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PAPER

Complexation of neutral 1,4-dihalobutanes with simple pillar[5]arenes that is dominated by dispersion forces†

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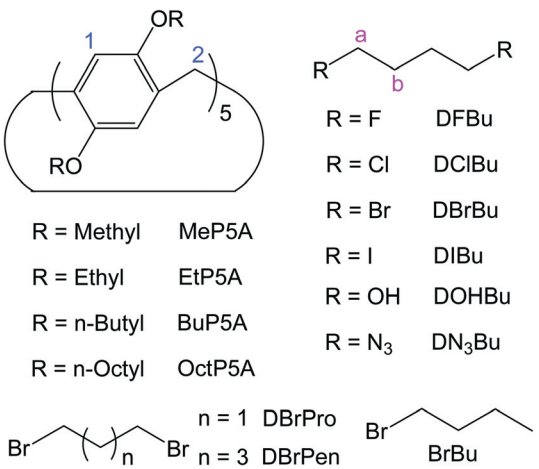
The complexation of neutral 1,4-dihalobutanes with simple pillar[5]arenes was investigated. The results indicate the formation of interpenetrated complexes, where the dispersive interactions dominate the complex stability. Typically, 1,4-diiodobutane displays the strongest binding strength with ethylpillar[5]-arene [$K_a = (1.0 \pm 0.1) \times 10^4\ M^{-1}$], up to 120 fold as compared with 1,4-difluorobutane.

Introduction

Pillararenes (PAs) are new calixarene (CA) analogues, and are described as "fascinating cyclophanes with a bright future".[1–4] They are made up of hydroquinone units linked by methylene bridges, and possess symmetrical pillar architectures. This structural feature makes PAs superior to CAs in the construction of threaded complexes. Furthermore, PAs are more rigid than traditional CAs, which affords the possibility of their highly effective binding of specially designed guests. Our recent works[4] have reported the surprising host–guest properties of simple alkyl-substituted pillar[5]arenes (AlkP5As)[5] towards the neutral bis(imidazole) and dinitrile guests. It is well known that CAs generally interact strongly with cationic guests,[6] except for calixpyrroles, which have shown considerable promise in the area of anion recognition and sensing. P5A's neutral guest recognition abilities are very unique. Searching new neutral axles and further clarifying the binding mechanisms (especially the driving forces) and the inclusion characteristics of this new class of supramolecular host are thus significantly interesting.

In this work, we choose a series of neutral dihaloalkane derivatives (Scheme 1) as guest molecules and screen their interactions with AlkP5As, which results in formation of some stable interpenetrated complexes both in solution and in the solid state.[7] The driving forces, binding geometries, and binding selectivities are comprehensively discussed. The results suggest that the dominant driving force for the complexation was van der Waals dispersion forces (also known as London forces). Although dispersion forces are relatively weak intermolecular interactions, they often play a large role in some supramolecular complexes.[8] Furthermore, their importance in the stacking between nucleobases and in the folding of proteins has also been recognized.



Scheme 1 Structure of AlkP5A hosts and neutral guests.

Results and discussion

Complexation of dihalobutanes by EtP5A

As shown in Fig. 1, in the presence of about 1 equiv. of EtP5A, the signals of DIBu's methylene protons (H_a and H_b) exhibit a very substantial upfield shift ($\Delta\delta = -2.85$ for H_b), and broadening effects compared to the free axle. Typically, the broadening effects were so remarkable that the signals of H_a could not be observed in the ^1H NMR spectrum. These results reveal that the

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†Electronic supplementary information (ESI) available: ^1H NMR and ^{13}C NMR spectra of hosts, Job plots, determination of the association constants; and crystal structures. CCDC 852484, 863689–863691. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25251a

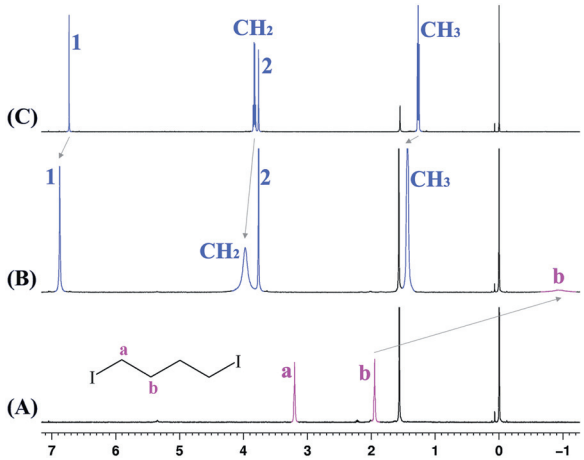

Fig. 1 ^{1}H NMR spectra (500 MHz) of (a) DIBu, (b) DIBu + EtP5A, and (c) EtP5A in $CDCl_3$ at 4.6–5.2 mM.

