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Alternative separation strategy for *o*-/*p*-dichlorobenzene mixtures through supramolecular chemistry protocols†

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N,*N*′-Bis(9-phenyl-9-xanthenyl)butane-1,4-diamine (**H**), a compound bearing two tricyclic fused ring systems linked by means of a four carbon diamino chain, was assessed for its host ability when presented with the three dichlorobenzene (DCB) isomers by means of crystallization experiments from each one. In this manner, it was shown that **H** was not capable of encapsulating *p*DCB, whilst both *o*DCB and *m*DCB successfully formed inclusion compounds with this host compound; host : guest (H : G) ratios were 1 : 1.5 in both instances. Host crystallization experiments from binary guest mixtures involving *o*DCB and *m*DCB demonstrated that **H** possessed only a moderate selectivity towards *o*DCB (the selectivity coefficients, *K*, were low and ranged between 2.1 and 5.4). However, remarkably, the preference of **H** towards *o*DCB when mixed in a 40 : 60 molar ratio with *p*DCB was overwhelming, and 89.3% of *o*DCB was measured in the crystals; *K* was significant (12.5). Of even greater prominence was the observation that when *o*DCB/*p*DCB were mixed in 80 : 20 molar proportions, only *o*DCB (100.0%) was observed in the complex, and *K* was infinite. These results demonstrate that *o*DCB/*p*DCB (40 : 60 and 80 : 20) may be separated/purified by means of **H** through supramolecular chemistry strategies, this being extremely challenging to achieve by means of more conventional fraction distillations due to similarities in the physical properties of these isomers. Meaningful single crystal X-ray diffraction (SCXRD) data were only possible for **H**·1.5(*o*DCB) as the crystal quality of complex **H**·1.5(*m*DCB) was poor (owing to extreme twinning). This complex (**H**·1.5(*o*DCB)) was also subjected to Hirshfeld surface analyses, while both complexes were analysed by means of thermoanalytical experiments as well: **H**·1.5(*o*DCB) experienced a multi-stepped guest release process whilst the guest in **H**·1.5(*m*DCB) escaped from the crystals of the complex in a single step. Finally, the thermal stability of the complex with preferred *o*DCB was higher than that with less favoured *m*DCB.

1. Introduction

Chloroaromatic compounds such as the dichlorobenzenes (DCBs) may be prepared by means of the chlorination of benzene with chlorine gas in the presence of a catalyst,[1] but this synthetic strategy furnishes a mixture of all three isomers (*o*DCB, *m*DCB and *p*DCB) in varying amounts. Another possible route towards the DCBs is through the Sandmeyer reaction, where aniline is converted first into an aryldiazonium salt using sodium nitrate and HCl, followed by the addition of cuprous chloride to the mixture to afford the desired aryl halide; in the case of the synthesis of dichlorobenzene, an appropriate chloro-substituted aniline is required as the starting material.[2–4]

Arguably, the most important DCB is the *para* substituted isomer, which is used commercially in products such as deodorants and moth controls, whilst nitration of *o*DCB affords 3,4-dichloroaniline which has important functions in the preparation of herbicides and insecticides.[5] Similarly, the *meta* isomer also finds application in the production of pesticides and has, furthermore, been used as a precursor in the synthesis of dyes and phamaceuticals.[1] The industrial importance of *p*DCB, moreover, includes its use in the preparation of polyphenylene sulfide,[6] an important polymer used in various industries including thermoplastics, while *o*DCB is employed in the synthesis towards toluene diisocyanate,[7] which has found broad applications in the production of polyurethane plastics, coatings and adhesives.[8]

Traditional separation methods of these isomers by using, for example, fractional distillations, are extremely intricate

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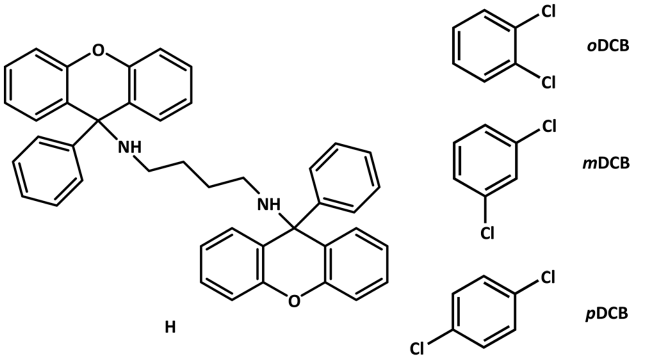
† Electronic supplementary information (ESI) available: Crystallographic data for H·1.5(oDCB) have been deposited at the Cambridge Crystallographic Data Centre under the CCDC number 2361243 and can be obtained from **https://www.ccdc.cam.ac.uk/structures/cif**. Other data supporting this article have been included as part of the ESI (Fig. S1 contains relevant ^{1}H-NMR spectra, Table S1, the *K* values obtained, and Tables S2–S5 measurements applicable to the SCXRD analyses). For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d4ce00684d**

owing to their narrow boiling point range (*o*DCB boils at 180.4 °C, *m*DCB at 173.0 °C, and *p*DCB at 174.0 °C),[9] resulting in a process that is exceedingly energy intensive and costly, while still producing isomers with purities that are wanting. It may be suggested that the separation of *m*DCB/*p*DCB mixtures through fractional crystallizations is a viable option (the melting point of *m*DCB is between −22 and −25 °C, while that of *p*DCB is distinctly different, 53.5 °C), but this binary system has a eutectic point when the mixture has an 88 : 12 composition (by weight) of *m*DCB, therefore affording only one of the two isomers in pure form. Additionally, the isolation of *m*DCB here requires very low temperatures, rendering the process economically impracticable.[10] Alternative greener separations for these isomers are therefore mandatory, especially when one considers the energy crisis currently facing our planet.

