Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Chopra, Naveen , Hardi, Michaele J. and Raston, Colin L.(2000) 'Discovery of a Novel C_{60} Receptor Based on Substituted Anthracene', Supramolecular Chemistry, 11: 4, 275 — 278

To link to this Article: DOI: 10.1080/10610270008049138

URL: http://dx.doi.org/10.1080/10610270008049138

SUPRAMOLECULAR CHEMISTRY, Vol. 11, pp. 275–278
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Discovery of a Novel C_{60} Receptor Based on Substituted Anthracene

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(Received 26 July 1999)

Anthracene diaryl bromide was prepared *via* the acid catalyzed condensation of veratrole with *p*-bromobenzaldehyde. Mixing of toluene solutions of anthracene diaryl bromide and C_{60} fullerene led to the formation of a 1:1 solid state complex. Evidence for the complex is based on microanalysis and FTIR. A crystal structure of the anthracene diaryl bromide is presented and a dimeric butterfly structure has been proposed for the supramolecular species in solution.

Keywords: Anthracenes, fullerenes, host-guest chemistry, supramolecular chemistry

INTRODUCTION

Cyclotriveratrylene (CTV) **1** is a bowl shaped container molecule derived from the acid catalyzed condensation of veratrole with formaldehyde [1]. The shallow cavity of **1** allows it to host globular molecules such as C_{60} and *o*-carborane, forming discrete "ball and socket" complexes such as **1** C_{60} [2]. We endeavoured to synthesize substituted CTV derivatives bearing functional groups on the methylene carbon centres. This would provide a means of coupling CTV molecules together to create a divergent receptor capable of multiple guest inclusion (Fig. 1).

RESULTS AND DISCUSSION

Reaction of veratrole with *p*-bromobenzaldehyde in sulfuric acid solution led to the formation of 2,3,6,7-tetramethoxy-9,10-di-(4-bromophenyl) anthracene **2** (hereafter referred to as anthracene **2**) in 19% yield [3–5] (Scheme 1).

Crystals of anthracene **2** were grown from toluene solution as a 1:1 toluene solvate, and an X-ray crystal structure was obtained in the triclinic space group $P\bar{1}$ [6]. The anthracene molecule lies over an inversion centre and the anthracene core is flat with a mean deviation of 0.02 Å from the plane. The bromophenyl groups are at close to right angles to the anthracene plane, with an angle of 95.2° between planes (Fig. 2). Solvent toluene is disordered over two positions and shows no close contacts to the anthracene molecule. There is no evidence of face-to-face or edge-to-face π interactions between

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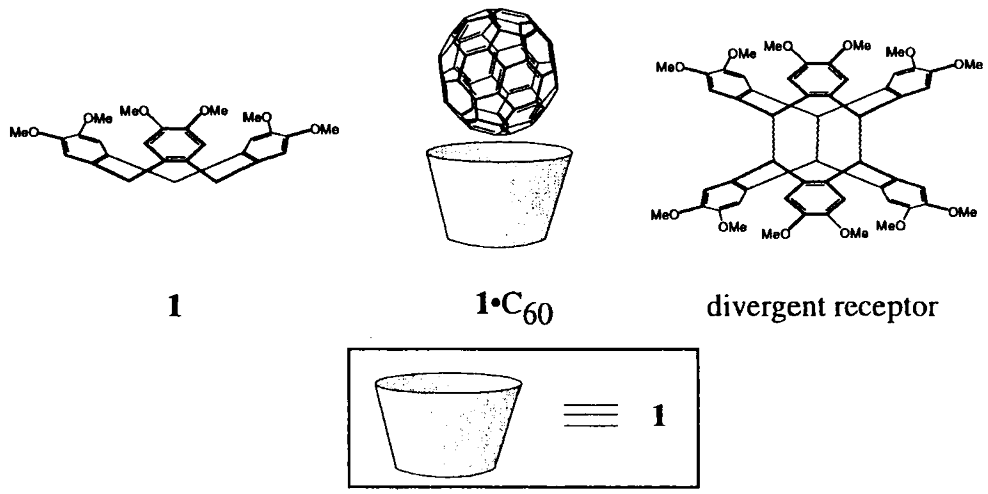
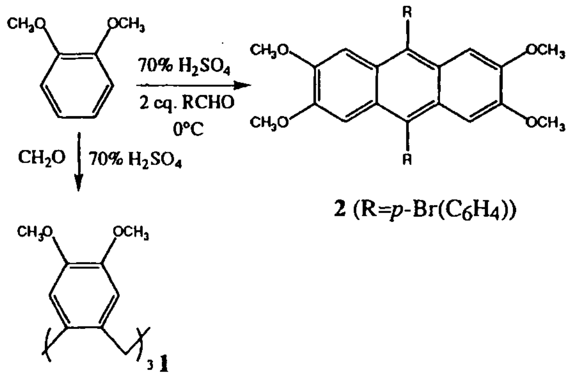


