ORIGINAL ARTICLE



DMT [(–)-(2*R*,3*R*)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol], a highly efficient host compound for nitroaromatic guests: selectivity, X-ray and thermal analyses

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Abstract

In this work, we reveal that the compound (-)-(2*R*,3*R*)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (DMT) is a highly efficient host material for nitroaromatics *o*-nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), *p*-nitrotoluene (*p*-NT) and nitrobenzene (NB). Each of these guests was included with a 2:1 host:guest ratio. The host displayed selectivity for *p*-NT and NB when these guests were mixed in equimolar proportions with any one of the other guest solvents, and the host recrystallized from this binary mixture. A selectivity order for the host in these conditions was thus noted to be NB \approx *p*-NT > *o*-NT > *m*-NT. Furthermore, guests were also mixed in non-equimolar proportions and the host behaviour analysed, the results of which were in accordance with observations from the equimolar studies. Additionally, an equimolar quaternary experiment of all four guests provided a somewhat adjusted host selectivity order [*p*-NT (39.9%) > NB (30.2%) > *m*-NT (17.1%) > *o*-NT (12.8%)]. Single crystal diffraction analyses of all four complexes showed the crystals to share the same host packing, and comparable host–guest interactions were observed in each. However, thermal analyses, both DSC and TG, showed that the preferred guests *p*-NT and NB formed complexes with increased relative thermal stabilities, and this observation correlated with the selective behaviour of the host in competition experiments.

Keywords Host-guest chemistry · Inclusion · Complexes · Selectivity · Nitrobenzene · Nitrotoluene

Introduction

Nitrobenzene (NB), *p*-nitrotoluene (*p*-NT), *m*-nitrotoluene (*m*-NT) and *o*-nitrotoluene (*o*-NT) (Scheme 1) are aromatic compounds that have myriad applications in the chemical industry [1-5]. Most of the nitrobenzene in production is converted to aniline, which has a variety of applications, but nitrobenzene is also sometimes used as a solvent for certain reactions. Industrially, it is produced through the mixed acid nitration of benzene. The nitrotoluene isomers see routine use as building blocks in the production of agricultural chemicals, explosives and dyes (commonly via

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Benita Barton benita.barton@mandela.ac.za reduction to their corresponding toluidines). Specifically, *p*-NT is often sulfonated to yield 4-nitrotoluene-2-sulfonic acid, which may be further utilized as a synthetic intermediate, or crystals thereof may be used in optical applications. The nitrotoluenes are synthesized through nitration of toluene, a process that affords a mixture of the nitrotoluene isomers with an *o*-NT:*p*-NT ratio of ~ 1.6 (with *m*-NT being the minor product). The boiling points of *o*-NT (222.0 °C) and *m*-NT (232.0 °C) are sufficiently different to allow their separation through fractional distillation, after which *p*-NT may be isolated through crystallization as it has a relatively high melting point (51.6 °C).

Much of the research conducted where one or more of these compounds behaves as a guest in host–guest applications deals with chemically sensing them. Examples include the work of Li et al. [6] who investigated the use of lanthanide(III) organic frameworks as fluorescent probes for sensing various nitroaromatics with high selectivity and sensitivity. Other workers considered triptycene-polytriazoles [7] and dendrimer-derived macromolecules [8] and their interactions with these guest types.

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Scheme 1 Structures of hosts DMT and TETROL, and guests NB, *o*-NT, *m*-NT and *p*-NT

(-)-(2R,3R)-2,3-Dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (DMT, Scheme 1) has been shown to be a highly efficient host compound that exhibited selectivity when recrystallized from mixtures of xylenes [9] and various anilines [10], with the potential of thus separating such mixtures. This compound is readily synthesized by methylation of the secondary hydroxyl groups of host TETROL [(+)-(2R,3R)-1,1-4,4-tetraphenylbutane-1,2,3,4-tetraol, Scheme 1]. A comparison of the behaviour of these two host materials when recrystallized in the presence of isomeric toluidine mixtures showed the hosts to possess differing host ability [11], despite their structural similarities, with DMT displaying significantly poorer selectivity than TETROL in these conditions. Since DMT is selective when presented with mixed guests, we investigated the behaviour of this host compound in the presence of o-NT, *m*-NT and *p*-NT (in addition to NB) to determine whether their separation would be feasible via host-guest chemistry rather than the more usual fractional distillations and crystallizations. Even though these nitroaromatics are successfully separated industrially, it remains attractive to probe alternative separation methodologies.

