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Clathrates of novel ethylenediamine derivatives: thermal, X-ray crystallographic and conformational analysis of inclusion complexes of *N*,*N*′-bis(5-phenyl-5-dibenzo[*a*,*d*]cycloheptenyl)ethylenediamine and its 10,11-dihydro analogue

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Novel compounds *N*,*N*′-bis(5-phenyl-10,11-dihydro-5-dibenzo[*a*,*d*]cycloheptenyl)ethylenediamine **3a** and *N*,*N*′-bis(5-phenyl-5-dibenzo[*a*,*d*]cycloheptenyl)ethylenediamine **3b** are efficient hosts, forming clathrates upon recrystallization from a wide variety of organic solvents. The 1:2 and 1:1 complexes of **3a** and **3b**, respectively, with dichloromethane, dibromomethane and diiodomethane were subjected to extensive thermal and X-ray crystallographic studies, and it was found that guests of the thermally less stable complexes reside in channels, while these are accommodated in discrete cavities in the more stable complexes. Host **3a** adopts similar conformations in its complexes with CH_2Cl_2 and CH_2Br_2, while a different conformer is involved with CH_2I_2. DFT (B3LYP/6-31G*) geometry optimizations revealed that these conformers are respectively, 8.7 and 7.5 kJ mol^{-1} less stable than the global minimum energy conformer of **3a**. Host **3b** adopts similar conformations in its three complexes, which optimize to the global minimum energy conformer. In the thermally more stable complexes, **3a** and **3b** exist as relatively low energy conformers.

1. Introduction

Molecular recognition phenomena have long been of interest owing to the manifold applications of structures that display affinity for other molecules. A prime example is TADDOL and its derivatives.[1] In enantiopure form, these compounds have found applications extending from the resolution of racemates to use in enantioselective transformations. These selectivity properties of TADDOL are attributable to its hydrogen bonding capabilities, allied with its underlying chirality. We have recently reported[2–4] on the selective inclusion properties of a related compound, (+)-(2*R*,3*R*)-1,1,4,4-tetraphenylbutane-1,2,3,4-tetraol (TETROL) which, remarkably, includes 3- and 4-methylcyclohexanone as their energetically unfavourable axial methyl conformers.[2,3]

We have previously described[5,6] achiral alcohols based on xanthenyl and related systems that also co-crystallize with a variety of organic compounds. This study is being extended to amino analogues of these alcohols, ultimately with a view to incorporating chirality into the host compounds. Our focus has been initially on achiral ethylenediamine derivatives, and we have described examples that are highly effective in forming inclusion complexes.[7,8] We now report on two further novel host compounds from this series, namely *N*,*N*′-bis(5-phenyl-10,11-dihydro-5-dibenzo[*a*,*d*] cycloheptenyl)ethylenediamine **3a** and *N*,*N*′-bis(5-phenyl-5-dibenzo-[*a*,*d*]cycloheptenyl)ethylenediamine **3b**.

2. Results and discussion

Compounds **3a** and **3b** were prepared by treating the appropriate triaryl bridged alcohols (**1a** and **1b**) with perchloric acid, and then the resultant perchlorate salts (**2a** and **2b**), with ethylenediamine (Scheme 1).

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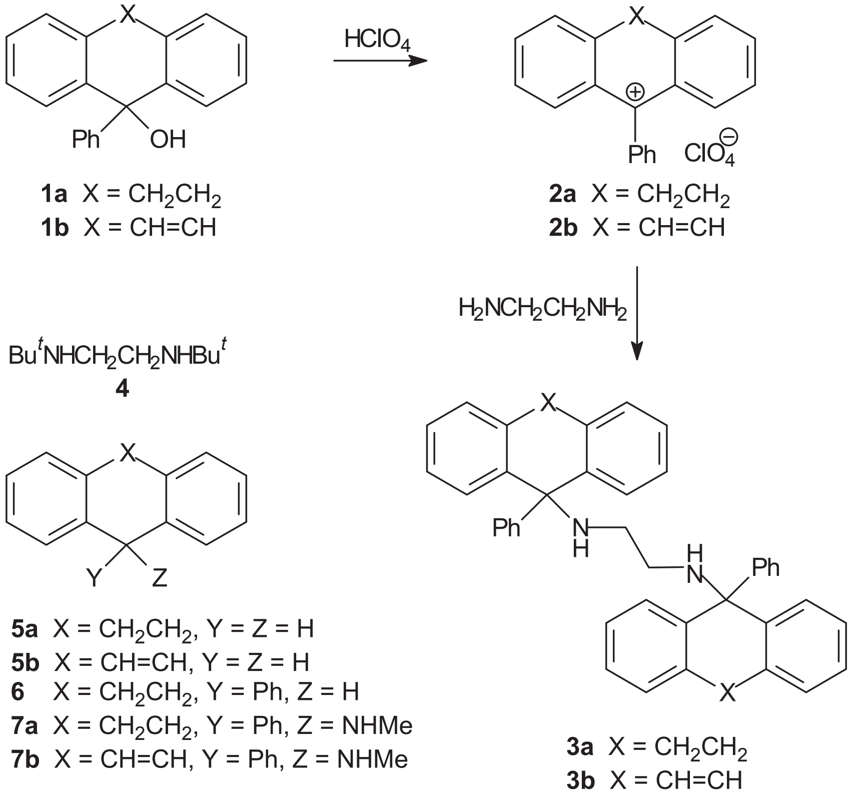

