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A comparison of the behaviour of two closely related xanthenylderived host compounds in the presence of vaporous dihaloalkanes

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Abstract

The behaviour of two closely related xanthone-derived host compounds, N,N'-bis(9-phenyl-9-xanthenyl)ethylenediamine and N,N'-bis(9-phenyl-9-thioxanthenyl)ethylenediamine, which formed complexes with CH₂Cl₂, CH₂Br₂ and CH₂I₂ after recrystallization from each of these solvents, was compared when subjected to these guest and guest mixtures in the vapour phase. Surprisingly, these hosts displayed entirely different behaviours under these conditions, with only the thioxanthenyl derivative possessing the ability to clathrate these guests (or guest mixtures) from the gas phase; this ability was entirely absent in the xanthenyl host. All novel complexes were subjected to single crystal diffraction analyses in order to investigate the interactions present, as well as thermal and Hirshfeld surface experiments. The host selectivity and host–guest interactions were correlated with the differences observed in the recrystallization and vapour experiments. Furthermore, data obtained for the novel complexes by employing various analytical techniques were related back to the observed selectivity order.

Keywords Host–guest chemistry \cdot Inclusion compounds \cdot Alkyl halides \cdot X-Ray crystallography \cdot Thermal stability \cdot Gas absorption

Introduction

Host–guest chemistry is a field of chemistry devoted to investigating the synthesis, properties and applications of new and successful host molecules for the formation of host–guest inclusion compounds. Inclusion compounds are "complexes" in which one chemical compound, the host, forms a cage, cavity or channel in which another compound, the guest, is located. The two compounds interact to form one new inclusion compound which does not obey the known definition of a complex, as there are no coordinate covalent/dative bonds between the guest and the host [1].

Hosts, usually solids, can form inclusion compounds with guests by simple recrystallization processes. The resultant solid inclusion compounds are analyzed by means of various

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Lize de Jager s213337665@mandela.ac.za techniques such as nuclear magnetic resonance (NMR) spectroscopy, gas chromatography (GC) and single crystal X-ray diffraction (SCXRD).

There exist numerous applications of host–guest chemistry: in the pharmaceutical industry, host compounds are used to clathrate drug molecules to improve transport, activity, resistance and solubility of such drugs, and to effect chiral resolution of important pharmaceutical products. Other applications include the removal of hazardous materials from the environment, improving taste and stability of food products, chromatography and asymmetric synthesis [1].

The storage of organic vapours by interstitial van der Waals confinement is an important application of host materials. The process of absorption of guests within these is fundamental in many industrial applications. In heterogenous catalysis, for example, the catalysts are solids whilst the great majority of reactants are gases or liquids [2, 3]. Absorption of guest molecules facilitates the trapping of highly volatile guests by forming thermally stable inclusion compounds, and the separation of mixtures of such compounds is contingent on the selectivity of the host material [4]. Absorption of guests is controlled by molecular recognition and relies on non-covalent interactions between host and guest under defined temperatures and

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pressures, the time of exposure and the porosity of the host material [2]. The most basic principle of organic solidstate chemistry is that molecules will arrange in a manner to balance the effects between optimization of space and intermolecular interactions [4]. Amombo et al. [2] investigated the guest exchange of tetrakis(4-halophenyl)ethylene hosts and noted significant halogen bonding $(d > 3 \text{ \AA})$ as the possible reason for complex stability, based on previous work that considered the size of the halogen atoms [5]. A calix[4]arene-derived host was explored by Atwood et al. [4] for its ability to capture small, highly volatile molecules that formed disordered complexes due to the guest's loose "fit" and the presence of high crystallographic site symmetry; they noted that the more symmetrical guests were not disordered [4]. Ziganshin et al. [6] studied the thermal stability, sorption capacity and change of morphology of amino acid derivatives with arenes, linear alcohols, alkanes and nitriles. The inclusion ability decreased with each added methylene group and, for the alcohols, the difference in host selectivity was correlated to the shape of the molecules, as linear *n*-propanol was highly preferred. Moreover, hosts were observed to form more stable clathrates at lower guest content.

