Calix[4]arene-5,17-dicarboxylic acids and their interactions with aliphatic amines. Part 2. A crystal engineering approach

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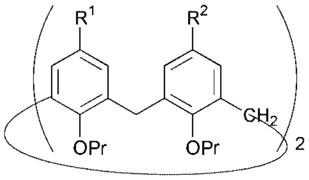
The possible interactions between diacid functionalised conformationally diverse calix[4]arene molecules and simple amines were investigated. The aim was to establish an understanding of the solid state constructions obtained upon crystallising the salts formed between the acids and the amines. Each component of the acid–base system was subject to variations through the degree of chemical substitution and conformational diversity of the calix[4]arene system and through the degree of chemical substitution for the amine system pertaining to primary, secondary and tertiary amines. Unlike the known solution behaviour where tertiary amines behave differently from secondary and primary amines as a group it was found that the solid state behaviour was further differentiated. In the solid state primary amines give rise to salt bridged closed networks whereas secondary amines give rise to open polymeric salt bridged networks and tertiary amines give rise to monomeric salts. Furthermore the patterns that were uncovered from the isolated studies could be used to predict the structural behaviour of a more complex case such as the biological molecule ephedrine for which a calix[4]arene based sensing system was developed in our previous paper.

Introduction

[*n*]Cyclophanes have attracted enormous attention since they were first characterised and the large interest in them stems from the fact that molecules of this sort have been contemplated as platforms for molecular receptors.[1–4] In our previous paper we reported how a calix[4]arene based receptor system for the biological molecule ephedrine was made and characterised.[5] While the molecular conformation[6] and interactions such as binding constants are easily studied in solution others like detailed salt bridges are more easily studied using X-ray structural characterisation. This prompted us to make a detailed study to map out the interactions as a function of the degree of substitution of the amine. The results obtained from the crystal structure analysis can thus be rationalised in terms of the packing motifs generally known for neutral or weakly interacting calixarenes and the interactions imposed upon the system by the substituents *i.e.* specific hydrogen interactions or salt bridges. It was anticipated that the conformation of the calix[4]arene diacid–amine salt in solution would be reflected in the crystal structure. This was however not observed in all instances and it was found necessary to analyse the effects properly since a detailed knowledge of how the receptor works is a prerequisite for further development. The original concept of the receptor was based on the conformational diversity of the calix[4]arene skeleton where the upper rim of the calix[4]arene system was derivatised with two sets of chemically different groups (compounds **1**–**5**): one set of groups that were to interact with the analyte and one set of groups that were to signal the conformational state of the calix[4]arene. In order for the system to work as a receptor the conformation of the calix[4]arene system (and thus the signal read from the sensor) has ideally to depend solely on the presence or absence of the analyte. The receptor system presented in our previous paper was based on the use of acid groups to interact (sense) with amines. As groups that would transduce a signal on the conformational state diazophenyl or stilbene groups were chosen, the former using UV-VIS techniques and the latter using fluorescence techniques for the detection. Schematically the mechanism in solution is shown to the left in Fig. 1 where the two possible so-called pinched cone conformers are different thus resulting in different signals detected using the external circuitry. In the solution experiments there was no distinction between primary and secondary amines but in the solid state it was found that primary, secondary and tertiary amines all give rise to different behaviour as can be seen in the right-hand part of Fig. 1.



1 (R^1 = Br, R^2 = Styryl)
2 (R^1 = Br, R^2 = COOH)
3 (R^1 = Azophenyl, R^2 = COOH)
4 (R^1 = Styryl, R^2 = COOH)
5 (R^1 = H, R^2 = COOH)

In this paper we throw some more light on the interactions between the calix[4]arene diacids and amines reported previously using X-ray crystallographic techniques. First of all we compare and contrast the findings obtained in the NMR experiments and, further, the detailed structural knowledge obtained from the X-ray experiments provides an explanation for the varying strengths of interactions between the calix[4]arene diacids and the amines observed in the solution experiments. Furthermore the solid state constructions thus uncovered are discussed in terms of crystal engineering and hold the explanation for some of the discrepancies between the results from solution and the solid state.

Results and discussion

In order to characterise the behaviour of the calix[4]arene diacid based salts a systematic study was undertaken which is presented in the following sections. Firstly the simple interactions that can be observed for neutral calix[4]arenes and calix[4]arene diacids are described. Following on from this the interactions between calix[4]arene diacids and in turn primary,

