**ORIGINAL ARTICLE** 



### *trans-N,N*<sup>'</sup>-Bis(9-phenyl-9-xanthenyl)cyclohexane-1,2-diamine and its thioxanthenyl derivative as potential host compounds for the separation of anilines through host—guest chemistry principles

Benita Barton<sup>1</sup> · Daniel V. Jooste<sup>1</sup> · Eric C. Hosten<sup>1</sup>

Received: 13 February 2020 / Accepted: 27 May 2020 © Springer Nature B.V. 2020

### Abstract

In this work, we investigate the potential of separating mixtures of the guest solvents aniline (ANI), *N*-methylaniline (NMA) and *N*,*N*-dimethylaniline (DMA) by means of host–guest chemistry principles employing two novel host compounds, namely *trans-N*,*N'*-bis(9-phenyl-9-xanthenyl)cyclohexane-1,2-diamine (1,2-DAX) and *trans-N*,*N'*-bis(9-phenyl-9-thioxanthenyl) cyclohexane-1,2-diamine (1,2-DAX) and the point are challenging. After recrystallization experiments of the two host compounds from various combinations of these anilines, it was revealed that host–guest chemistry certainly has the potential to serve as an alternative separation strategy for such mixtures. Equimolar ANI/DMA solutions proved most successful, where both 1,2-DAX and 1,2-DAT showed near-quantitative selectivity for DMA (90%). Both single crystal diffraction and thermal analyses were employed in order to understand the preferential behaviour displayed by each host compound.

Keywords Host-guest · Xanthenyl · Inclusion · Selectivity · Separation · Aniline

### Introduction

Industrially, aniline (ANI) is a valuable chemical that has applications in over 300 different products, with one of the more important of these being in the production of methylene diphenyl diisocyanate (MDI) [1]. MDI exists in three isomeric forms, with the 4,4'-isomer being the most valuable: reaction with alcohols produces the commerciallyimportant rigid polyurethane. ANI is additionally employed as an intermediate in the manufacture of dyes and pigments, as well as antidegradants in rubber processing. *N*-Methylaniline (NMA) is used as an antiknock agent to adjust the octane number in the production of many fuels, while

**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10847-020-01002-0) contains supplementary material, which is available to authorized users.

Benita Barton benita.barton@mandela.ac.za *N*,*N*-dimethylaniline (DMA) serves as an intermediate in the manufacture of dyes such as Crystal Violet [2, 3]. NMA is typically synthesized through the methylation of ANI with methanol, but this process is prone to selectivity concerns since the product (NMA) is more reactive than ANI, resulting in the formation of DMA due to overalkylation. Furthermore, upon heating, NMA and DMA undergo rearrangement to form unwanted *p*- and *o*-toluidine [4]. More recently, vapour phase methylation of aniline using Sn-MFI molecular sieves (tin silicalite-1) has been successful as an alternative aniline alkylation strategy; the molar ratio of SiO<sub>2</sub> and SnO<sub>2</sub> may be varied. Using this process, the aniline conversion is usually increased which, in turn, leads to either an increase or reduction in the production of NMA and DMA, dependent on this SiO<sub>2</sub>/SnO<sub>2</sub> ratio [5].

The separation of these aniline compounds (ANI, NMA and DMA) when they are found in mixtures, as would be the case when ANI is alkylated, is challenging owing to similarities in their boiling points (184.1, 196.2 and 193.5 °C, respectively), and methods other than fractional distillation are therefore appealing. An alternative separation strategy that may be considered to achieve this goal is host–guest

<sup>&</sup>lt;sup>1</sup> Department of Chemistry, Nelson Mandela University, 6031 Port Elizabeth, South Africa

chemistry. This field of science utilizes crystalline host compounds (typically the larger of the involved molecular species) to encapsulate the guest (the smaller species) through non-covalent interactions between the host and guest [6-8]. These interactions are more usually  $\pi \cdots \pi$ , XH $\cdots \pi$  and hydrogen bonding in nature, dependent on the characteristics of the two interacting species, though many other interaction types have been noted in the literature. Naturally, in order to facilitate separation in this context, the host compound is required to display preferential behaviour towards only one guest component in the presence of such mixtures. Host-guest chemistry presents an attractive alternative protocol for the separation of such compounds, especially since the host compounds are readily recycled in the process after removal of the enclathrated guest components through distillation.

Many investigations have been carried out that employ this method of separation. As examples, Nassimbeni et al. assessed the potential of three diol host compounds to effect the separation of various lutidine isomers with much success[9], while Caira and co-workers considered xylenol isomer separations using a cyclohexane host derivative [10]. Furthermore, Ni(NCS)<sub>2</sub>(*para*-phenylpyridine)<sub>4</sub>, a Werner complex, was shown by Barbour and Lusi [11] to be selective for *ortho*-xylene when present in a vaporous mixture of the three xylenes. Guests in mixtures, however, need not necessarily be related as isomers in order for the host to behave discriminatorily. As illustrations, our group has reported on the clear selectivity of various host materials when presented with aromatic/aliphatic [12] or ketone/alcohol/amine [13] combinations.

In this work, we report on the selectivity behaviour of two novel host compounds, trans-N,N'-bis(9-phenyl-9-xanthenyl)cyclohexane-1,2-diamine (1,2-DAX) and trans-N,N'-bis(9-phenyl-9-thioxanthenyl)cyclohexane-1,2-diamine (1,2-DAT), when these were recrystallized from various mixtures of ANI, NMA and DMA, in order to ascertain whether separations of these guest compounds are feasible by means of host-guest chemistry principles (Scheme 1). NMR spectroscopy, single crystal X-ray diffraction (SCXRD) and thermal analyses (TA) were selected as the analytical methods of choice with which to analyse any complexes formed in this work, as appropriate. Note that ANI/NMA/DMA guest combinations have been considered by our group previously, employing alternative known host compounds, namely (-)-(2R,3R)-2,3-dimethoxy-1,1,4,4tetraphenylbutane-1,4-diol (DMT) [14], (+)-(2R,3R)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol (TETROL) [15], N,N'-bis(9-phenyl-9-xanthenyl)ethylenediamine and N,N'bis(9-phenyl-9-thioxanthenyl)ethylenediamine [16]. In this way, both DMT and TETROL were revealed to possess poor selectivity in these conditions, while the two ethylenediamine derivatives were observed to be more capable.