Complexes that formed successfully were subjected to single crystal diffraction and thermal analyses in order to ascertain the nature of guest inclusion and the relative complex stabilities. The results of these studies are presented here.
 Table 1 Composition of complexes when DMT was recrystallized from mixed equimolar guests

NB	o-NT	m-NT	p-NT	Guest ratios (%e.s.d.'s)	Overall H:G ratio
	x	x		66.4 :33.6 (2.3)	2:1
	х		x	16.8: 83.2 (1.0)	2:1
		x	x	22.3: 77.7 (1.1)	2:1
	х	x	x	13.2:20.6: 66.2 (0.3)(0.5)(0.7)	2:1
x	х			71.9 :28.1 (1.2)	2:1
x		х		79.7 :20.3 (2.6)	2:1
x			x	49.6: 50.4 (1.2)	2:1
x	X	X	x	30.2:12.8:17.1: 39.9 (0.8)(1.2)(0.7)(1.0)	2:1

Ratios were determined using GC-MS analyses

Experiments were conducted in triplicate and averages are provided here, with %e.s.d.'s in parentheses

Results and discussion

Synthesis of DMT

DMT is derived directly from TETROL in moderate yield (65%) according to published procedures [9, 12].

Assessment of the host potential of DMT for singular guests NB, o-NT, m-NT and p-NT

After recrystallizing DMT from each of the individual nitroaromatic guests, ¹H-NMR spectroscopy of the isolated solids revealed that DMT clathrated each guest, and each complex shared the same host:guest (H:G) ratio (2:1).

Competition experiments employing mixed guests

Equimolar guest mixtures

Since each of the guests was clathrated individually, we conducted competition experiments by mixing guests in equimolar proportions and recrystallizing DMT from these mixtures. These experiments were carried out in order to ascertain whether DMT displayed selectivity when the guests competed. After GC-MS analyses of the crystals formed in this way, Table 1 was populated, displaying the composition of the complexes. For ease of distinction, the preferred guest is highlighted in bold italic font face.

In each experiment, the overall H:G ratio remained 2:1 (Table 1). A binary competition between *o*-NT and *m*-NT resulted in DMT preferentially including *o*-NT (66.4%). However, in the presence of *o*-NT and *p*-NT, the latter solvent was favoured (83.2%), and remained so also in the presence of *m*-NT, where 77.7% of *p*-NT was extracted from the mixture. A ternary competition experiment comprising only the nitrotoluenes resulted in a host selectivity order of *p*-NT (66.2%) > *m*-NT (20.6%) > *o*-NT (13.2%).

NB was also considered in experiments of this type, and this guest was selected for when competing against *o*-NT (71.9%) and *m*-NT (79.7%). However, very poor selectivity was displayed by DMT in a competition between NB and *p*-NT (*p*-NT, 50.4%).

When we considered only the binary competition experiments, a host selectivity order of NB $\approx p$ -NT > o-NT > m-NT was observed. Interestingly, however, when all four guests were mixed together, this selectivity order was altered: p-NT (39.9%) > NB (30.2%) > m-NT (17.1%) > o-NT (12.8%).

Non-equimolar guest mixtures

We subsequently varied the mole fractions of guests in binary mixtures (all combinations) and then recrystallized DMT from these. After analysing both the resultant crystals (Z) and the mother liquor from which they had formed (X) using GC-MS, we plotted the data points (Z vs X) in order to determine how the host behaviour changed as guest concentrations changed. The resultant plots are provided in Fig. 1a–f.

In these figures, the dashed straight-line plot represents an unselective host, and is hypothetical.