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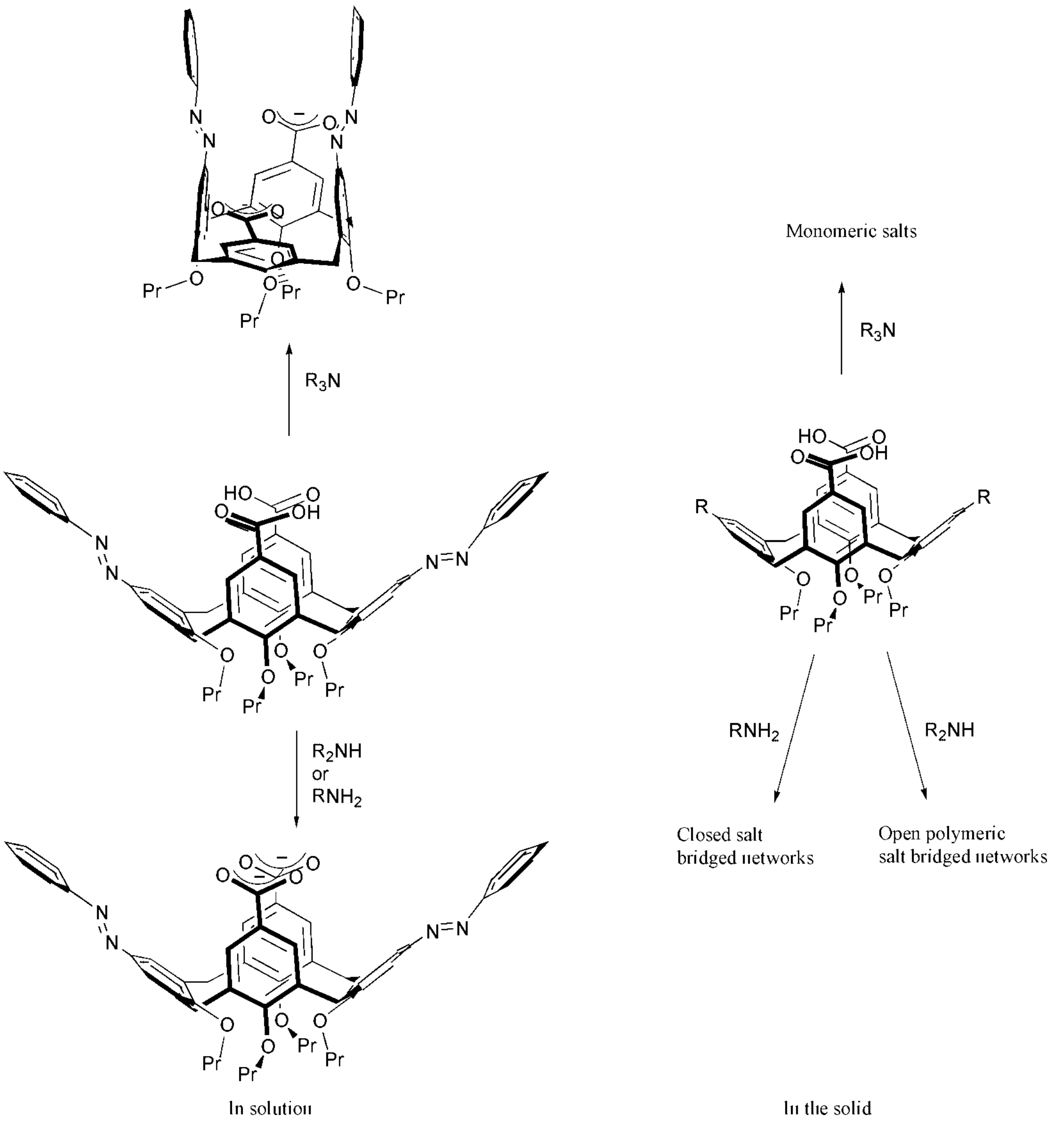

Fig. 1 The behaviour of the calix[4]arene diacid based system as established in solution using NMR. From this it is evident that there is no distinction between primary and secondary amines as a group but tertiary amines behave differently due mainly to coulombic repulsion (left). In the solid state however primary, secondary and tertiary amines are all distinguished by different trends of formation of salt bridged networks (right).

secondary and tertiary amines are described. Finally the interaction between a calix[4]arene diacid and the biological molecule ephedrine is described in the context of the preceding findings.

Interactions for neutral calix[4]arenes and calix[4]arene diacids

The simple calixarene **1** is seen to pack in a manner which conforms to the principles described in an earlier paper[7] where the side groups are splayed outwards and the molecules form stacks in a *head to tail* fashion. The subsequent introduction of an interacting substituent, an acid group, to this system is expected to significantly influence the resulting structure. There has been some discussion as to the possibilities of interaction between the calix[4]arene carboxylic acids. It has been suggested that a monomeric structure could be formed where two carboxylic acid groups interacted across the cavity.[8] This would imply a twist of the carboxylic acid group with respect to the aromatic ring. In one example based on a single crystal structure it was found that the calix[4]arene 5,17-diacid studied formed a dimer.[9] A comprehensive search of the CCDC database[10] for arylcarboxy occurrences (both acids and acid salts but not esters) was undertaken. The plot of the torsion angle formed between the phenyl ring and the carboxy group (see Fig. 2) clearly shows that carboxylate/aryl assemblies prefer a very nearly coplanar arrangement. In no instances were the 90° torsion angles (required for interaction across the calix[4]arene cavity) found, further substantiating the dimer arrangement as being preferred.

