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# The Synthesis of Novel Enclathration Compounds: Bis(9-amino-9-aryl-9*H*-thioxanthenes) and Investigations of their Host–Guest Inclusion Potential

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ABSTRACT

**Four novel bis(9-amino-9-aryl-9*H*-thioxanthenes) were synthesized and their inclusion potential assessed by allowing them to crystallize slowly from organic solvents (single and binary mixtures). Only two of the compounds studied displayed inclusion ability and enclathrated several of the solvents studied. The stoichiometries of the resultant inclusion complexes were determined by $^1$H-NMR studies, and the favoured host:guest ratios were found to be predominantly 1:1, with ratios 2:1, 4:3 and 3:2 occurring less frequently. The stability of the clathrate complexes has been investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Competition experiments were carried out with the compounds that successfully hosted solvent molecules in order to determine their relative affinity for these solvents. One of the hosts was also exposed to two vaporous guests in two separate experiments to assess its ability for entrapping molecules from the vapour phase.**

KEYWORDS

**Inclusion compounds, enclathration, host–guest compounds, 9*H*-thioxanthene derivatives, thermochemistry.**

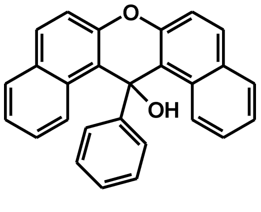
## 1. Introduction

Host–guest inclusion chemistry has recently generated interest due to its potential practical applications, while studies into the phenomenon are likely to also clarify the nature of the intermolecular forces that are involved in molecular recognition phenomena.[1] Effective host compounds are usually rigid and bulky so as to provide suitable cavities within the crystal structure into which guest molecules may be accommodated. Their effectiveness is frequently improved if a coordination site, e.g. a hydrogen-bonding donor or acceptor, which may enhance association between the host and guest molecules, is also present. Furthermore, optically active pure chiral hosts are able to provide a chiral trapping environment for guest molecules, and may be used to separate racemic mixtures of guests into their respective enantiomers.[2]

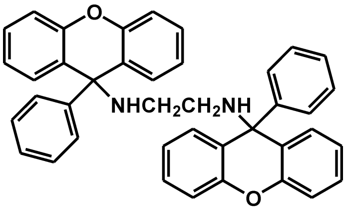
It has been reported that bridged triarylmethyl (trityl) derivatives are very effective at forming inclusion compounds with numerous organic guest molecules.[3] Examples of such systems are the xanthenyl derivatives **1** and **2**, which have previously been synthesized in our laboratories and shown to enclathrate a variety of solvents.[4,5]

The main purpose of the present study was to compare the enclathration ability of the novel thioxanthenyl compound **3** with its xanthenyl analogue **2**, and hence to determine the influence that the bridging sulphur atom has on its inclusion potential.

In addition, the chloro derivative **4** was also synthesized and tested as a potential host. Compounds **5** and **6** which contain variations in the diamino alkyl link were also investigated. Compound **5**, being chiral and prepared optically pure, was tested in the hope of selectively resolving racemic guest mixtures.

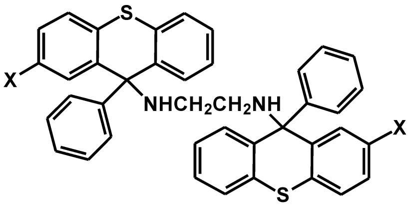


**1**



**2**

Competition experiments in which the host compound was crystallized from an equimolar mixture of two potential guest components, both of which were individually included in separate experiments, were also carried out with hosts **3** and **4**. Furthermore, thermal analysis studies on a number of the successfully formed inclusion complexes are reported.