Other separatory techniques that have been employed to isolate each of these dichlorobenzenes include zeolites and metal organic frameworks (MOFs).[11–14] These methodologies, however, are also expensive to carry out and have their own flaws. In the present investigation, we propose employing supramolecular chemistry strategies for these separations, more specifically the field of host-guest chemistry. This field of science is multidisciplinary in nature and finds rich applications in many industries,[15–18] including in drug stability and delivery, chemical sensing, and chromatographic procedures. Separations through host-guest chemistry is an extremely attractive methodology that is cost effective and environmentally friendly and, most importantly, the host compounds may readily be recovered and recycled in the process, adding to the appeal of this strategy. For effective separations of binary mixtures by means of host-guest chemistry, the selectivity coefficient (*K*, a measure of the host selectivity) must be 10 or greater, according to Nassimbeni and coworkers.[19] In our own laboratories, we employed various roof-shaped host compounds bearing the 9,10-dihydro-9,10-ethanoanthracene backbone for these separations with much success: *trans*-α,α,α',α'-tetra(*p*-chlorophenyl)-9,10-dihydro-9,10-ethano-anthracene-11,12-dimethanol demonstrated an overwhelming selectivity towards *m*DCB when presented with 20 : 80 and 50 : 50 *m*DCB/*p*DCB mixtures, and the *K* values were significant, 24.0 and 14.0, respectively.[20] Furthermore, the host system *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (DED) was remarkably selective for *p*DCB in both binary and ternary crystallization experiments, and near-quantitative amounts of *p*DCB were measured in the resultant crystals (96.4–100.0%) after host crystallization experiments from these mixtures.[21]

In the present work, *N*,*N*′-bis(9-phenyl-9-xanthenyl)butane-1,4-diamine (**H**), bearing two tricyclic fused ring systems linked together by means of a four carbon diamino chain, was investigated for its separation ability for DCB mixtures (Scheme 1) through host-guest chemistry principles, in an ongoing quest to identify capable host compounds with complementary selectivity behaviours. This proposed investigation was deemed an appropriate one since **H** has recently been demonstrated to possess selectivity in *p*-xylene/*m*-xylene (40 : 60, 50 : 50 and 60 : 40 mol%) mixtures (remarkable *K* values were calculated on many ocassions, in favour of *p*-xylene).[22] Any appropriate single solvent complexes produced in the present work were also subjected to SCXRD and Hirshfeld surface analyses where possible, together with thermoanalytical experiments, in order to observe the intermolecular interactions present in these complexes and their relative thermal stabilities. We report on all of these results now.



Scheme 1 Structures of the host compound *N*,*N*′-bis(9-phenyl-9-xanthenyl)butane-1,4-diamine (**H**) and the dichlorobenzene isomers (*o*-, *m*- and *p*DCB).

2. Experimental

2.1. General

All starting materials and guest compounds were purchased from Merck, South Africa, and were used without further purification.

^{1}H-NMR spectroscopic experiments were carried out by means of a Bruker Ultrashield Plus 400 MHz spectrometer; $CDCl_3$ was the deuterated solvent.

Thermal analyses were conducted on any successfully formed single solvent complexes by employing a Perkin Elmer simultaneous thermal analyser (STA) 6000. Data analysis was by means of Perkin Elmer Pyris 13 thermal analysis software. Samples were placed in ceramic pans and were heated from approximately 40 to 350 °C at a rate of 10 °C min^{-1}, and the purge gas was high purity nitrogen. An empty ceramic pan served as the reference.

GC experiments were carried out by means of a Young Lin YL6500 gas chromatograph, coupled to a flame ionization detector, fitted with an Agilent J&W Cyclosil-B column in order to quantify the guest compounds in the mixed complexes. The method involved an initial temperature of 50 °C with a hold time of 1 min followed by a ramp of 13 °C min^{-1} until 180 °C was reached (zero hold time). A split ratio of 1 : 40 was employed with a flow rate of 1.5 mL min^{-1}. The carrier gas was nitrogen, while the solvent was dichloromethane in all instances.

The complex **H**·1.5(*o*-DCB) was further subjected to single crystal X-ray diffraction (SCXRD) analysis. The applicable instrument was a Bruker Kappa Apex II diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). APEXII was used for data collection, whereas SAINT was employed for cell refinement and data reduction.[23] SHELXT-2018/2 (ref. 24) was employed to solve the structures, whilst refinement required least-squares procedures using SHELXT-2018/3 (ref. 25) together with SHELXLE[26] as a graphical interface. Carbon-bound hydrogen atoms were added in idealized geometrical positions in a riding model and all non-hydrogen atoms were refined anisotropically. Finally, by means of SADABS, data were corrected for absorption effects using the numerical methods in this program.[23] This crystal structure was deposited at the Cambridge Crystallographic Data Centre, and the applicable CCDC number is 2361243.

2.2. Synthesis of H

The host compound was prepared by considering a previous report.[22]

2.3. Single solvent crystallization experiments with H

To determine whether **H** has the ability to form complexes with each of the dichlorobenzene guest species, a spatula tip of **H** (±0.03 g, 0.05 mmol) was dissolved completely in an excess of the guest solvent with the aid of mild heating. In the case of *p*DCB, which is a solid at room temperature, 0.05 mmol of this guest was used together with ethylbenzene as a cosolvent. The vials were left open to the ambient conditions. The crystals that emanated from these solutions were collected under suction, washed with petroleum ether (b.p. 40–60 °C), and analysed by means of ^{1}H-NMR spectroscopy. The integrals of relevant host and guest resonance signals were then compared in order to obtain the host : guest (H : G) ratios.