In the case of **2** a dimeric structure was obtained similar to the one reported in ref. 9. Interestingly however the azo compound, **3**, forms a similar construct which seen in the light of the consequent *head to head* packing is in contrast to all calix[4]arenes with simple stilbenoid substituents like **1** and the ones found in the literature.[7] This suggest a higher strength in the interaction between the molecules through the acid groups (see Fig. 3).

This observation is further substantiated by an analysis of the interplanar angles defining the pinched cone conformation. In the case of **2** the angle between the molecular twofold axis and the phenyl ring bearing the bromine is 50° whereas for **3** the corresponding angles are 56° and 57° (respectively for the two molecules in the asymmetric unit) indicating some steric demand of the phenylazo groups.

A very useful way of distinguishing networks of specific hydrogen interactions is the use of graph set theory,[11–15] which described briefly is a way of classifying the interactions in much the same way organic chemists normally distinguish molecules through different bonds or arrangements of bonds. In the case of the acid dimers **2** and **3** an eight membered ring can be recognised involving two carbon atoms, four oxygen atoms and two hydrogen atoms as shown in Fig. 4.

The graph set description of this arrangement is $N_1 = R_2^2(8)$.† In spite of the different molecular structures for **2** and **3** the graph sets allow us to compare them and conclude that they are identical. The use of the graph sets will prove very useful in the later analysis of the salts. The dimer arrangements found in the solid state also exist in apolar solutions as evidenced by NMR.

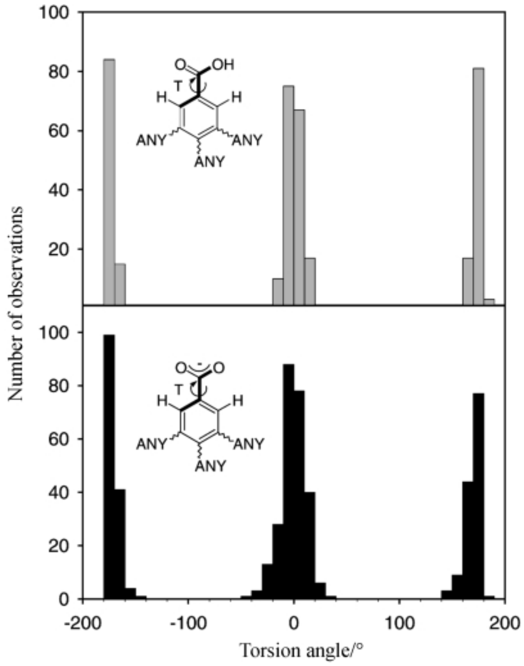

Fig. 2 *Vista* plots of occurrences in the CSD of arylcarboxylic acids (above) and arylcarboxylates (below) according to the search fragments shown as an inset. It is noteworthy that in no instances is a torsion angle of around 90° observed.

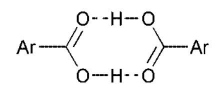

Fig. 4 An illustration of an arylcarboxylic acid dimer with the graph set $N_1 = R_2^2(8)$.

Interactions between primary amines and calix[4]arene diacids

A primary amine like benzylamine gives rise to a complex that in solution and in the solid state shows that the carboxylate groups are pinched together. Benzylamine can in its protonated state accommodate three different specific hydrogen interactions whereas the calixarene can accommodate at least one specific hydrogen interaction for each oxygen atom. The packing observed in the crystal of $\mathbf{2{\cdot}(BzNH_2)_2}$ is a complex arrangement consisting of four benzylamine molecules and two calixarene molecules. The assembly is shown in Fig. 5 where two benzylamine molecules keep each individual calixarene molecule in the pinched cone conformation with the acid groups

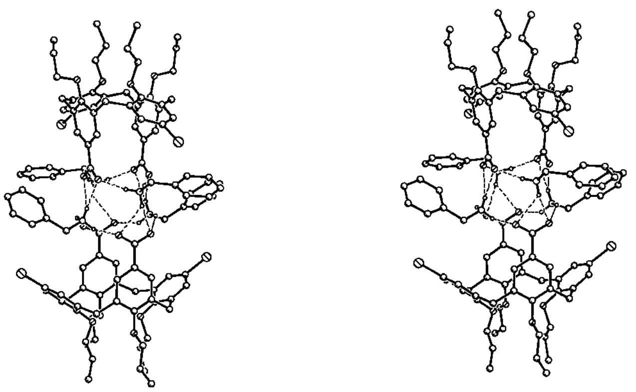

Fig. 5 Interactions with primary amines. A stereoview of the propeller shaped dimeric arrangement observed in the salt formed between benzylamine and **2**.