**X = H 3**
**X = Cl 4**

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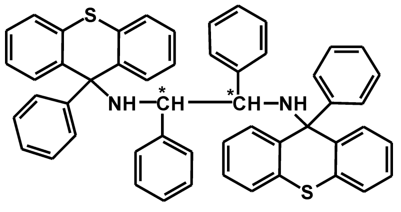
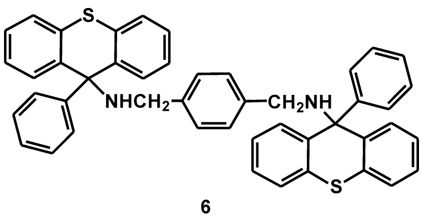


**5**



**6**

**Table 1** Inclusion complexes of host compounds **3** and **4**, with observed host–guest stoichiometries.

| Guest | Host:guest ratio | |
|---|---|---|
| | Host **3** | Host **4** |
| Acetone | 4:3 | – |
| DMF | 4:3 | 1:1 |
| THF | 1:1 | – |
| 1,4-Dioxane | 1:1 | 1:1 |
| Morpholine | 1:1 | 1:1 |
| Pyridine | 1:1 | – |
| Cyclohexane | 1:1, 2:1[a] | – |
| Benzene | 3:2, 2:1[a] | – |
| $CH_2Cl_2$ | 1:1 | – |
| $CHCl_3$ | 1:1 | – |

[a] Different ratios were obtained in duplicate experiments

## 2. Results and Discussion

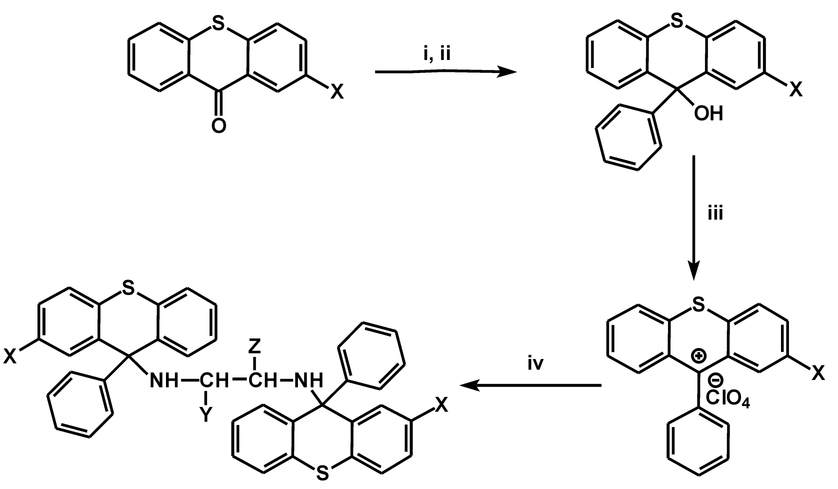
The four thioxanthenyl amines were prepared from the corresponding 9-phenyl-9*H*-thioxanthen-9-ols.[3,6] The latter were treated with perchloric acid to form the corresponding 9-phenyl-9*H*-thioxanth-9-ylium perchlorate salts,[7] which were then treated with the appropriate diamine, affording products **3**–**5** (Scheme 1). Similarly, treatment of two equivalents of 9-phenyl-9*H*-thioxanth-9-ylium perchlorate with one equivalent of 1,4-bis(aminomethyl)benzene produced compound **6.**

Of the four novel compounds prepared and investigated for their inclusion ability, only **3** and **4** were observed to function as host molecules, with compounds **5** and **6** incorporating none of the wide range of solvents used in this study. In addition to the solvents listed in Table 1, crystallizations of all four compounds were also carried out from methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol, acetonitrile, nitromethane, DMSO, piperidine, ether, menthol, menthone and carbon tetrachloride. None of these prospective guest compounds was included.

The sulphur-containing diamine **3** gave rise to inclusion complexes with 10 of the 22 solvents from which it was crystallized. A 1:1 host:guest (H:G) ratio was preferred in the majority of cases (Table 1). A comparison of the results obtained for the oxygen analogue **2** with host **3** shows the latter to have better inclusion ability than the former, for which only 8 of the 22 solvents studied were included.[5] Interestingly, the chlorinated solvents chloroform and dichloromethane were also enclathrated by **3**. The 1:1 H:G ratio was determined by elemental microanalysis of the complex.