2.4. The selectivity behaviour of H in equimolar mixed DCBs

In order to evaluate the selectivity of the host compound in mixed DCBs, **H** (0.04 g, 0.07 mmol) was crystallized from the various binary and ternary guest combinations where the guest species were present in equimolar amounts (the combined guest quantity was 3 mmol). Again, whenever *p*DCB was present, several drops of ethylbenzene were required to effect complete host dissolution. The vials were then sealed and, once more, kept at atmospheric pressure and temperature, which resulted in the formation of crystals. These were collected and treated in the same manner as in the single solvent experiments. The guest ratios in any mixed complexes formed in this manner were determined through GC-FID analyses.

2.5. The selectivity behaviour of H in binary mixtures of the DCBs where the molar concentrations of the guests were varied

The selectivity behaviour of **H** was further investigated by means of crystallization experiments from binary mixtures of the DCBs, where guest amounts were varied from 80 : 20, 40 : 60 and 60 : 40 to 20 : 80 (guest A (G_A) : guest B (G_B)). Therefore, **H** (0.04 g, 0.07 mmol) was dissolved, with mild heat being applied, in these guest solutions (3 mmol combined amount) (ethylbenzene, once more, served as the cosolvent in experiments involving *p*DCB) and the vials and the so-formed crystals were treated and isolated as in the equimolar experiments. The crystals were, once more, subjected to GC-FID analyses for guest quantification purposes. A plot of the guest ratio of G_A (or G_B) in the crystals (Z) against G_A (or G_B) in the original solution (X) afforded selectivity profiles, a visual manner in which to observe the host behaviour in these experimental conditions. The selectivity coefficient (K), which is a measure of the separation ability of the host compound for these binary guest mixtures, may be determined by means of the equation $K_{A:B} = Z_A/Z_B \times X_B/X_A$, where $X_A + X_B = 1$.[27] An unselective host compound has $K = 1$, which is represented by the straight diagonal lines in these plots.

2.6. Software

Program Mercury was used to prepare the unit cell, host-guest packing, inter- and intramolecular interaction, and void diagrams.[28] In the latter instance, the guest molecules were deleted from the packing calculations, and the resulting spaces were analysed by means of a spherical probe with a radius of 1.2 Å. Crystal Explorer software was employed in order to prepare Hirshfeld surface illustrations as well as the associated two-dimensional fingerprint plots, and to quantify the intermolecular guest⋯host interactions.[29,30]

3. Results and discussion

3.1. Single solvent crystallization experiments with H

Host compound **H** was crystallized independently from each of the three dichlorobenzene isomers. ^{1}H-NMR spectroscopic analysis on the resultant solids demonstrated that only *o*- and *m*DCB were enclathrated in this way, both complexes having 1 : 1.5 H : G ratios; guest-free host compound was isolated in the case of the guest species *p*DCB (and this guest, therefore, did not form a complex with **H**). Similarly, from a previous report,[20] *trans*-α,α,α',α'-tetra(*p*-chlorophenyl)-9,10-dihydro-9,10-ethano-anthracene-11,12-dimethanol, a host compound that was also presented with these DCB guest compounds, enclathrated only *o*DCB and *m*DCB (H : G 3 : 2 and 1 : 1), while DED formed a complex with all three guest compounds (H : G 2 : 3, 1 : 1 and 2 : 1 for *o*DCB, *m*DCB and *p*DCB, correspondingly).[21]

3.2. The selectivity behaviour of H in equimolar mixed DCBs

Table 1 contains a summary of the guest ratios, as obtained from GC-FID analyses, of the complexes that formed in the equimolar mixed guest experiments. To ensure the repeatability of these results, all experiments were performed in duplicate and, as such, the percentage estimated standard deviations (% e.s.d.s.) are also provided here (in parentheses). Preferred guests in each mixture are highlighted by means of bold font.

Table 1 Guest ratios of complexes formed in the equimolar experiments

*o*DCB	*m*DCB	*p*DCB	Averaged guest ratios[a] (% e.s.d.)
X	X		**71.3**:28.7 (0.3)
X		X	**90.3**:9.7 (2.9)
	X	X	[b]
X	X	X	**60.8**:27.8:11.4 (0.5)(0.5)(1.0)

[a] Guest ratios were obtained by means of GC-FID analyses. [b] The guest ratios were not reproducible since the% e.s.d.s. calculated were unacceptably high.

When **H** was crystallized from the equimolar binary mixtures of these DCBs, a distinct preference towards *o*DCB was observed: from the *o*DCB/*m*DCB and *o*DCB/*p*DCB solutions were isolated complexes with significant amounts of this guest species (71.3 and 90.3%) (Table 1). However, the results obtained from the *m*DCB/*p*DCB experiments could not be reproduced during multiple repeat experiments (the e.s.d.s were greater than 5% in all cases) and, thus, these data are not provided here. This observation may be as a result of the fact that both *m*DCB and *p*DCB appear to be disfavoured by **H**. Finally, crystals emanating from the solution containing all three of the DCBs (*o*DCB/*m*DCB/*p*DCB) furnished a complex with, once more, an enhanced quantity of *o*DCB (60.8%). From these results, the selectivity of **H** for these guests may be written as in the order *o*DCB ≫ *m*DCB > *p*DCB. These observations complement those of host compounds *trans*-α,α,α′,α′-tetra(*p*-chlorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol and DED from earlier reports,[20,21] where the host selectivity was overwhelmingly in favour of *m*DCB and *p*DCB, correspondingly.

3.3. The selectivity behaviour of H in binary mixtures of the DCBs where the molar concentrations of the guests were varied

The selectivity profiles that were obtained after plotting *Z* (the molar ratio of G_A or G_B in the mixed complex) against *X* (this molar ratio in the original solution) are provided in Fig. 1a–c after GC-FID analyses on the solids emanating from each crystallization experiment.

