individually from the six aromatic guests species.

Guest	TETROL	DMT
Toluene	[a]	2:1
Ethylbenzene	[a]	2:1
Cumene	[a]	2:1
Aniline	2:3	2:1[b]
N-Methylaniline	2:4[c]	2:1[b]
N,*N*-Dimethylaniline	[a]	2:1[b]

[a] These guests were not clathrated.
[b] These results were published on a prior occasion and are inserted here for ease of comparison [11].
[c] Subsequent diffraction analyses showed the asymmetric unit to contain two host and four guest molecules.

2.2.2. Equimolar mixed-solvent recrystallizations

We subsequently conducted competition experiments using various combinations of the three alkylated and, independently, the three aminated aromatics in order to determine the effect of the availability of multiple guests on the inclusion behaviour of the host. In each case, the host was recrystallized from equimolar combinations of the guest solvent. The equimolar condition was maintained by storing the vessels at 0 °C after dissolution of the host. Where crystals formed, these were processed as in the single-solvent experiments. Table 2 (aminated aromatics) and 3 (alkylated aromatics) summarise the data obtained. Note that since none of the alkylated aromatics were included by TETROL, competition studies for this class of compounds and this host were disregarded.

These data reveal that TETROL has a distinct preference for including aniline whenever this compound was present in the recrystallizing mixture (Table 2). From the aniline/*N*-methylaniline and aniline/*N*,*N*-dimethylaniline binary mixtures, TETROL extracted 68 and 95% aniline, respectively. An *N*-methylaniline/*N*,*N*-dimethylaniline experiment, on the other hand, failed to furnish crystals and when aniline was also added, a host preference order of aniline (67%) > *N*-methylaniline (29%) > *N*,*N*-dimethylaniline (4%) was noted. In contrast to TETROL, DMT afforded a host selectivity order of *N*,*N*-dimethylaniline (62%) > *N*-methylaniline (32%) > aniline (6%) [11]. Furthermore, it is noteworthy that the extent of these host selectivities are comparable (62, 32, 6 *versus* 67, 29, 4) though for different guests. The selectivity of DMT in the aniline series appears to correlate with increasing polarity of the aniline guest compound, while the opposite is true for TETROL.[1]

In the case of the alkyl benzenes, binary competition experiments showed that DMT selected toluene (67%) and ethylbenzene (63%) in preference to cumene (33 and 37%, respectively, Table 3). When the host was recrystallized from an equimolar toluene/ethylbenzene mixture, toluene was only marginally preferred (51% *vs* 49%). A ternary competition experiment comprising all three alkyl aromatics resulted in poor selectivity with an order ethylbenzene (39%) > toluene (35%) > cumene (26%) being obtained. On the face of it, the inclusion selectivity displayed by DMT seems to correlate with the polarities of the guest compounds insofar as it exhibited higher selectivity in a ternary mixture of the three anilines (Table 2), while the inclusion selectivity was poor in a ternary mixture of the relatively non-polar alkyl benzene guests.

[1] The dipole values for aniline, *N*-methylaniline and *N*,*N*-dimethylaniline, computed at the ωB97X-D/6-31G* level, are 1.69, 1.73 and 1.79, while those for toluene, ethylbenzene and cumene are 0.33, 0.29 and 0.27 Debye, respectively.

Table 2
Host:guest (H:G) ratios of complexes obtained when TETROL and DMT were recrystallized from equimolar mixtures of the aniline guests.[a]

Host	Aniline	*N*-Methylaniline	*N*,*N*-Dimethylaniline	Guest ratios (%e.s.d.s[b])	Overall H:G ratio
TETROL	***x***	x		***68***:32 (0.3)	2:3
TETROL	***x***		x	***95***:5 (0.7)	2:3
TETROL		x	x	[c] (N/A)	N/A
TETROL	***x***	x	x	***67***:29:4 (0.6)(0.6)(0.1)	2:3
DMT[c]	x	***x***		15:***85*** (0.1)	2:1
DMT[c]	x		***x***	15:***85*** (0.8)	2:1
DMT[c]		x	***x***	41:***59*** (0.3)	2:1
DMT[c]	x	x	***x***	6:32:***62*** (0.2)(0.2)(0.0)	2:1

Bold italic represents preferred guest.
[a] Determined using GC-MS (see General Methods) and/or ^{1}H NMR spectroscopy, as appropriate.
[b] Experiments were conducted in triplicate, and parentheses contain the percentage estimated standard deviations (%e.s.d.s).
[c] These results have been published on a prior occasion [11] and are inserted here for ease of comparison.

