Joining the rings: the preparation of 2- and 3-indenyl-triptycenes, and curious related processes

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Received 9th March 2007, Accepted 3rd May 2007
First published as an Advance Article on the web 17th May 2007
DOI: 10.1039/b703437g

The indenyltriptycenes, **1** and **2**, where the 3- or 2-indenyl, respectively, is attached at the 9-position of the triptycene, are attractive prototypes of molecular gearing systems that can also incorporate a brake. These molecules have been prepared from their respective indenylanthracenes, **3** and **4**, by the [4 + 2] cycloaddition of benzyne to the anthracene fragment, and the rotational barriers about the indenyl–triptycenyl single bonds in **1** (12 kcal mol^{-1}) and **2** (<9 kcal mol^{-1}) have been measured. The precursor anthracenes, **3** and **4**, were prepared by using palladium-catalysed coupling reactions. Unexpectedly, the Heck-type reaction of 9-bromoanthracene, **5**, with indene leads to the formation of 3-indenylanthracene **3**; moreover, this process is accompanied by a novel palladium-catalysed carbocyclisation reaction leading to the indenophenanthrylene **9**. The addition of benzyne to 9-(3-indenyl)anthracene, **3**, yields the corresponding indenyltriptycene, **1**, and, surprisingly, the anthracenyl methano-bridged phenanthrene **16**. It has been demonstrated that 2-arylindenes can act as 1,3-dienes in the [4 + 2] cycloadditions of benzyne. The products **2**, **7a**, **9** and **16** have been characterised by X-ray crystallography.

Introduction

Our zest to miniaturise everything in this world meets, unfortunately, a stern and impenetrable limit when it comes to the molecular world. That is, possibly, why nearly a generation of chemists has been involved in the design and preparation of exemplars of the ultimate microscopic machinery: molecular shuttles,[1] motors,[2] gears,[3] ratchets,[4] turnstiles[5] and even a nano-car![6] From a chemical point of view, the function of a given molecular machine involves the interconversion of several stereoisomeric forms by internal thermal molecular motion. Since the relative stability of stereoisomers can be controlled by applying a chemical, electrochemical or photochemical stimulus, the predominant configuration of the molecular machine can be controlled in solution and on the surface. Although fast thermal molecular motion provides dynamic linkage between the states of the molecular machine, it has been shown[4b] that, without the means to slow down or stop this process, the more complex functions (directional travel, sorting, *etc.*) are not attainable. Referring back to the macro-world, a machine, for example a car with no brakes, is not a marketable commodity.

In recent years, we have sought to prepare and test molecular gearing systems (Chart 1) incorporating a paddlewheel-shaped triptycene fragment ***P*** attached to the "stationary" molecular shuttle moiety ***S***.[7] The rotational barrier about the ***P***–***S*** single bond is determined in this case by the steric interactions of groups **X** at the C(1), C(8) and C(13) positions of the triptycene blades with the nearest adjacent group **Y** of the shuttle ***S***. It is anticipated that by dynamically modifying the position of the sterically demanding group **Y** it should be possible to control the rate of rotation of the triptycene moiety.

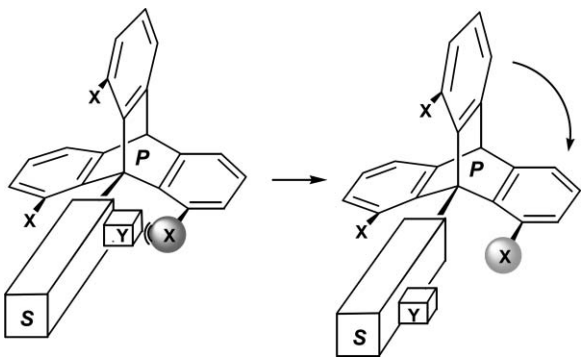

Chart 1 Molecular gearing system with brake: free rotation of the paddlewheel ***P*** is controlled by the "latch" ***Y*** of the shuttle ***S***.

An interesting approach to the construction of the shuttle ***S*** involves the introduction of a migrating metal fragment **Y** to control the rotational barrier of the paddlewheel moiety ***P***. For example, the protonation of η^5-indenyl-ML$_n$ (or deprotonation of η^6-indene-ML$_n$) complexes results in haptotropic migration of the metal between the five- and six-membered rings.[3a,8] Consequently, an indenyl-ML$_n$ unit attached to the triptycene moiety could, in principle, fulfil the desired function of a 'molecular brake'. We have previously reported the synthesis and characterisation of 9-(3-indenyl)triptycene, **1**, (Scheme 1), and also a tricarbonylchromium derivative.[7] However, the relatively high (12 kcal mol^{-1}) rotational barrier in **1**, precludes its use as a molecular brake which requires that the one of the states allows free rotation of the paddlewheel moiety. Herein, we describe convenient routes to both of the isomeric indenyl-triptycenes, **1** and **2**, and also compare their internal rotational behaviour. Moreover, we discuss several novel

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and fascinating reaction pathways that have been unveiled during the search for effective routes to couple anthracene and indene moieties.

Results and discussion

Indenyl-anthrancenes

Since the preparation of 9-(3-indenyl)triptycene, **1**, *via* the Stille coupling of 1-(tributylstannyl)indene and 9-bromoanthrancene to yield **3**, with subsequent addition of benzyne, has been described previously,[7] we chose to focus on the synthesis of the corresponding 2-indenyl-anthracene isomer, **4**. On the assumption that 9-(2-indenyl)triptycene, **2**, should likewise be preparable by the [4 + 2] cycloaddition of benzyne[9] to 9-(2-indenyl)anthracene, a straightforward route to **4** was required. Based on earlier precedents,[10] it was decided that the best approach would involve a Heck-type, palladium-catalysed reaction of indene with a 9-halo-anthracene, **5**, as depicted in Scheme 1.