The temperature at which the guest is released provides information on the relative stability of the host–guest inclusion complex. ($T_{on}$–$T_b$) data provides a measure of this stability: the larger the value obtained, the more stable the complex is, relative to another complex having a lower value. Large positive ($T_{on}$–$T_b$) values suggest that the guest molecules are held tightly within the host framework, either due to host–guest interactions such as hydrogen bonding, or due to a tight-fit of the guest in the cavity.

DSC analyses were carried out on all the inclusion complexes formed by host **3**. The DSC traces of its inclusion complexes formed with morpholine, acetone and DMF are included as representative examples (Figs 1, 2 and 3). These traces are relatively uncomplicated, showing two endotherms, the first corresponding to the guest-releasing process, followed by another one corresponding to the melting point of the host compound. From these temperature values, the ($T_{on}$–$T_b$) values,[8–10] where $T_{on}$ is the onset temperature and $T_b$ the boiling point of the pure guest compound, were calculated and are



3 : X = Y = Z = H
4 : X =Cl ; Y = Z = H
5 : X = H ; Y = Z = Ph

**Scheme 1**

Synthesis of the thioxanthenyl host compounds **3**–**5**. *Reagents and Conditions*: i, PhMgBr, THF; ii, Aq. $NH_4Cl$; iii, $HClO_4$, $Ac_2O$, Pet. Ether; iv, 1,2-ethylenediamine or (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine.

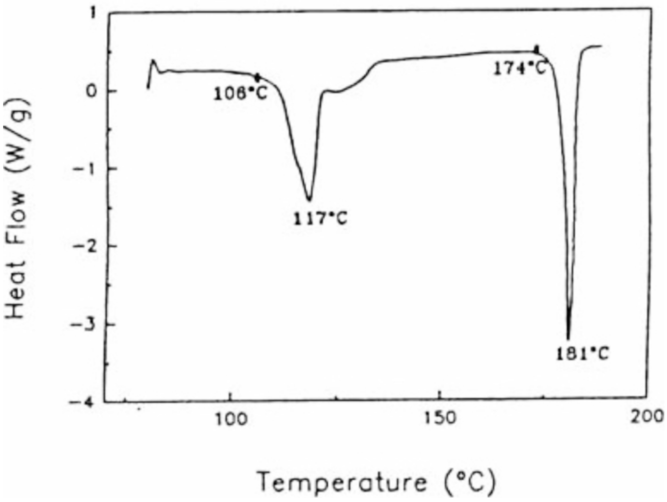


**Figure 1** DSC trace for the decomposition of the host **3**–morpholine complex.

**Table 2** Thermal data for complexes formed by host compounds **3** and **4**.

| Clathrate | $T_{on}$/°C | $T_b$/°C | ($T_{on}$–$T_b$)/°C |
|---|---|---|---|
| **3**-Acetone | 82.0 | 56.5 | +25.5 |
| **3**-DMF | 96.0 | 153.0 | –57.0 |
| **3**-THF | 106.0 | 66.0 | +40.0 |
| **3**-Dioxane | 96.0 | 101.1 | –5.1 |
| **3**-Morpholine | 106.0 | 128.9 | –22.9 |
| **3**-Pyridine | 133.0 | 115.5 | +17.5 |
| **3**-Cyclohexane | 64.0 | 80.5 | –16.5 |
| **3**-Benzene | 116.0 | 80.5 | +35.5 |
| **3**-Dichloromethane | 96.0 | 40.0 | +56.0 |
| **3**-Chloroform | 89.0 | 61.0 | +28.0 |
| **4**-Dioxane | 90.0 | 101.1 | –11.1 |
| **4**-Morpholine | 128.0 | 128.9 | –0.9 |

depicted in Table 2. From the magnitudes of the calculated values for host **3**, dichloromethane appears to be the most strongly enclathrated, followed by THF, benzene and chloroform. The DMF complex showed the lowest stability (Table 2).

A TG experiment was conducted on the **3**-DMF clathrate, which showed this guest to be released in a stepwise manner (Fig. 2). 9.44% of DMF is released at $T_{on}$ = 96°C and 1.76% at a later stage, commencing at 158°C. The total mass loss observed was therefore 11.20%, which is slightly higher than the 10.78% mass loss required for a 1:1 clathrate. The second endotherm represents melting of the host compound **3**, as well as further release of DMF. The DSC trace shows two endotherms, the first commencing at 96°C and a second having a long tail, starting at 144°C.