Table 3
Guest ratios in complexes obtained from competition experiments using DMT and equimolar mixtures of the alkylbenzene guests[a,b].

Toluene	Ethylbenzene	Cumene	Guest ratios (%e.s.d.s[c])	Overall H:G ratio
x	x		***51***:49 (0.4)	2:1
x		x	***67***:33 (0.9)	2:1
	x	x	***63***:37 (0.1)	2:1
x	***x***	x	35:***39***:26 (0.4, 0.1, 0.1)	2:1

Bold italic represents preferred guest.
[a] Ratios determined using GC-MS.
[b] TETROL's behaviour was not assessed in this investigation since it failed to include any of the alkylated aromatics.
[c] Experiments were conducted in triplicate, and percentage estimated standard deviations (%e.s.d.s) are given in parentheses.

2.3. Single crystal X-ray diffraction analyses

Crystals of DMT alone and also its complexes with toluene and cumene were subjected to these X-ray diffraction analyses, as were the complexes of TETROL with aniline and *N*-methylaniline. The diffractions were conducted at 200 K employing a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). APEXII [16] was used for data collection and SAINT [16] for cell refinement and data reduction. The structures were solved using SHELXT-2014 [17] and refined by least-squares procedures using SHELXL-2016 [18] with SHELXLE [19] as graphical interface. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized geometrical positions in a riding model. Data were corrected for absorption effects using the SADABS [16] numerical method. All relevant crystal data were deposited at the Cambridge Crystallographic Data Centre and may be accessed free of charge via www.ccdc.cam.ac.uk/data_request/cif [CCDC reference numbers 1828030 (2DMT·toluene), 1828031 (2DMT·cumene), 1828032 (DMT apohost), 1827895 (2TETROL·3aniline) and 1842472 (2TETROL·4N-methylaniline)]. [Diffraction data for 2DMT·ethylbenzene (CCDC 1487592), 2DMT·aniline (1577095), 2DMT·*N*-methylaniline (1577097) and 2DMT·*N*,*N*-dimethylaniline (1577096) were deposited on prior occasions [10,11].

Table 4 lists crystallographic data and refinement parameters for 2DMT·toluene, 2DMT·cumene, DMT apohost, 2TETROL·3aniline and 2TETROL·4N-methylaniline. Both the toluene and cumene complexes experience isostructural host packing, crystallizing in the monoclinic crystal system with *C*2 symmetry. In fact, all six complexes relevant to the present discussion shared this isostructurality [10,11]. The crystal packing, however, collapsed when guest was not present, as witnessed by the variation in crystal system (tetragonal) and space group ($I4_1$) of the apohost material (Table 4). The host packing in complexes with TETROL, on the other hand, was guest-dependent: enclathration of aniline resulted in solids which crystallised in the orthorhombic crystal system and $P2_12_12_1$ space group, while the *N*-alkylated guest complex differed from this (triclinic, *P*1).

Both toluene and cumene in complexes with DMT displayed disorder owing to rotation about a two-fold axis. (Ethylbenzene, on the other hand, showed several layers of disorder [10]). These relatively non-polar guests were entrapped within the host crystal by means of a number of weak π–π interactions ranging between 4.570(6) and 5.996(3) Å. Toluene experienced no further interaction types while only one other short contact was noted in the cumene inclusion compound involving the *meta*-aromatic C atom of the guest and the *para*-aromatic H atom of the host (2.89 Å, 168°). Overall, the number and type of host–guest interactions in these complexes are strikingly few.