Fig. 1a demonstrates that the selectivity behaviour of **H** depended upon the amounts of the two guest solvents present. The affinity was towards *m*DCB when the molar concentration of this guest species in the solution exceeded 80%. The crystals then contained 83.4% *m*DCB, and the selectivity coefficient (*K*, in favour of *m*DCB) was 1.3. In the remaining mixtures (40:60, 60:40 and 80:20 *o*DCB/*m*DCB), **H** favoured *o*DCB, but *K* values remained low, ranging between 2.2 and 5.4. According to Nassembeni *et al.*,[19] *K* values of 10 or greater are required for feasible separations of binary mixtures through supramolecular chemistry strategies. Clearly, in the present instance (*o*DCB/*m*DCB), these separations are not practicable with **H** as the host candidate.

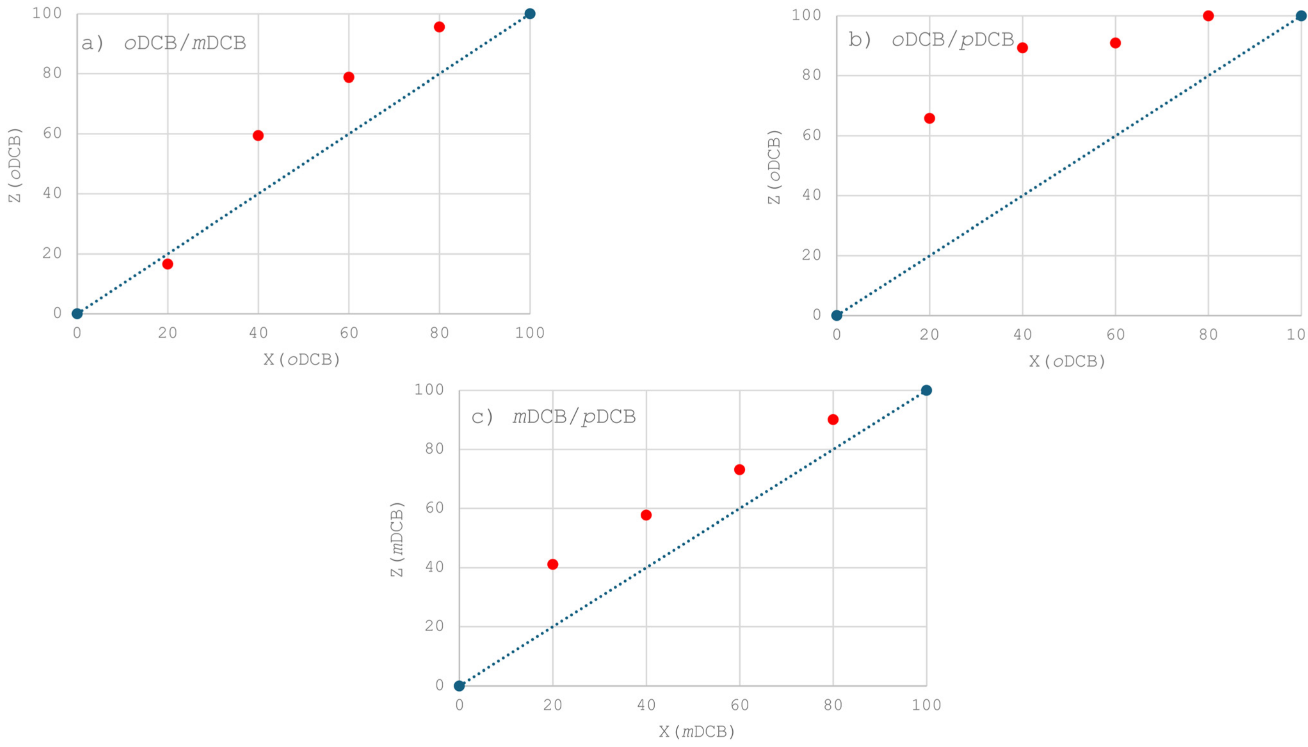


Fig. 1 Selectivity profiles of H when crystallized from the a) *o*DCB/*m*DCB, b) *o*DCB/*p*DCB and c) *m*DCB/*p*DCB binary mixtures. The straight diagonal lines represent an unselective host compound.

When considering the results obtained from all combinations of *o*DCB and *p*DCB (Fig. 1b), a remarkable host preference towards *o*DCB was consistently observed. From the 20 : 80 and 60 : 40 *o*DCB/*p*DCB experiments, the calculated *K* values, in favour of this guest, were 7.7 and 6.7, respectively, and hence **H** would not be able to separate these two mixtures effectively. However, the 40 : 60 mixture furnished a complex with as much as 89.3% *o*DCB, and *K* was a significant 12.5, while this value was infinite when **H** was crystallized from an 80 : 20 *o*DCB/*p*DCB solution, since only *o*DCB (100.0%) was detected in the crystals. These latter two mixtures may therefore be readily separated/purified by means of **H** through host-guest chemistry principles, a remarkable finding given the difficulty of separating such mixtures by the more conventional techniques.

From all of the experiments in *m*DCB/*p*DCB (Fig. 1c) were calculated low *K* values (K_{avg} 2.2), in favour of the *meta* isomer: **H**, therefore, does not possess the ability to separate any of these solutions.

Analogous experiments with host compounds *trans*-α,α,α′,α′-tetra(*p*-chlorophenyl)-9,10-dihydro-9,10-ethano-anthracene-11,12-dimethanol and DED[20,21] revealed that a number of these mixtures may also be separated efficiently by means of host-guest chemistry strategies (the first of these host compounds having an affinity for *m*DCB, and DED for *p*DCB). Clearly, the results of the present investigation, once more, complement those in these previous reports.

3.4. Thermal analysis

To assess the relative thermal stabilities of the two complexes produced in this work, thermal analyses were subsequently carried out on each one. The overlaid thermal curves (the thermogravimetric (TG), its derivative (dTG), and the differential scanning calorimetric (DSC)) provided in Fig. 2a and b were obtained by heating the samples from approximately 40 to 350 °C at 10 °C min^{-1}. A summary of the more relevant temperature and mass loss data from these curves is provided in Table 2, where T_{on} is the temperature at which the guest loss event commenced and serves as a measure of the thermal stability of the complex.