It has been reported that the arylation of indene with iodoarenes leads predominantly to the formation of 2-arylindenes, and to a lesser extent 3-arylindenes.[10b] These isomeric products were characterised on the basis of their ^{1}H NMR spectra since the chemical shift of the α-methylene protons is sensitive to the position of the aryl group; specifically, in 2-arylindenes this chemical shift is typically in the range 3.7–3.9 ppm, whereas in 3-arylindenes it is ~3.4 ppm.

To provide unambiguous confirmation of the regioselectivity of the palladium-catalysed indene arylation, we ran the reaction of 1-bromo-4-iodobenzene, **6**, with indene in the presence of palladium acetate as catalyst and triethylamine as base. After separation of the products by column chromatography, the structure of the major isomer, 2-(4-bromophenyl)indene, **7a**, was established by X-ray diffractometry (Fig. 1).[11] Interestingly, the indenyl and bromophenyl rings are not coplanar; there are two independent molecules in the unit cell with quite different torsion angles

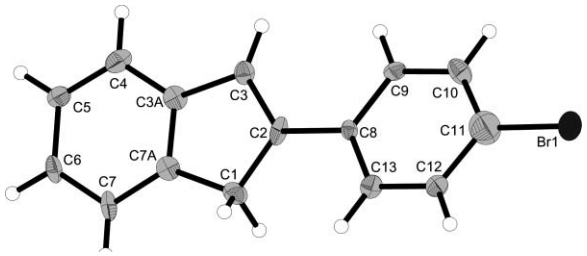


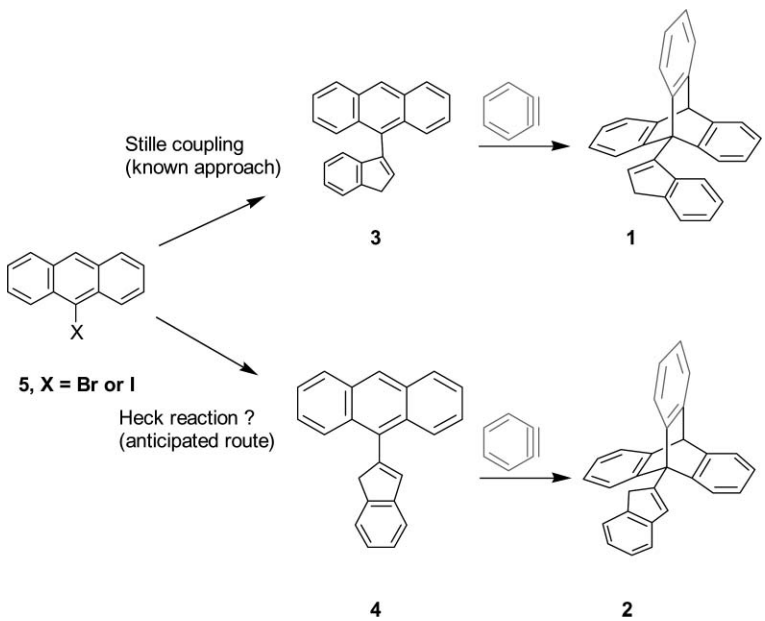
Fig. 1 Molecular structure of 2-(4-bromophenyl)indene, **7a**. Atoms are drawn with 50% ellipsoids.

−13.6° and 27.3°. X-ray crystallographic data on indenyl-arenes are sparse,[12] but it is perhaps relevant to note that the X-ray crystal structures of many biphenyls have been reported,[13] and it has been shown that not only their photophysical properties,[14] but also their biological activities,[15] are determined by this inter-planar twist angle.

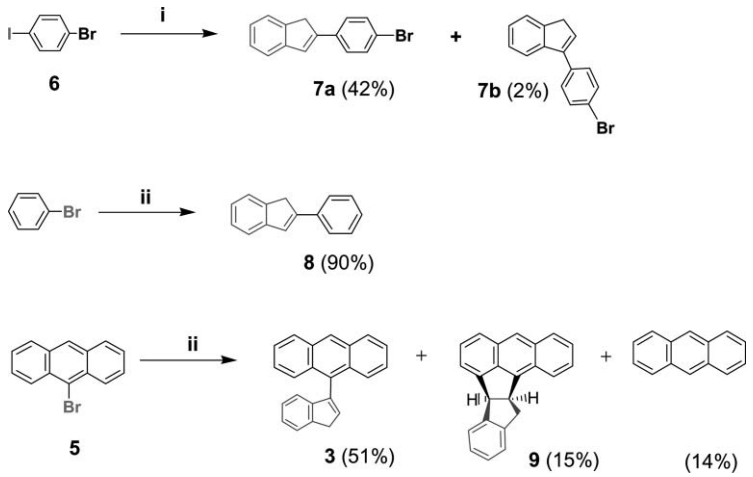
As expected, the methylene protons of **7a** resonated at 3.76 ppm, while those in the minor product, **7b**, were found at 3.5 ppm. Interestingly, 2-(4-iodophenyl)indene was not found in the reaction mixture, leading to the conclusions that (a) the arylation of indene with aromatic iodides catalysed by palladium acetate leads selectively to the formation of 2-isomers, and (b) that, as anticipated, iodoaromatic substrates are more reactive than are the corresponding bromides towards indene under the specified conditions.

Nevertheless, because of the relatively low availability of aryl iodides, we investigated the practicability of palladium-catalysed indene arylations using aryl bromides as the source of the aryl group (Scheme 2). It was found that the reaction of bromobenzene with indene in the presence of dichloro-bis(tri-*o*-tolylphosphine)palladium(II) (DMF, 100 °C, 6 h) led regiospecifically to the formation of 2-phenylindene, **8**, in high yield.

In light of the observed excellent selectivity of the palladium-catalysed arylation of indene with aryl bromides, we then ran the



Scheme 1 Proposed approaches to the isomeric triptycene molecular gearing systems.