Competition experiments, with one exception, have shown mixed inclusions to occur (Table 3). Preference was shown for the inclusion of THF in all three of the combinations investigated. In the other combinations, dichloromethane was favoured over acetone, as was benzene over cyclohexane. Pyridine was included exclusively when **3** was crystallized from an equimolar mixture of pyridine and benzene, but the overall H:G ratio was not stoichiometric. Furthermore, host:guest ratios obtained from the competition experiments do not correlate well with the ($T_{on}$–$T_b$) values calculated for the single solvent crystallizations (Table 1). For example, when crystallized from an equimolar ratio of THF and dichloromethane, host **3** favoured THF over $CH_2Cl_2$ (**3**:THF:$CH_2Cl_2$ = 1:0.75:0.15) even though ($T_{on}$–$T_b$) values suggest that $CH_2Cl_2$ is more strongly held than THF.

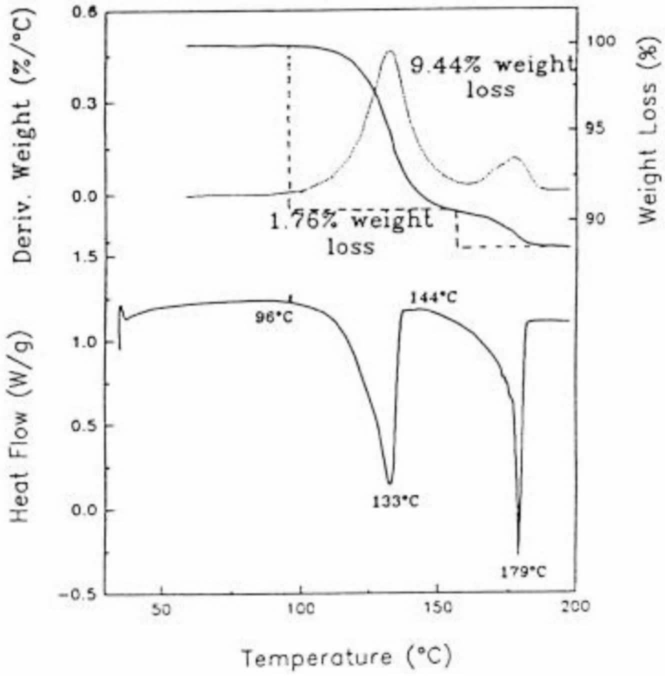


**Figure 2** DSC and TG traces for the decomposition of the host **3**-DMF complex.

In a further experiment, pure **3**, crystallized from dichloromethane/petroleum ether, was exposed in powder form to THF vapour for one week. ($^1$H-NMR spectroscopy showed no inclusion of dichloromethane using this method of crystallization.) After this period, the crystals were washed with methanol and air-dried, whereupon $^1$H-NMR spectroscopic analysis showed that THF had been absorbed from the gaseous phase to form a 2:1 H:G clathrate. This clathrate, when re-exposed to THF vapour for an extended period, led to a H:G ratio which closely approached the 1:1 ratio, which is the same as that obtained from the original recrystallization experiment with the pure solvent.

Surprisingly, THF vapour was not included by the oxygen analogue **2**, though it was enclathrated in the recrystallization experiment.[5] A similar experiment was conducted using host **3** and dichloromethane vapour. In this case, dichloromethane absorption was also observed, but appeared to take place more slowly, giving a complex with a H:G ratio of 1.44:1 after three

