SHORT PAPER

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Synthesis and molecular structure of a head-to-tail [4+4] dimer of a hexa-substituted anthracene†

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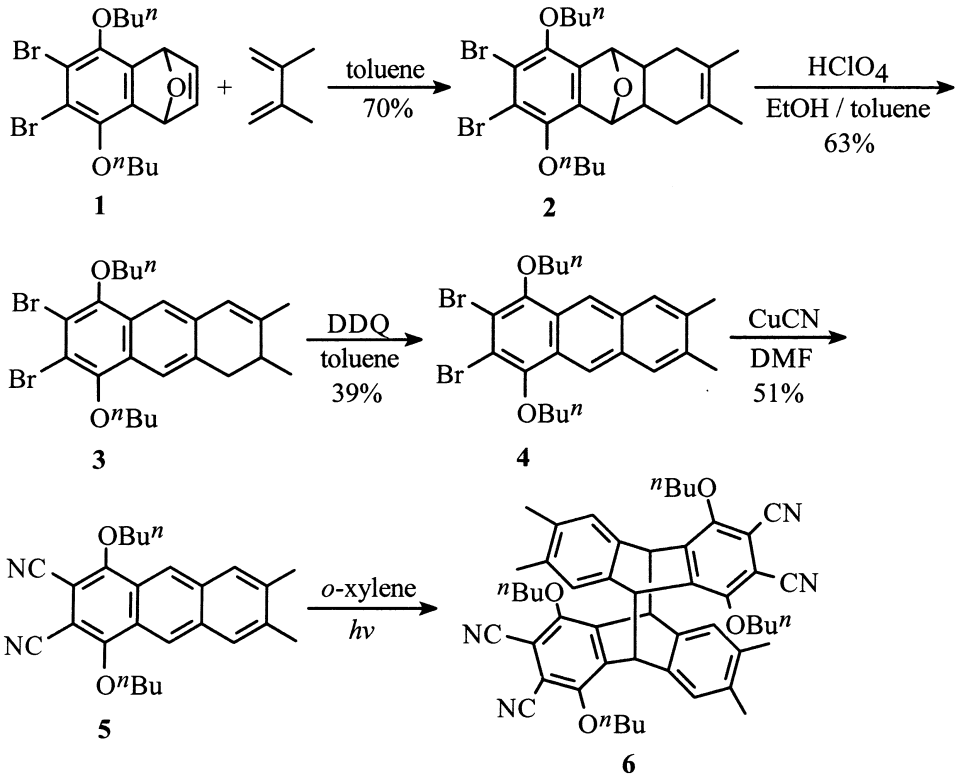
Two hexa-substituted anthracenes have been synthesised; the molecular structure of a [4+4] head-to-tail anthracene dimer has also been determined by X-ray diffraction analysis.

Keywords: anthracenes, Diels–Alder reactions, cycloaddition reactions, X-ray crystal structures

Anthracene and its derivatives are very common polycyclic aromatic compounds.[1] Owing to the ease of modification and strong fluorescence emission, these compounds have been widely used as luminophores in optically based chemosensors for a wide range of metal ions,[2] anions,[2a] diols,[3] glucose,[4] nucleotides,[2e] vitamin B13[2e] and saxitoxin[5] (that is responsible for some of the red tides). The use of these compounds as photo-responsive materials for data storage and optical switching[6] and as blue-light-emitting scaffolds in light-emitting devices[7] has also been investigated. Numerous anthracenes substituted with different moieties have been prepared, but it is noted that most of the them are functionalised at the 9- and/or 10-positions, presumably due to the ready availability of the corresponding precursors such as 9-anthraldehyde, 9-anthracenecarboxylic acid and 9,10-dihaloanthracenes, *etc.* Anthracene derivatives substituted at other positions, in particular those that are highly substituted remain relatively rare.[8] We describe herein a useful procedure to prepare hexa-substituted anthracenes, together with the molecular structure of a [4+4] head-to-tail dimeric adduct.