Scheme 2 Palladium-catalysed formation of arylindenes. *Reagents and conditions*: (i) indene, $Pd(OAc)_2$, Et_3N, DMF, 100 °C; (ii) as for (i), but using $PdCl_2(o\text{-}Tol_3P)_2$.

arylation of indene with 9-bromoanthracene (Scheme 2) with the aim of preparing the desired 2-indenyl-anthracene isomer, **4**. In this case the reaction was carried out at 100 °C for 24 h, but did not proceed to completion (12% of the unreacted 9-bromoanthracene starting material, **5**, was found). Unexpectedly, while the observed chemical shift of the methylene protons of the major product was 3.87 ppm, careful scrutiny of its NMR spectrum, in combination with single-crystal X-ray diffraction measurements, indisputably proved that this product was identical to the already known 9-(3-indenyl)anthracene, **3**.[7] Moreover, and completely unexpectedly, the minor product, **9**, of the palladium-catalysed arylation of indene with **5** did not contain an indenyl substituent; however, the elemental composition of **9** matched the expected formula, $C_{23}H_{16}$, of both isomers **3** and **4**. A detailed ^1H and ^{13}C NMR examination of this material by standard 1D, 2D and NOE techniques indicated that the former indenyl fragment was now attached to the anthracene system by two newly-formed C–C bonds as the result of a palladium-catalysed annulation.[16] This assignment was subsequently confirmed by X-ray crystallography,[17] as shown in Fig. 2 which emphasises the folded nature of the molecule about the common bond between the two five-membered rings. The third product found in the reaction mixture was shown to be anthracene.

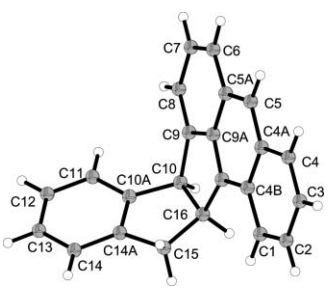


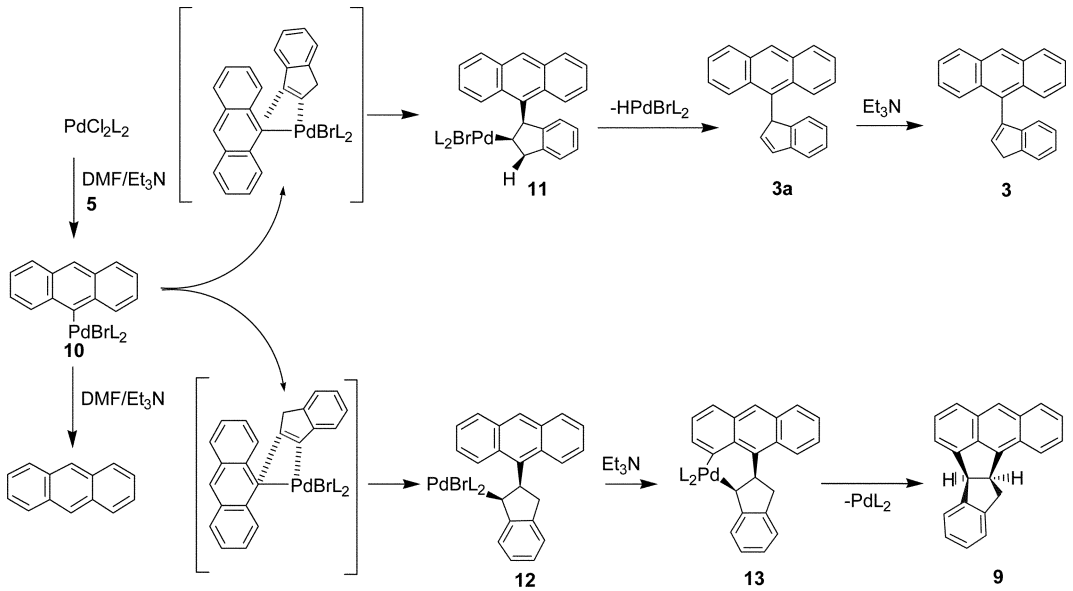
Fig. 2 Molecular structure of the indeno-dihydroaceanthrylene, **9**. Atoms are drawn with fixed radii.

Apparently, despite the precedents noted above, the Heck-type reaction of 9-bromoanthracene with indene is not a suitable route to 9-(2-indenyl)anthracene, **4**, but does provide a more convenient route to the 3-indenyl isomer, **3**. Moreover, the reaction is significantly different from other indene arylation reactions in terms of rate (*vide supra*) and selectivity, and a possible rationale for the observed results is offered in the stepwise mechanism illustrated in Scheme 3.

It is suggested that the formation of all three products proceeds *via* the key intermediate arylpalladium complex **10**.[10,16] One might postulate that this intermediate can undergo two major reactions: either (a) relatively slow insertion of indene by one of the two alternative pathways leading to the intermediates **11** and **12** (note that the addition of complex **10** across the C(2)=C(3) double bond of indene is a stereospecifically *cis*-process), or (b) base-promoted hydride reduction with DMF leading to anthracene. The formation of **11** is followed by a relatively fast *cis*-elimination of $HPdL_2Br$ giving rise initially to 9-(1-indenyl)anthracene, **3a**, and subsequent, possibly catalytic, isomerisation of **3a** into **3**. In contrast, lack of a suitably positioned hydrogen in intermediate **12** precludes the *cis*-elimination of $HPdL_2Br$. Instead, this complex undergoes an intramolecular palladation leading to the six-membered palladacycle, **13**, which subsequently undergoes reductive elimination of the product **9**, in which the protons at the junction of the two five-membered rings are *cis* to each other. We note that, although intramolecular aromatic palladation and the formation of palladacycles is well documented,[18] there are very few previous cases leading to the construction of a fused aromatic and aliphatic ring system by this mechanism.[19]