Only one of the three guests in the asymmetric unit of 2TETROL·3aniline is disordered. Here, the two ordered aniline molecules are anchored in position by means of strong hydrogen bonds with the secondary hydroxyl groups of the host, measuring 2.746(3) and 2.763(3) Å (O···N), with angles of 165 and 167°, respectively. The host functions as a H-bond donor in both cases. The disordered aniline molecule does not experience an interaction of this type. Similar observations were made when analysing TETROL's 2:3 H:G complexes with the toluidines [14]. The asymmetric unit of 2TETROL·4N-methylaniline comprises two host and four guest molecules. Two of the four guests function as hydrogen bond acceptors with secondary host hydroxyl groups, both measuring 2.738(2) Å (O···N), with angles 151 and 154°. Remarkably, the third is a donor to one of the tertiary host hydroxyls [O···N 3.019(3) Å, 152(2)°] which, to the best of our knowledge, is unprecedented in the literature – to date, TETROL has only ever been observed to function as a donor to guests that possess hydrogen bonding capability and [14,15], interestingly, it is the secondary hydroxyl groups that are largely involved. The fourth guest molecule, once more, does not experience hydrogen bonding with the host. Contrastingly, on no occasion does DMT retain its guests in the crystal by means of hydrogen bonding when such guests have the ability to perform as hydrogen bond donors and/or acceptors, as in the aniline series [11]. This suggests that TETROL favours this interaction type while DMT does not, which predisposes TETROL to complex less readily with the various guests, as witnessed in Table 1. DMT, however, does not employ hydrogen bonding to stabilize guest retention, and so a wider variety of guests are able to be enclathrated by it. This is affirmed by the fact that DMT readily forms complexes with the alkyl aromatics, while TETROL does not since these guests do not possess hydrogen bonding capability.

Fig. 1a–d depict the unit cells for 2DMT·toluene (as representative example of the isostructural complexes, with guests in magenta colour and ball-and-stick representation), apohost DMT,

Table 4
Crystallographic data for 2DMT·toluene, 2DMT·cumene, DMT alone, 2TETROL·3aniline and TETROL·2N-methylaniline.

	2DMT·toluene	2DMT·cumene	Apohost	2TETROL·3aniline	2TETROL·4N-methylaniline
Chemical formula	$2C_{30}H_{30}O_4 \cdot C_7H_8$	$2C_{30}H_{30}O_4 \cdot C_9H_{12}$	$C_{30}H_{30}O_4$	$2C_{28}H_{26}O_4 \cdot 2C_6H_7N, C_6H_5N$[a]	$2C_{28}H_{26}O_4 \cdot 4C_7H_9N$
Formula weight	1001.21	1029.27	454.54	1130.34	640.79
Crystal system	Monoclinic	Monoclinic	Tetragonal	Orthorhombic	Triclinic
Space group	*C*2	*C*2	$I4_1$	$P2_12_12_1$	*P*1
μ (Mo-Kα)/mm^{-1}	0.078	0.078	0.078	0.080	0.078
a/Å	17.3412(6)	17.1139(6)	10.2823(6)	17.3680(9)	11.5756(6)
b/Å	11.9827(4)	12.0772(5)	10.2823(6)	17.5435(9)	13.1533(7)
c/Å	14.0871(5)	14.3270(5)	23.8173(2)	20.0346(10)	13.6373(6)
alpha/°	90	90	90	90	62.163(2)
beta/°	109.892(2)	107.460(2)	90	90	89.734(2)
gamma/°	90	90	90	90	74.043(2)
V/Å [3]	2752.6(2)	2824.8(2)	2518.1(3)	6104.5(5)	1746.56(16)
Z	2	2	4	4	2
F(000)	1068	1100	968	2400	684
Temp./K	200	200	200	200	200
Restraints	5	1	1	6	3
Nref	6037	6398	3129	15216	16209
Npar	326	380	156	758	893
R	0.0377	0.0351	0.0307	0.0401	0.0338
wR2	0.1008	0.0899	0.0826	0.1135	0.0788
S	1.03	1.03	1.09	1.04	1.02
θ min–max/°	2.1, 28.3	2.1, 28.3	2.2, 28.3	1.5, 28.3	1.7, 28.3
Tot. data	19477	26304	39639	147780	62431
Unique data	6037	6398	3129	15216	16209
Observed data [I > 2.0 sigma(I)]	5479	5519	2982	12442	14356
R_{int}	0.017	0.020	0.020	0.023	0.020
Dffrn measured fraction θ full	0.999	1.000	1.000	1.000	1.000
Min. resd. dens. (e/Å^3)	−0.33	−0.17	−0.13	−0.32	−0.17
Max. resd. dens. (e/Å^3)	0.31	0.20	0.16	0.40	0.22

[a] Nitrogen-bound hydrogen atoms could not be located since these guest molecules displayed disorder.

and the complexes of TETROL with aniline (hydrogen bonded guests in yellow and those not hydrogen bonded in green) and *N*-methylaniline (hydrogen bonded guests, orange; non-hydrogen bonded guest, red), respectively. A stereoview is also provided in Fig. 2 to illustrate the unusual hydrogen bond acceptor behaviour of TETROL in the latter complex, involving the N–H hydrogen atom of *N*-methylaniline and the tertiary host hydroxyl group.