The synthetic route used to prepare hexa-substituted anthracenes is shown in Scheme 1. According to the procedure reported by Hart and co-workers,[9] the epoxydihydronaphthalene **1** was prepared from hydroquinone in three steps, involving a Diels–Alder reaction of benzyne, generated *in situ*, and furan as a key step. Having a dienophilic moiety, compound **1** underwent a further Diels-Alder reaction with 2,3-dimethyl-1,3-butadiene to give the adduct **2**. Upon treatment with $HClO_4$ in EtOH,[10] compound **2** was dehydrated to give 1,2-dihydroanthracene **3** instead of the expected 1,4-dihydroanthracene counterpart. It seemed that the former is



1 **2** **3** **4** **5** **6**

Scheme 1
Synthetic pathway for anthracene derivatives.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

thermodynamically more stable as a result of the higher conjugation. Treatment of **3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) led to dehydro-aromatisation giving the anthracene **4**. In the absence of the two *n*-butoxy substituents, the dehydrated product analogous to **3**, namely 6,7-dibromo-2,3-dimethyl-1,2-dihydroanthracene, could also be prepared by a similar procedure starting from 1,2,4,5-tetrabromobenzene.[11] However, upon treatment with DDQ, the resulting product was found to have a poor solubility in most organic solvents which hindered the isolation and purification processes. The additional *n*-butoxy groups are thus essential for the preparation and further modification of the anthracene derivatives.

The two bromo groups of compound **4** could be functionalised. Treatment with CuCN resulted in the formation of the dicyanoanthracene **5** in moderate yield (Scheme 1). This compound is of particular interest because of its electronically push (the methyl and *n*-butoxy groups) and pull (the cyano groups) nature and the fact that it can serve as a precursor for the highly conjugated 2,3-anthracocyanines, which are phthalocyanine analogues having a more extended π-system.[12] Compound **5** was purified by column chromatography and characterised by various spectroscopic methods.

Attempts to further purify this compound by recrystallisation from *o*-xylene led to the appearance of yellow needle-shaped crystals, which were suitable for X-ray diffraction analysis. Interestingly, the compound was found to be a [4+4] cycloadduct of **5** formed by sunlight-induced dimerisation. The dimer **6** crystallises in the triclinic system with two molecules per unit cell. The molecular structure, which contains an inversion centre relating the two halves of the molecule is given in Fig. 1. It can be seen that the two anthracene rings dimerise in a head-to-tail fashion. As a result of repulsion between the aromatic rings, the C5–C10′ bond is relatively long [1.618 (4) Å], compared to a C(sp^3)–C(sp^3) distance of 1.54 Å. The bond distances and angles for the dianthracene core of this compound (Table 1) appear to be normal and comparable with those of the unsubstituted analogue,[13] showing that the additional substituents do not induce substantial changes on the structure. The occurrence of dimerisation was also confirmed by ^{1}H NMR spectroscopy. The two aromatic signals at δ 8.62 and 7.85 for **6** were shifted upfield to δ 5.08 and 6.98 upon dimerisation.

In summary, we have reported the preparation of two highly substituted anthracenes. It is envisaged that this approach can be modified readily using different reacting components (*e.g.* furan and butadiene), and extended by further reactions of anthracenes with appropriate functionalities (*e.g.* bromo and cyano groups) to give a wide range of anthracenes for various purposes.

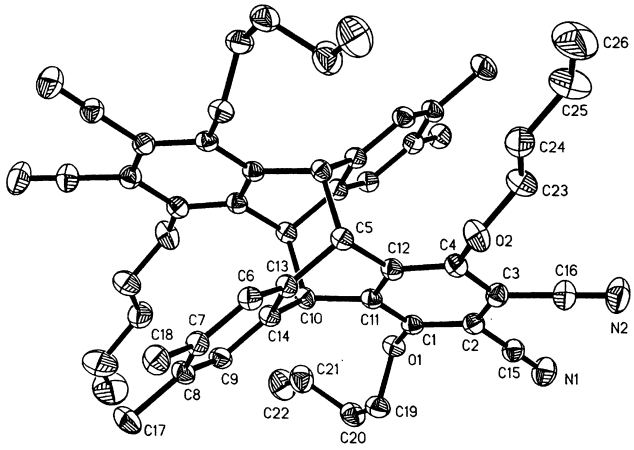

Fig. 1 Molecular structure of dimer **6** showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