Table 1 Association constants K_a for the host–guest inclusion complexation in $CDCl_3$ at 298 K

Host	Guest	K_a (M^{-1})
EtP5A	DFBu	$(8.6 \pm 0.5) \times 10$
EtP5A	DClBu	$(1.9 \pm 0.2) \times 10^3$
EtP5A	DBrBu	$(4.9 \pm 0.3) \times 10^3$
EtP5A	DIBu	$(1.0 \pm 0.1) \times 10^4$
EtP5A	DOHBu	$(5.4 \pm 0.3) \times 10^2$
EtP5A	DN_3Bu	$(3.5 \pm 0.4) \times 10^2$
EtP5A	DBrPro	$(3.0 \pm 0.2) \times 10^2$
EtP5A	DBrPen	$(1.4 \pm 0.1) \times 10^3$
EtP5A	BrBu	$(5.2 \pm 0.4) \times 10$
MeP5A	DBrBu	$(1.6 \pm 0.1) \times 10^3$
BuP5A	DBrBu	$(4.3 \pm 0.4) \times 10^3$
OctP5A	DBrBu	$(4.1 \pm 0.3) \times 10^3$

host engulfs the guest, which thus leads to an efficient shield[9] toward guest protons. On the other hand, the host is deshielded by the presence of a guest molecule, since proton signals of EtP5A derived from aromatic and ethyl protons display downfield displacement ($\Delta\delta$ = +0.15–+0.17 ppm). Other investigated 1,4-dihalobutane guest molecules (DFBu, DClBu, and DIBu) present a similar behavior (Fig. S9–S11†). Thus, these dihaloalkane axles must have a similar binding mode with EtP5A, *i.e.*, the wheel is fully threaded by the axles. These inclusion complexes can be considered to have [2]pseudorotaxane structures. In the present recognition motifs, multiple C–H···π interactions, C–H···halogen hydrogen bonds, dipole–dipole forces and dispersion forces may exist. Due to the high electronegativity of fluorine, the carbon–fluorine bond is very polar and the acidity of DFBu's methylenes is relatively strong, which should lead to the enhanced dipole–dipole, C–H···π, and hydrogen bonding interactions. However, the K_a value of DFBu with EtP5A [$(8.6 \pm 0.5) \times 10$ M^{-1}] is the smallest one among the four 1,4-dihalobutanes (Table 1). And the constant increases in the order of F < Cl < Br < I, *i.e.*, with the increasing polarizability of the guest. This undoubtedly indicates that the interaction is dominated by dispersion forces. It is well known that the dispersion forces depend on the movement of electrons to produce temporary (instantaneous) dipoles. The shared electron pair in the C–F bond gets dragged very firmly towards the fluorine atom. This makes the DFBu guest molecule much less polarizable, and therefore leads to weaker dispersion forces upon complexation with P5A host. In contrast, since iodine is highly polarizable and the C–I bond is almost nonpolar (the electronegativities of carbon and iodine are equal), the dispersion forces between DIBu and host are significantly strong. That is why DIBu displays the largest association constant of $(1.0 \pm 0.1) \times 10^4$ M^{-1}, up to 120 fold compared with DFBu. On the other hand, the size-fit between host and guest may be another, but not the crucial, reason for the large difference of K_a values. The van der Waals volume[10] (V_{vdw} = 89.9 Å^3) of DFBu represents a small fraction of the P5A cavity (*i.e.*, 225 Å^3),[3c] resulting in a weak binding.

For the mono-bromide guest, 1-bromobutane (BrBu), the host-induced NMR response in $CDCl_3$ was also a fast exchange (Fig. S14†). The complexation induced upfield shifts and broadening effects are obviously less remarkable than those for dibromoalkanes, indicating a weaker binding. As expected, the K_a value of BrBu with EtP5A [$(5.2 \pm 0.4) \times 10$ M^{-1}] is much smaller than that observed for dibromide guest DBrBu [$(4.9 \pm 0.3) \times 10^3$ M^{-1}]. This is mainly due to a clear advantage of cooperative dispersion, hydrogen bonding and C–H···π interactions in the DBrBu⊂EtP5A complex.

