The host potential of N,N'-bis(9-(4-methoxyphenyl)-9H-xanthen-9-yl)ethane-1,2-diamine for the xylene and ethylbenzene isomers, and its selectivity behaviour in mixed guest solutions

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Introduction

The separation of the aromatic isomers of xylene and ethylbenzene remains a significant industrial challenge due to their closely comparable physical properties, particularly their similar boiling points. In this study, the potential of host–guest chemistry as a potential alternative separation strategy.[1-5] The host compound N,N′-bis(9-(4-methoxyphenyl)-9H-xanthen-9-yl)ethane-1,2-diamine (H) was investigated to achieve this feat. Crystallization experiments were conducted with individual and mixed xylene/ethylbenzene systems to evaluate host selectivity and inclusion behaviour. Using single-crystal X-ray diffraction and thermal analysis guest incorporation modes and relative stability were further studied. The findings will provide insight into the selectivity profile of H and assess its viability as a means of separation and purification of xylene/ethylbenzene mixtures.

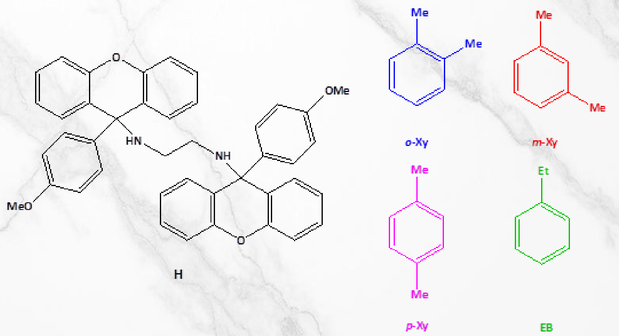
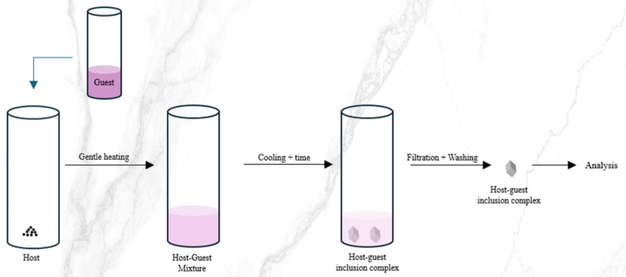


Figure 1. Structures of N,N'-bis(9-(4-methoxyphenyl)-9H-xanthen-9-yl)ethane-1,2-diamine (H), and the potential guest solvents o-xylene, m-xylene, p-xylene and ethylbenzene (o-Xy, m-Xy, p-Xy and EB).

Methods

The host molecule was produced using xanthone, 4-bromo-anisole and ethylene-diamine as described in *barton 1996*[6].
The formation of single inclusion complexes of host **H** with the corresponding guest.



To assess whether **H** possesses selectivity for a particular guest solvent, host crystallization experiments were conducted in mixed guest solutions in equimolar proportions. All possible Xy/EB combinations were considered here. Thus, H (0.05g, 0.08 mmol) was dissolved in the equimolar mixed guest solution (5 mmol combined amount), the vial lidded and sealed with parafilm and stored at ambient conditions. The resultant crystals were isolated and treated as in the single solvent experiments. The guest ratios in any mixed complexes that formed in this manner were determined through GC analysis.

H was crystallized from binary guest solutions (GA & GB) in which the molar ratio of each guest present was varied (20:80, 40:60, 60:40 and 80:20 GA:GB)in an identical fashion to the aforementioned equimolar guest experiments. Analyses of the crystals were by means of GC, which provided the guest amounts in the so formed mixed guest complexes. Selectivity profiles were then constructed by plotting ZA (or ZB), the amount of GA (or GB) in the crystals, against XA (or XB), the amount of GA (or GB) in the original solution, according to the equation of Pivovar and colleagues, K = ZA/ZB "×" XB/XA, where XA "+" XB = 1.[6] These plots provide a visual representation of the host selectivity behaviour in such varying guest proportions. K is the selectivity coefficient and may be calculated for each data point in these plots and serves as a measurement of the host selectivity. It has been reported that K values are required to be 10 or greater for effective separations of binary mixtures in a practical setting.[7] When K = 1, the host compound is not selective; this theoretical scenario is represented by the straight diagonal lines that have been inserted into each of these profiles for comparison.

Results

Table 1 summarises the results obtained when H was crystallized from each of the four isomers. Only EB was not enclathrated, while the H:G ratios of the three complexes that formed successfully were 1:1 (o-Xy and m-Xy) and 1:2 (p-Xy). (The applicable 1H-NMR spectra for these complexes are provided in the SI).