In this present work, we report on the inclusion ability and behaviour of host N,N'-bis(9-phenyl-9-xanthenyl)ethylenediamine 1 in the presence of dihaloalkanes CH₂Cl₂ (DCM), CH₂Br₂ (DBM) and CH₂I₂ (DIM). We also synthesised a closely related compound, N,N'-bis(9-phenyl-9thioxanthenyl)ethylenediamine 2, and compared the potential of both hosts for gaseous guest uptake, with surprising observations despite the similarities in each of these host materials. These hosts have never been assessed for their vapour inclusion ability.

HN Ν Η 1: X = O

2: X = S

Novel complexes were subjected to single crystal X-ray diffraction (SCXRD), Hirshfeld and thermal analyses in order to better understand the mode of guest inclusion, the nature of host-guest interactions and relative complex stabilities, and these observations were correlated with the selectivity and inclusion ability of the two hosts. We report these findings here.

Results and discussion

Synthesis of hosts 1 and 2

A simple Grignard reaction using phenylmagnesium bromide was carried out on xanthone and thioxanthone, independently, and the resultant alcohol reacted with perchloric acid to afford the perchlorate salt. Two of these xanthenyl units were then bridged with ethylenediamine to form the final product 1 and 2 (yield approx. 60-65%) [7].

Analysis of inclusion compounds

Complexation by recrystallization

Compound 1 was dissolved in each of the respective dihalo guest solvents. The resultant mixtures were left at ambient temperature and pressure to facilitate crystallization. The solid that formed was collected by vacuum filtration and washed efficiently with petroleum ether (40-60 °C). The crystals were analysed using proton NMR spectroscopy to determine whether inclusion had occurred and, if so, the host:guest (H:G) ratios were obtained by integration of relevant host and guest resonances. Table 1 is a summary of the results so-obtained.

Host 1 successfully formed inclusion compounds with all three dihaloalkanes, with DCM and its dibromo analogue preferring 1:2 H:G ratios, while diiodomethane was enclathrated with a 1:1 H:G ratio. Interestingly, the structurallysimilar sulfur analogue 2 showed the host to prefer the 1:1 H:G ratio consistently with the three guests [7].

Competition experiments with equimolar mixtures of guests by recrystallization

These experiments were carried out by dissolving host 1 in binary and ternary combinations of the guests (equimolar amounts). The crystallization vessels were closed and stored at 0 °C to maintain the equimolar condition. The resultant solids were processed and analysed in the same manner as the individual inclusions. Table 2 shows a summary of the results obtained, where italic bold font face was employed for preferred guests for better clarity.



Table 1Host:guest (H:G) ratiosof complexes formed by host 1

Guest (G)	H:G
DCM	1:2 ^a
DBM	1:2 ^a
DIM	1:1
	1

Determined using ¹H-NMR spectroscopy with CDCl₃ as the solvent

^aNMR spectra were deposited in the Supplementary Information (S1a–c). Thermal analyses showed that these inclusion compounds were unstable, which affected the integration values of the NMR resonance signals. The H:G ratios were, however, confirmed by means of SCXRD

 Table 2
 Results of competition experiments using host 1 and various equimolar mixtures of the guests

DCM	DBM	DIM	Average guest ratios (%)	Overall H:G ratio
x	x		38.46: 61.54	1:2
x		х	77.79:22.21	1:1
	x	х	84.16 :15.84	1:1
х	x	х	35.68: 51.72 :12.61	1:1

Ratios determined using ¹H-NMR spectroscopy with CDCl_3 as the solvent

Experiments were conducted in duplicate; % e.s.d.'s are provided in the Supplementary Information (S2)

Host **1** displayed selectivity for DBM when mixed in equimolar proportions with DCM and DIM in the binary experiments (61.54 and 84.16%, respectively, Table 2). In the presence of both DCM and DIM, the former was pre-ferred (77.79%), while an equimolar ternary experiment

Fig. 1 General selectivity curves obtainable for binary non-equimolar competition experiments [6]



provided a host selectivity order of DBM (51.72%) > DCM (35.68%) > DIM (12.61%). Interestingly, a different selectivity order was observed for the sulfur host analogue [DBM (46%) > DIM (38%) > DCM (16%)] [7].