Scheme 1 Molecular structures of host compounds 1,2-DAX and 1,2-DAT, as well as guests ANI, NMA and DMA



### Experimental

### **General methods**

All chemicals and solvents were purchased through Merck and used as received. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained by means of a 400 MHz Bruker Avance Ultrashield Plus 400 Spectrometer (CDCl<sub>3</sub> was the deuterated solvent). Melting points were carried out on a Stuart SMP10 digital melting point apparatus and these are uncorrected. Infrared analyses were conducted on a Bruker Tensor 27 Fourier Transform Infrared spectrometer, and data analysed by means of OPUS data analysis software. Gas chromatography (GC) was performed by means of an Agilent Technologies 7890 A gas chromatograph system fitted to an Agilent Technologies 5975 C VL MSD mass spectrometer (MS) with a Triple Axis Detector, or a YoungLin 6500 GC system with FID as detector, and data were analysed using Agilent MSD Productivity Chem-Station E.02.01.1177 and Delta 5.5 acquisition software, respectively. High purity helium was the carrier gas. An Agilent J&W GC DB-1MS column with a length of 30 m, a diameter of 0.25 mm and a film thickness of 0.25 um was applicable. This method involved heating the oven to 50 °C, with zero hold time, and then initiating an immediate ramp of 15 °C min<sup>-1</sup> to 200 °C, and culminating with a hold time of 1 min. The split ratio was 20:1 and inlet temperature 250 °C. Single crystal X-ray diffraction (SCXRD) experiments were performed at 200 K (for 1,2-DAX·ANI, 1,2-DAX·DMA and 1,2-DAT·DMA) or 296 K [1,2-DAT·2(ANI), 1,2-DAT·2(NMA)] using a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). APEXII [17] was used for data collection and SAINT [17] for cell refinement and data reduction. The structures were solved using SHELXT-2018/2 [18] and refined by least-squares procedures using SHELXL-2018/3 [19] with SHELXLE [20] as a graphical interface. All non-hydrogen atoms were refined anisotropically, and the carbon-bound hydrogen atoms were added in idealized geometrical positions in a riding model. The nitrogen-bound H atoms were located on a difference Fourier map and refined freely, where possible, or otherwise in calculated positions. Data were corrected for absorption effects using the numerical method implemented in SADABS [17]. Crystallographic data for these novel complexes were deposited at the Cambridge Crystallographic Data Centre {{CCDC-1982613 (1,2-DAX·ANI), 1982614 (1,2-DAX·DMA), 1982615 [1,2-DAT·2(ANI)], 1982616 [1,2-DAT·2(NMA)] and 1982617 (1,2-DAT·DMA)}}. Mercury CSD 3.10.2 (Build 189770) software was used to analyse the crystal structures [21]. Thermogravimetric (TG) and differential scanning calorimetry (DSC) traces were obtained using a Perkin Elmer STA6000 Simultaneous Thermal Analyser and analysed using Perkin Elmer Pyris 13 Thermal Analysis software. An empty ceramic pan was used as a reference, and the same open pan was subsequently employed for the sample run. High purity nitrogen was the purge gas, and all samples were heated from approximately 30 to 300 °C at a heating rate of 10 °C min<sup>-1</sup>.

#### Synthesis of host compounds 1,2-DAX and 1,2-DAT

1,2-DAX and 1,2-DAT were synthesized according to known procedures [22] in three distinct steps (Scheme 2):

### *trans-N*,N'-Bis(9-phenyl-9-xanthenyl) cyclohexane-1,2-diamine (Scheme 2, X = 0)

**9-Phenylxanthen-9-ol** This compound was prepared according to a general Grignard addition procedure. Magnesium turnings (2.4318 g, 0.1001 mol), bromobenzene (15.3602 g, 0.0978 mol) and xanthone (16.0083 g, 0.0816 mol) in anhydrous THF yielded a gum which was crystallized and recrystallized from CH<sub>2</sub>Cl/petroleum ether to afford 9-phenylxanthen-9-ol (13.8731 g, 62%) as a white solid, mp 158–162 °C (lit.,[22] mp 159 °C);  $v_{max}$  (solid)/ cm<sup>-1</sup> 3548 (OH) and 1600 (Ar C=C);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 2.71 (1H, s, OH), 7.09 (2H, t, ArH), 7.23 (3H, d, ArH) and 7.30–7.45 (8H, m, ArH);  $\delta_{\rm C}$ (CDCl<sub>3</sub>)/ppm 70.46 (PhCOH), 116.43 (ArC), 123.58 (ArC), 126.25 (ArC), 126.77 (ArC), 127.22 (quaternary ArC), 128.00 (ArC), 129.05 (ArC), 148.00 (quaternary ArC) and 149.71 (quaternary ArC).

**9-Phenylxanthen-9-ylium perchlorate** Perchloric acid (6.8952 g, 0.0686 mol) was added dropwise to a chilled, stirred solution of 9-phenylxanthen-9-ol (12.0199 g, 0.0439 mol) in a mixture of dichloromethane (250 mL) and diethyl ether (250 mL). Stirring was continued for 10 min before the resulting yellow precipitate was collected using vacuum filtration and washed with diethyl ether to yield 9-phenylx-anthen-9-ylium perchlorate (13.7007 g, 0.0384 mol, 87%) as a yellow solid, mp 285–287 °C (lit.,[22] mp 283–286 °C);  $v_{max}$  (solid)/cm<sup>-1</sup> 1597 (Ar C=C);  $\delta_{\rm H}$ (CDCl3)/ppm 7.79–7.82 (5H, m, ArH), 7.94 (2H, t, ArH), 8.19 (2H, d, ArH), 8.43 (2H, d, ArH) and 8.52 (2H, t, ArH).