Table 1 The H:G ratios of complexes of H when crystallized from each of the xylenes and EB.

Guest	H:G ratio
o-Xy	1:1
m-Xy	1:1
p-Xy	1:2
EB	*a*

[a]No inclusion occurred.

Table 2 contains a summary of the results obtained after analysing the solids emanating from the equimolar solutions through GC. These experiments were conducted in duplicate to determine their replicability and, thus, the percentage estimated standard deviations (% e.s.d.s) are also provided in this table. Preferred guests are indicated in bold text for ease of analysis.

Table 2. Results from the equimolar mixed Xy/EB experiments.

o-Xy	*m*-Xy	*p*-Xy	EB	Guest ratio	% e.s.d.s
X	X			**59.9** : 40.1	1.4
X		X		**86.7** : 13.3	0.3
X			X	**80.7** : 19.3	0.8
	X	X		**53.5** : 46.5	0.7
	X		X	45.9 : **54.1**	2.5
		X	X	41.2 : **58.8**	0.3
X	X	X		**53.8** : 34.5 : 11.7	0.5: 0.2 : 0.3
X	X		X	**48.1** : 9.6 : 42.3	1.9 : 0.3 : 1.56
X		X	X	**66.6** : 12.8 : 20.6	2.5 : 2.3 : 0.2
	X	X	X	9.2 : 9.5 : **81.3**	0.6 : 0.3 : 0.9
X	X	X	X	**36.2** : 19.8 : 8.2 : 35.8	1.2 : 1.4 :0.2 : 2.4

Table 3. Selectivity coefficients for the data points contained in the selectivity profiles.

	K Values					
Binary Mixture	20:80	40:60	50:50[a]	50:50[a]	60:40	80:20
o-Xy/*m*-Xy	1.8 (*o*-Xy)	1.3 (*o*-Xy)	1.4 (*o*-Xy)	1.6 (*o*-Xy)	1.9 (*o*-Xy)	2.4 (*o*-Xy)
o-Xy/*p*-Xy	8.8 (*p*-Xy)	1.8 (*o*-Xy	6.4 (*o*-Xy)	6.7 (*o*-Xy)	5.5 (*o*-Xy)	6.3 (*o*-Xy)
o-Xy/EB	**∞ (EB)**	1.5 (*o*-Xy)	4.3 (*o*-Xy)	4.0 (*o*-Xy)	5.5 (*o*-Xy)	5.2 (*o*-Xy)
m-Xy/*p*-Xy	4.5 (*p*-Xy)	1.4 (*m*-Xy)	1.1 (*m*-Xy)	1.2 (*m*-Xy)	1.4 (*m*-Xy)	4.9 (*m*-Xy)
EB/*m*-Xy	**∞ (*m*-Xy)**	1.5 (EB)	1.3 (EB)	1.1 (EB)	1.3 (EB)	1.6 (EB)
EB/*p*-Xy	1.2 (EB)	1.5 (EB)	1.4 (EB)	1.4 (EB)	1.5 (EB)	1.8 (EB)

[a]In all cases, the 50:50 experiments were conducted in duplicate

From Table 3, K was too low (1.1–8.8) in most instances to suggest that H would be an ideal host candidate for these separations through host-guest chemistry. Strikingly, though, two selectivity coefficients were calculated to be infinite as a result of the fact that only one guest species was observed in the so formed complexes. The applicable inclusion compounds were those obtained from the 20/80 o-Xy/EB and 20/80 EB/m-Xy solutions in which only EB and m-Xy, respectively, were detected in the crystals. These results indicate that H may behave as a purification tool for solvents EB and m-Xy that are tainted with, in turn, small quantities of o-Xy and EB.

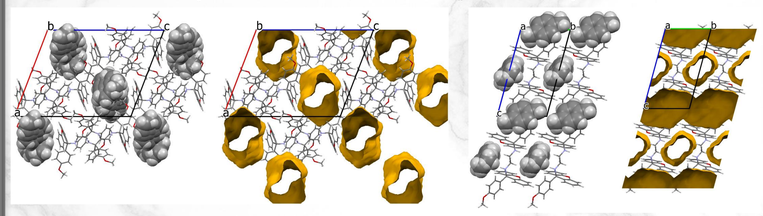


Figure 2. Unit cells for (left) H·o-Xy (representing also H·m-Xy) and (right) H·2(p-Xy); the void diagrams are provided on the right-hand side.