2.4. Thermal analyses

The stabilities of the novel complexes formed in this study, i.e. 2DMT·toluene, 2DMT·cumene, 2TETROL·3aniline and 2TETROL·4N-methylaniline, were determined through thermal analysis by heating in open platinum pans at 10 °C.min^{-1}. Fig. 3a–b illustrate the overlaid thermogravimetric (TG) and the derivative thereof (DTG) traces that were obtained for the DMT and TETROL inclusion compounds, respectively.

Table 5 summarises the relevant thermal data obtained from these traces.

The expected and observed mass losses experienced by the four complexes are all in close agreement (Table 5). Furthermore, thermal events experienced by the complexes with TETROL are generally more convoluted than those with DMT, as expected, owing to the isostructurailty of host packing in the latter and, additionally, the presence of only a few host–guest stabilizing interactions. T_{on}, the onset temperature of the guest release process which was estimated from the derivative of the TG (DTG), serves as a measure of the stabilities of the complexes, and these correlate exactly with the selectivity orders of the two hosts: toluene and aniline are released at significantly higher temperatures relative to cumene and *N*-methylaniline in their respective crystals with DMT and TETROL, reflecting the higher stabilities of the complexes of 2DMT·toluene and 2TETROL·3aniline, which explains the preference of the hosts for these guests as observed from competition experiments.

3. Conclusion

DMT and TETROL, compounds that are related closely in structure, display very different host abilities when recrystallized from two different classes of guest solvents, namely toluene, ethylbenzene, cumene on one hand, and aniline, *N*-methylaniline, *N*,*N*-dimethylaniline on the other. TETROL failed to form complexes with the alkyl aromatics, while each of these was included by DMT with a 2:1 host:guest ratio. An equimolar ternary experiment comprising these three guests showed that DMT was poorly selective under these conditions. However, TETROL did form complexes with aniline and *N*-methylaniline, while *N*,*N*-dimethylaniline was not clathrated. Host:guest ratios differed for the two complexes formed. When TETROL was recrystallized from an aniline/*N*-methylaniline/*N*,*N*-dimethylaniline mixture, it displayed a high preference for aniline; these results contrasted with similar experiments conducted using these guests and DMT, where the opposite selectivity order was observed. Single crystal X-ray diffraction analyses showed that TETROL employs hydrogen bonding with the aniline guests in order to stabilize each complex. Previously, TETROL has been observed to behave as the donor in such interactions, utilizing the secondary hydroxyl hydrogen atoms. In the present case, TETROL functions unusually as a hydrogen bond acceptor, employing the tertiary hydroxyls to achieve this. This was revealed in the inclusion compound with *N*-methylaniline, where one of these guests in the asymmetric unit donated a hydrogen towards the tertiary host hydroxyl group. The increased complexation ability of DMT relative to TETROL was ascribed to the fact that TETROL, in this investigation, relies on hydrogen bonding for guest retention, and so the guest should have this capability. Therefore the three non-polar alkyl benzene guests were not complexed while two of the anilines were. DMT is less discerning since it does not rely on this interaction type in order to stabilize the guest in the crystal. Finally, thermal analyses showed that the stabilities of the novel complexes produced in this

