



Host compounds (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol (**TETROL**) and (2*R*,3*R*)-(–)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (**DMT**) with guests *o*-, *m*- and *p*- toluidine: A comparative investigation

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ABSTRACT

In this work, we have compared the host abilities of closely related compounds (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol (**TETROL**) and (2*R*,3*R*)-(–)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (**DMT**) when these were recrystallized from single and mixed toluidine guests. Significant differences in host behaviour and selectivities were revealed and these were explained by means of single crystal diffraction experiments. Thermal analyses were used to determine the relative complex stabilities, and these data correlated exactly with the host selectivity orders for both **TETROL** and **DMT**.

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1. Introduction

Host-guest chemistry is that field of supramolecular chemistry¹ in which host compounds, in the presence of particular guests, are able to enclathrate these and, in so doing, form complexes with them. Typically, the host material is a crystalline solid, while the guests may be gases, liquids or solids, but more usually liquids. Host-guest complexes are ordinarily held together by means of non-covalent interactions such as van der Waals attractive forces, π - π and CH- π interactions, ion pairing and hydrogen bonding.²

There have been a number of proposed general structures for the design of novel and effective host compounds,^{3–7} and it is possible to summarise the more salient characteristics of these. Successful host compounds oftentimes (i) have hydrogen bonding capabilities in order to stabilize the host-guest interaction, (ii) have bulky, hydrophobic substituents (such as aromatic moieties) that provide a *surrounding factor* which surround the guest molecules in the crystal, (iii) are crystalline to facilitate separation of the guest from the host, and (iv) have rigid frameworks which

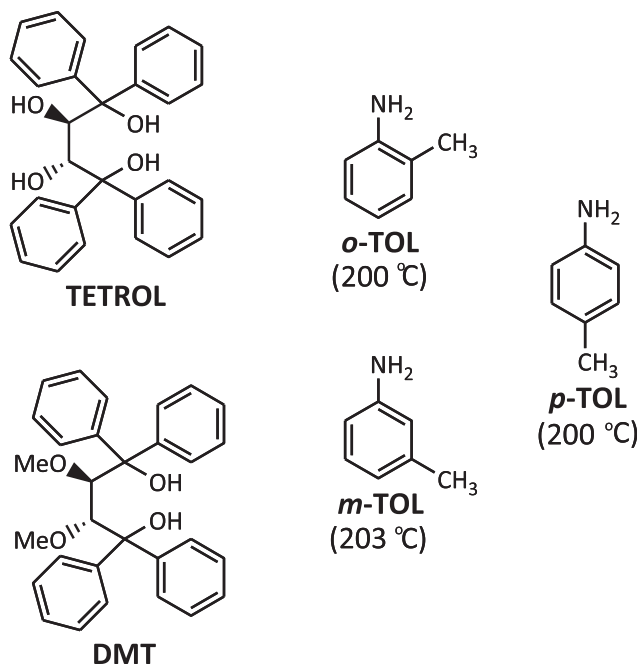
contribute towards their crystallinity.

The number of literature reports each year covering aspects of host-guest chemistry is overwhelming as chemists attempt to understand better the underlying principles involved. Not only this, but host-guest chemistry has a myriad useful applications in the chemistry realm. Host compounds are able to serve as separation agents for racemates⁸ as well as structural isomers,^{9–14} and have been utilized in modified stationary phases for chromatographic applications.¹⁵ Furthermore, host materials find application in both chemosensors and biosensors,^{16–18} while optically pure host compounds often find further use as catalysts in asymmetric syntheses, as demonstrated by the TADDOL class of compounds.¹⁵

Our research team focuses on the employment of host compounds for the separation of structural isomers, which is ordinarily quite difficult to achieve by conventional means owing to their similar physical properties. During these investigations, we found that both (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol (**TETROL**) and a dimethoxy derivative thereof, (2*R*,3*R*)-(–)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (**DMT**), have the ability to form inclusion complexes with selected toluidine (methylaniline) isomers [*o*-toluidine (***o*-TOL**), *m*-toluidine (***m*-TOL**) and *p*-toluidine (***p*-TOL**)], the boiling points of which range between 200 and 203 °C (Scheme 1). The toluidines are important

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Scheme 1. Structures of host compounds (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol (**TETROL**) and (2*R*,3*R*)-(-)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol (**DMT**), and guests *o*-toluidine (**o-TOL**), *m*-toluidine (**m-TOL**) and *p*-toluidine (**p-TOL**). In brackets beneath each guest structure is listed its boiling point.

industrial chemicals in that they are predominantly used as solvents and chemical intermediates for the production of antioxidants, pharmaceuticals, agricultural and rubber chemicals, and hence our interest in their facile separation.¹⁹ We discovered that the two title host compounds display marked differences in the extent of their selectivities for these guests, despite their structural similarities, and explore this phenomenon using single crystal X-ray diffraction experiments and thermal analyses, and report on these findings here.