Competition experiments with varied molar ratios of guests by recrystallization

These experiments involved preparing binary mixtures of two guests but varying their molar ratios beyond equimolar in order to determine whether the host selectivity changes with guest concentration change. The series of competition experiments in which pairs of guest molecules A and B cocrystallize with host H may be characterized by:

 $H(\alpha, s) + nA(l \text{ or } g) + mB(l \text{ or } g)/H \cdot A_n(s, \beta) + mB(l \text{ or } g)$

where H represents the apohost in its non-porous α -phase which, when placed in contact with a mixture of the guests A and B, selects A and forms a solid inclusion compound H·A_n, the β -phase, and excludes B [8]. In practice, however, usually both guests are found in the host crystal.

A selectivity coefficient can be defined as

$$K_{A:B} = Z_A/Z_B \times X_B/X_A$$
, where $X_A + X_B = 1$

where X_A is the mole fraction of guest A in the liquid mixture and Z_A that of guest A enclathrated in the crystal (Fig. 1). Here, plot 'i' represents no selectivity and $K_{A:B} =$ 1, curve 'ii' results when A is preferentially enclathrated with respect to B over the entire concentration range, while curve 'iii' is the case where the host selectivity is guestconcentration dependent [9].

We therefore prepared binary mixtures with host **1** and guest 1(G1):guest 2(G2) ratios approximating 100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100, and the results of these experiments are represented as the selectivity profiles in Fig. 2a–c. The x- and y-axes are given as mole fractions ($X_{dihaloalkane}$ and $Z_{dihaloalkane}$, respectively), and the



Fig. 2 Selectivity profiles of host 1 when recrystallized from a DBM/DCM, b DBM/DIM and c DCM/DIM

straight-line plot represents the line of no selectivity (K=1) and is hypothetical.

Figure 2a, b clearly show that host 1 is selective for DBM over the entire concentration range assessed, even at low molar fractions of this guest in the recrystallizing liquid mixture (<50%). Furthermore, Fig. 2b shows a significant deviation of the experimental data points relative to the hypothetical line of no selectivity compared with Fig. 2a, where

the data points lie closer to the straight-line plot, which confirms the preference of dichloromethane over diiodomethane when the second solvent is DBM. This correlates with the observed host selectivity order in the equimolar solvent experiments. Finally, and as expected, DCM was preferred consistently relative to DIM (Fig. 2c).

In comparison, host **2** was selective for DBM over the entire concentration range, even at low concentrations of

this guest. In the absence of DBM, however, the host initially showed selectivity for DIM at low concentrations, up until 66%, and beyond this point the host preferred DCM [7]. In order to understand the observed selectivity order, we analysed suitable crystals by means of SCXRD in order to establish the nature and type of intermolecular interactions present between host and guest.

Single crystal X-ray diffraction analyses

X-Ray diffraction studies were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromated Mo K α radiation (λ =0.71073 Å). APEXII [10] was used for data collection and SAINT [10] for cell refinement and data reduction. The structure was solved using SHELXT-2014 [11] and refined by least-squares procedures using SHELXL-2017/1 [11] with SHELXLE [12] as a graphical interface. Data were corrected for absorption effects using the numerical method implemented in SAD-ABS [10] All non-hydrogen atoms were refined anisotropically. Carbon–bound hydrogen atoms were added in idealized geometrical positions in a riding model. For both 1·2DCM and 1·2DBM, the nitrogen–bound hydrogen atoms are disordered over two positions which were located on the difference Fourier map but refined riding. The solvent molecules have positional disorder and were refined with the carbon–halide bonds restrained to be the same length. These crystallographic data were deposited at the Cambridge Crystallographic Data Centre [1·2DCM (1824152) and 1·2DBM (1824153)]. The crystal structure of the inclusion compound 1·DIM could not be determined due to poor crystal quality.

The relevant crystallographic data for these experiments are summarized in Table 3.

Both inclusion compounds display isostructural host packing, crystallizing in the triclinic *P*-1 crystal system with very similar unit cell dimensions.

