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Binding of an acetonitrile molecule inside the ethereal cavity of a hexaarylbenzene-based receptor *via* a synergy of C–H···O/C–H···π interactions†

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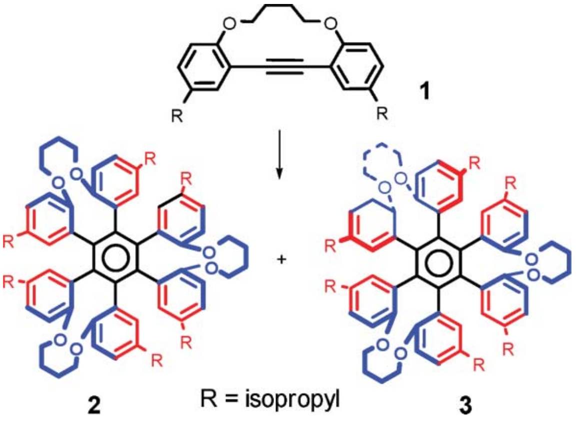
A pair of hexaarylbenzene-based receptors, which contain a circular, as well as a partially-broken, ethereal fence around the central benzene ring, bind acetonitrile molecules *via* a synergy of C–H···O and C–H···π interactions, as probed by X-ray crystallography.

Weak molecular forces play a vital role both in supramolecular chemistry and biological sciences.[1] Scores of studies have demonstrated that C–H···O and C–H···π interactions are the two most notable weak molecular forces, besides hydrogen bonding, that control the crystal packing, as well as the stabilization, of both natural and unnatural supramolecular assemblies.[2] It has also been suggested that these weak molecular forces play an important role in controlling the selectivity/reactivity of a variety of chemical transformations.[3]

We have recently uncovered that a $Co_2(CO)_8$-catalysed trimerization of (bridged) *ortho*-substituted diarylacetylenes[4] allows the selective formation of only two easily-separable rotamers of hexaarylbenzenes (Scheme 1).[5] Note that simple *ortho*-substituted diarylacetylenes produce (multiple) inseparable mixtures of rotamers![6] The ready availability of well-defined rotamers and especially symmetrical rotamers **2**, in which the six ethereal oxygens are arranged in a circular array on one face of the central benzene ring, prompted us to investigate their C–H···O and C–H···π interactions[1–3] towards the binding of different guests.[5]



Scheme 1 Synthesis of a pair of hexaarylbenzene rotamers.

Accordingly, herein, we report the binding of acetonitrile to hexaarylbenzene (HAB) derivatives **2** and **3**, and delineate that the binding of acetonitrile to these HAB derivatives occurs from a synergistic interplay of both C–H···O and C–H···π forces, as established by X-ray crystallography.

The hexaarylbenzene rotamers **2** and **3** were synthesized by a $Co_2(CO)_8$-catalysed trimerization of the corresponding bridged *ortho*-substituted diarylacetylene. The characterization data of the various compounds are included in the ESI.† Excellent single crystals of **2** (or **3**) were obtained by a slow evaporation of its solution in a 9 : 1 mixture of dichloromethane–acetonitrile during the course of 2 d at 22 °C. The crystal structure of the symmetrical rotamer **2** showed that it contained two symmetrically-independent but (almost) identical molecules of a [**2**·CH_3CN] complex.‡ Fig. 1 shows that the CH_3 group of the guest acetonitrile nestles deep inside the bowl-shaped cavity of **2**, which is comprised of an aromatic bottom (*i.e.* central benzene ring) and an ethereal rim formed by six oxygens from the peripheral aryl groups. The depth of the cavity, *i.e.* the distance between the aromatic bottom and the ethereal rim, is ~2.1 Å. The radius of the cavity in **2** is ~3.15 Å, which is significantly larger than the cavity found in 18-crown-6 (*i.e.* ~2.85 Å),[7] and thus allows a CH_3 group to reside inside it.