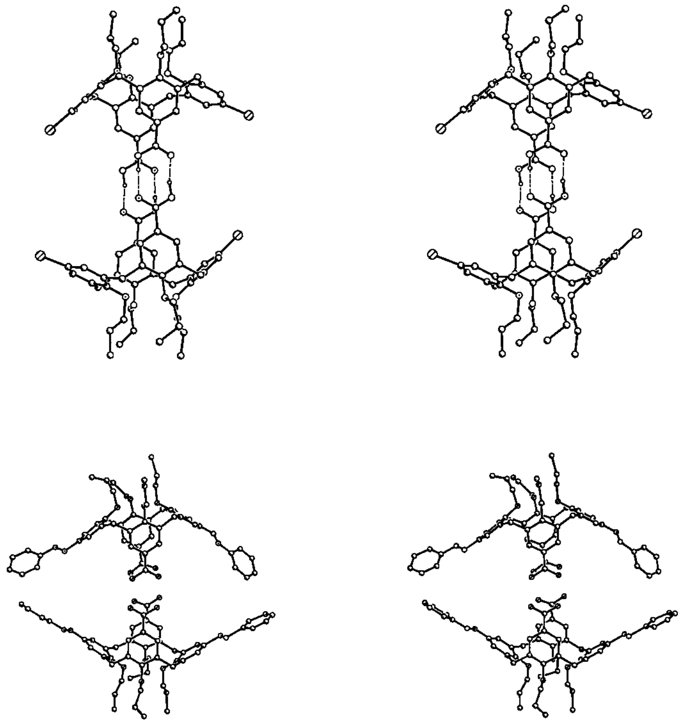

Fig. 3 Stereoviews of the dimeric arrangements observed for **2** (above) and **3** (below) in the crystal.

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† The graph set description encompasses the number of specific hydrogen interactions according to their nature (donor or acceptor) and their arrangement (ring (*R*), chain (*C*) *etc.*). A graph set involving one type of specific hydrogen interactions is a unitary (or first) level graph set (written N_1), a graph set involving two specific hydrogen interactions is termed a second level graph set (written N_2) and so on. The *R* signifies that it is a ring arrangement with eight atoms involved. There are further two hydrogen donors (shown as the superscript) and two hydrogen acceptors (shown as the subscript).

together. This aggregate then forms a dimer thus having the four benzylamine molecules arranged in a cyclic propeller-like fashion capped by a calixarene molecule at either side of the propeller plane.

In this case two distinct specific hydrogen interactions can be identified, one type involving one hydrogen atom from the benzylammonium ion and two oxygens from the same carboxylate ion, and another involving two hydrogen atoms from the benzylammonium ions and two oxygens from different carboxylate ions. The unitary level graph set can thus be described as $N_1 = R^2_1(4)R^4_4(12)$. It is however much more appropriate to consider a smaller ring involving both specific hydrogen interactions and describe it as the secondary level graph set $N_2 = R^2_4(8)$. For the system to work as a receptor it has to rely on a conformational change upon complexation with the analyte and in the case of calix[4]arene diacids this implies that the acid groups become splayed outwards. If coulombic interactions were to govern the conformation of the calix[4]arene system it was expected that the full deprotonisation of the acid with salt formation and the consequent development of two negative charges would make the phenyl rings carrying the negatively charged carboxylate groups become splayed outwards (see Fig. 1 for tertiary amines). In the case of a cation that can interact in a manner that not only involves the coulombic interactions but also for instance through specific hydrogen interactions the behaviour to expect does not necessarily imply that the acid groups become splayed outwards.

Interactions between secondary amines and calix[4]arene diacids

The obvious extension to this study is to analyse the interactions that are observed with a secondary amine where only two specific hydrogen interactions are possible in the protonated state. This obviously should influence the structure and while it is still possible to have the acid groups pinched together it would not be feasible to get dimerisation. The reason for this is apparent when considering the structure in Fig. 5. In the case of a secondary amine one of the hydrogen atoms for the primary ammonium ion would be replaced by an alkyl substituent and this substituent would be pointing straight towards the carboxylate anion with which interaction is required for dimerisation. The secondary amine diethylamine is such a case and it confirms the above expectation. In fact we have discovered that it crystallises in at least two different forms. The first form, **2·(Et$_2$NH)$_2$ Early**, termed the early growth phase is the first crystals that develop. They present a thin plate like crystal morphology and have a low density relative to the late growth phase which is obtained upon leaving the mixture. In time the early growth phase completely transforms into a different form, **2·(Et$_2$NH)$_2$ Late**, termed the late growth phase with a needle like morphology. It is believed that the late growth phase is the stable form. A similar observation has been made recently[16] where a supramolecular system changes crystal morphology, crystal system and space group. No crystallographic details in the form of atomic positions and packing arrangements were given however. The interesting point to note is that the two forms are very dissimilar with respect to crystal morphology, space group symmetry, packing, molecular conformation of the calix[4]arene skeleton and the graph set for the specific hydrogen interactions. The different specific hydrogen interactions observed in the two cases are shown in Fig. 6.