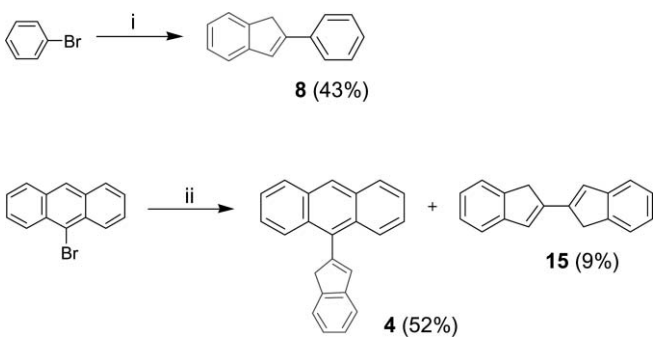
Having established that the Heck-type reaction of indene with 9-bromoanthracene was a convenient route to the 3-indenyl-anthracene, **3**, rather than to the desired 2-indenyl isomer, **4**, we chose to try a palladium-catalysed Suzuki-type cross-coupling reaction. Since it has been shown previously that 2-indenylboronic acid, **14**, and aryl iodides react to give cross-coupling products,[20] we decided to use this approach for the preparation of 9-(2-indenyl)anthracene.

A test experiment using bromobenzene as the substrate and dichloro-bis(triphenylphosphine)palladium(II), $PdCl_2(Ph_3P)_2$, as the catalyst precursor, verified that the boronic acid, **14**, was a useful coupling reagent. The reaction was carried out at 75 °C in ethanol–toluene in the presence of Na_2CO_3 as base. The analogous reaction of 9-bromoanthracene with **14** was run, but instead using dichloro-bis(diphenylphosphinoferrocene)palladium(II),



Scheme 3 Possible mechanistic routes for the indenylation of 9-bromoanthracene, **5** (L is a phosphine ligand).

(dppf)$PdCl_2$, as the catalyst. Gratifyingly, this led to the desired 9-(2-indenyl)anthracene, **4**, in 52% yield (Scheme 4), and the product was readily separated from unreacted **5**, and co-formed 2,2′-diindenyl, **15**, by column chromatography on silica. An X-ray diffraction study of 9-(2-indenyl)anthracene, **4**, revealed that, in the solid state, it exhibits a substantial degree of interlayer packing disorder, which prevents determination of the molecular parameters.



Scheme 4 Palladium-catalysed coupling of aryl bromides with 2-indenylboronic acid (**14**). *Reaction conditions*: (i) **14**, $(Ph_3P)_2PdCl_2$ (1 mol%), ethanol–toluene, Na_2CO_3, 30 h, 75 °C. (ii) as for (i), but using (dppf)$PdCl_2$.

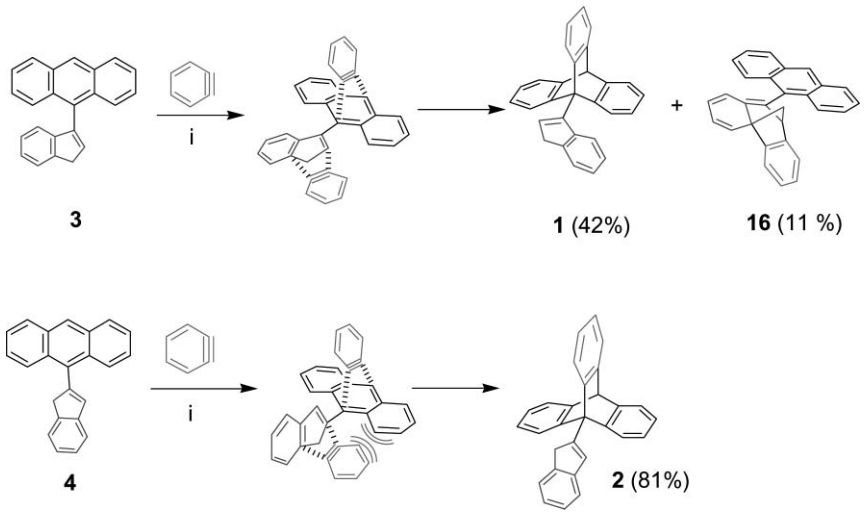
However, a simple molecular orbital calculation[21] at the extended Hückel level indicated that rotation of the indenyl fragment towards coplanarity with the anthracenyl moiety was electronically disfavoured, and indicated that the indenyl and anthracenyl rings adopt a dihedral angle of approximately 70°. Further calculations at the DFT level are planned and may provide a more quantitatively reliable and clearer rationale. Nevertheless, this finding, as discussed later, is relevant to the reactivity of the isomers in cycloaddition processes. Interestingly, as had been shown earlier, in the isomeric 9-(3-indenyl)anthracene, **3**, whose structure was well resolved, the corresponding interplanar angle was 74°.[7]

Indenyl-triptycenes

As noted above, we have previously reported the preparation of 9-(3-indenyl)triptycene, **1**, in 29% yield, by a [4 + 2] cycloaddition of *in situ* generated benzyne to 9-(3-indenyl)anthracene, **3**.[7] Since typical yields of triptycenes in reactions of this class can reach 60–70%,[9] we attempted to improve the process by varying the solvent, temperature and reagent addition rate. Thus, when 1,2-dichloroethane and 1,4-dioxane were used as the bulk- and the co-solvent, respectively, at 80 °C, addition of anthranilic acid to a mixture of **3** and excess isoamyl nitrite over a 15 minute period furnished 9-(3-indenyl)triptycene, **1**, in 42% yield, as characterised by comparison with its known NMR spectroscopic and X-ray crystallographic data (Scheme 5).[7]

Having achieved such a significant improvement in the overall yield, it was also possible to separate from the reaction mixture a previously unknown second product, **16**, apparently resulting from the [4 + 2] cycloaddition of benzyne at the C(2) and C(7a) positions of the original indenyl moiety in **3**. The identity of the product **16** was established by standard NMR techniques, and by X-ray crystallography.[22] The structure of **16** appears as Fig. 3, and reveals that, at least in the solid state, the dihedral angle between the anthracene system and the plane defined by atoms C(9), C(10) and C(10a) is 56°.