FIGURE 1 Molecular receptors.



SCHEME 1

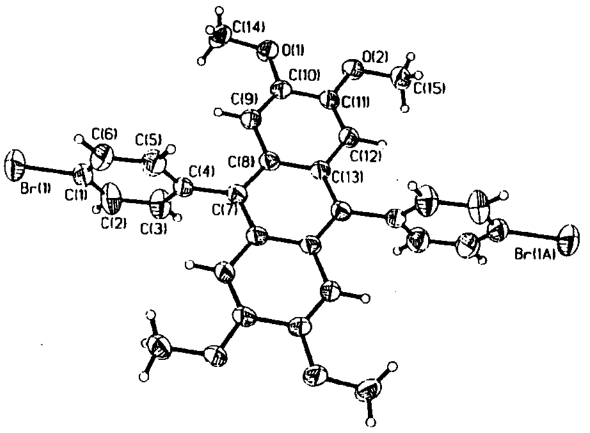


FIGURE 2 ORTEP diagram of 2. Ellipsoids are shown at 50% probability level.

molecules of 2 in the crystal lattice. The bond lengths and angles show no unusual features.

The supramolecular chemistry of anthracene 2 was probed by performing complexation experiments with C_{60} in toluene [7]. Anthracene derivatives have been previously shown to form Diels-Alder adducts with C_{60} [8]. Mixing of toluene solutions of anthracene 2 and C_{60} fullerene in a 4:1 ratio led to discharge of the magenta solution and the formation of a shiny black-magenta solid. Using ratios of anthracene 2 and C_{60} fullerene of less than 4:1 failed to form any solid complex, either crystallizing from solution, or on evaporation to dryness. FTIR analysis of the black-magenta solid revealed the superposition of fullerene and anthracene absorption bands, confirming that the solid contained both anthracene 2 and fullerene. Microanalysis of the solid was consistent with a 1:1 complex. Suspension of the powder in $CHCl_3$ destroyed the complex, yielding free anthracene 2 and fullerene components, thus confirming that the complex is noncovalent in nature; this was also borne out in the ^1H and ^{13}C NMR spectroscopy, as only free anthracene 2 was observed. Furthermore, an ESMS of the complex revealed only the individual anthracene and fullerene components.

Interestingly, when the ^1H NMR spectrum of anthracene **2** in toluene-d_8 was measured after several minutes time, a second set of signals was observed; these new signals were assigned to anthracene dimer **3**, a butterfly-shaped compound [9]. The ^1H NMR spectrum of anthracene **2** in toluene displays a pair of doublets at 7.49 and 7.15 ppm for the aryl protons of the *p*-bromophenyl substituent, a singlet at 6.87 ppm for the aryl protons, and a singlet at 3.31 for the methoxy protons. Anthracene dimer **3** has an AB quartet centred at 7.44 ppm, a singlet at 6.62 ppm, and a singlet at 3.24 ppm. The ^{13}C NMR also revealed two sets of signals. The most notable chemical shift changes were the 3.2 ppm shift (from 126.8 to 130.0 ppm) and the 3.4 ppm shift (from 140.1 to 143.5 ppm); either change would be consistent with a change in hybridization of the C-9 and C-10 carbons from sp^2 in anthracene **2** to sp^3 in anthracene dimer **3**. Attempts to isolate anthracene dimer **3** by chromatography were unsuccessful, only anthracene **2** was isolated; hence the dimer formation is reversible.