The acetonitrile molecule approaches the central benzene ring of **2** in a highly symmetrical fashion, with the 3-fold axis of both molecules coinciding within 7° and with a distance as close as 3.24 Å. Although acetonitrile usually forms directed (linear) C–H···O bonds (*vide infra*), in this complex, however, it forms

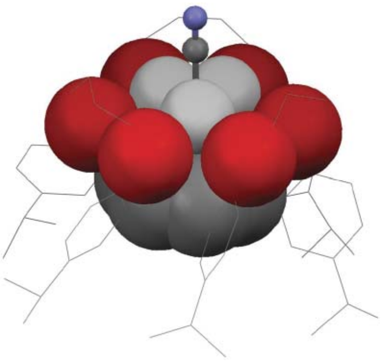


Fig. 1 A partial space-filling representation of the [**2**·CH_3CN] complex showing the symmetrical juxtaposition of the CH_3 group inside the bowl-shaped cavity of **2**.

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† Electronic supplementary information (ESI) available: Synthetic details and spectral data of various compounds in Scheme 1. See DOI: 10.1039/b707237f

symmetrically-bifurcated C–H···O bonds,[8] where each H atom of the methyl group is equally shared between two neighbouring ethereal oxygens. The average H···O distance of 2.48 Å is considerably shorter than the equilibrium van der Waals separation of 2.72 Å, and is also shorter than the value of ~2.6 Å expected from the average C–H···O angle of ~137° (Fig. 1).[9]

As such, the staggered orientation of the CH_3 group of the acetonitrile molecule with respect to six ethereal oxygens in **2** results in its H atoms being positioned within the largest openings between the pairs of ethereal oxygens from the rim of the cavity. Moreover, such an arrangement of the methyl H atoms (Fig. 1) allows optimum access to the central benzene ring surface. Indeed, all the H atoms of the methyl group simultaneously approach the carbon atoms of the central benzene ring at an average H···C separation of 2.92 Å, which is comparable with the standard value of 2.90 Å.§ Also note that the C–H···C_{Ar} bond angle in the [**2**·CH_3CN] complex is 117°, which is a deviation from the optimal value of ~150°—a statistically preferred angle for effective C–H···π interactions.§

The observed mutual orientation of the acetonitrile within the bowl-shaped cavity of **2** in Fig. 1 leads to a rather stable complex¶ despite the absence of optimal geometric conditions for the discrete C–H···O and C–H···π interactions. This most likely arises due to the mutual cooperativity of two weak molecular forces.

Interestingly, the unsymmetrical rotamer **3**, with two faces of the central benzene ring containing 4 and 2 ethereal oxygens, respectively, shows more localized C–H···O and C–H···π interactions with a pair of complexed acetonitrile molecules. For example, the crystal structure of the [**3**·2CH_3CN] complex consists of *three* symmetrically-independent but structurally similar molecular complexes. As shown in Fig. 2, unsymmetrical complex **3** interacts with *two* acetonitrile molecules above and below the plane of the central benzene ring to produce a 2 : 1 molecular complex.

The mutual orientation of the two acetonitrile molecules relative to the central benzene ring is surprisingly invariable in all three independent molecules—with one H–C–H plane singularly perpendicular (within just 2°) to the plane of the central benzene ring. Such an orientation allows the H atoms to effectively interact with the central benzene ring *via* C–H···π bonding, whereas the remaining H atoms are chiefly involved in C–H···O interactions. The acetonitrile molecule on the face of the benzene ring containing four ethereal oxygens shows that the H atoms facing the benzene ring have an average H···O distance of 2.45 Å and a C–H···O angle of 156°, while the remaining H atom lies at an average H···C distance of 2.67 Å and a C–H···C angle of 151°. On the opposite side of the benzene ring, having just two ethereal oxygens, the observed H···O distance is longer, 2.60 Å, with a C–H···O angle of 157°, whereas the C–H···C_{Ar} interactions across the ring are similar, *i.e.* 2.66 Å and 157°, respectively.