*trans*-N,N<sup>'</sup>-Bis(9-phenyl-9-xanthenyl)cyclohexane-1,2-diamine (1,2-DAX) 9-Phenylxanthen-9-ylium perchlorate (7.9050 g, 0.0222 mol), in CH<sub>2</sub>Cl<sub>2</sub> (250 mL), was added to *trans*-1,2-cyclohexanediamine (1.2651 g, 0.0111 mol),



9-Phenylxanthen-9-ylium perchlorate (X = O) 9-Phenylthioxanthen-9-ylium perchlorate (X = S)

also in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The reaction mixture was stirred at room temperature for 30 min whereafter triethylamine (5 mL, 3.630 g, 0.0359 mol) was added, resulting in a colour change from orange to colourless. Following an additional 30 min of stirring, the solution was washed with water and the organic layer dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue crystallized and recrystallized from ethanol/CH2Cl2 to afford trans-N,N'-bis(9-phenyl-9-xanthenyl)cyclohexane-1,2-diamine (1,2-DAX) (6.1411 g, 9.798 mmol, 88%) as a white solid, mp 227–230 °C; v<sub>max</sub> (solid)/cm<sup>-1</sup> 3271 (NH), 3070 (ArCH), 3028 (ArCH), 2920 (alkyl CH), 2856 (alkyl CH) and 1601 (Ar C=C);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 0.26–0.53 (2H, m, cyclohexyl H), 0.54-0.79 (4H, m, cyclohexyl H), 1.01-1.21 (2H, m, cyclohexyl H), 1.92-2.09 (2H, m, NHCH), 2.18 (2H, br s, NH) and 6.88-7.37 (26H, m, ArH); δC(CDCl3)/ ppm 25.02 (CH<sub>2</sub>), 33.91 (CH<sub>2</sub>), 57.36 (NHCH), 59.76 (quaternary CNH), 115.90 (ArC), 116.10 (ArC), 122.84 (ArC), 123.30 (ArC), 126.29 (ArC), 127.59 (ArC), 128.00 (ArC), 128.18 (ArC), 130.73 (ArC), 130.84 (ArC), 150.45 (quaternary ArC), 150.78 (quaternary ArC) and 151.72 (quaternary ArC). After recrystallization from o-xylene, a 1:1 complex was obtained. [Found: C, 85.44; H, 6.82; N, 3.72. C<sub>44</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub>·C<sub>8</sub>H<sub>10</sub> (1:1) requires C, 85.27; H, 6.61; N, 3.82%.]

Scheme 2 Synthetic strategy towards 1,2-DAX and 1,2-DAT

*trans-N*,N'-Bis(9-phenyl-9-thioxanthenyl) cyclohexane-1,2-diamine 1 (Scheme 2, X = S)

9-Phenylthioxanthen-9-ol This compound was also prepared by means of a general Grignard addition procedure. Magnesium turnings (2.7332 g, 0.1125 mol), bromobenzene (16.6532 g, 0.1061 mol) and thioxanthone (10.0113 g, 0.0472 mol) in anhydrous THF yielded a gum-like residue which was crystallized and recrystallized from benzene/ petroleum ether to afford 9-phenylthioxanthen-9-ol (8.5690 g, 63%) as a mustard yellow solid, mp 103-106 °C (lit.,[22] mp 105–106 °C);  $v_{max}$  (solid)/cm<sup>-1</sup> 3297 (OH) and 1589 (Ar C=C);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 2.85 (1H, s, OH), 6.96–7.07 (2H, m, ArH), 7.15-7.25 (3H, m, ArH), 7.28-7.47 (6H, m, ArH) and 8.06 (2H, d, ArH); δ<sub>c</sub>(CDCl<sub>3</sub>)/ppm 77.02 (PhCOH), 126.13 (ArC), 126.52 (ArC), 126.69 (ArC), 126.97 (ArC), 127.34 (ArC), 127.80 (ArC), 128.09 (ArC), 131.64 (quaternary ArC), 140.01 (quaternary ArC) and 143.41 (quaternary ArC).

**9-Phenylthioxanthen-9-ylium** perchlorate Perchloric acid (14.1440 g, 0.1408 mol) was added dropwise to a chilled, stirred solution of 9-phenylthioxanthen-9-ol (6.0066 g, 0.0207 mol) in a mixture of  $CH_2Cl_2$  (50 mL) and diethyl ether (50 mL). Following an additional 5 min

of stirring, the resulting intense red precipitate was collected using vacuum filtration and washed with diethyl ether to yield 9-phenylthioxanthen-9-ylium perchlorate (6.2753 g, 0.0168 mol, 81%) as a red solid, mp 238–240 °C (decomp.) [lit.,[22] mp 239 °C (decomp.)];  $v_{max}$  (solid)/cm<sup>-1</sup> 1591 (Ar C = C);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 7.59–7.61 (2H, m, ArH), 7.77–7.79 (3H, m, ArH), 8.01 (2H, t, ArH), 8.27 (2H, d, ArH), 8.35 (2H, t, ArH) and 8.84 (2H, d, ArH).

trans-N,N'-Bis(9-phenyl-9-thioxanthenyl)cyclohexane-1,2-diamine (1,2-DAT) 9-Phenylthioxanthen-9-ylium perchlorate (3.0135 g, 0.0081 mol), in CH<sub>2</sub>Cl<sub>2</sub>, was added to a solution of trans-1,2-cyclohexanediamine (0.4685 g, 0.0041 mol), also in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), and the solution stirred for 30 min. A portion of triethylamine (4.4 mL, 3.194 g, 0.0316 mol) was then added which resulted in a colour change of the solution from deep red to orange. Stirring at room temperature was continued for 30 min before the solution was washed with water and the organic layer dried over anhydrous Na2SO4. The solvent was removed under reduced pressure, yielding an orange gum which was crystallized and recrystallized from ethanol/CH2Cl2 to afford trans-N,N'-bis(9-phenyl-9 thioxanthenyl)cyclohexane-1,2-diamine (1,2-DAT) (1.4138 g, 2.146 mmol, 52%) as a cream solid, mp 175–181 °C; v<sub>max</sub> (solid)/cm<sup>-1</sup> 3269 (NH), 3054 (ArCH), 2913 (alkyl CH), 2848 (alkyl CH) and 1588 (Ar C = C);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ ppm 0.37-0.59 (2H, m, cyclohexyl H), 0.62-0.98 (4H, m, cyclohexyl H), 1.03-1.29 (2H, m, cyclohexyl H), 1.99-1.21 (2H, m, NHCH), 2.36 (2H, br s, NH) and 6.74–7.39 (26H, m, ArH); δ<sub>C</sub>(CDCl<sub>3</sub>)/ppm 25.32 (CH<sub>2</sub>), 34.08 (CH<sub>2</sub>), 58.10 (NHCH), 65.29 (quaternary CNH), 124.76 (ArC), 124.91 (ArC), 125.38 (ArC), 125.81 (ArC), 126.25 (ArC), 126.62 (ArC), 126.66 (ArC), 127.40 (ArC), 128.724 (ArC), 132.13 (ArC), 132.22 (ArC), 138.54 (quaternary ArC) 138.80 (quaternary ArC) and 150.43 (quaternary ArC). After recrystallization from p-xylene, a 1:1 complex was obtained. [Found: C, 81.88; H, 6.82; N, 3.38; S, 8.03. C<sub>44</sub>H<sub>38</sub>N<sub>2</sub>S<sub>2</sub>·C<sub>8</sub>H<sub>10</sub> (1:1) requires C, 81.64; H, 6.32; N, 3.66; S, 8.38%.]