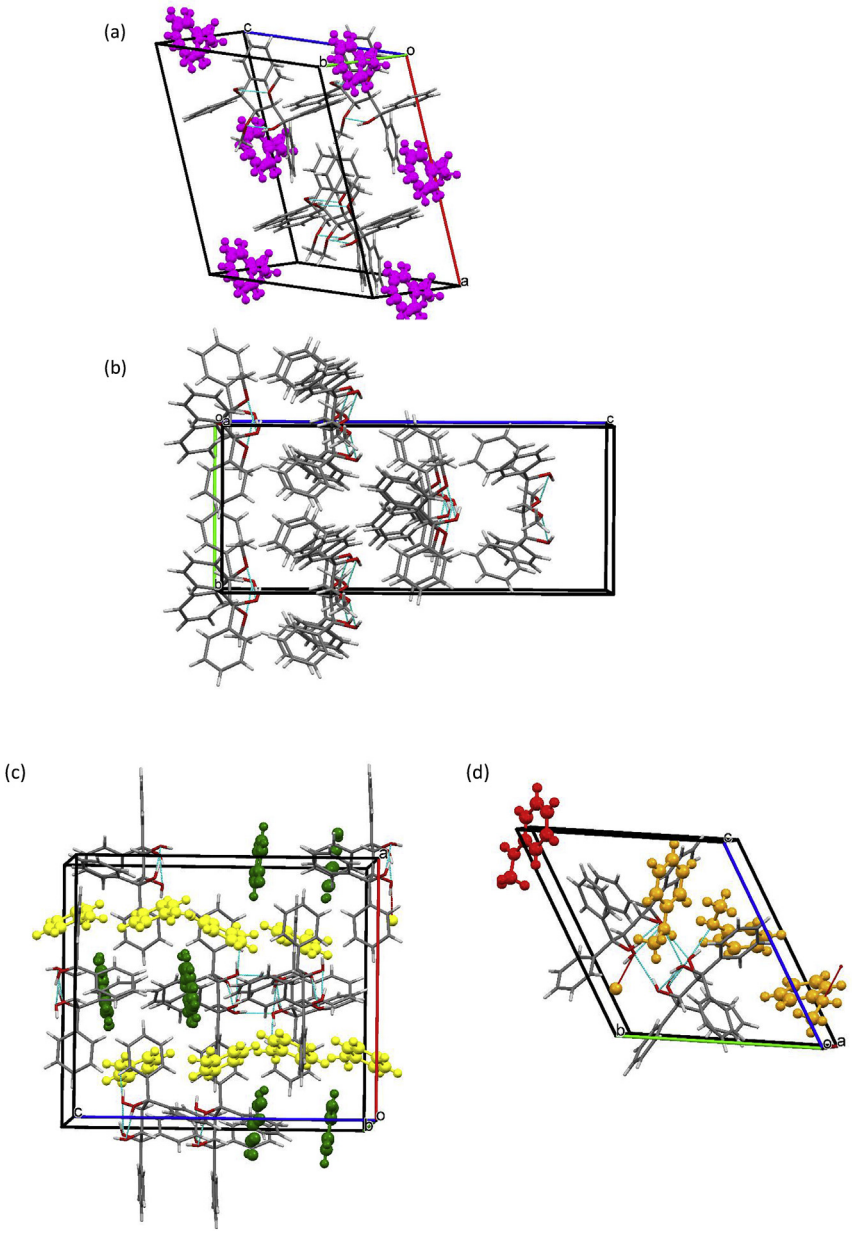

Fig. 1. Unit cells for (a) 2DMT·toluene, (b) DMT alone, (c) 2TETROL·3aniline, and (d) 2TETROL·4N-methylaniline.

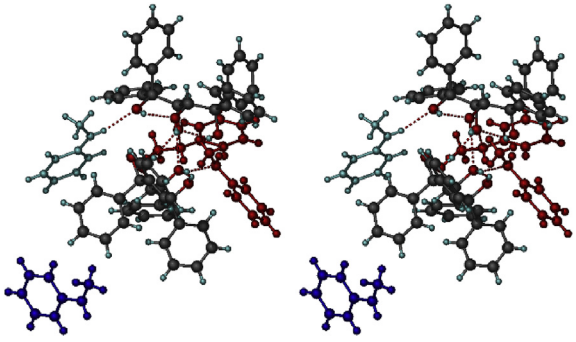

Fig. 2. Stereoview depicting the unusual behaviour of TETROL as a hydrogen bond acceptor to one of the four *N*-methylaniline guests (turquoise); the guest that does not hydrogen bond to the host is shown in blue.

work correlate exactly with the guest preference order.