From the *p*-NT/*m*-NT competition experiment (Fig. 1a), it is clear that DMT is consistently selective for the para isomer over the entire concentration range. However, *p*-NT/*o*-NT mixtures revealed that, at low concentrations of the para isomer, the host was unselective (up until approximately 20% p-NT), and only displayed increased selectivity for *p*-NT at increased concentrations of this guest (Fig. 1b). On the other hand, the behaviour of DMT when recrystallized from o-NT/m-NT mixtures was guestconcentration dependent, showing preferential inclusion of *m*-NT at low concentrations of the *ortho* isomer, and preferring o-NT at higher concentrations of this guest. The point of inflection occurred at approximately 36% o-NT (Fig. 1c). The behaviour of DMT in the presence of both p-NT and NB was comparable to the o-NT/m-NT experiment (Fig. 1c), being guest-concentration dependent, but the point of inflection occurred at a higher concentration of *p*-NT (52%, Fig. 1d). A competition experiment comprising NB/*m*-NT (Fig. 1e) resembled that of *p*-NT/*o*-NT (Fig. 1b), and the host was unselective at low concentrations of NB (up until ~ 18%), after which point its preference for NB increased significantly. Finally, NB/*o*-NT mixtures showed DMT to consistently discriminate against *o*-NT in favour of NB (Fig. 1f).

We also investigated the behaviour of DMT in the simultaneous presence of all three of the nitrotoluene isomers. Once more, the mother liquors (circles, A–G) and crystalline solids (squares, A'–G') were analysed and resulted in the ternary plot provided in Fig. 2. The general trend indicates a substantial shift towards higher *p*-NT concentrations in the complexes when compared with the mother liquors.

Single crystal X-ray crystallographic analyses of complexes of DMT with *o*-NT, *m*-NT, *p*-NT and NB

We analysed each of the four complexes of DMT using single crystal diffraction experiments on suitable quality crystals in order to understand better the mode of retention of the guests within the host. These experiments were conducted at 200 K using a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). APEXII and SAINT were used for data collection, and cell refinement and data reduction, respectively [13]. SHELXT-2014 [14] was used to solve the structures, and refined by least-squares procedures using SHELXL-2017/1 [14] together with SHELXLE [15] as a graphical interface. Data were corrected for absorption effects using the numerical method implemented in SADABS [13]. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were added in idealized geometrical positions in a riding model, and the hydrogen atoms of the methyl groups were allowed to rotate with a fixed angle around the C-C bonds to best fit the experimental electron density. For disordered methyl groups, the hydrogen atoms were added in idealized geometrical positions, while the hydrogen atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C-O bonds to best fit the experimental electron density. The solvent molecules are disordered around a twofold rotational axis necessitating the use of various constraints and restraints. The phenyl rings of the disordered solvents were forced into a regular hexagon with bond lengths of 1.39 Å. The relevant crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [CCDC Reference Numbers 1847990 (2DMT-o-NT), 1847991 (2DMT·m-NT), 1847992 (2DMT·p-NT) and 1847993 (2DMT·NB)].

Table 2 lists the relevant crystallographic and refinement parameters for these experiments.



Fig. 1 Selectivity profiles of DMT when recrystallized from a *p*-NT/*m*-NT, b *p*-NT/*o*-NT, c *o*-NT/*m*-NT, d *p*-NT/NB, e NB/*m*-NT and f NB/*o*-NT mixtures

All four complexes of DMT crystallize in the monoclinic crystal system and C2 space group. A close analysis of unit cell angles and dimensions revealed that each of the four complexes are, in fact, isostructural. Furthermore, all guests exhibit well-modelled symmetry-generated disorder. Figure 3 displays the unit cell for the *p*-NT complex as representative example, where the guest is in ball-and-stick and the host in stick representation.

The isostructural nature of the host packing is a characteristic of DMT, and this host consistently packs in the same manner [9–11]. The geometry of the host molecule is stabilized by 1,3- and 2,4-intramolecular hydrogen bonds which range between 2.624(2) and 2.679(2) Å (O···O) with angles of $140^{\circ}-142^{\circ}$ (Fig. 3, dashed lines). These are the only classic hydrogen bonds present in the crystal—no bonds of this type exist intermolecularly with other host molecules nor with the guests.