Scheme 1.

2.1. Assessment of the host potential of 3a and 3b

2.1.1. Formation of complexes. Compounds **3a** and **3b** were recrystallized from a range of organic solvents through dissolution followed by slow evaporation of the solvent under ambient conditions. The resulting crystals were collected under vacuum, washed with methanol (a solvent that was previously ascertained not to be included), and dried by suction filtration. ^{1}H NMR spectroscopy was used to determine whether any enclathration of the solvent had occurred and, if so, the stoichiometric ratio of the resulting host-guest complex (Table 1).

Table 1
Host **3a**:guest (**3a**:G) and host **3b**:guest (**3b**:G) stoichiometric ratios of complexes formed

Guest (G)[a]	**3a**:G	**3b**:G
Acetone	1:1	1:1
CH_3CN	—	4:3
CH_3NO_2	1:1	1:1
DMSO	1:1	—
THF	—	1:1
1,4-Dioxane	1:1	1:1
DMF	1:2	1:2
Pyridine	—	[b]
CH_2Cl_2	1:2	1:1
CH_2Br_2	1:2	1:1
CH_2I_2[c]	1:2	1:1

[a] No inclusion occurred when recrystallizations were done from MeOH, EtOH, *i*-PrOH, *t*-BuOH, benzene, morpholine, piperidine, pyridine, cyclohexane, diethyl ether, menthol, menthone, $CHCl_3$ and CCl_4.
[b] The complex was non-stoichiometric.
[c] Dissolution required facilitation by adding co-solvent $CHCl_3$.

Both compounds produced inclusion complexes for most of the solvents tested (Table 1). Notwithstanding the structural similarities between the two host compounds, some significant differences are noted in their inclusion abilities: **3b** includes CH_3CN and THF while **3a** does not, and **3a** has an affinity for DMSO while **3b** does not. Interestingly, the dihalomethanes CH_2Cl_2, CH_2Br_2 and CH_2I_2 all form complexes with **3a** and **3b**, but the former host includes the three dihaloalkanes with a 1:2 H:G ratio while **3b** leads to 1:1 ratios. It seems that small changes in host structure have a significant impact on inclusion ability.

2.1.2. Thermal analyses. Relative thermal stabilities of the six complexes of **3a** and **3b** with CH_2Cl_2, CH_2Br_2 and CH_2I_2 were investigated further by means of thermogravimetric (TG) analysis. Table 2 summarizes the results of these experiments when each of the complexes was heated at a rate of 10 °C/min, and Figs. 1a–c and 2a–c are the TG traces (with overlaid derivatives) for the six complexes, where T_{on} is the onset temperature for guest release, as estimated from the derivatives of the TG traces.

Table 2
Thermal properties of complexes formed by **3a** and **3b**

Host (H)	Guest (G)	T_{on}/°C	Mass loss expected/%	Actual mass loss measured/%
3a	CH_2Cl_2	*d*	22.2	19.6
3a	CH_2Br_2	*d*	36.8	32.6
3a	CH_2I_2	77	47.3	46.3
3b	CH_2Cl_2	~100	12.5	12.1
3b	CH_2Br_2	~100	22.7	21.9
3b	CH_2I_2	~100	31.1	31.3

d–T_{on} could not be stated here with conviction since mass loss appeared to occur right from the outset.

Data given in Table 2 suggest that the dichloro- and dibromomethane complexes formed with **3a** have significantly lower relative thermal stabilities compared with the complex of **3a** with