The early growth phase presents a simple graph set consisting of infinite chains involving four different crystallographically distinct specific hydrogen interactions and it can be described by the quaternary graph set $N_4 = C^4_4(12)$. It is noteworthy that the graph set for the late growth phase resembles that of the benzylamine dimer except that a third type of specific hydrogen interaction is observed because the network is not closed around a cylinder but closed in a plane. The graph set is thus a tertiary level graph set that can be described as $N_3 = R^3_4(10)$.

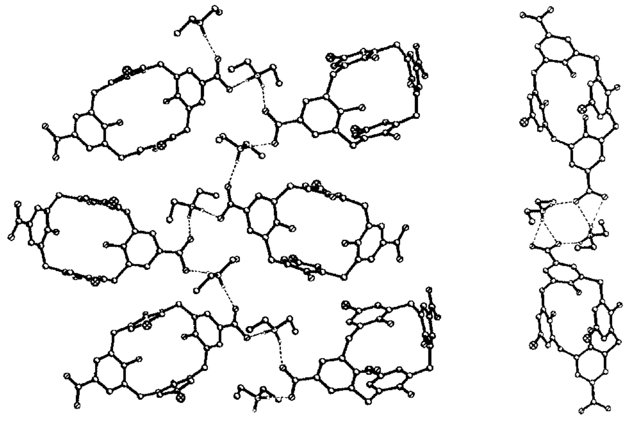

Fig. 6 Interactions with secondary amines. The outline of the different salt bridges observed for the two different crystal forms of the salt between **2** and diethylamine. The early growth phase is shown to the left and the late growth phase to the right.

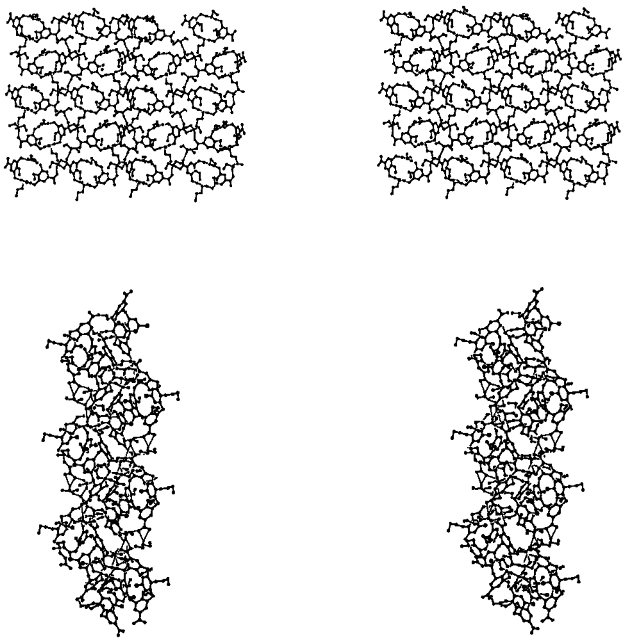

Fig. 7 Two stereoviews emphasising the very different packing topology for the two crystal forms of the salt formed between **2** and diethylamine. The early growth phase (above) presents a sheet like topology whereas the late growth phase (below) presents a string like topology.

While both structures present polymeric networks the nature of the graph set is reflected in the structure. The early growth phase has an open chain infinite graph set linking the molecules together in infinite sheets in the orthorhombic space group *Pbca*. On the contrary the late growth phase has closed graph sets linking the molecules together in infinite strings along the unique axis (4_3-axis) in the tetragonal space group $P4_32_12$. The different outlines of the two structures are shown in Fig. 7.

The only other well documented example of a calix[4]arene based supramolecular system that exhibits polymorphism is one that does not contain solvent and where conformational differences distinguish the two polymorphs[17] or as in our case pseudopolymorphs[18–20] where the two forms also differ in the amount of included solvent. In our case the conformation of the calixarene is less pinched in the early growth phase than in the late growth phase. For instance, the bromine–bromine distance is 5.501(7) Å and 4.477(8) Å for the early and late growth phase respectively. The splay and pinch angles (the angle formed between the plane of the aromatic ring and the molecular C_2-axis) are 39.4° and 3.9° respectively for the early growth phase and 57.8° and −6.3° respectively for the late growth

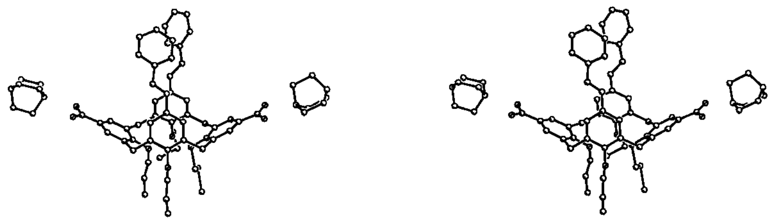

Fig. 8 Interactions with tertiary amines. Coulombic repulsion and resulting pinching of the stilbene substituents observed for the salt formed between **4** and DABCO. Shown as a stereoview.