The host molecules in the crystal of H·2(p-Xy) (Figure 3c) possessed an inversion of symmetry and, consequently, the two NH groups of the linker units were positioned in an antiperiplanar orientation (180.00°) with respect to one another. However, these molecules in the H·o-Xy and H·m-Xy complexes (which demonstrated an isostructural host packing motif) had these NH moieties in a more gauche orientation (66.61 and 66.08°). Moreover, after guest removal from the packing calculations and an analysis of the resulting spaces by means of a probe with a 1.2 Å radius, it was possible to prepare the void diagrams as demonstrated on the right-hand side in Figure 3. In all of these complexes, guests were accommodated in endless channels, unidirectional in the case of H·o-Xy and H·m-Xy (left) and bidirectional in the complex with p-xylene (right, with the disordered guest species in a different channel to the ordered guest molecules).

Table 4. Thermal data for the inclusion compounds of H with the xylene isomers.

Complex	T_{on}[a] (°C)	Mass loss (%) (expected)	Mass loss (%) (experimental)
H·*o*-Xy	41.7	14.4	13.6
H·*m*-Xy	39.2	14.4	15.4
H·2(*p*-Xy)	41.3	25.1	25.2

[a]T_{on} is the onset temperature for the guest release event and was estimated from the DTG trace in each case.

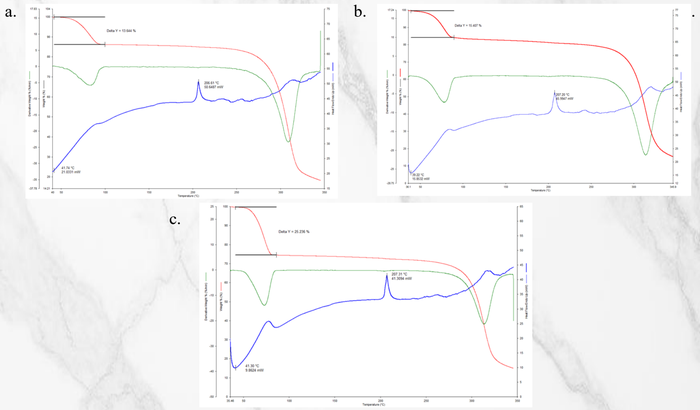


Figure 3. Overlaid TG (red), DTG (green) and DSC (blue, endo up) traces for the inclusion complexes with a) H·o-Xy, b) H·m-Xy and c) H·2(p-Xy).

Figures 3a–c depict the overlaid thermogravimetric (TG, red), its derivative (DTG, green) and differential scanning calorimetric (DSC, blue, endo up) for the thermal experiments conducted on each of H·o-Xy, H·m-Xy and H·2(p-Xy), while the more applicable thermal data from these traces have been summarised in Table 4. Each of the guest species in the three complexes was released in a distinct single-stepped process . Furthermore, the onset temperatures for this guest release event (Ton) in each of the three experiments were extremely comparable (41.7, 39.2 and 41.3 °C for H·o-Xy, H·m-Xy and H·2(p-Xy), respectively), suggesting that these inclusion compounds possess very similar relative thermal stabilities. This observation is not entirely surprising in the case of H·o-Xy and H·m-Xy since these complexes shared a host packing. These thermal data do not, as a result, provide a rationalization for the selectivity behaviour of H when presented with guest mixtures in that the more preferred guests did not form the more stable complexes, according to these data.

Conclusions

In the present investigation, the host compound *N,N'*-bis(9-(4-methoxyphenyl)-9*H*-xanthen-9-yl)ethane-1,2-diamine (**H**) was demonstrated to possess inclusion ability for *o*-Xy, *m*-Xy and *p*-Xy, while EB was not enclathrated in analogous experimental conditions and only apohost **H** was isolated in this particular instance. The H:G ratios of the three successfully furnished complexes were 1:1, 1:1 and 1:2 (*o*-Xy, *m*-Xy and *p*-Xy). When **H** was crystallized from guest solutions, a host selectivity order of *o*-Xy > EB > *m*-Xy > *p*-Xy was noted. In fact, it was shown that **H** may serve to purify EB and *m*-Xy solvents when contaminated with small quantities of *o*-Xy and EB, respectively. SCXRD experiments demonstrated that more preferred *o*-Xy and *m*-Xy always experienced a (guest)C–H···π(host) close contact with **H**, facilitating guest retention, while not all of the guest molecules in **H**·2(*p*-Xy) were involved in these types of stabilizing interactions with the host species, thus explaining the low preference of **H** for *p*-Xy. The relative thermal stabilities of the three single solvent complexes were, moreover, established to be equivalent through thermoanalytical experiments since T_{on}, the onset temperatures of the guest release events, ranged between only 39.2 and 41.7 °C.

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