X-ray crystallographic analysis

Further support for formation of the interpenetrated geometries came from X-ray crystallographic analysis of the single crystals by slow evaporation of the host–guest solutions in dichloromethane. We obtained the crystal structures of four complexes: DClBu⊂EtP5A, DIBu⊂BuP5A, DFBu⊂BuP5A, and DClBu⊂OctP5A (Fig. 2, S18–S20†). In the solid state the guest is included in the center of the AlkP5A host, which is consistent with the result in solution. THe typical crystal structure of DClBu⊂EtP5A complex is shown in Fig. 2. There exit multiple C–H···π interactions between axle's methylenes and host's dialkoxybenzene units (Fig. 2a), weak C–H···Cl hydrogen bonds between the host's ethyls and the guest's chlorine atoms (Fig. 2b), and weak C–H···O hydrogen bonds between the axle's methylenes and the host's oxygen atoms (Fig. 2c).

Complexation of DBrBu by different AlkP5As

The interactions of DBrBu with other simple AlkP5As, MeP5A, BuP5A and OctP5A, have also been investigated (Fig. S15–S17†). Similar NMR changes are observed, representing the interpenetrated complex formation. Among these four hosts, MeP5A gives the smallest K_a value [$(1.6 \pm 0.1) \times 10^3$ M^{-1}], and the other three hosts (EtP5A, BuP5A and OctP5A) exhibit similar binding affinities. For example, the binding constant of DBrBu with EtP5A is 3.1 times larger than that for MeP5A. One reasonable explanation is that there may be more C–H···Br and dispersive interactions between the ethyls of EtP5A with the axle than the methyls of MeP5A.

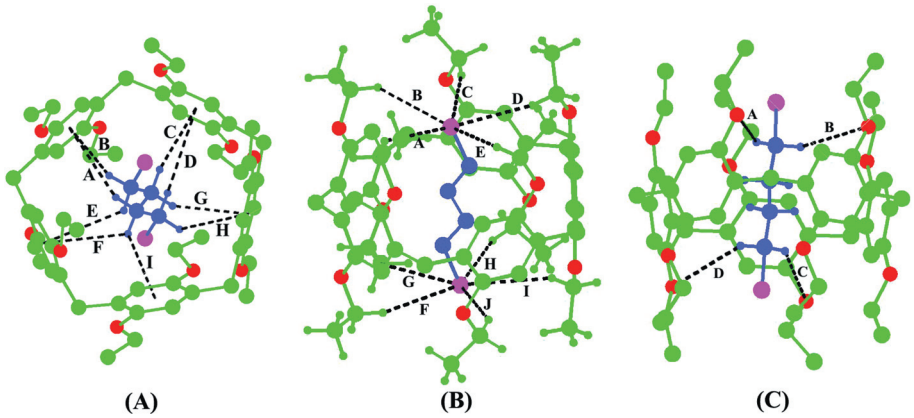

Fig. 2 Crystal structure of the DClBu⊂EtP5A complex. EtP5A is green, DClBu is blue, oxygens are red, and chlorines are magenta. Dashes represent C–H···π interactions or hydrogen bonds. (A) C–H···π parameters: H···ring centre distances (Å), C–H···ring angles (°) A, 3.15, 148; B, 3.07, 151; C, 2.90, 169; D, 3.50, 147; E, 3.38, 118; F, 3.41, 120; G, 2.89, 146; H, 3.27, 138; I, 3.33, 137. (B) C–H···Cl hydrogen-bond parameters: H···Cl distances (Å), C–H···Cl angles (°) A, 3.17, 136; B, 3.20, 140; C, 2.99, 167; D, 3.05, 167; E, 3.19, 148; F, 3.43, 154; G, 3.31, 137; H, 3.28, 151; I, 3.28, 139; J, 3.11, 141. (C) C–H···O hydrogen-bond parameters: H···O distances (Å), C–H···O angles (°) A, 3.14, 148; B, 2.80, 162; C, 3.33, 142; 3.10, 150.

Linker length effect

The linker length effect was then studied. From Table 1, the K_a values for DBrPro and DBrPen with the host are reduced by factors of 16 and 3.5, respectively, compared with that for DBrBu. That is to say, DBrBu, possessing four methylenes in its linker, is the most suitable axle for an EtP5A wheel. Both the increase and the decrease of methylene linker length will reduce the dispersion interactions, and thus lead to an obviously unfavorable effect on the complex formation.