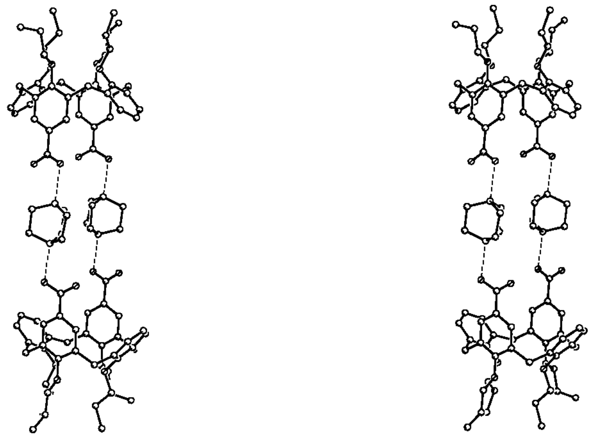

Fig. 9 A stereoview of the dimeric arrangement observed in the salt formed between **5** and DABCO.

phase. A possible explanation for the appearance of the early growth phase could be that it is a result of the rapid crystal growth from the supersaturated solution obtained when mixing initially. At a later stage once supersaturation has receded the more stable late growth phase starts growing or nucleates from the early growth phase. The early growth phase subsequently transforms into pure late growth phase. It was shown by powder diffraction that the early and late growth phases were pure (within the experimental limits of powder diffraction techniques). It was also found possible to nucleate the initial mixture with the late growth phase thus obtaining the late growth phase directly. It is interesting to speculate on the consequences of this as they may be suggestive of a large crystallographic complexity for supramolecules and macromolecules.

Interactions between tertiary amines and calix[4]arene diacids

With tertiary amines only one interaction is possible and therefore simpler structures are to be expected. Several attempts were made to crystallise salts of the calix[4]arene diacids with simple tertiary amines like triethylamine and quinuclidine but we only succeeded in obtaining crystals with the tertiary diamine DABCO (1,4-diazabicyclo[2.2.2]octane). In the case of the salt formed between the calix[4]arene diacid **4** and DABCO (**4·(DABCO)**$_2$, Fig. 8) the electrostatic repulsion would be expected to force the phenyl rings carrying the carboxylate groups outwards and thus make the stilbene units come into contact as observed. This effect is expected when considering the results from the experiments in solution. The electrostatic argument however is perhaps not so rigid as we did obtain crystals of the salt formed between the calix[4]arene diacid **5** and DABCO (**5·DABCO**, Fig. 9). In this case in the DABCO dimer type arrangement, the DABCO molecules behave as divalent tertiary amines interacting at both ends contrary to the case with **4**.

Graph sets describing the interactions in both structures are simply *D*. An analysis of the C–O bond lengths in the carboxylates and the different N–O distances between the DABCO and the carboxylate groups does seem to indicate that DABCO is doubly protonated in the dimer case. As this would imply that four cations are placed close together the electrostatic argument is questionable and more analysis has to be done to provide conclusive evidence for this. Certainly the choice of a divalent tertiary amine like DABCO is undesirable as the effects of this added complexity are not easily discerned from the pure acid base and coulombic interactions.

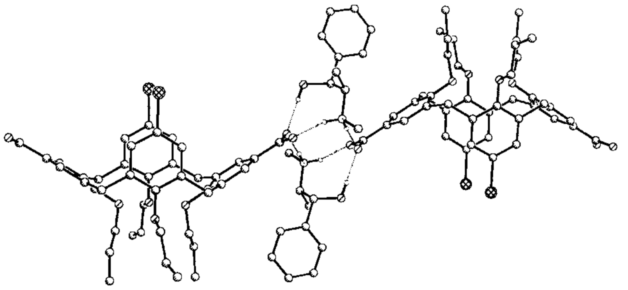

Fig. 10 The salt bridging network observed in the salt between **2** and (±)-ephedrine. It is noteworthy that the interactions for the pure secondary amines can be recognised and in addition the additional hydroxy group participates in the interaction.