Table 3Crystallographic datafor 1.2DCM and 1.2DBM

	1.2DCM	1.2DBM
Chemical formula	$C_{40}H_{32}N_2O_2\cdot 2CH_2Cl_2$	$C_{40}H_{32}N_2O_2 \cdot 2CH_2Br_2$
Formula weight	906.87	920.37
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
μ (Mo-K α)/mm ⁻¹	0.366	4.415
a/Å	8.8213 (4)	8.8555 (4)
b/Å	8.8657 (4)	8.8981 (4)
c/Å	13.5055 (6)	13.5996 (6)
Alpha/°	73.237 (2)	72.633 (2)
Beta/°	72.035 (2)	72.998 (2)
Gamma/°	66.861 (2)	66.578 (2)
$V/Å^3$	906.87 (7)	919.83 (7)
Z	1	1
F (000)	386	458
Temp./K	200	200
Restraints	6	6
N _{ref}	4501	4561
N _{par}	251	251
R	0.0467	0.0387
wR ²	0.1369	0.1013
S	1.03	1.05
θ min–max/°	1.6, 28.3	1.6, 28.4
Tot. data	24,198	28,553
Unique data	4501	4561
Observed data [I > 2.0 sigma (I)]	3477	3360
R _{int}	0.023	0.028
Dffrn measured fraction θ full	0.999	1
Min. resd. dens. (e/Å ³)	-0.38	-0.60
Max. resd. dens. (e/Å ³)	0.34	0.37

The 1.DIM complex was characterized by poor crystal quality and could not be analysed by SCXRD

Figure 3 shows unit cells of the complexes, where the host is represented by ball-and-stick and the guests with space-fill representation. The crystal packing of the two unit cells are clearly isostructural.

The experimental powder pattern obtained when employing powder X-ray diffraction (PXRD) on the DIM complex was compared to the calculated powder patterns of the other two complexes (using the Mercury software). As expected, the host packing in the DIM complex was not isostructural with the other dihalo-analogue complexes since clear differences between these patterns were observed (Supplementary Information S3).

From the SCXRD data, we obtained the significant host – guest interactions present in the complexes, and these are summarized in Table 4.

The two inclusion compounds experience no π - π , CH- π or classical hydrogen bonding interactions (Table 4). While the complex 1·2DCM does not display non-classical hydrogen bonding interactions, two of these interaction types are



Fig.3 Unit cells for a 1·2DCM and b 1·2DBM; isostructural host packing is evident

present in 1.2DBM. This observation may be the reason for the observed selectivity of host 1 for DBM (Table 2; Fig. 2a). In addition, the 1.2DCM complex is held in the crystal by means of only four short contacts (Table 4), whereas the 1.2DBM experiences a further two of these. The complex of host 2 with DBM (the preferred guest) also experienced a greater number of host–guest interactions compared with the other two guests [7]. Furthermore, its diiodomethane complex was stabilized by guest–guest interactions owing to these molecules being in close proximity to one another as a consequence of their increased molecular size.

We subsequently carried out Hirshfeld surface analyses to elucidate, quantitatively, the intermolecular interactions in the crystal.

Hirshfeld surface analysis

Hirshfeld surfaces describe the immediate environs of molecules. Figure 4a–d are depictions of the two-dimensional fingerprint plots which were derived from the three-dimensional Hirshfeld surfaces generated using Crystal Explorer 17 [13]. These surfaces were obtained using data files (.cif files) from the crystal structure analyses. (Note that all surfaces were generated around the guest molecules.) Here, *de* and *di* correspond to the distances to the nearest atom outside and inside the surface, respectively. Figure 5 illustrates the comparison of the percentage of the appropriate intermolecular interactions (G…H/H…G). Since the guests in both 1.2DCM and 1.2DBM showed disorder, care had to be taken and Hirshfeld surfaces were mapped for both major and minor components.

Unfortunately, these Hirshfeld surface analyses did not provide any information which could be used to explain the selectivity order of the host. X–H and H–H interactions were most predominant, where X represents the halogen atoms, as expected since hydrogen atoms are on the periphery of the molecules and are therefore more likely to experience these interaction types.

We subsequently investigated the nature of the guest accommodation.

Guest accommodation

The nature of the guest accommodation is shown in Fig. 6, and these voids were calculated using the Mercury software after the guests had been removed from the packing calculation [14]. Since 1.2DCM and 1.2DBM were isostructural, only the voids for the chloro derivative were calculated, as representative example.