4. Experimental

4.1. General methods

Melting points were recorded on a Stuart SMP10 melting point apparatus and are uncorrected. ^{1}H- and ^{13}C- NMR spectra were obtained by means of a 400 MHz Bruker Avance Ultrashield Plus 400 spectrometer, and infrared spectra using a Bruker Tensor 27 Fourier Transform Infrared spectrophotometer. Gas chromatography was performed using an Agilent Technologies 7890 A gas chromatograph system connected to an Agilent Technologies 5975 C VL MSD mass spectrometer with a triple-axis detector. High purity helium gas was used as the carrier gas. An Agilent J&W Cyclosil-B column was used for the alkyl aromatics analyses, and the parameters were 30 m × 250 μm x 0.25 μm (calibrated). From

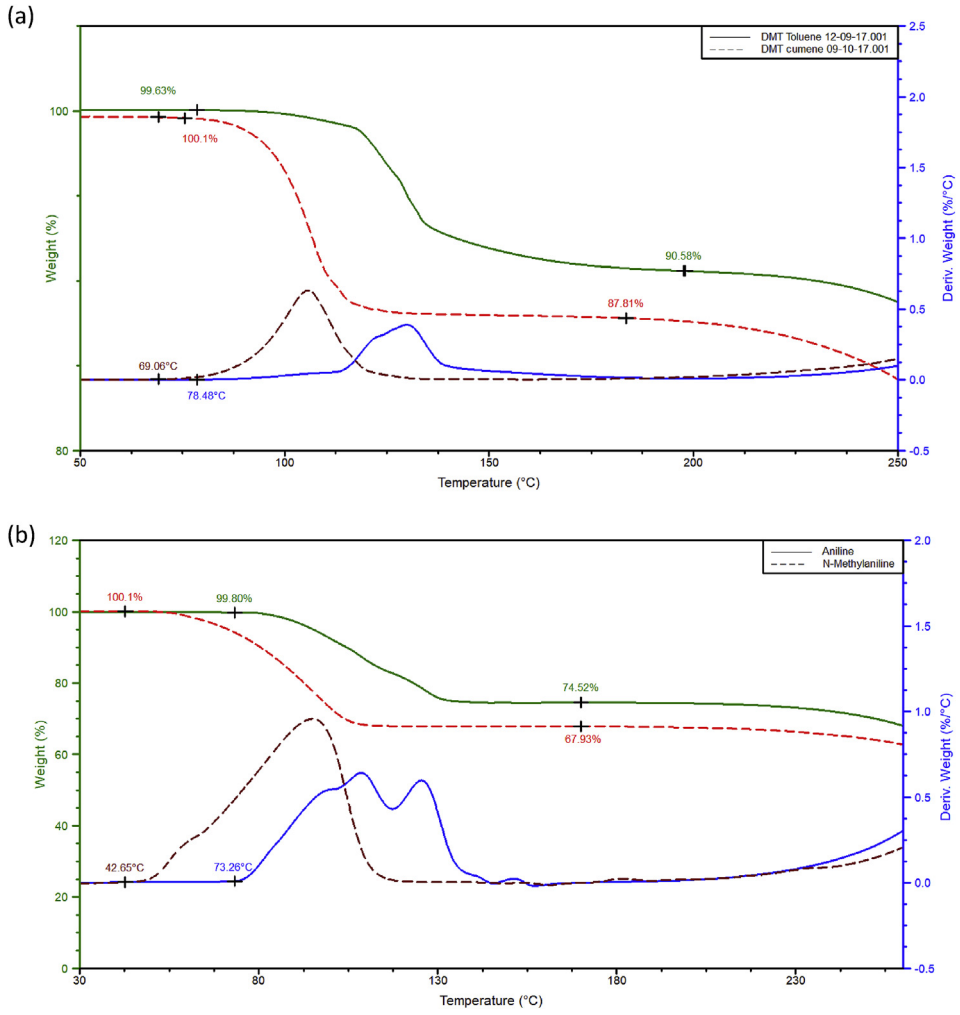

Fig. 3. Overlaid TG and DTG traces for (a) 2DMT·toluene and 2DMT·cumene, and (b) 2TETROL·3aniline and 2TETROL·4N-methylaniline.

an initial temperature of 50 °C, a heating rate of 2.5 °C.min^{-1} was employed up to 90 °C with a final hold time of 1 min. For the anilines analyses, an HP-5 column (30 m) was employed. The method involved an initial 2 min hold time at 40 °C, followed by a ramp of 2 °C.min^{-1} until 160 °C was reached, and then a hold time at this temperature for 5 min, and lastly a ramp of 20 °C.min^{-1} until 220 °C was attained, and then a final hold time at this temperature for 10 min. The split ratio was 100:1 and inlet temperature 250 °C. Thermal analyses were carried out on a TA SDT Q600 Module system and analysed using TA Universal Analysis 2000 data analysis software. The solid complexes were placed in open platinum pans. An empty platinum pan was employed as a reference, and high purity nitrogen gas was used as the purge gas.