A stereoview was also prepared to illustrate more clearly the host–guest packing for this complex (Fig. 4).





The guest molecules are retained in the complexes by various modes of interaction with the host, and these host–guest interactions are summarized in Table 3.

All of the guests experience comparable and weak $\pi-\pi$ stacking interactions with the host, with more of these contact types existing for NB (9 contacts), a highly preferred guest. Host-guest CH- π interactions are, furthermore, entirely absent in all complexes, while other short contacts between host and guest are present in the 2DMT·*o*-NT, 2DMT·*m*-NT and 2DMT·NB complexes (Table 3). Overall, these data do not convincingly explain the observed preference of DMT for NB and *p*-NT, and so we resorted to analysing the various complexes by means of thermal analyses.

Thermal analyses

In order to assess the relative thermal stabilities of the four complexes, these were subjected to thermal analyses

Table 2 Crystallographic data for 2DMT·o-NT, 2DMT·m-NT, 2DMT·p-NT and 2DMT·NB

	2DMT·o-NT	2DMT· <i>m</i> -NT	2DMT·p-NT	2DMT·NB
Chemical formula	$2C_{30}H_{30}O_4 \cdot C_7H_7NO_2$	$2C_{30}H_{30}O_4 \cdot C_7H_7NO_2$	$2C_{30}H_{30}O_4 \cdot C_7H_7NO_2$	$2C_{30}H_{30}O_4 \cdot C_6H_5NO_2$
Formula weight	1046.22	1046.22	1046.22	1032.19
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2	<i>C</i> 2	<i>C</i> 2	<i>C</i> 2
μ (Mo-K α)/mm ⁻¹	0.082	0.083	0.084	0.083
a/Å	17.4337 (9)	17.4167 (10)	17.155 (2)	17.2792 (9)
b/Å	12.0313 (7)	12.1276 (7)	12.2752 (17)	12.0018 (7)
c/Å	14.3683 (8)	14.0545 (9)	13.9597 (19)	13.9820 (8)
alpha/°	90	90	90	90
beta/°	110.512 (2)	109.768 (3)	109.557 (6)	108.757 (2)
gamma/°	90	90	90	90
V/Å ³	2822.7 (3)	2793.7 (3)	2770.1 (6)	2745.6 (3)
Z	2	2	2	2
F(000)	1112	1112	1112	1096
Temp./K	200	200	200	200
Restraints	5	2	1	2
Nref	6814	6824	6853	6787
Npar	347	389	359	380
R	0.0475	0.0366	0.0338	0.0340
wR2	0.1383	0.0980	0.0886	0.0895
S	1.06	1.04	1.03	1.02
θ min–max/°	2.1, 28.3	1.5, 28.3	2.1, 28.4	2.1, 28.3
Tot. data	28,821	29,120	27,460	26,189
Unique data	6814	6824	6853	6787
Observed data [I > 2.0 sigma(I)]	5903	6040	6447	6177
R _{int}	0.017	0.019	0.017	0.018
Dffrn measured fraction θ full	1.000	0.999	0.999	0.999
Min. resd. dens. (e/Å ³)	-0.33	-0.16	-0.23	-0.17
Max. resd. dens. $(e/Å^3)$	0.47	0.20	0.20	0.18



Fig. 3 Unit cell of the 2DMT·*p*-NT complex (as representative example)



Fig. 4 Stereoview to illustrate the host–guest packing in the 2DMT \cdot *p*-NT complex (as representative example); intramolecular host–host hydrogen bonding is shown by means of dashed lines

by heating at 10 °C min⁻¹ in open platinum pans. The soobtained thermogravimetric (TG, overlaid for each complex) and differential scanning calorimetry (DSC, also overlaid) traces are presented in Fig. 5a, b, respectively.

From the overlaid TG traces in Fig. 5a, it is evident that *p*-NT and NB, the preferred guests, are held more tightly in the host crystal (the onset temperatures for their guest release processes are higher) relative to the complexes comprising

o- and *m*-NT, guests that were discriminated against by DMT. Furthermore, DSC traces correspond favourably with these observations: although guest release occurs concomitantly with the host melt, both NB and *p*-NT experience this event at higher temperatures relative to the guests in the other two complexes (Fig. 5b).