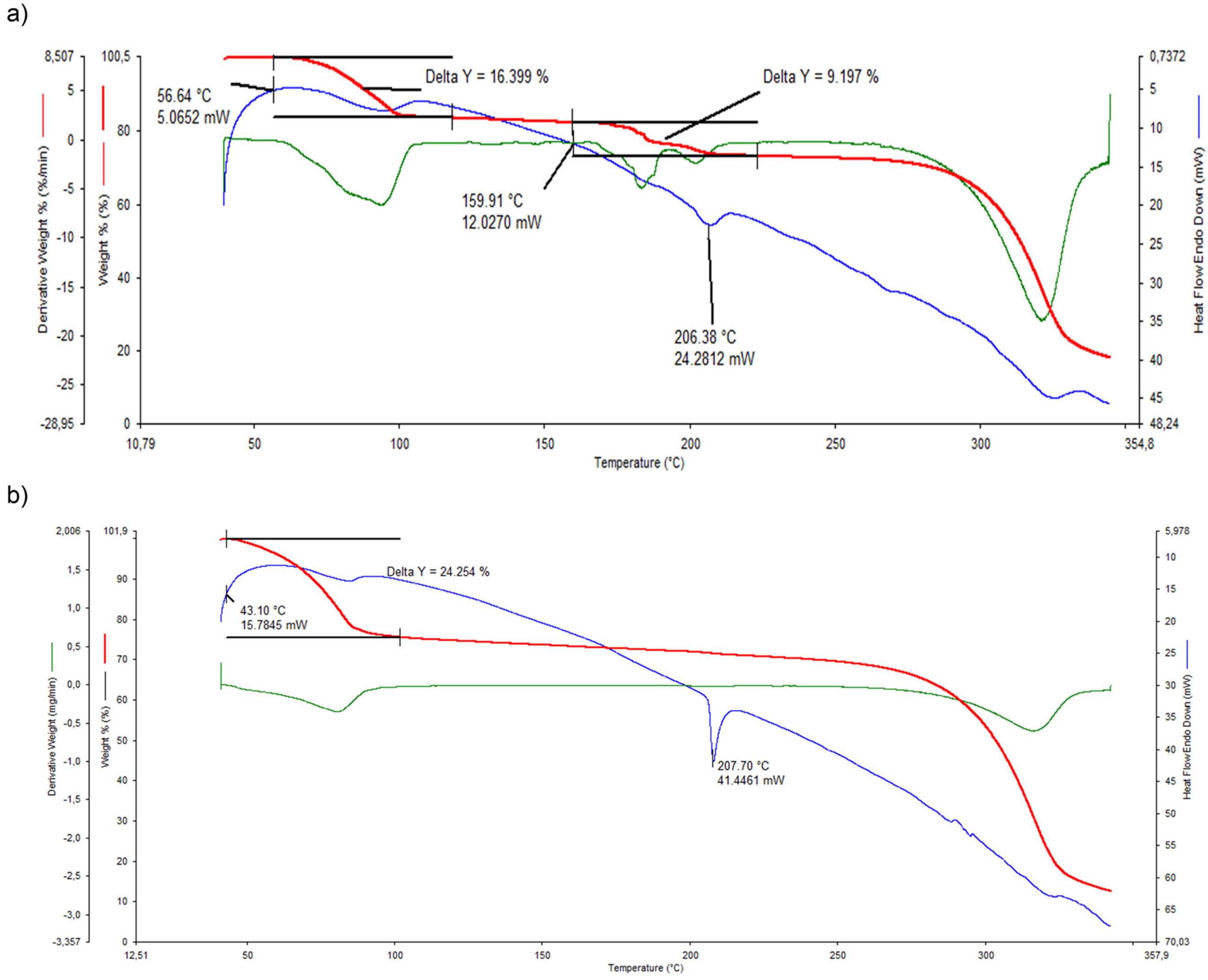


Fig. 2 Overlaid TG (red), DSC (blue) and DTG (green) curves for a) **H**·1.5(*o*DCB) and b) **H**·1.5(*m*DCB).

Table 2 Thermal data obtained for the complexes of H with *o*DCB and *m*DCB

Complex	T_{on} (°C)	Experiential mass loss (%)	Theoretical mass loss (%)
H·1.5(*o*DCB)	56.6	25.6	26.9
H·1.5(*m*DCB)	43.1	24.3	26.9

In the case of **H**·1.5(*o*DCB), the guest release process occurred in more than one step, and T_{on} was 56.6 °C (Fig. 2a, Table 2): nearly two thirds of the total guest amount (64.1%) were released from the complex during the first broad decomposition step while, in a second convoluted process (commencing at approximately 159.9 °C), the remainder of the guest species escaped from the crystals of the complex. With the H : G ratio being 1 : 1.5 for this complex, this observation effectively implies that first 1 and then 0.5 of the guest species escaped in these two broad guest release events. When considering these curves for **H**·1.5(*m*DCB) (Fig. 2b, Table 2), the guest release event initiated at 43.1 °C and was single stepped. Clearly, the complex with the preferred guest compound (*o*DCB) possessed the higher thermal stability compared with that containing less favoured *m*DCB. This observation plausibly explains the selectivity behaviour of **H** in DCB mixtures. Finally, for both complexes, the expected (26.9%) and experimentally determined (25.6 and 24.3%, respectively) mass losses were in reasonable agreement.

3.5. SCXRD analyses

The relevant crystallographic data from the SCXRD experiment on the complex **H**·1.5(*o*DCB) are provided in Table 3. This inclusion compound crystallized in the triclinic crystal system and space group $P\bar{1}$. One guest molecule in the unit cell was disordered around an inversion point while the other guest species present experienced no disorder.