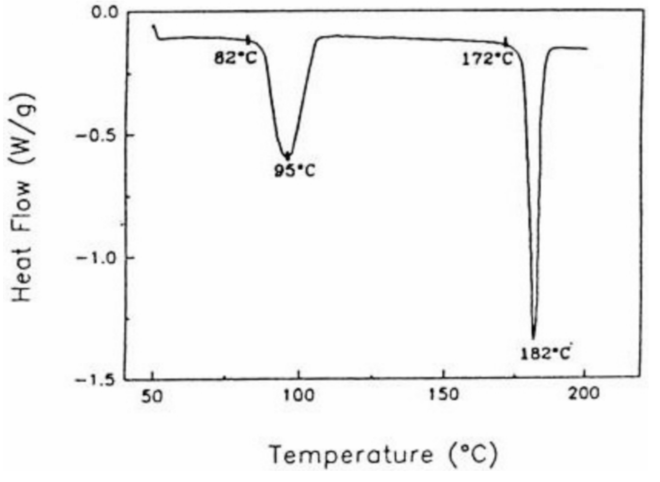


**Figure 3** DSC trace for the thermal decomposition of the **3**-acetone 1:1 complex.

**Table 3** Competition experiments involving host **3**.

| Guest 1 (G1) | Guest (G2) | Host **3**:G1:G2 ratio | **3**:(G1+G2) ratio |
|---|---|---|---|
| THF | Acetone | 1:0.64:0.14 | 1:0.78 |
| THF | Dioxane | 1:0.59:0.38 | 1:0.97 |
| THF | $CH_2Cl_2$ | 1:0.75:0.15 | 1:0.90 |
| $CH_2Cl_2$ | Acetone | 1:0.52:0.36 | 1:0.88 |
| Benzene | Cyclohexane | 1:0.59:0.12 | 1:0.71 |
| Pyridine | Benzene | 1:0.68:0.00 | 1:0.68 |

weeks.

The chloro derivative **4** was less effective at inclusion than **2** or **3**; only three different guests species were included, and all with the ratio of 1:1. A DSC experiment carried out on the morpholine inclusion complex (Fig. 4) also displays two endotherms, the first for guest desorption and the second corresponding to melting of the host. The dioxane inclusion complex appears to be thermally less stable than the morpholine complex according to the data contained in Table 2. In a competition experiment, however, dioxane was found to be enclathrated exclusively at the expense of morpholine when host **4** was crystallized from an equimolar mixture of the two solvents.

The optically pure chiral thioxanthenyl analogue **5** was investigated next in order to assess its ability to effect possible enantiomeric separations. However, **5** included none of the pure solvents investigated, nor menthol and menthone, respectively.

Bis(9*H*-thioxanthenyl)diamine **6**, which incorporates a *para*-disubstituted benzene unit as spacer group in the diamine linkage, was crystallized from the standard range of solvents, but no evidence for enclathration of solvent could be obtained.

## 3. Conclusions

The diamine **3**, having an ethylenediamine bridging moiety between the two thioxanthenyl groups, has been demonstrated to function as an effective host, being more successful than its oxygen analogue **2**, enclathrating several solvents from which it was crystallized. DSC and TGA thermal decomposition data showed that of the solvents included, dichloromethane was retained the strongest, while the complex with DMF was found to be thermally the least stable. Competition experiments showed that strongly-held solvents such as dichloromethane are not necessarily preferred by the host when crystallized from equimolar amounts of solvent mixtures. Compound **3** also showed the ability to absorb THF and dichloromethane from the vapour phase.

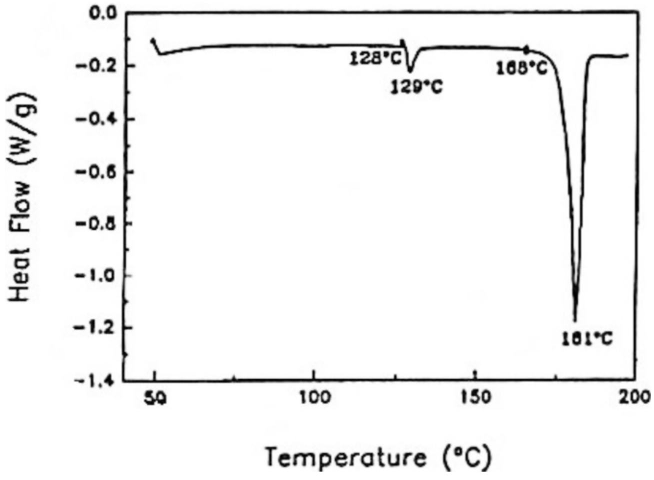


**Figure 4** DSC trace for the decomposition of the host 4-morpholine complex.

Host **4** only included three solvents and showed a preference for a 1:1 host:guest ratio. It is surmised that the presence of the chloro substituent on the 2-position of the thioxanthenyl moiety, being substantially larger than the hydrogen atom in the substituted derivative **3**, results in an alternative type of the packing in the crystal structure, thus affecting the cavity size and resulting in less effective enclathration by the host compound.