This conformation appears to be determined by multiple steric repulsion interactions of the anthracenyl hydrogens at positions C(12) and C(20) with those at C(9) and C(1), respectively, in the methano-bridged phenanthrenyl fragment. Consequently, the anthracenyl moiety in **16** is constrained, and is also twisted such that the interplanar angle between the opposite aromatic systems C(12)–C(15) and C(17)–C(20) is 9°. Accordingly, in solution ($CDCl_3$, 25 °C) all the protons and carbons of the two opposite anthracene blades are unique as a result of the rotational barrier about the C(10)–C(20B) single bond. Nuclear Overhauser measurements on molecule **16** suggested that its solid state and solution conformations were very similar. Strong NOE interactions between the protons at the C(1) and C(20)



Scheme 5 Additions of benzyne to 9-(3-indenyl)anthracene, **3**, and to 9-(2-indenyl)anthracene, **4**. *Reagents and conditions*: (i) anthranilic acid, isoamyl nitrite, CH_2ClCH_2Cl, 80 °C.

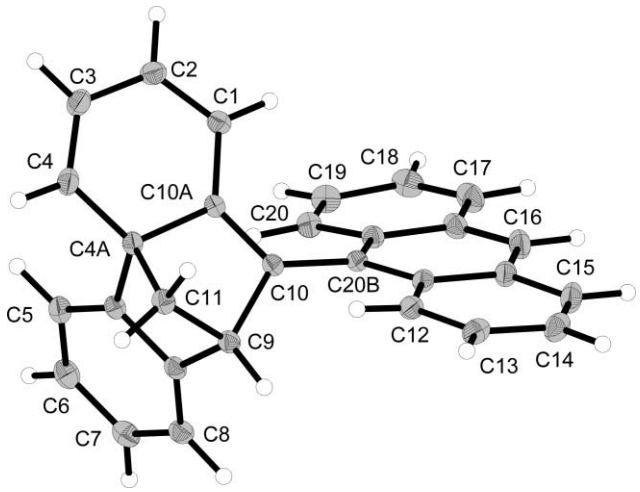
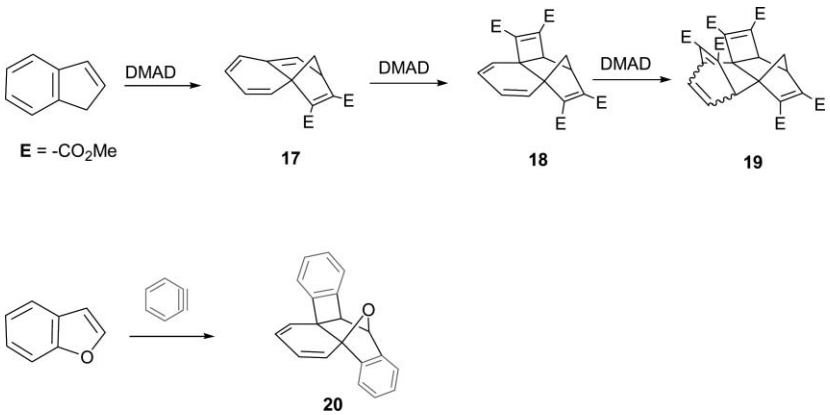


Fig. 3 Molecular structure of the Diels–Alder adduct **16**. Atoms are drawn with 50% ellipsoids.

positions were observed, and also H_{20} was significantly shielded by the nearby aromatic system, originally derived from benzyne. Furthermore, the variable-temperature ^1H and ^{13}C NMR spectra of **16** ($CDCl_2CDCl_2$, at 500 MHz and 125 MHz, respectively) over the temperature range 25–90 °C showed no significant changes, indicating slowed rotation about the C(10)–C(20B) single bond on the NMR time-scale. Thus, one can only calculate a minimum rotational barrier on the basis of the chemical shift difference between two non-coalescing signals, such as C(13) and C(19), that would have been equilibrated at 90 °C, if rotation were to have occurred. These data yield a minimum value for the rotational barrier of 18 kcal mol^{-1}, but it is undoubtedly substantially higher.

Although we are unaware of any previous reports of benzyne adding in such a fashion to indene, resulting in loss of aromaticity in the six-membered ring, the analogous reaction of dimethyl acetylenedicarboxylate (DMAD) to form **17** has been reported,[23] as in Scheme 6. Moreover, DMAD can add a second time, in a [2 + 2] process to yield **18** and, under more forcing conditions, a third time in yet another Diels–Alder reaction to produce the triple adduct **19**.[23,24] Likewise, there is a report of the double addition to benzofuran in which, according to the NMR data, the benzyne units have added to give the *anti*-isomer **20**.[25]

We have shown that benzyne can undergo [4 + 2] cycloaddition to either the anthracenyl or indenyl fragments of 9-(3-indenyl)anthracene, **3**, to form the triptycene, **1**, or the previously



Scheme 6 Cycloaddition reactions to indene and benzofuran.

unknown adduct, **16**, respectively. In contrast, the reaction of benzyne with 9-(2-indenyl)anthracene, **4**, furnished the desired 9-(2-indenyl)triptycene, **2**, in excellent yield (81%). The molecular structure of **2**, as determined X-ray crystallography,[26] appears in Fig. 4; the molecule has a crystallographically imposed mirror plane passing through one of the triptycene blades and bisecting the indenyl moiety. This gives rise to a minor disorder since the CH and CH_2 units can be either side of the five-membered ring which straddles this pseudo-mirror plane. The C(9)–C(17) single bond (1.514(4) Å) linking the indenyl and triptycenyl moieties is not significantly different from the corresponding distance (1.520(4) Å) in the 3-indenyl-triptycene system, **1**. However, unlike the situation in **1**, whereby the proximity of the six-membered ring of the indenyl moiety to the paddlewheel engenders a 12 kcal mol^{-1} rotation barrier,[7] the variable-temperature NMR spectra of the 2-indenyl-triptycene, **2**, are unchanged down to 193 K indicating essentially free rotation on the NMR time scale.