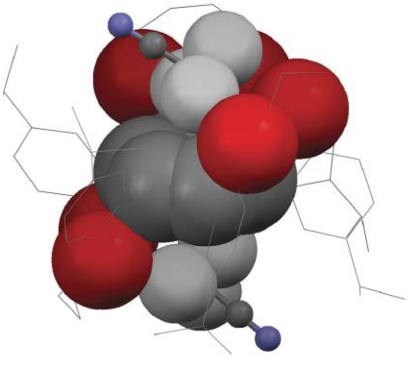

Fig. 2 A partial space-filling representation of the [**3**·2CH_3CN] complex showing the binding of two acetonitrile molecules to **3**.

It should be noted that the observed geometrical parameters are optimal for effective (individualized) C–H···O and C–H···π interactions in the [**3**·2CH_3CN] complex, as opposed to the geometrical parameters observed for the interaction of acetonitrile with symmetrical rotamer **2** (Fig. 1). It is believed that the symmetrical juxtaposition of the acetonitrile molecule in rotamer **2**, containing all the ethereal oxygens on one face, arises due to an effective synergy between C–H···O and C–H···π forces, despite less than optimal geometric conditions for the discrete C–H···O and C–H···π interactions.§

These findings suggest that the synergy of various weak molecular forces can play an important role in designing molecular receptors for the effective binding of different guests for practical applications. The construction of new receptors based on the molecular motifs presented herein is being actively pursued.

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Notes and references

‡ *Crystal structure data for [**2**·CH_3CN].* A suitable crystal (0.49 × 0.37 × 0.21 mm) of [**2**·CH_3CN] was obtained from a mixture of dichloromethane–acetonitrile solution at 22 °C. MW = 1108.97, $C_{75}H_{88.50}N_{1.50}O_{6.13}$, triclinic, space group *P*-1, $a = 14.1227(6)$, $b = 216227(10)$, $c = 23.5476(10)$ Å, $\alpha = 107.8180(10)$, $\beta = 92.4520(10)$, $\gamma = 102.2070(10)°$, $D_c = 1.108$ Mg m^{-3}, $V = 6646.3(5)$ Å^3, $Z = 4$. The total number of reflections measured were 73492, of which 27031 reflections were symmetrically non-equivalent (R(int) = 0.0259). Final residuals were $R1 = 0.0584$ and w$R2 = 0.1561$ for 27031 reflections with $I > 2\sigma(I)$. Also note that the two isopropyl groups in one of the molecules are rotationally disordered over 2 and 3 positions, respectively, and were refined with appropriate geometrical restrains. CCDC 647363.

*Crystal structure data for [**3**·2CH_3CN].* A suitable crystal (0.33 × 0.14 × 0.09 mm^3) of [**3**·2CH_3CN] was obtained from a mixture of dichloromethane–acetonitrile solution at 22 °C. MW = 1127.72, $C_{75.76}H_{89.68}Cl_{0.16}N_{1.84}O_6$, monoclinic, space group $P2_1/n$, $a = 11.1865(6)$, $b = 40.7401(19)$, $c = 42.484(2)$ Å, $\alpha = 90$, $\beta = 95.9670(10)$, $\gamma = 90°$, $D_c = 1.167$ Mg m^{-3}, $V = 19256.5(17)$ Å^3, $Z = 12$. The total number of reflections measured were 89746, of which 27724 reflections were symmetrically non-equivalent (R(int) = 0.0741). Final residuals were $R1 = 0.0635$ and w$R2 = 0.1415$ for 27724 reflections with $I > 2\sigma(I)$. Also note that in the second and third symmetrically-independent units of the molecular complex, acetonitrile molecules are partially substituted with dichloromethane molecules. They were refined with a geometry restrained to be the same as that of the unaffected acetonitrile molecules from the first unit. CCDC 647364. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707237f