In both complexes, the guest is accommodated in infinite multidirectional channels. Interestingly and in direct contrast to this host, the thio derivative **2** accommodated its guests as pairs in discrete cavities [7]. Therefore, significant host

Non-covalent interaction	1.2DCM	1·2DBM	Symmetry operator
π–π	None present	None present	
CH···π (host–guest)	None present	None present	
H-bonding (host-guest)	None present	Non-classical	
		3.50 Å, 144°	x, 1 + y, z
		(C–H···Br)	
		3.77 Å, 145° (C–H···Br)	-x, 1-y, 1-z
Short contacts (host/guest and guest/guest) ^{a,b}			
	2.77 Å, 1113° (<) [(host Ar)C–C···H–C(guest 2)]		x, y, z
	2.77 Å, 107° (<) [(host Ar)C–C···H–C(guest 1)]		1 - x, 1 - y, 1 - z
	2.82 Å, 156° (<) [(host NH)N–H…Cl–C(guest 2)]		1 + x, y, z
	2.80 Å, 145° (<) [(guest 2)N–H···Cl–C(host Ar)]		1 - x, 1 - y, 1 - z
		2.70 Å, 116° (<<) [(host Ar)C–C…H–C(guest 2)]	x, y, z
		2.90 Å, 154° (<) [(host NH)N–H…Br–C(guest 1)]	1 – x, y, z
		2.91 Å, 145° (<) [(host CH ₂)C–H…Br–C(guest 2)]	-x, 1-y, 1-z
		2.83 Å, 143° (<) [(guest 2)C–H···C–C(host Ar)]	1 - x, 1 - y, 1 - z
		2.87 Å, 137° (<) [(guest 1)C–Br…H–N(host NH)]	-1+x, y, z
		2.91 Å, 160° (<) [(guest 1)C–Br…H–C(host CH ₂)]	x, -1 + y, z

^aDistances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å

^bTwo-fold disorder is evident, and guest 1 is the major component and guest 2 the minor component, respectively

behaviour differences are clearly evident even though the two hosts are so similar in structure.

It has been reported that higher thermal stabilities are associated with complexes in which guests are accommodated in discrete cavities compared with instances where guests are found in channels [15]. We therefore conducted thermal analyses of the three complexes with **1** in order to determine whether this was indeed the case here.

Thermal analysis

Thermal analyses were carried out on each of the three complexes of host 1, and thermogravimetric (TG), the derivative of the TG (DTG) and differential scanning calorimetry (DSC) (overlaid) traces are provided in Fig. 7a–c. The temperature range used was 20–250 °C, and the heating rate was 10 °C/min.

The relevant thermal data from these traces have been summarized in Table 5. The term T_{on} is the onset

temperature for the guest release process and is estimated from the DTG traces in Fig. 7a–c.

Figure 7a, b show that the DBM and DCM complexes are unstable at room temperature and pressure since these complexes experienced mass loss from the outset of these experiments as is observed in the two relevant TG traces. However, the diiodomethane complex is significantly more stable than the latter two: when 1.DIM was heated, mass loss was only experienced at approximately 81.5 °C.

The T_{on} is the temperature at which the first of the guest is released from the host crystal and T_b the boiling point of pure guest solvent. The value of T_{on} is estimated from the derivative of the TG curve. Taking into account these T_{on} values for the three guest release processes, the DIM complex is the most stable, followed by complexes containing DBM and DCM. These data do not correlate with the selectivity order observed for host **1**, which was also the case for the thioxanthenyl-derived host compound **2** [7].



Fig. 4 Two-dimensional fingerprint plots for a 1-2DCM major component, b 1-2DCM minor component, c 1-2DBM major component, and d 1-2DBM minor component

What is, however, evident is that complexes with 1:1 H:G ratios had higher relative thermal stabilities than 1·2DCM and 1·2DBM. Furthermore, all three complexes with 2, with H:G ratios of 1:1, were also thermally stable at room temperature [7] These results correlate exactly with the findings of Zinganshin et al. [6] who reported that hosts form more stable inclusion compounds when their guest content is lower (e.g., 1:1 H:G ratios) relative to complexes with higher guest content (e.g., 1:2 H:G ratios), as in the present study.

Vapour inclusions experiments were subsequently conducted with both hosts to determine whether the host behaviour is dependent on the method employed for complex formation.

Vapour inclusion

Vapour inclusion has, to date, not been experimentally investigated for hosts 1 and 2, and we therefore carried out applicable experiments in order to assess the behaviour of these hosts in the presence of gaseous guests.