Interactions between the complex amine ephedrine and calix[4]arene diacids

The above treatise dealt with the structural behaviour of the salts obtained with simple amines. In the case of the secondary amine ephedrine we would expect a behaviour similar to that of diethylamine with the added possibility of further interaction through the hydroxy group. Also this may give some clues as to why the calix[4]arene systems descibed in this paper show a strong binding of ephedrine. While the strength of the binding was easily monitored by NMR, and this gave some hints on the interactions observed in solution, data from a crystal could give more detailed information on the geometry of the complex even though it might not be identical to the geometry observed in solution. In spite of many attempts it was in our hands not possible to obtain crystals of the (−)-ephedrine salt. The explanation might be that the binding of two chiral amines to the same calix[4]arene diacid gives rise to a chiral complex that in this case finds difficulty in growing suitable crystals. This prompted us to try and grow crystals using the racemic form (±)-ephedrine. Using this strategy it became possible to grow crystals and the structure could be solved. Indeed the expectations of an interacting hydroxy group were fulfilled thus giving rise to a stronger complexation. The conformation of the calix[4]arene system however has the carboxylate groups splayed outwards contrary to the observation in solution. The nature of the interactions however shows very nicely that a complex network is obtained as shown in Fig. 10.

A tertiary level graph set that can be used to describe the network is $N_3 = R_4^3(13)$. Based on the nature of the ephedrine complex and the observed interactions it is likely that the stronger binding observed for ephedrine is due to the extra hydroxy group.

Conclusion

In this paper we have through crystal structure analysis demonstrated how calix[4]arene diacids form salts with amines that appear as dimers or networks in the solid state as a function of the complexity of the amine, and further provided an explanation of the strength of interactions observed in solution for a receptor system based on these molecules. Several interesting aspects of salt formation of these macromolecules were uncovered, in particular the ability to form diverse polymeric networks bearing a polymorphic or pseudopolymorphic relationship. A definite trend was observed showing how the number of interactions available controlled the complexity of the salt bridged networks. It was thus shown that primary amines offering the largest degree of interaction formed complex networks that were closed giving rise to a dimeric arrangement. Secondary amines gave rise to networks that were open or closed but leading to polymeric arrangements. Tertiary amines gave rise to simple monomeric salts. It is noteworthy that the salts formed between the calix[4]arene diacids and primary and secondary amines give rise to different interactions in the solid state as opposed to solution. An explanation for this can be found by comparing the dimeric arrangement observed for **2·(BzNH$_2$)$_2$** with what the same arrangement would look like if benzylamine was replaced by diethylamine. A complex with two diethylamine molecules keeping the acid groups pinched together is possible and this is what is believed to exist in solution. Upon crystallising there is no possible way of creating a favourable interaction leading to a dimeric arrangement between two such calix[4]arene diacid salts. To satisfy the number of possible interactions the salts with secondary amines such as diethylamine have to adopt the other pinched cone conformation with the acid groups splayed outwards leading to extended networks. In general the networks follow distinct patterns reminiscent of crystal engineering which makes it possible to predict the behaviour for a more complex system like ephedrine that offers further interactions based on the results from the isolated study of simple amines.

Experimental

The crystals were grown from solution by fully dissolving the calix[4]arene diacid (50 mg) with heating in methylene chloride (0.5 mL) followed by addition of the amine (50 mg) to the warm solution. Finally acetonitrile was added (1–2 mL). Crystal growth initiated shortly after mixing and upon cooling crystals of a quality sufficient for X-ray crystallography were obtained. Experimental details can be found in Table 1.‡ All crystals were drawn from the mother liquor, coated with a thin layer of oil, mounted on glass capillaries with grease and transferred quickly to the cold nitrogen stream on the diffractometer. All data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector using MoKα radiation at 120(2) K. Absorption corrections were made for all compounds using SADABS.[21] Direct methods for the structure solution and full-matrix least-squares refinements were used for all compounds. Hydrogen atoms were included in calculated positions for all compounds. The Programs used were SMART, SAINT from Siemens[22,23] and SHELX-97.[24] All structures were checked for overlooked symmetry using MISSYM and for voids in PLATON.[25] Some disorder of the propoxy groups was observed for compounds **2**, **2·(BzNH$_2$)$_2$** and **5·(DABCO)**. This was in all three instances modelled as two mutually exclusive groups and refined with respect to the sof (Site Occupation Factor). For compound **3**, **2·(Et$_2$NH)$_2$ Early** and **4·(DABCO)$_2$** large thermal ellipsoids were observed for some of the carbon atoms of the propoxy groups. In all instances a disordered model similar to the above was attempted without success. The best representation was thus found to be the acceptance of these large ellipsoids. For compound **2·(Et$_2$NH)$_2$ Late** two dis-