Conclusions

(-)-(2R,3R)-2,3-Dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (DMT) is a highly efficient host compound for nitroaromatic guest compounds, including nitrobenzene and the three isomers of nitrotoluene, each with a 2:1 host:guest ratio. When two guests were mixed in equimolar proportions and the host recrystallized from these mixtures, it was observed that DMT displayed preferential behaviour, and the host selectivity order was noted to be NB $\approx p$ -NT > o-NT > m-NT. An equimolar mixture of all four guests, however, showed this order to change under these conditions [*p*-NT (39.9%) > NB (30.2%) > *m*-NT (17.1%) > o-NT (12.8%)]. Non-equimolar competition experiments revealed that DMT was selective for p-NT and NB over the entire concentration range when this host was recrystallized from p-NT/m-NT and NB/o-NT mixtures. p-NT was also preferred when using p-NT/o-NT, but with the host displaying non-selective behaviour at low concentrations of this guest. The case was similar for the NB/m-NT experiment, preferring NB but only after a certain minimum concentration of this guest in the solution had been reached. For the o-NT/m-NT and p-NT/NB experiments, the host preference was guest-concentration dependent as witnessed by the sigmoidal nature of the resulting data points. Single crystal diffraction analyses revealed that NB, a highly preferred guest, experienced a larger number of $\pi - \pi$ stacking interactions but, overall, the host-guest interactions were comparable and did not convincingly explain the selectivity displayed by the host. However, TG and DSC experiments showed that complexes containing the preferred guests p-NT and NB displayed higher relative thermal stabilities than those comprising o- and m-NT, as mass loss and concomitant guest release/host melt events occurred at increased temperatures for these complexes. This correlated favourably with the host selectivity order.

Interaction	2DMT·o-NT	2DMT·m-NT	2DMT·p-NT	2DMT·NB
π-π	4.826(4) – 5.994(3) Å (7 contacts)	4.842(2) – 5.883(3) Å (8 contacts)	5.191(1) – 5.788(1) Å (8 contacts)	5.217(4) – 5.845(3) Å (9 contacts)
СН–π	None	None	None	None
Other short contacts	2.61 Å, 134° < (host) <i>m</i> -ArH…O- N(guest) 2.72 Å, 163° < (host) <i>p</i> - ArH…ArC(guest) 2.33 Å, 153°, < (guest)CH… <i>m</i> - ArH(host)	2.69 Å, 150° ≪ (host) <i>o</i> -ArC… <i>o</i> - ArH(guest) 2.25 Å, 113°, < (host) <i>m</i> - ArH…HC(guest)	None	2.66 Å, 160° < (host) <i>p</i> -ArH…O-N(guest)

Table 3 Summary of the significant host-guest interactions in the complexes of DMT with o-NT, m-NT, p-NT and NB

< denotes contacts less than the sum of the van der Waals radii, while \ll denotes contacts less than this sum minus 0.2 Å



Fig. 5 Overlaid a TG and b DSC traces for the complexes of DMT with o-NT, m-NT, p-NT and NB

Experimental

General methods

Melting points were recorded on an Electrothermal IA9000 Series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 Fourier Transform Infrared spectrophotometer, and ¹H-NMR and ¹³C-NMR spectra on a 400 MHz Bruker Avance Ultrashield Plus 400 spectrometer. Thermal experiments were conducted using a TA SDT Q600 Module system and analysed using TA Universal Analysis 2000 data analysis software. Samples were placed in open platinum pans with an empty platinum pan functioning as

a reference. High purity nitrogen gas was used as purge gas. 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 Cyclodex-B column was used. From an initial temperature of 60 °C, a heating rate of 4 °C min⁻¹ was employed up to 145 °C with a final hold time of 1 min.

Synthesis of DMT

DMT was prepared from TETROL according to previous reports [9, 12].