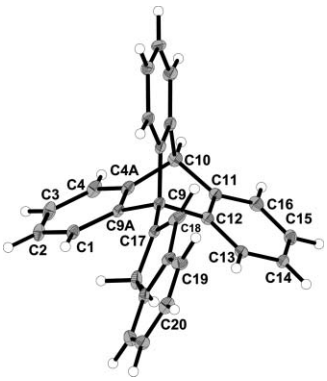


Fig. 4 Molecular structure of the triptycene **2**. Atoms are drawn with 50% ellipsoids.

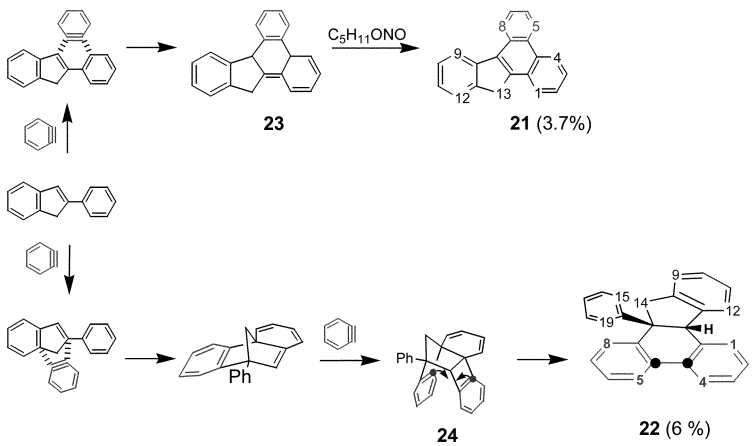
As depicted in Scheme 5, it is evident that the trajectory of approach for a potential [4 + 2] cycloaddition of benzyne to the five-membered ring of **4**, is blocked by the 2-anthracenyl moiety which, according to the molecular orbital calculations noted above, is rotated through ~70° relative to the plane of the indene. This may account for the formation of the 2-indenyl-triptycene, **2**, as the sole product in such high yield.

The simplicity of the ^1H and ^{13}C NMR spectrum of **2** at 303 K, and also at 193 K, clearly demonstrates the chemical shift equivalence of the three blades of the triptycene, indicating a low rotational barrier about the C(9)–C(17) single bond. On the basis of the previously observed chemical shift differences within the triptycene blades for the 3-isomer, **1**, under conditions of slowed rotation on the NMR time-scale, one can estimate probable peak separations for the 2-indenyl-triptycenyl, **2**. Thus, in **1** the chemical shift difference between H(2) and H(14) is 0.3 ppm (150 Hz on a 500 MHz spectrometer); if one were to assume a similar value for **2**, and if decoalescence had become evident at 193 K, this would have indicated a rotation barrier of approximately 9 kcal mol^{-1}; since there is no indication of decoalescence, the barrier in **2** is presumably considerably less than this estimated value.

Cycloaddition reactions of 2-phenylindene

Stimulated and intrigued by the unexpected cycloaddition of benzyne to the indenyl unit of **3**, we chose to extend this study by investigating the reactivity of benzyne towards 2-phenylindene. In this case, the majority (88%) of the 2-phenylindene was recovered unchanged; however, the reaction furnished significant amounts of two products, **21** (3.7%) and **22** (6%) (Scheme 7). The former was characterised by NMR spectroscopy as the known indenophenanthrene, **21**,[27] apparently the result of the addition of one benzyne unit to 2-phenylindene. The latter was identified from its one- and two-dimensional ^1H and ^{13}C NMR spectra as the double benzyne adduct, **22**.

One might speculate that **21** resulted from the [4 + 2] cycloaddition of benzyne to 2-phenylindene to give the dihydrophenanthrene, **23**, which, in the presence of excess isoamyl nitrite, was oxidised into the fully aromatic system **21** The second product, **22**, is formally the result of a [2 + 2 + 2] cycloaddition of 2-phenylindene with two benzynes; however, in the absence of a template, such a trimolecular process is rather improbable. Another, perhaps more reasonable, pathway invokes successive [4 + 2] and [2 + 2] additions of benzyne, somewhat analogous to the previously described behaviour of DMAD with indene,[23] or of benzyne with benzofuran.[25] However, because of the presence of the phenyl substituent at the 2-position of the original indene, it is hypothesised that the double benzyne adduct adopts the *syn*,



Scheme 7 Cycloaddition reactions of benzyne to 2-phenylindene, **8**.

24, rather than the *anti* configuration, as depicted in Scheme 7. Subsequent thermolysis could then cleave the benzyne–indene-C(7a) linkage, open the four-membered ring and rearrange to form the observed product **22**. The thermodynamic driving force for such a process would be the relief of cyclobutane ring strain in **24** and the recovery of aromatic character in the original six-membered ring of the indene.

Conclusions

The palladium-catalysed coupling of indene with 9-bromoanthracene under Heck conditions led to 9-(3-indenyl)anthracene, **3**; the reaction also yields the novel cyclic product, **9**, *via* an aromatic cyclisation process. In contrast, Suzuki coupling, catalysed by dichloro-bis(diphenylphosphinoferrocene)palladium, yielded 9-(2-indenyl)anthracene, **4**. While the 2-isomer, **4**, reacted smoothly with benzyne to furnish the required 2-indenyltrypticene, **2**, in good yield, the 3-isomer **3**, unexpectedly, formed two isomeric benzyne adducts—the previously described 3-indenyltriptycene, **1**, and the [4 + 2] adduct to the indenyl moiety of **3**. Subsequently, the addition of benzyne to 2-phenylindene was shown to yield unexpected products of one and two-fold benzyne cycloaddition. The structures and dynamic behaviour of the isomeric triptycenes **1** and **2** have been studied; in the former the barrier to rotation about the indenyl-triptycene linkage is 12 kcal mol^{-1} whereas in the latter system there is essentially free rotation on the NMR time-scale, making it a potentially attractive molecular machinery prototype system.