For comparison purposes, we also selected for our study another two neutral 1,4-butylene derivatives, *i.e.*, 1,4-butanediol (DOHBu) and 1,4-diazidobutane (DN_3Bu). From Fig. S12 and S13,† the formation of [2]pseudorotaxane-type complexes was observed since methylene protons H_a and H_b broadened and shifted upfield upon complexation with EtP5A. The association constants are both in the vicinity of 10^2 M^{-1} in $CDCl_3$ (Table 1). Since oxygen and nitrogen are less polarizable than chlorine, bromine and iodine, the resulting weaker dispersive interactions between the host with DOHBu and DN_3Bu bring about the weaker host–guest binding affinities.

Conclusions

In conclusion, we have demonstrated the inclusion complexation behaviors of neutral 1,4-dihalobutanes with simple alkyl-substituted pillar[5]arenes. The results obtained indicate undoubtedly the formation of interpenetrated complexes, where the dispersion forces are the dominant contributions. The halogen-substituent pattern on 1,4-butylene unit drastically affects the binding abilities and selectivities. The association constant increases in the order of F < Cl < Br < I. The present study will further clarify the recognition mechanisms and the inclusion characteristics of the new supramolecular building block, pillararene, and can provide new opportunities for supramolecular chemists in this field. The formation of interpenetrated geometries, the easy availability of both the wheels[5] and axles, and the highly selective binding behaviors imply broad applications of the new recognition motifs in the construction of new pillararene-based functional supramolecular systems, such as mechanically interlocked structures and supramolecular polymers.

Experimental

Materials and methods

AlkP5A hosts[2f] (MeP5A, EtP5A, BuP5A and OctP5A) were prepared by condensation of the corresponding 1,4-dialkoxybenzene with paraformaldehyde and $BF_3{\cdot}O(C_2H_5)_2$ as a catalyst. All of the halogenated guest compounds were commercially available and used as received. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 instrument.

Determination of the association constants

For each of the host–guest complex, chemical exchange is fast on the NMR time scale. To determine the association constant, NMR titrations were done with solutions which had a constant concentration of AlkP5A and varying concentrations of guest. Using the nonlinear curve-fitting method, the association constant was obtained for each host–guest combination from the following equation[11]:

$$A = (A_\infty/[\mathrm{P5A}]_0)\ (0.5[\mathrm{G}]_0 + 0.5([\mathrm{P5A}]_0 + 1/K_a) - (0.5\ ([\mathrm{G}]_0{}^2 + (2[\mathrm{G}]_0(1/K_a - [\mathrm{P5A}]_0)) + (1/K_a + [\mathrm{P5A}]_0)^2)^{0.5}))$$

where A is the chemical shift change of aromatic proton (H_1) on AlkP5A host at $[G]_0$, A_∞ is the chemical shift change of H_1 when the host is completely complexed, $[P5A]_0$ is the fixed initial concentration of the AlkP5A host, and $[G]_0$ is the initial concentration of guest. (Fig. 3 and 4) Assuming 1 : 1 inclusion complexation stoichiometry between AlkP5As and these neutral guests, the plot of $\Delta\delta$ (the chemical shift change of AlkP5A's aromatic proton H_1) as a function of $[guest]_0$ for each examined

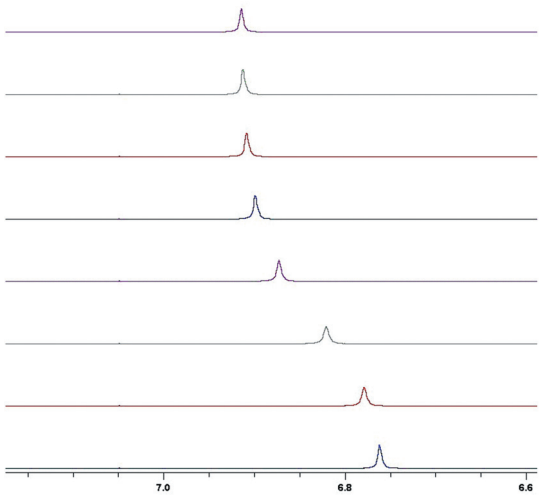

Fig. 3 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of MeP5A at a concentration of 1.0 mM upon addition of DBrBu. From bottom to top, the concentration of DBrBu was 0, 0.3, 0.8, 2.0, 4.3, 8.1, 13.4, 20.3 mM.