### Single guest solvent experiments

The host compounds were recrystallized independently from each of ANI, NMA and DMA. This was achieved by placing each host material (~0.05 g) in a glass vial and dissolving it in an excess of the liquid guest; heat was applied to facilitate dissolution in need. The vials were capped and left to stand at ambient temperature and pressure after which recrystallization occurred within 1–3 days. Should crystallization not have been successful during this time, the capped vial was then placed in a refrigerator set to 0 °C to further encourage the process. Resultant solids were collected by vacuum filtration, washed with petroleum ether to remove any guest solvent adhering to the crystal surfaces, and dried under vacuum filtration. The dried crystals were analysed by means of <sup>1</sup>H-NMR spectroscopy (CDCl<sub>3</sub> was the deuterated solvent) to establish whether inclusion of the guest by the host species had taken place and, if so, the overall host:guest (H:G) ratio through integration of relevant host and guest resonance signals on this spectrum.

### **Mixed guest solvent experiments**

# Using equimolar binary and ternary mixtures of ANI, NMA and DMA

Equimolar guest/guest competition experiments were carried out in order to ascertain whether either of the host compounds possessed selectivity for any one of the guests present in various binary and ternary combinations of these guest solvents. This was accomplished by dissolving the host (~0.05 g) in such mixtures (made up of 5 mmol of each guest). The capped vials were stored at 0 °C and, once crystallization occurred, the crystals treated as in the single solvent experiments. Analyses to obtain the amounts of each guest compound present in the host crystals was accomplished by means of GC-MS (with CH<sub>2</sub>Cl<sub>2</sub> as the dissolution solvent) and not <sup>1</sup>H-NMR spectroscopy owing to the overlapping of guest/guest and/or host/guest resonance signals on the <sup>1</sup>H-NMR spectra. All experiments were carried out in duplicate for confirmatory purposes.

### Using binary mixtures of ANI, NMA and DMA where their concentrations were sequentially varied

In these binary guest/guest ( $G_A$  and  $G_B$ ) competition experiments, the molar ratio of each guest solvent present was varied sequentially between approximately 10:90 and 90:10 mol%, and the host compound dissolved in these mixtures. The vials were capped and stored at 0 °C so that crystallization could occur, and the solid filtered under vacuum, washed and dried, analogously to the procedure for the equimolar guest/guest experiments. Here, both the solution (the liquid guest mixture from which crystallization occurred) and the so-formed crystals were analysed using GC-MS which allowed for the determination of the amounts of both  $G_{A}$  and  $G_{B}$  in both of these phases  $(X_{\text{\tiny A}}$ and  $X_B$ , and  $Z_A$  and  $Z_B$ , respectively). A plot of  $Z_A$  (or  $Z_B$ ) against X<sub>A</sub> (or X<sub>B</sub>) resulted in host selectivity profiles, a manner of visually establishing the host behaviour as guest concentrations changed. The selectivity coefficient (K), a measure of the host selectivity, was determined by means of employing the equation  $K_A:_B = (Z_A/Z_B) \times (X_B/Z_B)$  $X_A$ ) where  $X_A + X_B = 1$  [23].

### **Results and discussion**

### Synthesis of host compounds 1,2-DAX and 1,2-DAT

Novel host compounds 1,2-DAX and 1,2-DAT were prepared in three distinct steps using methods that have been reported on a prior occasion [22]. This involved a Grignard addition reaction (phenylmagnesium bromide) on either xanthone or thioxanthone (Scheme 2), as applicable. The resultant alcohols were subsequently reacted with perchloric acid to afford highly coloured crystalline perchlorate salts, which were then treated with trans-cyclohexane-1,2-diamine to yield the required compounds in moderate to excellent yields.

### Single guest solvent experiments

The H:G ratios after <sup>1</sup>H-NMR analysis of the crystals emanating from the recrystallization experiments of each host independently from ANI, NMA and DMA are summarized in Table 1.

Both host compounds were efficient for the enclathration of each of the three aniline solvents (Table 1). While 1,2-DAX unfailingly preferred the 1:1 H:G ratio, 1,2-DAT formed 1:2 complexes with ANI and NMA, but a 1:1 ratio was also obtained when this host was recrystallized from DMA.

Guest	1,2-DAX	1,2-DAT	
ANI	1:1	1:2	
NMA	1:1	1:2	
DMA	1:1	1:1	

<sup>a</sup>Determined using <sup>1</sup>H-NMR spectroscopy, with CDCl<sub>3</sub> as the deuterated solvent

**Mixed guest solvent experiments** 

### Using equimolar binary and ternary mixtures of ANI, NMA and DMA

Recrystallization of the host compounds from the various equimolar combinations of ANI/NMA/DMA resulted in mixed complexes in each instance; both hosts, additionally, demonstrated selectivity behaviour. These data are summarised in Table 2. Note that the experiments were conducted in duplicate, and tabulated ratios are averages; percentage estimated standard deviations (%e.s.d.s) are provided in this table in parentheses. Furthermore, bold numbering was employed to distinguish the preferred guest species in each experiment for each host compound.

Overall, some similarities are evident in the selectivity behaviour of the two host compounds (Table 2). Upon recrystallization of 1,2-DAX from ANI/NMA, NMA was favoured (66.5%); 1,2-DAT also preferred NMA in these conditions but the selectivity for this guest was much reduced here (51.1%). Results from ANI/DMA mixtures were striking in that both host compounds almost exclusively selected DMA [91.8% (1,2-DAX) and 90.3% (1,2-DAT)]. Therefore, ANI was consistently discriminated against when the solutions employed were ANI/NMA and ANI/DMA. In the absence of ANI, 1,2-DAX displayed an enhanced preference for DMA (82.5%) while 1,2-DAT differed and preferred NMA (61.7%). The selectivity of both hosts for these guests, as obtained from the ternary mixture experiment, was therefore in the same order (DMA > NMA > ANI) and, additionally, the extent of selectivity was similar for both (80.1, 10.8, 9.1 compared with 80.3, 12.9, 6.8%).

These results indicate that both host compounds may serve as separation agents for such guest mixtures, particularly when ANI/DMA combinations arise from synthetic procedures.