Experimental

All reactions were carried out under a nitrogen atmosphere. Column chromatography separations were carried out on a Buchi Sepacore machine with UV absorbance detector using silica gel particle size 40–63 mm. NMR spectra were acquired on Varian Inova 300 MHz and 500 MHz spectrometers. Assignments were based on standard ^{1}H–^{1}H and ^{1}H–^{13}C two-dimensional techniques, and NOE measurements. 2-Indeneboronic acid (**14**) was prepared in 86% yield according to a literature procedure.[20]

2-(4-Bromophenyl)indene (7a)

To a solution of *p*-bromoiodobenzene (0.308 g, 1.09 mmol), indene (0.29 g, 2.5 mmol), and triethylamine (0.6 mL) in DMF (5 mL) was added palladium acetate (10 mg, 4%). The reaction mixture was stirred at 100 °C for 4 h after which it was concentrated under reduced pressure and separated by chromatography, eluting with 3% dichloromethane in cyclohexane to give the 2-isomer **7a** as a pale yellow solid (0.122 g, 42%): mp 158 °C; δ_H (300 MHz, $CDCl_3$): 7.5 (4H, m), 7.40 (1H, d, *J* 7.3), 7.25 (4H, m), 3.76 (2H, s); the 3-isomer **7b** was obtained as a glass (6 mg, 2%):[28] δ_H (300 MHz, $CDCl_3$): 7.4–7.6 (5H, m), 7.3 (3H, m), 6.60 (1H, s), 3.50 (2H, s).

2-Phenylindene (8)

To a solution of bromobenzene (0.314 g, 2 mmol), indene (0.29 g, 2.5 mmol) and triethylamine (0.6 mL) in DMF (5 mL) was added bis(tri-*o*-tolylphosphine)dichloropalladium (16 mg, 1%). The reaction mixture was stirred at 100 °C for 6 h, after which it was concentrated under reduced pressure and separated by chromatography eluting with 3% dichloromethane in cyclohexane to give the 2-isomer, **8** as a pale solid (0.344 g, 90%):[28] mp 165 °C; δ_H (300 MHz, $CDCl_3$): 7.63 (2H, d, *J* 7.1), 7.47 (1H, d, *J* 7.1), 7.4 (3H, m), 7.24 (4H, m), 3.79 (2H, s). The 1-isomer, a colourless oil, δ_H 3.50 (2H, s),[29] was not found.

9-(Inden-3-yl)anthracene (3); indeno[1,2-*a*]-10,16-dihydroaceanthrylene (9)

To a solution of 9-bromoanthracene, **5** (2.06 g, 8 mmol), indene (1.16 g, 10 mmol) and triethylamine (2.2 mL) in DMF (25 mL) was added dichloro-bis-(tri-*o*-tolylphosphine)palladium (100 mg, 1.6%). The reaction mixture was stirred at 100 °C for 24 h, after which it was concentrated under reduced pressure and separated by chromatography eluting with 3% dichloromethane in cyclohexane to give anthracene (200 mg, 14%), **3** (1.2 g, 51%) and **9** (0.34 g, 14%) in order of elution. The 3-isomer **3** was obtained as a yellowish solid:[7] mp 141 °C. The compound **9** was obtained as yellow needles: mp 158 °C (Found: C, 93.71; H, 5.76. $C_{23}H_{16}$ requires C, 94.48; H, 5.52); δ_H (500 MHz, $CDCl_3$, numbering in accord with Fig. 2): 8.19 (1H, s, H_5), 8.11 (1H, d, H_1, *J* 8.8), 8.05 (1H, d, H_4, *J* 8.3), 7.70 (1H, H_6, *J* 8.3), 7.64 (1H, d, H_{11}, *J* 7.5), 7.50 (4H, m, H_2, H_3, H_7, H_8), 7.20 (1H, pseudo-t, H_{12}, *J* 8.5), 7.11 (2H, m), 5.43 (1H, d, H_{10}, *J* 7.5), 5.05 (1H, m, H_{16}), 3.93 (1H, dd, H_{15}, *J* 16.5 and 10.5), 3.42 (1H, dd, H_{15}, *J* 16.5 and 4.0); δ_C ($CDCl_3$, 125 MHz): 148.6 (C_9), 144.8 (C_{16a}), 143.8 (C_{10}), 142.6 (C_{14a}), 135.6 (C_{9a}), 134.2 (C_{4a}), 129.8 (C_4), 129.7 (C_{5a}), 127.8 (C_7), 127.2 (C_{13}), 126.9 (C_{4b}), 126.9 (C_{12}), 125.3 (C_{14}), 125.0 (C_3), 124.9 (C_2), 124.6 (C_1), 124.3 (C_{11}), 123.1 (C_6), 122.4 (C_5), 117.1 (C_8), 56.6 (C_{10}), 46.9 (C_{16}), 38.9 (C_{15}).

9-(1*H*-Inden-2-yl)-anthracene (4); 2,2′-biindenyl (15)