The atomic labelling of the asymmetric unit of complex **H**·1.5(*o*DCB) is presented in Fig. 3, whilst Fig. 4 illustrates the unit cell and the voids, by means of stereoscopic views, which were prepared using program Mercury.[29] Here, guests were housed in multidirectional channels which occupied 26.7% of the unit cell volume (554.15 Å^3). (Note that in the case of the complex **H**·1.5(*m*DCB), data collection indicated that three-component twinning was present. The host molecule was located but its refinement afforded negative values for the thermal parameters of the atoms. Furthermore, refinement of the guest molecule had an *R* factor of 28%, and so these SCXRD data were thus not reliable and are not provided here.)

The angle between the planes of the free aromatic rings and that between the planes of the xanthenyl moieties were measured to be 6.39 (11) and between 22.80 and 19.95 (11)°, respectively (Fig. 5). Previously, this host compound was crystallized from guest species *o*- and *p*-xylene, and these angles in the host molecule were then measured to be between 5.40 (6) and 10.78 (7)°, and 21.42 (5) and 26.63 (5)°, correspondingly.[22] In another investigation involving cyclohexanone guest species,[31] both of these angles were exactly parallel (180°). Finally, the geometry of the diamino linker of the host molecule in **H**·1.5(*o*DCB) was similar to those in the previous two reports, where a "zigzag" pattern was observed and where the two nitrogen atoms were oriented periplanar with respect to one another. Clearly the geometry of the host molecule is dependent upon the nature of the guest species present.

Although no significant π···π interactions between any of the species were observed, (guest)C–H···π(host) and (guest)C–Cl···π(host) (halogen bonding) interactions were identified in **H**·1.5(*o*DCB). The former interaction involved the aromatic hydrogen atom of the ordered guest species (*ortho* to the chlorine atom) and a centroid of one of the aromatic rings of the xanthenyl moiety of the host molecule; the H···π and C···π distances were 2.73 and 3.646 (3) Å, respectively, while the C–H···π angle was 161°. In the case of the halogen bond, one chlorine atom of both disorder guest components interacted with an aromatic ring of the xanthenyl moiety of the host molecule once more. The Cl···π and C···π bond distances were 3.614 and 5.135 (3) Å, and the C–Cl···π angle was 146.1 (3)°. These interactions are illustrated in Fig. 6.

Table 3 Relevant crystallographic data and structure refinement for H·1.5(*o*DCB)

Identification code	H·1.5(*o*DCB)
Empirical formula	$C_{51}H_{42}Cl_3N_2O_2$
Formula weight	821.21
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.8318 (4) Å b = 14.6939 (6) Å c = 16.5191 (7) Å
Volume	2074.76 (15) Å^3
Z	2
Density (calculated)	1.315 mg m^{-3}
Absorption coefficient	0.265 mm^{-1}
F(000)	858
Crystal size	0.394 × 0.355 × 0.328 mm^3
Theta range for data collection	1.941 to 28.295°
Index ranges	$-11 \leqq h \leqq 11$, $-19 \leqq k \leqq 19$, $-21 \leqq l \leqq 21$
Reflections collected	170 208
Independent reflections	10 290 [R(int) = 0.0498]
Completeness to theta = 25.242°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10 290/66/568
Goodness-of-fit on F^2	1.112
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0576$, w$R_2 = 0.1372$
R indices (all data)	$R_1 = 0.0927$, w$R_2 = 0.1807$
Extinction coefficient	0.0102(14)
Largest diff. peak and hole	0.780 and −0.643 e.Å^{-3}

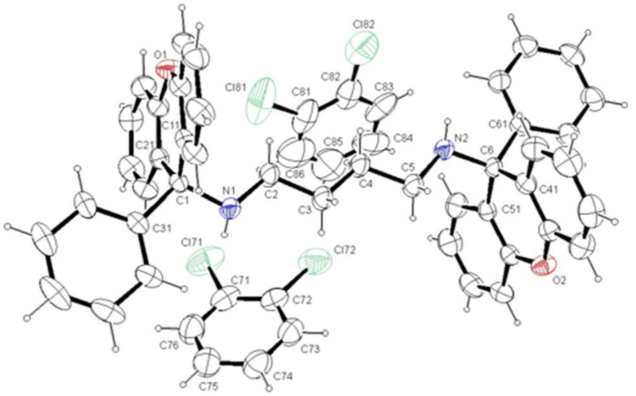


Fig. 3 Atomic labelling of the asymmetric unit of complex **H**·1.5(*o*DCB). Both host and guest atoms are presented as thermal ellipsoids.

Furthermore, non-classical hydrogen bonding interactions were identified in **H**·1.5(*o*DCB). One such contact type was intramolecular in nature and involved a host hydrogen atom of the free aromatic ring and a nitrogen atom of the diamino linker moiety; there were two such interactions (Fig. 7), and applicable H⋯N bond distances were 2.46 Å (C⋯N 2.803 (3) Å) and 2.42 Å (C⋯N 2.779 (3) Å), while their angles both measured 102°. The other interaction was an intermolecular one and involved the hydrogen atom of the free aromatic ring of the host molecule and the oxygen atom of the xanthenyl moiety of an adjacent host species (also shown in Fig. 7). The H⋯O and C⋯O distances were 2.46 and 3.389 (3) Å, with a bond angle of 167°.