Experimental

Experimental details regarding the purification of solvents and reagents, and spectroscopic measurements were described elsewhere.[14]

6,7-Dibromo-5,8-di-n-butoxy-9,10-epoxy-2,3-dimethyl-1,4,4a,9,9a,10-hexahydroanthracene (**2**): A mixture of **1** (10 g, 22 mmol) and 2,3-dimethyl-1,3-butadiene (15 ml, 0.13 mol) in toluene (300 ml) was refluxed for 20 h. After removing the volatiles *in vacuo*, the crude product was purified by column chromatography using hexane / ethyl acetate (9:1) as eluent (8.3 g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.13 (s, 2 H, OCH), 3.98 (t, J = 6.6 Hz, 4 H, OCH_2), 1.93–2.24 (m, 6 H, CH and CH_2), 1.74–1.83 (m, 4 H, CH_2), 1.69 (s, 6 H, Me), 1.48–1.60 (m, 4 H, CH_2), 0.99 (t, J = 7.5 Hz, 6 H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 145.3, 137.4, 127.2, 118.5, 83.2, 73.7, 42.4, 34.1, 32.0, 19.2, 18.8, 13.8. MS (EI): *m/z* 528 (M^+). Anal. Calc. for $C_{24}H_{32}Br_2O_3$: C, 54.56; H, 6.11. Found: C, 54.60; H, 6.33.

6,7-Dibromo-5,8-di-n-butoxy-2,3-dimethyl-1,2-dihydroanthracene (**3**): Perchloric acid (70%, 50 ml) in ethanol (70 ml) was added dropwise to a mixture of endoxide **2** (9.4 g, 17.8 mmol) in toluene (300 ml). The mixture was refluxed for 8 h, then allowed to cool to room temperature. The resulting brown mixture was extracted with CH_2Cl_2 (2 × 100 ml) and the combined extracts was washed with water (150 ml) and dried over anhydrous $CaCl_2$. After removing the volatiles *in vacuo*, the residue was subjected to column chromatography using hexane / $CHCl_3$ (7:3) as eluent (5.69 g, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (s, 1 H, ArH), 7.57 (s, 1 H, ArH), 6.38 (s, 1 H, ArH), 4.02–4.08 (m, 4 H, OCH_2), 3.09–3.21 (m, 1 H, CH_2), 2.72–2.82 (m, 1 H, CH_2), 2.36–2.48 (m, 1 H, CH), 1.88–1.98 (m, 7 H, CH_2 and Me), 1.61–1.70 (m, 4 H, CH_2), 1.02–1.09 (m, 9 H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 150.0, 149.7, 145.7, 134.4, 134.2, 128.0, 127.4, 122.2, 120.7, 117.3, 115.4, 115.2, 73.9 (two overlapping signals), 36.6, 33.5, 32.3 (two overlapping signals), 22.0, 19.3 (two overlapping signals), 17.6, 14.0 (two overlapping signals). MS (EI): *m/z* 510 (M^+). Anal. Calc. for $C_{24}H_{30}Br_2O_2$: C, 56.49; H, 5.93. Found: C, 57.02; H, 6.03.