Table 2 Applicable G:G ratios<sup>a</sup> of complexes formed when 1,2-DAX and 1,2-DAT were recrystallized from the equimolar mixed anilines<sup>b</sup>

ANI	NMA	DMA	Guest ratios (%e.s.d.s <sup>c</sup> ) (for 1,2-DAX)	Guest ratios (%e.s.d.s <sup>c</sup> ) (for 1,2-DAT)	
x	х		33.5: <b>66.5</b> (0.8)	48.9: <b>51.1</b> (0.6)	
x		х	8.2: <b>91.8</b> (0.7)	9.7: <b>90.3</b> (0.6)	
	х	х	17.5: <b>82.5</b> (0.6)	<b>61.7</b> :38.3 (0.8)	
x	х	х	9.1:10.8: <b>80.1</b> (0.4:0.1:0.5)	6.8:12.9: <b>80.3</b> (0.5:0.7:1.1)	

<sup>a</sup>Determined using GC-MS with CH<sub>2</sub>Cl<sub>2</sub> as the dissolution solvent

<sup>b</sup>Overall H:G ratios, obtained using <sup>1</sup>H-NMR spectroscopy, were 1:1 in all cases with the exception of the mixed complex obtained when 1,2-DAT was recrystallized from ANI/NMA (overall H:G 1:2) <sup>c</sup>Percentage estimated standard deviations (%e.s.d.s)

# Using binary mixtures of ANI, NMA and DMA where their concentrations were sequentially varied

Selectivity profiles, upon performing host recrystallization experiments from binary mixtures of ANI, NMA and DMA but changing the mol% of each guest in these mixtures, are provided in Fig. 1a-c (1,2-DAX) and 2a-c (1,2-DAT). Figure 1a shows that 1,2-DAX discriminated against ANI in favour of NMA across the entire concentration range, with an average K value of 2.2 calculated. When the mother liquor contained 57.2% NMA, the crystals of the so-formed complex possessed a significant amount of this guest (74.7%). In DMA/ANI and DMA/NMA binary mixtures (Fig. 1b and c, respectively), the host selectivity was significantly and consistently in favour of DMA, and the average K values were calculated to be 14.2 and 3.7, respectively. Even at low mother liquor concentrations of DMA in the DMA/ANI experiment (10.7%, Fig. 1b), the resultant crystals already contained 80.4% of this guest. Increasing the DMA content in solution after this point facilitated a gradual increase of DMA in the crystals: when 91.6% of the solution was DMA, the crystals contained almost exclusively DMA (98.5%). As alluded to by the K values obtained from the DMA/ANI (14.2) and DMA/NMA (3.7) experiments, the extent of selectivity of 1,2-DAX for DMA was reduced when ANI was replaced by NMA. For example, when the mother liquor contained 26.6% DMA, the resultant crystals possessed only 62.8% of this guest.

Analogous experiments with 1,2-DAT showed the selectivity of this host, in each case, to be guest concentrationdependent (in stark contrast to the results obtained for 1,2-DAX, where selectivity was for one guest only, irrespective of concentration). Figure 2a shows that at lower concentrations of NMA ([NMA]  $\leq$  30.4), 1,2-DAT displayed a preference for ANI, and the average  $K_{\text{NMA:ANI}}$  value calculated was 0.2 for the three experiments in question. However, as the concentration of NMA in the solution increased, the host selectivity changed in favour of this guest. The average selectivity coefficient for the remainder of the experiments ([NMA]  $\geq$  53.3%) was 1.1, alluding to a marginal NMA preference at higher NMA concentrations: when the guest mixture contained 63.5 and 82.5% NMA, the crystals had 67.6 and 84.6% of this guest, respectively. From the DMA/ANI and DMA/NMA binary guest experiments (Figures b and c, respectively), the host was consistently selective for DMA at higher DMA concentrations ( $\geq$  48.6 and 60.5%, respectively): when the DMA/ANI solution comprised 48.6% DMA or more, the average K value was 9.8 in favour of DMA (a solution with 48.6% DMA afforded crystals containing 88.9% of this guest). The converse was true also: at low concentrations of DMA, ANI (Fig. 2b) and NMA (Fig. 2c) were selected. In the former case, when the concentration of ANI in solution was equal to or greater than 72.3%,  $K_{DMA:ANI}$  was calculated to be 0.5. In the latter case, when [NMA]  $\geq$  47.4%, the average K<sub>DMA:NMA</sub> was 0.6, and here the host selectivity change (in favour of DMA)



Fig. 1 Host selectivity profiles obtained for 1,2-DAX in the presence of a NMA/ANI, b DMA/ANI and c DMA/NMA binary mixtures



Fig. 2 Host selectivity profiles obtained for 1,2-DAT in the presence of a NMA/ANI, b DMA/ANI and c DMA/NMA binary mixtures

occurred at DMA concentrations above 60.5% (where the average  $K_{DMA:NMA}$  value was calculated to be 4.1).

In conclusion, of the two host compounds, 1,2-DAX may be regarded as superior in its selectivity behaviour, and may certainly behave as an efficient separating agent, especially in the presence of mixtures of ANI and DMA, irrespective of the concentrations of either guest present (Fig. 1b). 1,2-DAT is less discerning in these conditions, and its selectivity behaviour is dependent on guest concentration, regardless of the types of guest anilines present in the binary mixture.

#### Single crystal X-ray diffraction (SCXRD) analyses

The three single solvent complexes formed by 1,2-DAT and the aniline guests were subjected to SCXRD analyses, while only the ANI- and DMA-containing inclusion compounds of 1,2-DAX produced crystals of suitable quality for this analytical technique; the crystal quality of 1,2-DAX·NMA was inappropriate. Table 3 summarises the relevant crystallographic data that were thus obtained. Both 1,2-DAX·ANI and 1,2-DAX·DMA crystallized in the monoclinic crystal system and C2/c space group, and experienced isostructural host packing as is evident from the unit cell dimensions provided in this table. Similarly, all three complexes of 1,2-DAT crystallized in the monoclinic crystal system, 1,2-DAT·2(ANI) and 1,2-DAT·2(NMA) in the I2/a space

group, and the DMA complex in C2/c. Furthermore, this last complex shared host packing type with the two 1,2-DAX complexes. Disorder was observed in both 1,2-DAX·ANI and 1,2-DAX·DMA, with the guest species positioned around a two-fold rotational axis. Furthermore, the hydrogen atom on the host nitrogen was disordered over two positions in both complexes. All three complexes with 1,2-DAT also experienced disorder, and two different non-symmetrical orientations were possible for the guest species in 1,2-DAT·2(ANI). However, the disorder in the DMA complex was due to the guest being positioned near a symmetry element resulting in this disorder being symmetry generated, whilst NMA in 1,2-DAT·2(NMA) was severely disordered: three guest components  $(G_1, G_2, and G_3)$  were present in the unit cell, with one  $[G_1 MJ (major disordered component)$ and G1 MN (minor disordered component)] oriented in two directions (s.o.f.'s of 0.529 and 0.471, respectively), while the remaining two guest molecules experienced disorder owing to a symmetry element (s.o.f.'s of 0.50 each for G<sub>2</sub> and  $G_3$ ). Additionally, the nitrogen-bound hydrogen atoms of the host were disordered in the ANI and DMA complexes of 1,2-DAT.