In closed glass vials, the crystalline host compound 1 and 2 (0.5 mmol) were separately suspended on a plastic tray well above each of liquid phase guests (30 mmol) (Fig. 8). In this way, the solid host was effectively subjected to vaporous guest. The vials were fitted with lids and parafilmed to allow the gaseous guest to saturate the vessel. In addition, a similar experiment was conducted but using an equimolar mixture of the three guests (10 mmol each). The crystals were treated







and analysed as before after monitoring the progress *via* proton NMR over several days (1–31 days).

Host 1 did not include any of the three guests over the allocated time (1-31 days) period. Additionally, this host also displayed no inclusion ability in the presence of the mixture of gaseous guests. Surprisingly, and in direct contrast, host 2 possessed the ability to absorb guests from the gaseous phase, and Fig. 9 illustrates the results obtained when this host was subjected to these gaseous guests. The y-axis indicates the percentage of guest inclusion that was calculated using the integration of applicable resonances from the ¹H-NMR spectra, and the x-axis displays the amount of time the host was subjected to these gases.

From Fig. 9a, it is clear that DCM was included with a H:G ratio of 1:1 after only 6 h, and this ratio remained relatively consistent until 54 h had lapsed. DBM uptake was much slower, with a 1:1 ratio being observed at 24 h, while DIM only reached 67% after 54 h. These results are in accordance with the volatility of the three guests as DCM is the most volatile, followed by DBM and DIM.

In the mixed guest experiment (Fig. 9b), **2** initially selected for the guests in the order DCM > DBM > DIM, according to guest volatility once more. After 3 days, however, a guest exchange was observed to occur, and while the DBM percentage remained relatively constant (since the 3-day analysis), DCM was exchanged by DIM molecules. This observation correlated with the recrystallization experiments (DBM > DIM > DCM) [7] where **2** showed increased selectivity for DIM relative to DCM as the amount of DCM decreased from 45 to 35%, while that of DIM increased from 10 to 23%. The overall H:G ratio remained 1:1 throughout the entire experiment.

The fact that host 1 did not include any guest from the gas phase was thought-provoking. Host 2 is generally less selective than host 1, and guests taken up by 2 experience fewer host-guest interactions compared with host 1



Fig. 7 TG, DTG and DSC traces for a 1.2DCM, b 1.2DBM and c 1.DIM

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 Table 5
 Thermal properties of the complexes of host 1 with the three dihalomethanes

Guest (G)	T _{on} /°C	Mass loss expected/%	Actual mass loss meas- ured/%
DCM	21.0	22.9	12.8 ^a
DBM	24.2	37.8	32.3 ^a
DIM	81.5	32.6	28.8

^aThe inclusion compounds with DCM and DBM were unstable at room temperature; therefore, the observed mass loss is significantly lower than that expected due to loss of some guest during sample preparation

[7]. Therefore it is plausible that guests are readily taken up from the gas phase by the less-discerning 2 compared with 1 (which did not take up guest from the gas phase). Furthermore, we observed that host 2 recrystallized from all three dihaloalkanes to form stable inclusion complexes with a H:G ratio of 1:1 and, in contrast, host 1 only formed one stable complex, that with DIM. It is thus conceivable that host 2 successfully included these guests from the vapour phase since the resulting complexes were stable. The experiment of this host with a mixture of guests was initially affected by volatility and, after a period of time, the selectivity of the host became more prominent, and guest exchange was observed to occur, with the more preferred guest (DIM) being absorbed in favour of the less favoured one (DCM)-this process was possibly facilitated by the fact that the host packing in all the complexes was isostructural. Host 1, on the other hand, did not form complexes with the preferred guests DBM and DCM when these were in vapour phase and this may be as a result of the fact that the resultant complexes would have been unstable, and hence inclusion was not favoured. However, this host formed a stable inclusion compound with DIM in the recrystallization process but was possibly unsuccessfully absorbed owing to the low preference of this host for DIM (DBM > DCM > DIM).