§ Statistical analysis of C–H···O intermolecular interactions between acetonitrile molecules and ethereal oxygens in various reported crystal structures (based on 83 structures from the Cambridge Structural Database) has revealed that 224 prospective H···O contacts are shorter than 3.0 Å, 116 contacts are shorter than the van der Waals separation (2.7 Å), and there are 30 contacts shorter than 2.4 Å. These contacts show strong correlation with the corresponding C–H···O angles, *i.e.* the shorter the C–H···O distance the more linear (close to 180°) is the angle. For example, the shortest contacts only have angle variations between 140 and 180°. There are larger geometrical variations in C–H···π intermolecular interactions between acetonitrile molecules and benzene rings in various crystal structures. 2328 prospective H···C contacts shorter than 3.2 Å were found in 418 structures. Furthermore, 859 of these contacts are shorter than the van der Waals separation (*i.e.* 2.9 Å), whereas 72 of them are shorter than 2.6 Å. These contacts exhibit a strong correlation with the corresponding C–H···C angle, similar to that observed for C–H···O interactions. For the purposes of a uniform comparison, all C–H bonds in acetonitrile molecules were normalized throughout the search to a standard neutronographic value of 1.083 Å

¶ It is noteworthy that an exposure of a solution of **2** in $CDCl_3$ to ~10–20 equiv. acetonitrile at 22 °C showed considerable shifts of the aromatic ^1H NMR signals. However, it could not be ruled out that these changes in chemical shift occurred due to the change in solvent polarity. The crystallization of the molecular complexes of **1** and **2** is being pursued with a variety of other guests such as nitromethane, toluene, methanol, ammonium cation, *etc.*, and will be reported in due course.

1 (*a*) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999; (*b*) G. R. Desiraju, *Chem. Commun.*, 2005, 2995; (*c*) M. Nishio, M. Hirota and Y. Umezawa, *The CH/π Interaction. Evidence, Nature, and Consequences*, Wiley-VCH, New York, 1998.

2 (*a*) G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565 and references cited therein; (*b*) C. A. Hunter, *Angew. Chem., Int. Ed.*, 2004, **43**, 5310; (*c*) O. Takahashi, Y. Kohno, S. Iwasaki, K. Saito, M. Iwaoka, S. Tomoda, Y. Umezawa, S. Tsuboyama and M. Nishio, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 2421; (*d*) M. Nishio, *CrystEngComm*, 2004, **6**, 130.

3 (*a*) M. Nishio, *Tetrahedron*, 2005, **61**, 6923 and references cited therein; (*b*) W. B. Jennings, B. M. Farrell and J. F. Malone, *J. Org. Chem.*, 2006, **71**, 2277; (*c*) O. Takahashi, K. Saito, Y. Kohno, H. Suezawa, S. Ishihara and M. Nishio, *New J. Chem.*, 2004, **28**, 355.

4 R. Shukla, S. V. Lindeman and R. Rathore, *J. Org. Chem.*, 2006, **71**, 6124.

5 (*a*) R. Shukla, S. V. Lindeman and R. Rathore, *J. Am. Chem. Soc.*, 2006, **128**, 5328; (*b*) R. Shukla, S. V. Lindeman and R. Rathore, *Org. Lett.*, 2007, **9**, 1291.

6 H. Pepermans, R. Willem, M. Gielen and C. Hoogzand, *J. Org. Chem.*, 1986, **51**, 301.

7 R. D. Rogers, P. D. Richards and E. J. Voss, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1988, **6**, 65.

8 A. N. Chekhlov, A. I. Yurtanov and I. V. Martynov, *Russ. Chem. Bull.*, 1987, 1198 and references therein.

9 The standard van der Waals separations for H···O (2.72 Å) and H···C (2.92 Å) are given according to: A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.