Host-guest packing diagrams are provided for 1,2-DAX·ANI (as representative of the three complexes sharing host-guest packing type), 1,2-DAT·2(ANI) and 1,2-DAT·2(NMA) in Fig. 3a-c (left), respectively, together

	1,2-DAX·ANI <sup>b</sup>	1,2-DAX·DMA <sup>b</sup>	1,2-DAT·2(ANI)	1,2-DAT·2(NMA)	1,2-DAT·DMA <sup>b</sup>
Chemical formula	$C_{44}H_{38}N_2O_2 \cdot C_6H_5N$	$C_{44}H_{38}N_2O_2 \cdot C_8H_{11}N$	$C_{44}H_{38}N_2S_2 \cdot 2(C_6H_5N)$	$C_{44}H_{38}N_2S_2 \cdot 2(C_7H_9N)$	$C_{44}H_{38}N_2S_2 \cdot C_8H_{11}N$
Formula weight (g/mol)	717.87	747.94	841.10	873.19	780.06
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	<i>I</i> 2/a	<i>I</i> 2/a	C2/c
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.073	0.075	0.159	0.156	0.167
a/Å	14.2367(9)	14.2849(7)	21.2117(14)	18.950(2)	15.4768(9)
b/Å	14.2099(9)	14.2602(6)	9.1358(5)	15.0422(19)	13.9742(7)
c/Å	19.6234(13)	19.6725(9)	24.4234(17)	33.561(4)	19.3645(10)
<b>α/°</b>	90	90	90	90	90
β/°	92.451(3)	90.302(2)	104.641(5)	97.784(7)	91.465(2)
γ/°	90	90	90	90	90
$V/Å^3$	3966.2(4)	4007.3(3)	4579.2(5)	9478.4(19)	4186.7(4)
Z	4	4	4	8	4
F (000)	1520	1592	1776	3712	1656
Temp (K)	200	200	296	296	200
Restraints	42	0	16	102	0
Nref	4932	5013	5765	11873	5199
Npar	276	296	249	552	296
R	0.0487	0.0427	0.0738	0.0630	0.0432
wR2	0.1353	0.1197	0.2568	0.2135	0.1207
S	1.02	1.04	1.05	1.03	1.03
$\Theta$ min, max/°	2.0, 28.4	2.0, 28.3	1.7, 28.7	1.5, 28.4	2.0, 28.3
Tot. data	37253	54421	62581	129352	32707
Unique data	4932	5013	5765	11873	5199
Observed data [ $I > 2.0\sigma(I)$ ]	3594	4058	3758	7663	4270
R <sub>int</sub>	0.023	0.022	0.028	0.033	0.023
Completeness	1.000	1.000	1.000	1.000	1.000
Min. and Max. resd. dens. $(e/Å^3)$	-0.24, 0.24	-0.18, 0.29	-0.57, 0.61	-0.50, 0.49	-0.54, 0.41

Table 3	Crystallographic data for	1,2-DAX·ANI, 1,2-DAX·DMA,	, 1,2-DAT·2(ANI),	1,2-DAT-2(NMA)	and 1,2-DAT·DMA <sup>a</sup>
---------	---------------------------	---------------------------	-------------------	----------------	------------------------------

<sup>a</sup>1,2-DAX·NMA was characterised by poor crystal quality, and SCXRD analysis was not possible for this complex.

<sup>b</sup>These three complexes experienced isostructural host packing.

with void diagrams (right), which were prepared by removing each guest species and recalculating the spaces remaining using a probe radius of 1.2 Å.

The guest components in 1,2-DAX·ANI, 1,2-DAX·DMA and 1,2-DAT·DMA all occupied isolated cavities in the host crystal (Fig. 3a) while both ANI and NMA were accommodated in channels in 1,2-DAT (Fig. 3b and c). It is clear from these figures that the preferred guest for both host compounds, DMA, was always found in discrete cavities and the host packing, too, was identical in each; a prior report by Caira et al. [24] associated this accommodation type (discrete cavities) with enhanced complex stability. A close analysis of the host-guest interactions responsible for guest retention was subsequently undertaken in each case.

1,2-DAX interacted with both ANI and DMA by means of numerous but very weak (host) $\pi$ ··· $\pi$ (guest) interactions ranging between 5.082(5) and 5.946(5), and 4.970(1) and 5.911(2) Å, respectively. Furthermore, ANI also experienced a classical hydrogen bond with this host [Fig. 4, 3.413(9) Å, 164(3)°], where ANI behaved as an acceptor, while an interaction of this kind with DMA was absent. However, DMA was additionally involved in two (guest)CH··· $\pi$ (host) contacts [2.94 Å (140°), 2.93 Å (141°)] and also a (guest)



Fig. 3 Host-guest packing (left) and void (right) diagrams for a 1,2-DAX·ANI (as representative for the three isostructural complexes), b 1,2-DAT·2(ANI) and c 1,2-DAT·2(NMA)

ArH…HAr(host) interaction. Overall, DMA therefore experienced a greater number and type of interactions with the host, in accordance with the preference of 1,2-DAX for this guest.