2. Results and discussion

Hosts **TETROL** and **DMT** were readily prepared in moderate yield according to published procedures.^{10,11}

2.1. Single solvent complex formation

TETROL and **DMT** were individually assessed for their host abilities in the presence of each of the toluidine isomers. Therefore, each host (approximately 0.1 g) was dissolved in an excess of the guest (in the case of **p-TOL**, which is a solid at room temperature, ethanol was added as co-solvent to achieve this). The vials were left open to the ambient atmosphere, which facilitated the crystallization process. The so-formed crystals were collected by means of vacuum filtration, washed efficiently with low boiling petroleum ether (40–60 °C) to remove superficial guest solvent, and dried. These solids were analysed by means of ¹H NMR spectroscopy, using CDCl₃ as the deuterated solvent, to determine if inclusion had occurred. Integration of relevant host and guest resonances provided the host:guest (H:G) ratio in each case, and these are summarized in Table 1.

TETROL favoured the 2:3 H:G ratio when including guest solvents **m-TOL** and **p-TOL** (Table 1). **o-TOL** was not enclathrated in this way. On the other hand, **DMT** included all three of these isomers and consistently with a H:G ratio of 2:1 (In the Supplementary

Table 1

H:G ratios^a for the single solvent experiments using **TETROL** and **DMT** as hosts, and the toluidine isomers as guests.

Host	Guest	H:G ratio
TETROL	o-TOL	— ^b
TETROL	m-TOL	2:3
TETROL	p-TOL	2:3
DMT	o-TOL	2:1
DMT	m-TOL	2:1
DMT	p-TOL	2:1

^a Determined using ¹H NMR spectroscopy with CDCl₃ as the deuterated solvent.

^b No inclusion occurred.

Information, Figs. 1S and 2S show the ¹H NMR spectra for **2TET**·**3m-TOL** and **2DMT**·**o-TOL**, respectively, as representative examples).

2.2. Competition experiments

In order to ascertain whether these host compounds display any selective behaviour in the presence of mixed guests, each host material (approximately 0.3 mmol) was dissolved, in vials, in equimolar binary and ternary mixtures of these guests (approximately 5 mmol of each). The vessels were closed and stored at 0 °C so as to maintain the equimolar condition. Once crystallization occurred, the formed solids were treated as in the single solvent experiments. GC-MS was selected as the more appropriate quantitative analytical technique for these complexes owing to the overlap of guest-guest resonance signals in the ¹H NMR spectra. CH₂Cl₂ was used as the dissolution solvent in each instance. Table 2 summarizes the data so-obtained, where the preferred guest is shown in bold.

The recrystallization of **TETROL** and **DMT** from the various equimolar guest mixtures afforded mixed complexes in each case, with the exception of the experiment comprising **TETROL** and the equimolar binary guest mixture **o-TOL/m-TOL**, where crystallization failed to occur. However, **DMT**, in an equivalent experiment, did indeed furnish crystals, and these contained a significantly larger amount of **o-TOL** (72.5%) relative to **m-TOL**. When **TETROL** was recrystallized from **o-TOL/p-TOL**, the host displayed high selectivity for the *para* isomer, extracting 83.5% of this isomer from the mixture, while **DMT** was somewhat more ambivalent, showing

Table 2

H:G ratios^a for the equimolar mixed solvent experiments using **TETROL** and **DMT** as hosts, and the toluidine isomers as guests.

Host	o-TOL	m-TOL	p-TOL	Guest ratios (%e.s.d.s) ^b	H:G ratio
TETROL	x	x	—	— ^c	— ^c
TETROL	x	—	x	16.5: 83.5 (0.3)	2:3
TETROL	—	x	x	29.9: 70.1 (0.4)	2:3
TETROL	x	x	x	14.2:27.3: 58.5 (0.1) (0.6) (0.7)	2:3
DMT	x	x	—	72.5 :27.5 (0.1)	2:1
DMT	x	—	x	46.7: 53.3 (0.1)	2:1
DMT	—	x	x	28.7: 71.3 90.8)	2:1
DMT	x	x	x	40.1:15.7: 44.2 (0.6) (1.1) (0.4)	2:1

^a Determined using GC-MS with CH₂Cl₂ as the dissolution solvent.

^b These experiments were carried out in triplicate, and percentage estimated standard deviations (%e.s.d.s) are provided in parentheses.

^c Crystals failed to form.

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