Table 1 Bond lengths (Å) and angles (°) for the dianthracene core of **6**

C5–C10′	1.618 (4)	C10–C14	1.512 (3)
C5–C12	1.514 (4)	C10–C11	1.508 (4)
C5–C13	1.514 (4)	C11–C12	1.387 (4)
C13–C14	1.380 (4)		

C10′–C5–C12	111.0 (2)	C5′–C10–C11	110.6 (2)
C10′–C5–C13	112.3 (2)	C5′–C10–C14	112.3 (2)
C12–C5–C13	108.0 (2)	C11–C10–C14	107.3 (2)
C5–C12–C11	116.9 (2)	C10–C14–C13	116.9 (2)
C10–C11–C12	118.0 (2)	C5–C13–C14	118.3 (2)

2,3-Dibromo-1,4-di-n-butoxy-6,7-dimethylanthracene (**4**): A mixture of **3** (1.0 g, 2.0 mmol) and DDQ (0.9 g, 4.0 mmol) in toluene (100 ml) was refluxed under nitrogen for 8 h, then filtered while hot. The filtrate was rotary-evaporated and the residue was purified by column chromatography using hexane / $CHCl_3$ (3:2) as eluent (0.39 g, 39%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.49 (s, 2 H, ArH), 7.79 (s, 2 H, ArH), 4.14 (t, J = 6.6 Hz, 4 H, OCH_2), 2.48 (s, 6 H, Me), 2.02 (quintet, J = 7.2 Hz, 4 H, CH_2), 1.70 (sextet, J = 7.5 Hz, 4 H, CH_2), 1.08 (t, J = 7.5 Hz, 6 H, Me). MS (EI): m/z 508 (M^+). Anal. Calc. for $C_{24}H_{28}Br_2O_2$: C, 56.71; H, 5.55. Found: C, 57.70; H, 5.45.

1,4-Di-n-butoxy-2,3-dicyano-6,7-dimethylanthracene (**5**): A mixture of **4** (0.50 g, 1.0 mmol) and CuCN (0.27 g, 3.0 mmol) in *N*,*N*-dimethylformamide (DMF) (10 ml) was refluxed under nitrogen for 10 h. After being cooled to room temperature, the mixture was poured into a 35% ammonia solution, then bubbled with air for 3 h. The mixture was then filtered and the residue was washed with diethyl ether (4 × 50 ml). The combined organic portions was washed with water, dried over anhydrous $CaCl_2$, then rotary-evaporated. The residue was purified by column chromatography using hexane / $CHCl_3$ (3:7) as eluent (0.20 g, 51%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.62 (s, 2 H, ArH), 7.85 (s, 2 H, ArH), 4.53 (t, J = 6.6 Hz, 4 H, OCH_2), 2.53 (s, 6 H, Me), 2.02 (quintet, J = 6.9 Hz, 4 H, CH_2), 1.66 (sextet, J = 7.5 Hz, 4 H, CH_2), 1.07 (t, J = 7.5 Hz, 6 H, Me). MS (EI): m/z 400 (M^+). Anal. Calc. for $C_{26}H_{28}N_2O_2$: C, 77.97; H, 7.05; N, 6.99. Found: C, 77.56; H, 7.41; N, 6.57.

[4+4] Dimer of 1,4-di-n-butoxy-2,3-dicyano-6,7-dimethylanthracene (**6**): A concentrated solution of **5** in *o*-xylene was allowed to stand at room temperature in the presence of sunlight. After a few days, yellow needle-shaped crystals appeared which were collected by filtration and dried *in vacuo*. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.98 (s, 4 H, ArH), 5.08 (s, 4 H, CH), 4.26–4.39 (m, 8 H, OCH_2), 2.32 (s, 12 H, Me), 2.07–2.16 (m, 8 H, CH_2), 1.83–1.91 (m, 8 H, CH_2), 1.29–1.34 (m, 12 H, Me). Crystallographic data: $C_{52}H_{56}N_4O_4$, fw 801.00, triclinic space group $P\bar{1}$, with a = 9.247(2) Å, b = 11.385(2) Å, c = 11.565(2) Å, α = 77.54(3)°, β = 81.10(3)°, γ = 74.56(3)°, V = 1139.8(4) Å^3, and D_{calcd} = 1.167 g/cm^3 for Z = 2. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 2541 data to a conventional R value of 0.0838 (R_w = 0.2119). Crystallographic data (excluding structure factors) for this compound have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-187769. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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