With respect to those complexes formed by 1,2-DAT, a large number of weak host–guest  $\pi \cdots \pi$  interactions were witnessed in all three, ranging between 4.771(3) and 5.981(2) Å, while guest–guest interactions of this kind were additionally

evident in the ANI and NMA complexes [4.999(6)–5.884(8) Å]. A further five XH… $\pi$  bonds, absent in 1,2-DAT·2(ANI), were also observed in 1,2-DAT·2(NMA). Two of these occurred between the NH group of one guest moiety and the  $\pi$  system of another guest molecule (2.73 and 2.47 Å, 164 and 148°). A single (guest)CH… $\pi$ (host) contact was also evident in the 1,2-DAT·DMA complex (2.91 Å, 141°). Notably, classical host–guest hydrogen bonds were absent in all three

**Fig. 4** A classical host-guest hydrogen bond (green) present in 1,2-DAX·ANI; here, ANI serves as the acceptor and the host compound as the donor molecule



inclusion compounds, but an abundance of other short contacts was observed, ranging from 2.31 to 2.87 Å (134–169°), while guest–guest short contacts ranged between 1.87 and 3.231(2) Å (108–164°). The preference of 1,2-DAT for DMA, upon close analyses of these interactions, is therefore not clear from these SCXRD data alone. However, as noted before, DMA was the only guest to be accommodated in cavities, while ANI and NMA occupied unconstricted and infinite channels in the crystal, an observation that may be responsible for the host preference for DMA, owing to the enhanced thermal stability associated with discrete cavity occupation [24].

Thermal [thermogravimetric (TG), its derivative (DTG) and differential scanning calorimetry (DSC)] analyses of all of the complexes formed in this investigation were subsequently conducted in order to confirm the thermal stability predictions that have been alluded to before. Figure 5a-c and 6a-c are the overlaid thermal traces thus obtained upon heating of the samples from approximately room temperature to 300 °C.

Table 4 summarises the relevant thermal data from Figs. 5a-c and 6a-c.

The guest release processes for the complexes with 1,2-DAX, largely, occurred in a single step (Fig. 5a–c). The endotherm peak temperatures (blue trace) representing this process ( $T_p$ ) decreased in the order DMA (181.8 °C) > NMA (173.2 °C) > ANI (164.8 °C), which correlates exactly with selectivity observations made before. Furthermore, expected and measured mass losses for these 1:1 complexes were in

close agreement (Table 4). Finally, the host melt occurred between 227.2 and 229.1 °C (the peak temperatures obtained from the host melt endotherms).

The thermal traces obtained for the three complexes with 1,2-DAT (Fig. 6a-c) were strikingly more convoluted than those for 1,2-DAX: 1,2-DAT·2(ANI) released the guest in what appeared to be two or more indistinct steps, and the host melt was not discernable on the trace. A similar scenario was observed for both 1,2-DAT·2(NMA) and 1,2-DAT·DMA, with the absence of a clear host melt endotherm on each. Additionally, the experimentally obtained mass losses for these complexes upon complete guest removal were significantly lower than those calculated. An explanation for these discrepancies may be that the TG (the red trace), with its continual downward slope in each instance, ensured difficulty in determining the temperatures at which guest loss was complete. However, the endotherm peak temperatures, as was the case for the complexes of 1,2-DAX, correlated satisfactorily with the host selectivity order noted before [DMA (157.1 °C) > NMA (125.1 °C) > ANI (110.2 °C)]. The observation of Caira et al. [24] that host-guest complexes display increased relative thermal stabilities when guests are retained in cavities compared with those where these are accommodated in channels is therefore supported by the results of experiments in this current investigation (DMA was the only guest to be accommodated in discrete cavities by 1,2-DAT, while ANI and NMA occupied unconstricted and infinite channels; the complex containing DMA did indeed possess a higher thermal stability (T<sub>p</sub> 157.1 °C)



Fig. 5 Thermal (TG, DTG and DSC) traces for a 1,2-DAX·ANI, b 1,2-DAX·NMA and c 1,2-DAX·DMA



Fig. 5 (continued)

than 1,2-DAT·2(ANI) (T<sub>p</sub> 110.2 °C) and 1,2-DAT·2(NMA) (T<sub>p</sub> 125.1 °C).

### Conclusion

This work sought to answer the question as to whether host– guest chemistry may be employed in order to separate ANI/ NMA/DMA mixtures using either 1,2-DAX and 1,2-DAT, novel compounds, as hosts. Such mixtures are industrially relevant since NMA and DMA are synthesized from ANI. It was revealed that both host compounds possess enhanced selectivities for DMA, more especially when recrystallized from equimolar binary mixtures where the other guest was ANI (ANI:DMA 8.2:91.8 and 9.7:90.3 for 1,2-DAX and 1,2-DAT, respectively). Furthermore, 1,2-DAX fared significantly better than 1,2-DAT if the molar amounts of DMA in binary mixtures were varied: while 1,2-DAX consistently favoured DMA (irrespective of its concentration), the behaviour of the sulfur-containing host depended on guest concentration, only preferring that guest that was present in increased amounts. SCXRD analyses were used to understand the host selectivity for DMA: 1,2-DAX experienced a greater number and type of host—guest interactions with this guest, while the preference of 1,2-DAT for DMA was less clear using this analytical technique. However, thermal analyses undoubtedly showed that the relative thermal stabilities of the complexes were in the order DMA > NMA > ANI for both host compounds, which correlated exactly with their selectivity behaviours when recrystallized from such guest mixtures. 1,2-DAX and 1,2-DAT may therefore be employed successfully to purify various mixtures of ANI/NMA/DMA.



 $\label{eq:Fig.6} \textit{Fig.6} \quad \textit{Thermal} (TG, DTG \textit{ and } DSC) \textit{ traces for } a 1,2\text{-} \textit{DAT} \cdot 2(\textit{ANI}), b 1,2\text{-} \textit{DAT} \cdot 2(\textit{NMA}) \textit{ and } c 1,2\text{-} \textit{DAT} \cdot \textit{DMA} \textit{ and } c 1,2\text{-} \textit{DAT} \cdot \textit{DAT} \cdot \textit{DMA} \textit{ and } c 1,2\text{-} \textit{DAT} \cdot \textit{DA} \textit{ and } c 1,2\text{-} \textit{DAT} \cdot \textit{DA} \textit{ and } c 1,2\text{-} \textit{DAT} \cdot \textit{DA} \textit{ and } c 1,2\text{-} m a 1,2\text{-} ma a 1,2\text{-}$ 





Table 4Relevant thermal datafor complexes formed by 1,2-DAX and 1,2-DAT

Guest	1,2-DAX			1,2-DAT		
	T <sub>p</sub> <sup>a</sup> ∕°C	Mass loss observed/%	Mass loss expected/%	T <sup>a</sup> /°C	Mass loss observed/%	Mass loss expected/%
ANI	164.8	12.9	12.9	110.2, 172.2	17.7	22.0
NMA	173.2	14.6	14.6	125.1	13.0	24.5
DMA	181.8	17.7	16.2	157.1	13.7	15.5

 ${}^{a}T_{p}$  is the endotherm peak temperature that represents the guest release process, is where guest loss is most rapid, and may be used as a measure of relative thermal stability

### **Supplementary information**

Crystallographic data for the novel complexes were deposited at the Cambridge Crystallographic Data Centre, where SCXRD analyses were possible {{CCDC-1982613 (1,2-DAX·ANI), 1982614 (1,2-DAX·DMA), 1982615 [1,2-DAT·2(ANI)], 1982616 [1,2-DAT·2(NMA)] and 1982617 (1,2-DAT·DMA)}}. These data may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Acknowledgements Financial support is acknowledged from the Nelson Mandela University and the National Research Foundation (NRF).