Similarly, both compounds **5** and **6** were unsuccessful as host compounds for the guest compounds studied, suggesting that the structure of the bridging unit between the two thioxanthenyl moieties plays a crucial role in the enclathration ability of the host compound. An unsubstituted ethylenediamine bridge is effective in this respect, whereas the introduction of substituted ethylenediamines such as 1,2-diphenylethylenediamine, and diamines such as α,α′-diamino-*p*-xylenes do not lead to effective host compounds as borne out by our observations.

## 4. Experimental

Melting points were determined on an Electrochemical IA9000 Series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 series Fourier Transform Infrared Spectrometer, and $^1$H-NMR (200 MHz) and $^{13}$C-NMR (50 MHz) spectra on a Varian Gemini 200MHz Spectrometer. Differential scanning calorimetry (DSC) experiments were determined on a Du Pont 910 standard DSC module, connected to a Du Pont 9000 Thermal Analyser. High purity dinitrogen gas was used for purging. A heating rate of 5°C min$^{-1}$ was applied. Compounds were sealed in aluminium pans and their lids pierced, while an empty aluminium pan served as a reference.

### *Synthesis of* N,N′*-bis(9-phenyl-9*H*-thioxanthen-9-yl)ethylenediamine* **3**

9-Phenyl-9*H*-thioxanthen-9-ol, synthesized by previously reported methods in 96% yield,[3,6] was converted into 9-phenyl-9*H*-thioxanth-9-ylium perchlorate by a similar procedure previously described by us (Scheme 1).[7] 9-Phenyl-9*H*-thioxanth-9-ylium perchlorate (1.00 g, 2.68 mmol) dissolved in $CH_2Cl_2$ (20 ml) was added to a stirred solution of ethylenediamine (0.32 g, 5.36 mmol) in $CH_2Cl_2$ (10 ml) at ambient temperature. After stirring for 30 min, the solution was washed with water (3 × 100 ml), dried ($Na_2SO_4$), and concentrated under reduced pressure. Crystallization of the residue from chloroform gave a 1:1 complex, N,N′*-bis(9-phenyl-9*H*-thioxanthen-9-yl) ethylenediamine* **3**–$CHCl_3$ as a white solid (0.70 g, 90%); mp 174–175°C (decomp.) [Found: C, 68.2; H, 4.7; N, 3.9. $C_{40}H_{32}N_2S_2$ $CHCl_3$ (1:1) requires C, 68.0; H, 4.6; N, 3.9%]; $\nu_{max}$ ($CHCl_3$)/cm$^{-1}$ 3347 (NH) and 1587 (Ar); $\delta_H$ ($CDCl_3$) 2.42 (2H, br, s, N*H*), 2.50 (4H, s, $CH_2CH_2$) and 7.10–7.80 (26H, m, Ar); $\delta_C$ ($CDCl_3$) 46.41 ($CH_2CH_2$), 68.21 (PhCNH), 127.84, 128.07, 128.89, 128.99, 130.00 and 131.83 (Ar), 133.60, 139.89 and 148.53 (quaternary Ar); *m/z* 604 (M$^+$, 0.2%), 527 (M–Ph, 0.1), 303 (2.2), 273 (100), 226 (2.1), 212 (2.2), 197 (11.8), and 77 ($C_6H_5$, 0.5).