Table 5
Thermal data for 2DMT·toluene, 2DMT·cumene, 2TETROL·3aniline and 2TETROL·4N-methylaniline.

Complex	T_{on} (°C)[a]	Mass loss expected (%)	Mass loss observed (%)
2DMT·toluene	78.5	9.2	9.1
2DMT·cumene	69.1	11.7	12.3
2TETROL·3aniline	70.9	24.7	25.9
2TETROL·4N-methylaniline	41.1	33.4	32.2

[a] Estimated from the DTG trace and is the onset temperature of the guest release process.

4.2. Preparation of hosts DMT and TETROL

These host compounds were prepared according to published procedures [10,15].

4.2.1. Synthesis of TETROL [15].

(*R*,*R*)-(+)-Diethyl L-tartrate (5.71 g, 27.7 mmol), phenylmagnesium bromide [prepared from magnesium turnings (4.06 g, 167 mmol) and bromobenzene (23.12 g, 147 mmol)] afforded a gum which was dissolved in methanol, from which TETROL crystallised (7.98 g, 18.7 mmol, 68%), mp 148–150 °C (lit., [20], mp 150–151 °C); $[\alpha]_D^{23}$ +163° (*c*. 3.18, CH_2Cl_2) {lit., [20], $[\alpha]_D^{25}$ +154° (*c*. 1.2, $CHCl_3$)}; ν_{max}(solid)/cm^{-1} 3525–3380 (br, OH), 3392–3146 (br, OH), 3057 (Ar), 3031 (Ar), 1597 (Ar) and 1493 (Ar); δ_H($CDCl_3$)/ppm 3.82 (4H, br, 2HCOH and 2CPh_2OH), 4.31 (2H, s, 2HCOH) and 7.00–7.30 (20H, m, Ar); δ_C($CDCl_3$)/ppm 72.1 (HCOH), 81.7 (CPh_2OH), 125.0 (Ar), 126.1 (Ar), 127.1 (Ar), 127.3 (Ar), 128.4 (Ar), 128.6 (Ar), 143.9 (quaternary Ar) and 144.2 (quaternary Ar) (See Supplementary data, Figs. 1S and 2S).

4.2.2. Synthesis of DMT [10].

Excess sodium hydride (6.0125 g, 55–65% suspension in mineral oil), TETROL (5.48 g, 12.8 mmol) and methyl iodide (3.65 g, 25.9 mmol) afforded a gum which was triturated with petroleum ether (40–60 °C); this resulted in a white precipitate which was recrystallized from methanol/petroleum ether to yield DMT (3.76 g,

8.27 mmol, 65%), mp 124–126 °C (lit. [21], mp 125–126 °C); $[\alpha]_D^{23}$ −154.5° (*c*. 0.27, CH_2Cl_2) {lit. [21], $[\alpha]_D$ −153° (*c*. 0.8, $CHCl_3$)}; ν_{max}(solid)/cm^{-1} 3576–3271 (br, OH), 3025 (Ar), 2836 (O–CH_3), and 1567 (Ar); δ_H($CDCl_3$)/ppm δ_H($CDCl_3$)/ppm 2.59 (6H, s, 2OCH_3), 4.44 (2H, s, 2$HCOCH_3$), 4.87 (2H, s, 2CPh_2OH [disappears upon addition of D_2O]), 7.15 (2H, m, Ar), 7.24 (4H, m, Ar), 7.32 (2H, m, Ar), 7.46 (4H, m, Ar) and 7.63 (8H, m, *ortho*-Ar); δ_C($CDCl_3$)/ppm 61.0 (OCH_3), 80.1 (CPh_2OH), 85.3 ($HCOCH_3$), 125.9 (Ar), 126.1 (Ar), 126.8 (Ar), 127.2 (Ar), 128.0 (Ar), 128.5 (Ar), 144.9 (quaternary Ar) and 145.6 (quaternary Ar). (See Supplementary data, Figs. 3S and 4S).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.07.044.

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