Conclusion

In this investigation, the inclusion ability of N,N'-bis(9phenyl-9-thioxanthenyl)ethylenediamine 2, from a previous report, was compared with that of the oxygen derivative, N, N'-bis(9-phenyl-9-xanthenyl)ethylenediamine **1**. Both compounds included the dihalomethanes CH₂Cl₂, CH₂Br₂ and CH₂I₂, but while 2 preferred a 1:1 H:G ratio consistently, 1 complexed with CH₂Cl₂ and CH₂Br₂ with 1:2 ratios, and only CH₂I₂ experienced a 1:1 ratio. Equimolar binary and ternary competition experiments were correlated to results from single solvent experiments. For both hosts, the bromine derivative was the preferred guest, and SCXRD showed that this guest experienced a significantly larger number of host-guest interactions, in accordance with the selectivity order. Whilst 2 accommodated its guests consistently in discrete cavities, with two guests found in each, the CH_2Cl_2 and CH_2Br_2 guests in complexes with 1 were always found in multidirectional and infinite channels. For both host materials, Hirshfeld surface analyses and relative complex stabilities (based on onset temperatures) did not correlate with the selectivity orders. Vapour inclusion experiments indicated that 1 did not clathrate any of the three guests from this phase, whilst 2 clathrated all three, with the host selectivity correlating exactly with guest volatility, initially, and then, later, the preference mimicked the selectivity order from the recrystallization experiments. Complex stabilities explained these observations.

Experimental

General methods

Melting points were recorded on an Electrothermal IA9000 Series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 Infrared spectrometer (analysing with OPUS software), and ¹H-NMR and ¹³C-NMR spectra on a Bruker Ultrashield Plus 400 MHz



Fig. 8 Vapour inclusion experimental setup



Fig. 9 Graphical representation of the inclusion behaviour of 2 with a independent gaseous guests, and b an equimolar mixture of the three guests

spectrometer. Thermal experiments were conducted using a TA SDT Q600 Module system and analysed using TA Universal Analysis 2000 data analysis software. Samples were placed in open platinum pans with an empty platinum pan functioning as a reference. High purity nitrogen gas was used as purge gas in both cases. PXRD experiments were carried out using a Bruker D2 PHASER X-ray diffractometer. The resultant trace has been placed in the Supplementary Information. All starting materials and guest solvents were purchased from Sigma Aldrich, South Africa.

Synthesis of *N,N'*-bis(9-phenyl-9-xanthenyl) ethylenediamine 1

9-Phenylxanthen-9-ol (Y=O) (Supplementary Information, S4) [16]

Magnesium turnings (0.78 g, 32 mmol), bromobenzene (5.40 g, 34 mmol) and xanthone (5.39 g, 27.5 mmol) afforded 9-hydroxy-9-phenylxanthene (5.12 g, 74.7%) as a cream solid, m.p. 160–162 °C (lit., [16] 159 °C); ν (film)/

cm⁻¹ 3294 (OH) and 1582 (Ar); $\delta_{\rm H}$ (CDCl₃, 400 MHz)/ppm 2.67 (s, 1H, O<u>H</u>) and 7.07–7.45 (m, 13H, Ar<u>H</u>); $\delta_{\rm C}$ (CDCl₃, 400 MHz)/ppm 70.5 (<u>C</u>OH), 116.4 (Ar<u>C</u>), 123.6 (Ar<u>C</u>), 126.2 (Ar<u>C</u>), 126.8 (Ar<u>C</u>), 127.2 (Ar<u>C</u>), 128.0 (Ar<u>C</u>), 129.0 (Ar<u>C</u>), 129.1 (Ar<u>C</u>), 148.0 (quaternary Ar<u>C</u>) and 149.7 (quaternary Ar<u>C</u>).

9-Phenylxanthen-9-ylium perchlorate (Y=O), (Supplementary Information, S5) [16]

Perchloric acid (6.60 mL) and xanthenol (5.00 g, 8.2 mmol) afforded 9-phenylxanth-9-ylium perchlorate (6.08 g, 93.7%) as a bright yellow solid, m.p. 284–286 °C (lit., [16] 280–281 °C); ν (film)/cm⁻¹ 1595 (Ar); $\delta_{\rm H}$ (CDCl₃, 400 MHz)/ ppm 7.8–8.5 (m, 13H, Ar<u>H</u>).