### N,N′*-bis(2-chloro-9-phenyl-9*H*-thioxanthen-9-yl)ethylenediamine* **4**

2-Chloro-9-phenyl-9*H*-thioxanthen-9-ol, synthesized in 73% yield by a published method,[3] was converted into the perchlorate salt.[7] (Scheme 1). 2-Chloro-9-phenyl-9*H*-thioxanth-9-ylium perchlorate (2.00 g, 4.91 mmol) in $CH_2Cl_2$ (50 ml) was added to a stirred solution of ethylenediamine (0.59 g; 9.82 mmol) in $CH_2Cl_2$ (20 ml) at room temperature. After stirring for 30 min., the solution was washed with water (3 × 100 ml), dried ($Na_2SO_4$) and concentrated under reduced pressure. The residue was crystallized from dichloromethane to give N,N′-*bis(2-chloro-9-phenyl-9*H-*thioxanthen-9-yl)ethylenediamine* **4** as a white solid (1.42 g, 86%), mp 170–172°C (Found: C, 71.0; H, 4.6; N, 4.1. $C_{40}H_{30}Cl_2N_2S_2$ requires C, 71.3; H, 4.5; N, 4.2%); $\nu_{max}$ ($CHCl_3$)/cm$^{-1}$ 3352 (NH) and 1591 (Ar); $\delta_H$ ($CDCl_3$) 2.40 (2H, br, s, N*H*), 2.50 (4H, s, C*H*$_2$C*H*$_2$), 7.00–7.50 (20H, m, Ar*H*) and 7.56 (4H, dd, $J_1$ = 1.8 Hz and $J_2$ = 5.5 Hz, Ar); $\delta_C$ ($CDCl_3$) 46.24 ($CH_2CH_2$), 68.19 (PhCNH), 127.87, 128.35, 129.02, 129.16, 129.28, 129.71, 130.21, 131.56 and 131.68 (Ar), 132.11, 132.16, 133.10, 133.18, 134.01, 139.22, 141.68, 141.77 and 147.80 (quaternary Ar); *m/z* 672 (M$^+$, 0.01%), 307 (100), 246 (26.8),and 231 (41.1).

*(1R, 2R)-(+)-*N,N′-*bis(9-phenyl-9*H-*thioxanthen-9-yl)-1,2-diphenylethylenediamine* ***5***

9-Phenyl-9*H*-thioxanth-9-ylium perchlorate (0.439 g, 1.18 mmol) in dichloromethane (30 ml) was added to a stirred solution of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (0.125 g, 0.589 mmol) in dichloromethane (20 ml) and triethylamine (30 drops) at room temperature and stirring was continued for a further 30 min. The solution, processed as outlined above, gave a residue which crystallized from chloroform to give *(1*R*,2*R*)-(+)-*N,N′-*bis(9-phenyl-9*H-*thioxanthen-9-yl)-1,2-diphenylethylenediamine* **5** as a white powder (0.43 g, 96%), mp 207°C (Found: C, 82.4; H, 5.2; N, 3.8. $C_{52}H_{40}N_2S_2$ requires C, 82.5; H, 5.3; N, 3.7%); $[\alpha]_D^{17}$ +72.1 (*c* 1.10, $CHCl_3$); $\nu_{max}$ ($CCl_4$)/cm$^{-1}$ 3271 (NH) and 1589 (Ar); $\delta_H$ ($CDCl_3$) 3.27 (2H, s, N*H*), 3.55 (2H, s, C*H*Ph) and 6.15–7.50 (36H, m, Ar); $\delta_C$ ($CDCl_3$) 66.63 (*CHPh), 67.57 (PhCNH), 126.12, 126.73, 126.90, 127.03, 127.90, 128.27, 128.36, 128.49, 128.82, 129.26, 129.54 and 130.60 (Ar), 131.77, 133.42, 134.40, 135.00, 138.31, 139.84, 144.75 and 152.58 (quaternary Ar); *m/z* 756 (M$^+$, 0.1%), 273 (100) and 197 (16.3).