Table 1 Crystallographic data for the calix[4]arene diacids and their salts

Compound	**1**	**2**	**3**	**2·(BzNH$_2$)$_2$**	**2·(Et$_2$NH)$_2$ Early**	**2·(Et$_2$NH)$_2$ Late**	**4·(DABCO)$_2$**	**5·DABCO**	**2·(Ephedrine)$_2$**
Formula	$C_{56}H_{58}O_4Br_2$	$C_{42}H_{46}O_8Br_2$	$C_{54}H_{56}O_8N_4$	$C_{56}H_{64}O_8Br_2N_2$·CH_2Cl_2	$C_{50}H_{68}O_8Br_2N_2$·$\frac{1}{2}CH_2Cl_2$, $\frac{1}{2}CH_3CN$	$C_{50}H_{68}O_8Br_2N_2$·CH_2Cl_2, CH_3CN	$C_{70}H_{84}O_8N_4$·CH_3CN	$C_{48}H_{60}O_8N_2$·$3CH_3CN$	$C_{62}H_{76}Br_2N_2O_{10}$·$3CH_3CN$
Formula wt	954.84	838.61	889.03	1137.84	1047.87	1110.86	1150.47	916.14	1292.23
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Tetragonal	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$	$C2/c$	$Pbca$	$P4_32_12$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	4	8	8	8	4	2	2	4
a/Å	25.7135(4)	12.505(3)	22.391(5)	24.817(5)	17.394(6)	17.865(3)	13.062(3)	10.754(2)	14.1546(10)
b/Å	9.52320(10)	24.822(5)	13.024(3)	25.026(5)	23.820(6)	17.865(3)	13.325(3)	12.014(2)	16.0715(11)
c/Å	19.8894(3)	12.722(3)	33.539(7)	17.854(4)	27.882(7)	17.263(4)	20.365(4)	21.851(4)	29.805(2)
α/°	90	90	90	90	90	90	96.75(3)	100.97(3)	90
β/°	105.57	94.80(3)	97.64(3)	99.88(3)	90	90	93.04(3)	96.83(3)	99.4010(10)
γ/°	90	90	90	90	90	90	110.93(3)	110.11(3)	90
V/Å^3	4691.62(11)	3935.0(14)	9694(3)	10924(4)	11552(6)	5509.6(16)	3270.4(11)	2550.0(9)	6689.2(8)
ρ/g cm^{-3}	1.352	1.416	1.218	1.384	1.205	1.339	1.168	1.193	1.283
Crystal dimensions/mm	0.63 × 0.63 × 0.13	0.50 × 0.15 × 0.15	0.30 × 0.25 × 0.13	0.50 × 0.10 × 0.10	0.38 × 0.13 × 0.03	0.50 × 0.33 × 0.15	0.35 × 0.18 × 0.13	0.28 × 0.18 × 0.08	0.65 × 0.30 × 0.20
μ/mm^{-1}	1.774	2.111	0.082	1.637	1.497	1.621	0.076	0.080	1.271
Number of reflections	24364	40482	97941	45803	41459	58853	34859	26915	71230
$R(F)$, $R_w(F^2)$ all data	0.0277, 0.0749	0.0470, 0.1157	0.1481, 0.3724	0.0814, 0.2043	0.1663, 0.4245	0.0426, 0.1350	0.1352, 0.4616	0.0796, 0.2110	0.0543, 0.1708

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‡ CCDC reference number 188/261. See http://www.rsc.org/suppdata/p2/b0/b002409k/ for crystallographic files in .cif format.

ordered solvent molecules were found for each calixarene. The disorder was modelled as CH_3CN and CH_2Cl_2 occupying the same site but in a mutually exclusive manner. This model was refined with respect to the sof and found to have CH_3CN and CH_2Cl_2 in a ratio of 1 : 1. For compound **2·(Et$_2$NH)$_2$ Early** one disordered solvent molecule was found for each calixarene. The disorder was modelled as above but the CH_3CN and CH_2Cl_2 were not occupying the same site. The model was refined in a mutually exclusive manner and with respect to the sof and found to have CH_3CN and CH_2Cl_2 in a ratio of 40 : 60. Several models were attempted both with one and two CH_3CN molecules (disordered or fully occupied), similarly with CH_2Cl_2. Of all the attempts made only the model presented here refined well. The disorder is quite pronounced and the atoms of the solvent molecules have only been refined at the isotropic level. For **2**, **2·(Et$_2$NH)$_2$ Early** and **4·(DABCO)$_2$** the max/min residual electron densities were quite large: 1.643/−1.399, 2.479/−1.829 and 1.023/−0.568 (e $Å^{-3}$) respectively. For the first two these large residual electron densities were found close to a bromine atom and attempts to include disorder as two alternate bromophenyl rings did not prove fruitful. In the case of **4·(DABCO)$_2$** the residual density was found close to one of the stilbene phenyl rings. Again a disordered model was attempted but did not refine well. The information that could be obtained safely from compounds **3**, **2·(Et$_2$NH)$_2$ Early** and **4·(DABCO)$_2$** due to the relatively poor data quality and their rather large *R*-factors were the unambiguous determination of connectivity, molecular conformation, packing pattern and the spatial relationship between neighbouring molecules.

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