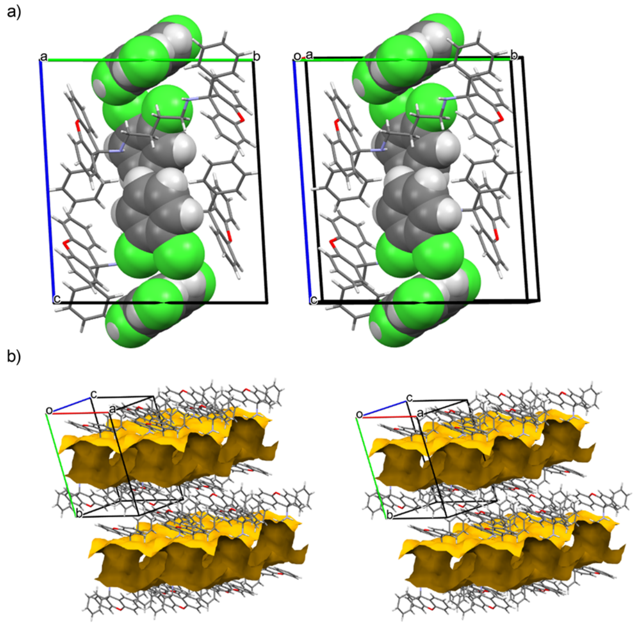


Fig. 4 Stereoviews of the a) unit cell (top) and b) voids (bottom, in yellow/orange/brown) depicting the multidirectional channels that housed the guest species in **H**·1.5(*o*DCB). The guest species are in spacefill representation and the host molecules in capped stick form.

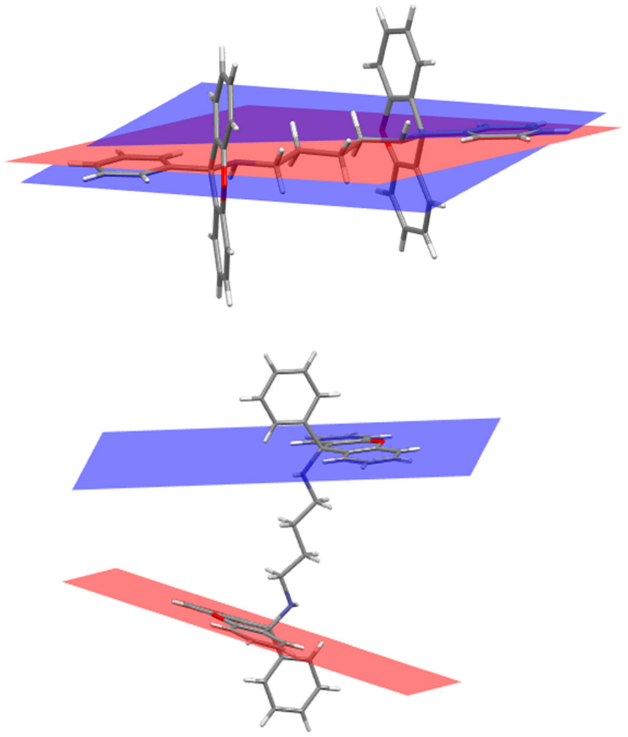


Fig. 5 Calculated planes of the two free phenyl rings (top) and the two xanthenyl moieties (bottom) in **H**·1.5(*o*DCB).

Several other short contacts, the distances of which measured less than the sum of the van der Waals radii of the involved atoms were also identified. The first of these involved a xanthenyl hydrogen atom and the aromatic carbon atom of a disorder guest component. Here, H⋯C and C⋯C were 2.84 Å and 3.767 Å, with a bond angle of 167°. Furthermore, a pair of guest chlorine atoms interacted with either a xanthenyl or a free aromatic hydrogen atom of the host molecule (Fig. 8). The Cl⋯H bond distances were 2.83 Å (C⋯H 3.379 Å) and 2.93 (C⋯H 4.587 Å), with bond angles of 152 and 160°, respectively. Finally, a Cl⋯Cl interaction was also observed, involving two disordered guest components. The Cl⋯Cl bond length was 3.315 (4) Å (C⋯Cl 4.950 Å) and the bond angle 157.6 (8).

Finally, we considered Hirshfeld surface analysis to further quantify the intermolecular host⋯guest interactions in **H**·1.5(*o*DCB) using program Crystal Explorer,[29,30] where a three-dimensional surface was generated around the guest molecule. This surface was subsequently converted into a two-dimensional (2D) fingerprint plot, which represents the distance between a guest atom inside the surface (*di*) and the nearest host atom outside this surface (*de*). Due to the nature of the guest disorder in one of the guest species in the complex **H**·1.5(*o*DCB), these analyses were not possible, and only the results for the ordered guest component are provided here. Fig. 9 illustrates the 2D fingerprint plot obtained representing all the intermolecular interactions between the guest and host species, where the 'spikes' (1 and 2) signify the Cl⋯H and H⋯N interactions, whilst the

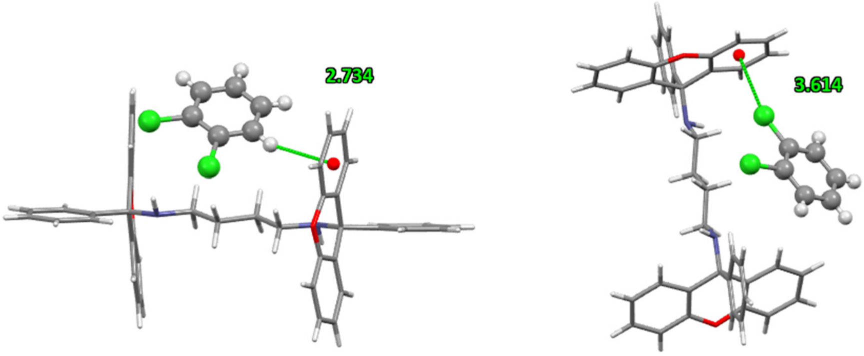


Fig. 6 The (guest)C–H⋯π(host) (left) and (guest)C–Cl⋯π(host) (right) interactions present in **H**·1.5(*o*DCB). For clarity, the interaction on the right is illustrated with one disorder guest component only. Host and guest species are presented in stick and ball-and-stick notation, respectively.

'wings' (3 and 4) represent the C⋯H and H⋯H interactions.