N,N′- *bis(9-Phenyl-9*H-*thioxanthen-9-yl)-α,α′-diamino-*p-*xylene* ***6***

9-Phenyl-9*H*-thioxanth-9-ylium perchlorate (1.37 g, 3.67 mmol) in dichloromethane (20 ml) was added to a hot stirred solution of α,α-diamino-*p*-xylene (0.25 g, 1.8 mmol) in dichloromethane (10 ml) and triethylamine (2 ml). After processing the mixture as outlined above, the residue was crystallized from chloroform/methanol to afford N,N′-*bis(9-phenyl-9*H-*thioxanthen-9-yl)-α,α′-diamino-*p-*xylene* **6** as a white solid (0.76 g, 61%). mp 207-208°C (Found: C, 80.8; H, 5.3; N, 4.2. $C_{46}H_{36}N_2S_2$ requires C, 81.1; H, 5.3; N, 4.1%); $\nu_{max}$ (nujol)/cm$^{-1}$ 3310 (NH), 1619 (Ar) and 1579 (Ar); $\delta_H$ ($CDCl_3$) 2.35 (2H, br s, N*H*), 3.50 (4H, s, C*H*$_2$), 7.10–7.45 (26H, m, Ar) and 7.50–7.60 (4H, dd, $J_1$ = 3.7Hz and $J_2$ = 5.1Hz); $\delta_C$ ($CDCl_3$) 49.98 ($CH_2$), 68.49 (PhCNH), 127.95, 128.14, 128.92, 129.05, 129.94, 129, 130.07, 130.35 and 131.58 (Ar), 133.72, 139.63, 141.28, and 148.00 (quaternary Ar); *m/z* 680 (M$^+$, 0.2%), 602 (M–Ph, 0.2), 407 (1.1), 273 (40.2), 272 (100), 197 (28.7) and 77 ($C_6H_5$, 2.3).

*Synthesis and analysis of inclusion complexes*

The potential host compounds **3–6** were crystallized from a range of organic solvents by dissolution in excess solvent, which was allowed to evaporate slowly at ambient temperature. The resulting crystals were then washed with methanol and air-dried. No evidence could be obtained from $^1$H-NMR spectroscopy for the inclusion of methanol into the crystal structures. Even crystallization of host **1** from methanol did not result in its inclusion. $^1$H-NMR spectroscopy was used to ascertain whether any inclusion of solvent had occurred and, where appropriate, to determine host–guest stoichiometries (Table 1). The stoichiometries were determined through integrating suitable $^1$H-NMR signals arising from the host and guest compounds. These signals were selected at positions in the spectra where no interference of signals occurred. The hydrogen atoms on the bridging units in all of the hosts were suitable for this purpose. Therefore the linking methylene groups in hosts **3**, **4** and **6**, and the methine hydrogen atom at the chiral centre in host **5** were selected for integration purposes. Similarly, resonance signals emanating from the solvent that did not interfere with the host's analytically useful resonance peaks were selected. The analytical technique has an accuracy limited by that of the integration of the NMR spectrometer. Ratios in the order of 1.44:1 may thus very well be 1.5:1. In some cases, values were rounded off, but in most cases, this was not necessary.

The inclusion complexes were further characterized by differential scanning calorimetry (DSC). DSC traces were obtained for most of these complexes in order to determine their relative stabilities. Representative examples are depicted in Figs 1 and 2. The onset temperatures ($T_{on}$) for the release of the guest compounds determined from these traces, as well as the boiling points of the pure guest compounds ($T_b$), are listed in Table 2. The ($T_{on}$–$T_b$) values, which have previously been proposed to be a measure of the strength of enclathration of the guest by the host, have also been calculated (Table 2).[8–10]

Competition experiments were carried out by dissolving the host compound by heating in an equimolar mixture of two selected solvents, both of which had previously been shown to be independently included by the host. The solution was then cooled to 0°C and the resulting crystals filtered, rinsed with methanol, dried, and analysed by $^1$H-NMR spectroscopy. These results for host **3** are contained in Table 3.

Absorption experiments were performed by placing the pure host species in an open container and this, in turn, was placed in a vessel lined with absorbent paper and containing some of the liquid guest. The larger vessel was then sealed for a few weeks. The resulting crystals were rinsed thoroughly with methanol and after drying, the host:guest ratios were determined by $^1$H-NMR spectroscopy.

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