TETROL¹²

A standard Grignard addition reaction to (*R*,*R*)-(+)-diethyl L-tartrate using phenylmagnesium bromide afforded a gum which crystallized from methanol (68%), mp 148–150 °C (lit. [16], mp 150–151 °C); $[\alpha]_D^{23}$ + 163 (*c*. 3.18, CH₂Cl₂) {lit. [16], $[\alpha]_D^{25}$ + 154 (*c*. 1.2, CHCl₃)}; ν_{max} (solid)/cm⁻¹ 3525–3380 (br, OH), 3392–3146 (br, OH), 3057 (Ar), 3031 (Ar), 1597 (Ar) and 1493 (Ar); δ_H (CDCl₃)/ppm 3.82 (4H, br, 2HCOH and 2CPh₂OH), 4.31 (2H, s, 2HCOH) and 7.00–7.30 (20H, m, Ar); δ_C (CDCl₃)/ppm 72.1 (HCOH), 81.7 (CPh₂OH), 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).

DMT⁹

Excess sodium hydride, TETROL and methyl iodide afforded a gum which precipitated out in petroleum ether (40–60 °C). This precipitate crystallized from methanol/ petroleum ether to yield DMT (65%), mp 124–126 °C (lit. [17], mp 125–126 °C); $[\alpha]_D^{23}$ – 154.5 (*c*. 0.27, CH₂Cl₂) {lit. [17], $[\alpha]_D$ – 153 (*c*. 0.8, CHCl₃)}; ν_{max} (solid)/cm⁻¹ 3576–3271 (br, OH), 3025 (Ar), 2836 (O–CH₃), and 1567 (Ar); $\delta_{\rm H}$ (CDCl₃)/ppm 2.59 (6H, s, 2OCH₃), 4.44 (2H, s, 2HCOCH₃), 4.87 (2H, s, 2CPh₂OH [disappears upon addition of D₂O]), 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); $\delta_{\rm C}$ (CDCl₃)/ppm 61.0 (OCH₃), 80.1 (CPh₂OH), 85.3 (HCOCH₃), 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).

Assessment of the host potential of DMT for guests NB, *o*-NT, *m*-NT and *p*-NT

DMT was dissolved in an excess of each individual guest solvent. In the case of *p*-NT, which is a solid at room temperature, a co-solvent (ethanol) was necessary to effect this dissolution. The vials in which these experiments were conducted were kept open to the atmosphere which allowed for supersaturation to occur through evaporation of some solvent. This resulted in crystallization, and each solid was isolated by means of vacuum filtration, during which the crystals were washed well with petroleum ether (40–60 °C), and then analysed by means of ¹H-NMR spectroscopy. By comparing the integrals of host and guest resonances, the H:G ratios could be determined.

Competition experiments employing mixed guests

Equimolar guest mixtures

Various combinations of binary, ternary and quaternary guests were mixed together in equimolar quantities, and the host dissolved in each of these mixtures. The vials were closed and stored at 0 $^{\circ}$ C so that the guest proportions remained equimolar. After crystallization occurred, the solids were recovered, washed (petroleum ether, 40–60 $^{\circ}$ C), and analysed by means of GC-MS experiments. The results were provided in Table 1.

Non-equimolar guest mixtures

Two guest solvents were mixed together in a range of nonequimolar proportions. Here we considered all four of the relevant guest solvents. The solids that resulted after the host was dissolved and recrystallized from each of these (also at 0 °C) were treated as before, and also analysed via GC-MS. Additionally, we analysed the mother liquors from which these crystals had formed. We then plotted the amounts of guest 1 in the crystal (Z) against the amount of this guest in the mother liquor (X) in order to obtain selectivity profiles for DMT as guest molar ratios varied (see Fig. 1a–f). We repeated this exercise for a ternary solvent mixture comprising the nitrotoluenes, which resulted in the ternary plot provided in Fig. 2. In this way, we could observe how the host selectivity changes as the guest concentrations change.

Supplementary data

CCDC-1847990 (2DMT·*o*-NT), 1847991 (2DMT·*m*-NT), 1847992 (2DMT·*p*-NT) and 1847993 (2DMT·NB) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc. cam.ac.uk/data_request/cif.

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