The ^1H NMR spectrum of the supramolecular complex in toluene revealed the presence of only anthracene **2**. However, when the same sample was rerun 48 hours later, only signals corresponding to the anthracene dimer **3** were observed. In contrast, a ^1H NMR spectrum of anthracene **2** in toluene after standing for 48 hours revealed a mixture of the two products **2** and **3**; after 20 days interconversion was still incomplete (Fig. 2). It is conceivable that C_{60} acts as a sensitizer thereby facilitating the dimerization of anthracene **2** to form anthracene dimer **3**. Moreover, dimer **3** possesses the gentle curvature to embrace a C_{60} molecule at both ends, which is further augmented by the outward directed *p*-bromophenyl groups (Fig. 3). These van der Waals interactions between the fullerene and the arene units of the dimer may be at play in driving the equilibrium towards formation of anthracene dimer **3**. Currently, attempts to grow crystals of the supramolecular complex suitable for X-ray crystallography are in progress.

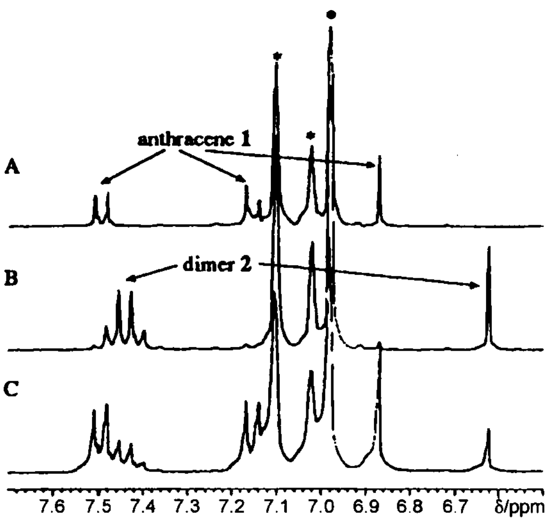
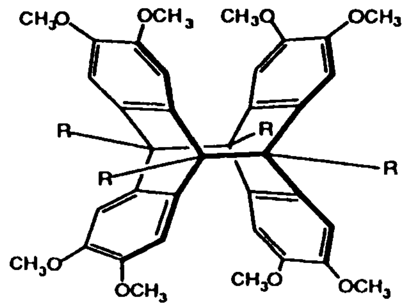


FIGURE 3 300 MHz ^1H NMR spectra (toluene-d_8) of (A) anthracene **2**; (B) supramolecular complex after 2 days; (C) anthracene **2** after 20 days. * denotes residual toluene in toluene-d_8.



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Acknowledgement

The authors wish to acknowledge the Australian Research Council for support of this work.

References and Notes

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[3] The syntheses of similar anthracene derivatives have been documented earlier, see (a) Müller, A., Raltschewa, M. and Papp, M. (1942). *Chem. Ber.*, **75**, 692 (R = Et); (b) Aubry, J. M., Schmitz, C., Rigaudy, J. and Cuong, N. K. (1983). *Tetrahedron*, **39**, 623 (R = Ph).

[4] Anthracene-crown ether species endowed with aliphatic groups have also been previously reported in the literature, see Ostaszewski, R. (1998). *Tetrahedron*, **54**, 6897.