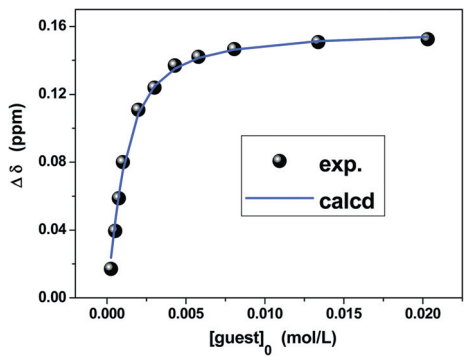

Fig. 4 The non-linear curve-fitting (NMR titrations) for the complexation of MeP5A host (1.0 mM) with DBrBu in $CDCl_3$ at 298 K. The concentration of DBrBu was 0, 0.3, 0.5, 0.8, 1.0, 2.0, 3.0, 4.3, 5.8, 8.1, 13.4, 20.3 mM.

host–guest pair gave an excellent fit, verifying the validity of the 1 : 1 inclusion complexation stoichiometry assumed. Additionally, Job plots based on proton NMR data also showed the 1 : 1 stoichiometries (Fig. S21†).

X-ray crystal data for DClBu⊂EtP5A. Crystallographic data: colorless, $C_{59}H_{78}Cl_2O_{10}$, *FW* 1018.11, orthorhombic, space group *Pbcn*, a = 42.526 (8), b = 15.758 (3), c = 16.686 (3), $\alpha = \beta = \gamma$ = 90.00°, V = 11 181 (3) Å^3, Z = 8, D_c = 1.210 g cm^{-3}, T = 173 (2) K, μ = 0.172 mm^{-1}, 49 628 measured reflections, 10 399 independent reflections, 650 parameters, 7 restraint, F(000) = 4368, R_1 = 0.1516, wR_2 = 0.3259 (all data), R_1 = 0.1193, wR_2 = 0.2971 [$I > 2\sigma(I)$], max. residual density 1.073 e Å^{-3}, and goodness-of-fit (F^2) = 1.096. CCDC 852484.

X-ray crystal data for DIBu⊂BuP5A. Crystallographic data: colorless, $C_{79}H_{118}I_2O_{10}$, *FW* 1481.53, triclinic, space group $P\bar{1}$, a = 15.136 (2), b = 24.590 (4), c = 24.775 (4), α = 61.226 (2), β = 81.302 (2), γ = 74.159 (2), V = 7774 (2) Å^3, Z = 4, D_c = 1.266 g cm^{-3}, T = 173 (2) K, μ = 0.863 mm^{-1}, 42 356 measured reflections, 26 098 independent reflections, 1639 parameters, 25 restraint, F(000) = 3112, R_1 = 0.2447, wR_2 = 0.5428 (all data), R_1 = 0.1970, wR_2 = 0.4940 [$I > 2\sigma(I)$], max. residual density 10.302 e Å^{-3}, and goodness-of-fit (F^2) = 2.082. CCDC 863691.

X-ray crystal data for DFBu⊂BuP5A. Crystallographic data: colorless, $C_{19.75}H_{29.50}FO_{2.50}$, *FW* 325.93, triclinic, space group $P\bar{1}$, a = 12.2219 (11), b = 14.4860 (13), c = 21.9366 (19), α = 89.672 (2), β = 89.514 (2), γ = 76.1320 (10), V = 3770.4 (6) Å^3, Z = 8, D_c = 1.148 g cm^{-3}, T = 296 (2) K, μ = 0.080 mm^{-1}, 24 029 measured reflections, 13 910 independent reflections, 820 parameters, 0 restraint, F(000) = 1416, R_1 = 0.1521, wR_2 = 0.2913 (all data), R_1 = 0.0911, wR_2 = 0.2284 [$I > 2\sigma(I)$], max. residual density 1.396 e Å^{-3}, and goodness-of-fit (F^2) = 1.031. CCDC 863690.

X-ray crystal data for DClBu⊂OctP5A. Crystallographic data: colorless, $C_{59.50}H_{99}ClO_5$, *FW* 929.84, monoclinic, space group $P2(1)/c$, a = 21.897 (4), b = 21.540 (4), c = 25.200 (5), $\alpha = \gamma$ = 90.00, β = 98.280 (4), V = 11 761 (4) Å^3, Z = 8, D_c = 1.050 g cm^{-3}, T = 173 (2) K, μ = 0.108 mm^{-1}, 55 903 measured reflections, 20 013 independent reflections, 1171 parameters, 18 restraint, F(000) = 4104, R_1 = 0.2188, wR_2 = 0.3894 (all data), R_1 = 0.1394, wR_2 = 0.3347 [$I > 2\sigma(I)$], max. residual density 1.130 e·Å^{-3}, and goodness-of-fit (F^2) = 1.508. CCDC 863689.

Acknowledgements

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