N,N'-Bis(9-phenyl-9-xanthenyl)ethylenediamine (Supplementary Information, S6) [16]

Perchlorate salt (3.00 g, 8.4 mmol) and ethylenediamine (0.30 g, 5.0 mmol) afforded *N*,*N*'-bis(9-phenyl-9-xanthenyl)ethylenediamine (1.54 g, 58.7%) as a white solid, m.p. 202–203 °C (lit., [16] 204–206 °C); ν (film)/ cm⁻¹ 3019 (CH) and 1573 (Ar); $\delta_{\rm H}$ (CDCl₃, 400 MHz)/ppm 2.32 (2H, broad s, NH), 2.25 (4H, s, CH₂) and 7.02–7.43 (m, 26H, ArH); $\delta_{\rm C}$ (CDCl₃, 400 MHz)/ppm 43.4 (CH₂), 59.9 (Ph–C–NH), 116.2 (ArC), 123.3 (ArC), 125.7 (ArC), 126.5 (ArC), 127.2 (ArC), 128.0 (ArC), 128.2 (ArC), 129.0 (ArC), 149.9 (quaternary ArC) and 151.3 (quaternary ArC).

Synthesis of *N*,*N*′-bis(9-phenyl-9-thioxanthenyl) ethylenediamine 2

9-Phenylthioxanthen-9-ol (Y=S) (Supplementary Information, S7) [16]

Magnesium turnings (1.82 g, 75 mmol), bromobenzene (11.1 g, 70.7 mmol) and thioxanthone (15.00 g, 75 mmol) afforded 9-hydroxy-9-phenylxanthene (5.12 g, 74.74%) as a white solid, m.p. 105–107 °C (lit., [16] 105–106 °C); ν (film)/ cm⁻¹ 3294 (OH) and 1443 (Ar); $\delta_{\rm H}$ (CDCl₃, 400 MHz)/ppm 2.89 (s, 1H, O<u>H</u>) and 7.05 – 8.07 (m, 13H, Ar<u>H</u>); $\delta_{\rm C}$ (CDCl₃, 400 MHz)/ppm 77.1 (COH), 126.2 (Ar<u>C</u>), 126.6 (Ar<u>C</u>), 126.7 (Ar<u>C</u>), 127.0 (Ar<u>C</u>), 127.4 (Ar<u>C</u>), 127.8 (Ar<u>C</u>), 128.1 (Ar<u>C</u>), 131.6 (Ar<u>C</u>), 140.0 (quaternary Ar<u>C</u>) and 143.4 (quaternary Ar<u>C</u>).

9-Phenylthioxanthen-9-ylium perchlorate (Y=S), (Supplementary Information, S8) [16]

Perchloric acid (4 ml, 66.5 mmol) and thioxanthenol (3 g, 10.3 mmol) afforded 9-phenylxanth-9-ylium perchlorate (3.58 g, 93%) as a bright yellow solid, m.p. 230–235 °C

°C (lit., [16] 239 °C); ν (film)/cm⁻¹ 1448 (Ar); $\delta_{\rm H}$ (CDCl₃, 400 MHz)/ppm 7.3–8.8 (m, 13H, Ar<u>H</u>).

N,N'-Bis(9-phenyl-9-thioxanthenyl)ethylenediamine (Supplementary Information, S9) [16]

Perchlorate salt (3.58 g, 9.6 mmol) and ethylenediamine (0.322 g, 5.36 mmol) afforded *N*,*N'*-bis(9-phenyl-9-xanthenyl)ethylenediamine (1.9009 g, 58.72%) as a white solid, m.p. 174–176 °C (lit., [16] 174–175 °C); ν (film)/cm⁻¹ 3056 (CH) and 1432(Ar); $\delta_{\rm H}$ (CDCl₃, 400 MHz)/ppm 2.48 (2H, broad s, N<u>H</u>), 2.48 (4H, s, C<u>H</u>₂) and 7.19–7.47 (m, 26H, Ar<u>H</u>); $\delta_{\rm C}$ (CDCl₃, 400 MHz)/ppm 44.4 (CH₂), 66.2 (Ph–C–NH), 125.8 (Ar<u>C</u>), 126.0 (Ar<u>C</u>), 126.8 (Ar<u>C</u>), 126.9 (Ar<u>C</u>), 128.0 (Ar<u>C</u>), 129.8 (Ar<u>C</u>), 131.6 (Ar<u>C</u>), 137.9 (quaternary Ar<u>C</u>) and 146.5 (quaternary Ar<u>C</u>).

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