### References

- Kahl, T., Schröder, K.-W., Lawrence, F.R., Marshall, W.J., Höke, H., Jäckh, R.: Ullmann's Encyclopedia of Industrial Chemistry, 7th edn. Weinheim, VCH (2011) Germany
- Mamytov, K.Z., Beisenbayev, O.K., Shvets, V.F., Syrmanova, K.K.: The Multifunctional Automobile Gasoline Additive on the Basis of Amino-Aromatic Hydrocarbons and Oxygen-Containing Compounds. Eurasian Chem.-Technol. J. 14, 249–252 (2012)
- Taber, D.F., Meagley, R.P., Supplee, D.: A colorful grignard reaction: preparation of the triarylmethane dyes from 4-bromo-*N*,*N*dimethylaniline. J. Chem. Educ. **73**, 259–260 (1996)
- Badr, M., Aly, M.: Molecular rearrangements. Part IV. Aryl (Alkyl) Amines (1), thermal rearrangement of *N*-Benzyl-*N*-methylaniline. Can. J. Chem. **52**, 293–298 (1974)
- Niphadkar, P.S., Joshi, P.N., Gurav, H.R., Deshpande, S.S., Bokade, V.V.: Synthesis of *N*-methylaniline by aniline alkylation with methanol over Sn-MFI molecular sieve. Catal. Lett. 133, 175–184 (2009)

- Atwood, J.L., Suslick, K.S., Lehn, J.-M.: Comprehensive Supramolecular Chemistry: Supramolecular Reactivity and Transport: Bioinorganic Systems. Elsevier, Amsterdam (1996)
- Atwood, J.L., Steed, J.W.: Encyclopedia of Supramolecular Chemistry. CRC Press, Marcel Dekker, Inc. New York (2004)
- Steed, J.W., Atwood, J.L.: Supramolecular, &Nbsp;Chemistry. Wiley, New Yok (2009)
- Samipillai, M., Batisai, E., Nassimbeni, L.R., Weber, E.: Separation of lutidines by enclathration. CrystEngComm 17, 8332–8338 (2015)
- Caira, M.R., Nassimbeni, L.R., Vujovic, D., Toda, F.: Separation of xylenols by inclusion. J. Phys. Chem. 13, 75–79 (2000)
- Lusi, M., Barbour, L.J.: Solid-vapor sorption of xylenes: prioritized selectivity as a means of separating all three isomers using a single substrate. Angew. Chem. Int. Ed. Engl. 51, 3928–3931 (2012)
- Barton, B., de Jager, L., Hosten, E.C.: Host behaviour of *N*,*N*'-Bis(9-phenyl-9-thioxanthenyl)ethylenediamine in the presence of aromatic and aliphatic five-membered heterocyclic guests: selectivity correlations with Hirshfeld surface analyses. Cryst. Growth Des. **19**, 1268–1281 (2019)
- Barton, B., Dorfling, S.-L., Hosten, E.C.: Inclusion ability of host TETROL [(+)-(2R,3R)-1,1-4,4-tetraphenylbutane-1,2,3,4tetraol] for selected saturated cyclic and aromatic alcohol, ketone and amine guest compounds. J. Incl. Phenom. Macrocycl. Chem. 95, 331–340 (2019)
- Barton, B., Hosten, E.C., Pohl, P.L.: Host (-)-(2R,3R)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol and guests aniline, *N*-methylaniline and *N*,*N*-dimethylaniline: a selectivity study. Aust. J. Chem. **71**, 133–141 (2018)
- Barton, B., de Jager, L., Dorfling, S.-L., Hosten, E.C., McCleland, C.W., Pohl, P.L.: Host behaviour of related compounds, TETROL

and DMT, in the presence of two different classes of aromatic guest compounds. Tetrahedron **74**, 4754–4760 (2018)

- Barton, B., de Jager, L., Hosten, E.C.: Comparing the host behaviour of *N*,*N*'-bis(9-phenyl-9-thioxanthenyl)ethylenediamine and *N*,*N*'-bis(9-phenyl-9-xanthenyl)ethylenediamine in the presence of various alkylated aromatic and aniline guests: crystal engineering considerations. CrystEngComm. **21**, 4387–4400 (2019)
- 17. Bruker, A.X.S., APEX2, S.A.D.A.B.S., Bruker, S.A.I.N.T.: A.X.S., Madison, WI (2010)
- 18. Sheldrick, G.M.: SHELXT-integrated space-group and crystal structure determination. Acta Crystallogr. A **71**, 3 (2015)
- Sheldrick, G.M.: Crystal structure refinement with SHELXL. Acta Crystallogr. C 71, 3 (2015)
- Hübschle, C.B., Sheldrick, G.M., Dittrich, B.: ShelXle: a Qt graphical user interface for SHELXL. J. Appl. Crystallogr. 44, 1281 (2011)
- Mercury 3.10.2: (Build 189770), http://www.ccdc.cam.ac.uk/ mercury/. Accessed 2019.]
- Barton, B.: Host–Guest Chemistry: The Synthesis and Assessment of Host Compounds Based on the 9-Arylxanthenyl and Related Systems. University of Port Elizabeth, Port Elizabeth (1996)
- Sykes, N.M., Su, H., Weber, E., Bourne, S.A., Nassimbeni, L.R.: Selective enclathration of methyl- and dimethylpiperidines by fluorenol hosts. Cryst. Growth Des. 17, 819–826 (2017)
- Tanaka, K., Hori, K., Tsuyuhara, S., Motoki, S., Shide, S., Arakawa, R., Caira, M.R.: Role of halogen bonding in clathrate formation of tetra- and hexasalicylides derived from halogenated salicylic acids. Tetrahedron 69, 1120–1127 (2013)

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.