These calculations showed that 46.0% of all of these intermolecular guest⋯host interactions involved the Cl atom of the guest species, while 37.9 and 16.1% pertained to the hydrogen and carbon atoms of the guest interacting with the host molecule. Finally, the amount of guest hydrogen atoms interacting with the nitrogen of the host molecule amounted to only 1.0%.

4. Conclusions

The crystallization of the host compound *N*,*N*′-bis(9-phenyl-9-xanthenyl) butane-1,4-diamine (**H**) from each of the DCBs revealed that inclusion compounds were obtained for both *o*DCB and *m*DCB, and the H : G ratios were 1 : 1.5 in each instance, while *p*DCB did not form a complex with **H**. When the host compound was crystallized from equimolar guest mixtures, a significant preference towards *o*DCB was observed. The selectivity of **H** was thus demonstrated to be in the order *o*DCB ≫ *m*DCB > *p*DCB. In binary mixtures of *o*DCB/*m*DCB and *m*DCB/*p*DCB, the selectivity coefficients (*K*) that were calculated were low and **H** would, therefore, not be able to separate any of these mixtures on an industrial platform. However, from the 40 : 60 and 80 : 20 *o*DCB/*p*DCB experiments were calculated significant *K* values (12.5 and infinite, in favour of *o*DCB) and **H** possesses the ability to separate or purify these mixtures efficiently. These observations are welcome given the difficulty of these separations by means of fractional distillations/crystallizations. Thermal analyses showed that the complex with the favoured guest compound (*o*DCB) had the greater thermal stability compared to the complex with unpreferred *m*DCB. SCXRD analyses revealed that the guest molecules in **H**·1.5(*o*-DCB) were housed in multidirectional channels, and interactions such as (guest)C–H⋯π(host), (guest)C–Cl⋯π(host) and other significant short contacts ((guest)C–Cl⋯H–C(host)) assisted in the retention of favoured *o*DCB in the crystals of the complex, while a number of intramolecular non-classical hydrogen bonds within each host molecule served to maintain its molecular geometry. Finally, the results from Hirshfeld surface analyses demonstrated that nearly 50% of the intermolecular guest⋯host interactions occurred between the chlorine of the ordered guest molecule and the host species.

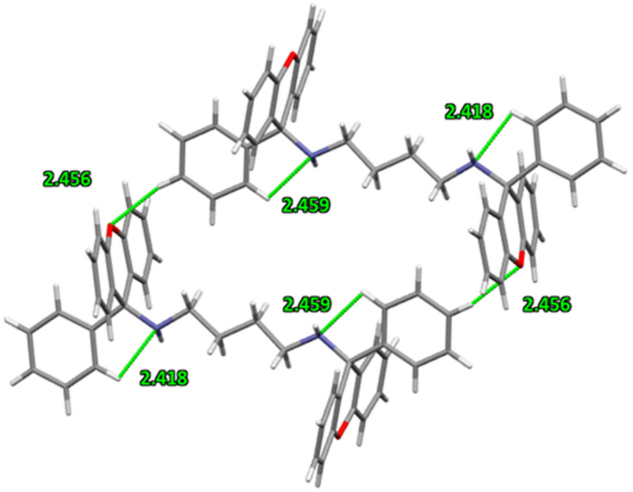


Fig. 7 The non-classical hydrogen bonds in **H**·1.5(*o*DCB). For clarity, hydrogen atoms not involved in these interactions have been deleted; the host molecules are presented in capped stick notation.

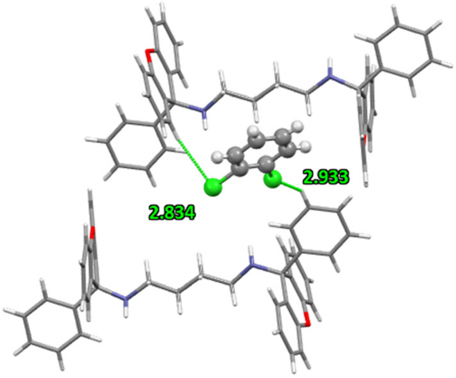


Fig. 8 A pair of short contacts in **H**·1.5(*o*DCB). For clarity, host molecules are presented in capped stick notation whilst the guest is in ball-and-stick representation.

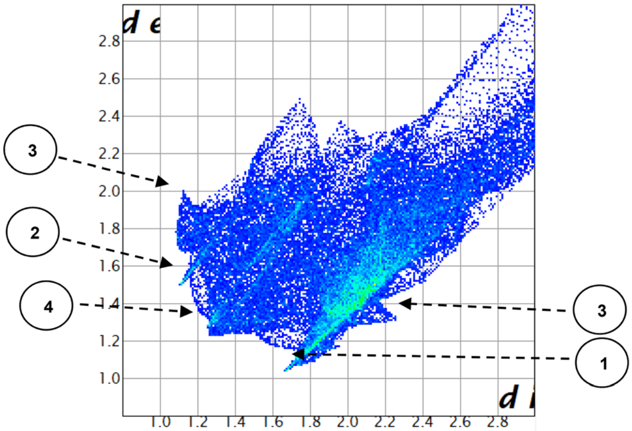


Fig. 9 The 2D fingerprint plot showing all the intermolecular interactions between the ordered guest and the host molecules present in **H**·1.5(*o*DCB).

Data availability

The crystallographic data for **H**·1.5(*o*DCB) has been deposited at the Cambridge Crystallographic Data Centre, and the applicable CCDC number is 2361243. These data may be obtained from **https://www.ccdc.cam.ac.uk/structures/cif**.

Author contributions

Brandon Barnardo: conceptualization; visualization; methodology; writing – original draft. Benita Barton: conceptualization; methodology; funding acquisition; project administration; resources; supervision; visualization. Eric C. Hosten: data curation; formal analysis.

Conflicts of interest

There are no conflicts of interest to declare.

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