[5] **Synthesis and Selected Physical Data**

Anthracene 2 **(R = *p*-bromophenyl): Typical Experimental Procedure:** To an ice-cold solution of 70% sulfuric acid (100 ml, degassed with N_2) and veratrole (2.0 ml, 16 mmol) was added 6.0 g of *p*-bromobenzaldehyde (32 mmol, 2 eq.) over 1 hour's time *via* a side-arm, while maintaining the reaction at 0°C. An intense red colour was observed as the aldehyde was added. Stirring was continued overnight, and the reaction was allowed to warm to room temperature. 100 ml of MeOH was added to the reaction flask, sonicated, and filtered, giving an off-white residue. The solid was chromatographed on silica gel using 1 : 1 CH_2Cl_2 : hexanes as eluent and the final product was recrystallized from CH_2Cl_2 : hexanes yielding 958 mg (1.57 mmol, 19%) of anthracene **2**. The product was unstable in chloroform, and decomposition was observed after 48 hours on standing in solution. ^{1}H NMR ($CDCl_3$) δ 7.73 (4H, d, J = 8.4 Hz, ArH), 7.34 (4H, d, J = 8.4 Hz, ArH), 6.73 (4H, s, ArH), 3.74 (12H, s, $ArOCH_3$); (toluene-d_8) δ 7.49 (4H, d, J = 8.4 Hz, ArH), 7.15 (4H, d, J = 8.4 Hz, ArH), 6.87 (4H, s, ArH), 3.31 (12H, s, $ArOCH_3$); 13C NMR ($CDCl_3$) δ 149.0, 138.6, 132.6, 131.9, 131.7, 125.6, 121.6, 103.5, 55.6; (toluene-d_8) δ 150.8, 140.1, 133.7, 132.7, 132.4, 126.8, 122.3, 104.6, 55.4; FTIR (KBr) ν 1636, 1530, 1498, 1460, 1433, 1241, 1207, 1124, 1041, 1013, 849, 755, 583 cm^{-1}.

Anthracene 2 · C_{60} complex: To 20 ml of toluene were added 20 mg of C_{60} (1.4 mM) followed by sonication until dissolution was complete (15 minutes). The magenta solution was then filtered to remove any traces of undissolved C_{60}, and 4 molar equivalents of anthracene host **2** were added. After sonication and gentle warming, the solution was filtered again, and allowed to stand in a vial. Precipitate formation occurred after a week, and the complex was isolated *via* vacuum filtration. FTIR (KBr) ν 1633, 1527, 1491, 1458, 1429, 1401, 1238, 1204, 1181, 1122, 1038, 1012, 843, 753, 582, 527 cm^{-1} Anal. Calcd. for $C_{30}H_{24}O_4Br_4 \cdot C_{60}$: C, 81.34; H, 1.82; Br, 12.02. Found: C, 81.02; H, 1.98.

Anthracene Dimer 3 (not isolated): ^{1}H NMR (toluene-d_8) δ 7.44 (16H, abq, J = 8.7 Hz, ArH), 6.62 (8H, s, ArH), 3.24 (24H, s, $ArOCH_3$); ^{13}C NMR (toluene-d_8) δ 56.3, 109.7, 123.2, 130.0, 132.2, 134.0, 134.5, 143.5, 143.5, 149.7.

[6] **X-ray structure of 2 · C_6H_8**: Data were collected at 180(1) K on an Enraf-Nonius KappaCCD single crystal diffractometer with Mo$K\alpha$ radiation (λ = 0.70173 Å). $C_{18.50}H_{16}BrO_2$, Mr = 350.22, triclinic, $P\bar{1}$, a = 7.8864(2), b = 9.1699(4), c = 11.6985(5) Å, α = 73.034(5), β = 85.665(5), γ = 76.879(5)°, U = 788.02(5) Å^3, Z = 2, crystal dimensions 0.30 × 0.20 × 0.15 mm, 6409 data collected, 2659 unique (R_{int} = 0.03), 256 parameters, R_1 = 0.0420 ($I > 2\sigma(I)$), wR_2 = 0.1112 (all data), S = 1.100. Structure was solved by direct methods and refined by full matrix least squares on F^2 (SHELXTL). All nonhydrogen atoms were refined anisotropically and hydrogens on **2** were fully refined. Hydrogens on the disordered toluene were not included.

[7] Leading references on Diels-Alder adducts of C_{60} and anthracene. (a) Lamparth, I., Maichle-Mössmer, C. and Hirsch, A. (1995). *Angew. Chem. Int. Ed. Engl.*, **34**, 1607. (reversible Diels-Alder adducts of anthracene : C_{60}); (b) Mikami, K., Matsumoto, S., Tonoi, T., Okubo, Y., Suenobu, T. and Fukuzumi, S. (1998). *Tetrahedron Lett.*, **39**, 3733. (solid state photochemistry of C_{60} and anthracenes).

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