9-Bromoanthracene, **5** (0.257 g, 1 mmol), boronic acid **14** (0.12 g, 0.75 mmol), and sodium carbonate (0.212 g, 2 mmol) were stirred in a mixture of ethanol (6 mL) and toluene (3 mL) for 0.5 h, after which bis(1,1-diphenylphosphinoferrocene)dichloropalladium (8 mg, 1%) was added. The reaction mixture was stirred at 75 °C for 30 h, filtered, concentrated under reduced pressure, extracted with dichloromethane and separated by chromatography eluting with 3% dichloromethane in cyclohexane to give the 2-isomer **4** (0.115 g, 52% with respect to the boronic acid **14**) as a off white solid (Found C, 94.23; H, 5.66. $C_{23}H_{16}$ requires: C, 94.48; H, 5.52); mp 211 °C; δ_H (500 MHz, $CDCl_3$): 8.48 (1H, s, H_{10}), 8.05 (2H, d, H_4, *J* 8.4), 7.97 (2H, d, H_{15}, *J* 8.7), 7.58 (1H, d, H_1, *J* 7.8), 7.56 (1H, d, H_{12}, *J* 7.5), 7.48 (2H, dd, H_3, *J* 8 and 6.5), 7.43 (1H, dd, H_{13}, *J* 7.5 and 7.0), 7.41 (2H, dd, H_2, *J* 8.5 and 7.0), 7.32 (1H, dd, H_{14}, *J* 8.0 and 7.8), 7.07 (1H, s, H_{11}), 3.81 (2H, s, H_{16}); δ_C ($CDCl_3$, 125 MHz): 145.3 (C_{16a}), 145.3 (C_{11a}), 143.9 (C_{15a}), 133.3 (C_{11}), 133.3 (C_9), 131.3 (C_{4a}, C_{10a}), 130.2 (C_{8a}, C_{9a}), 128.5 (C_4, C_5), 126.7 (C_{13}), 126.6 (C_{10}), 126.4 (C_1), 126.4 (C_8), 125.5 (C_2, C_7), 125.2 (C_3, C_6), 124.8 (C_{14}), 123.8 (C_{15}), 121.1 (C_{12}), 44.5 (C_{16}).

15 (10 mg, 9%) was obtained as a colourless solid (Found C, 93.42; H 6.14. $C_{18}H_{14}$ requires: C, 93.91; H, 6.09); mp 225 °C;[30] δ_H (300 MHz, $CDCl_3$): 7.44 (2 H, d, *J* 7.5), 7.36 (2 H, d, *J* 7.5), 7.25 (2 H, pseudo t, *J* 7.5), 7.17 (2 H, pseudo t, *J* 7.5), 6.93 (2 H, s), 3.74 (4 H, s).

9-(1-Indenyl)triptycene (1) and 10-(anthracen-9′-yl)-[4a,9]-methano-4a,9-dihydro-phenanthrene (16)

To a hot (80 °C) stirred solution of **3** (292 mg, 1 mmol) and isopentyl nitrite (380 mg, 3.2 mmol) in dichloroethane (6 mL) was added a solution of anthranilic acid (440 mg, 3.2 mmol) in dioxane (2.5 mL) over a period of 30 min. The reaction mixture was extracted with dichloromethane and separated by chromatography eluting with 5% dichloromethane in cyclohexane to give **3** (82 mg, 28%), **16** (42 mg, 11%) and the triptycene **1** (156 mg, 42%).[7] The adduct **16** as a yellow solid (Found C, 94.11; H, 5.51. $C_{29}H_{20}$ requires C, 94.53; H, 5.47); mp 155 °C; δ_H (500 MHz, $CDCl_3$, numbering in accord with Fig. 3): 8.41 (1H, s, H_{16}), 8.24 (1H, d, H_{12}, *J* 9.9), 8.06 (1H, d, H_{15}, *J* 9.6), 7.92 (1H, d, 1H, H_{17}, *J* 8.8), 7.52 (2H, m, H_{14}, H_{13}), 7.31 (1H, pseudo-t, H_{18}, *J* 7.6), 7.23 (1H, d, H_5, *J* 6.7), 7.12 (1H, pseudo-t, H_6, *J* 6.8), 7.11 (1H, d, H_8, *J* 7.2), 7.03 (1H, pseudo-t, H_7, *J* 7.2), 6.95 (1H, ddd, H_{19}, *J* 9.2, 6.5, 1.6), 6.62 (1H, d, H_4, *J* 9.5), 6.55 (1H, dd, H_3, *J* 9.5 and 6.5), 6.45 (1H, d, H_{20}, *J* 9.2), 6.05 (1H, dd, H_2, *J* 9.2 and 5.2), 5.95 (1H, d, H_1, *J* 9.2), 4.46 (1H, s, H_9), 2.94 and 2.89 (CH_2, each d, 1H, H_{11}, *J* 7.2); δ_C ($CDCl_3$, 125 MHz): 156.2 (C_{4b}), 149.6 (C_{10a}), 145.9 (C_{8a}), 144.7 (C_{10}), 131.9 (C_{20b}), 131.7 (C_{16a}), 131.5 (C_{15a}), 130.6 (C_4), 130.2 (C_{20c}), 129.4 (C_{20a}), 128.7 (C_{15}), 128.1 (C_{17}), 126.8 (C_3), 126.4 (C_{16}), 126.3 (C_{20}), 125.6 (C_7), 125.5 (C_{14}), 125.2 (C_{13}), 125.1 (C_{18}), 125.1 (C_{19}), 124.8 (C_8), 124.1 (C_2), 123.4 (C_6), 121.4 (C_5), 121.4 (C_1), 78.5 (C_{11}), 60.6 (C_{4a}), 57.9 (C_9).

9-(2-Indenyl)triptycene (2)

To a hot stirred solution of **4** (117 mg, 0.4 mmol) and isopentyl nitrite (187 mg, 1.6 mmol) in dichloroethane (3 mL) was added a solution of anthranilic acid (205 mg, 1.5 mmol) in dioxane (1 mL) over a period of 30 min. The reaction mixture was extracted with dichloromethane and separated by chromatography eluting with 5% dichloromethane in cyclohexane to give starting **4** (14 mg, 12%), and triptycene **2** (120 mg, 81%) as a white solid (Found C, 94.25; H, 5.59. $C_{29}H_{20}$ requires: C, 94.53; H, 5.47); mp 308 °C; δ_H (500 MHz, CD_2Cl_2, numbering in accord with Fig. 4): 7.70 (1H, d, H_{22}, *J* 7.5), 7.62 (1H, d, H_{19}, *J* 7.5), 7.56 (3H, d, $H_{4,5,16}$, *J* 6.9), 7.49 (3H, d, $H_{1,8,13}$, *J* 7.5), 7.48 (1H, s, H_{18}), 7.45 (1H, pseudo-t, H_{20}, *J* 7.5), 7.37 (1H, pseudo-t, H_{21}, *J* 7.5), 7.08 (3H, pseudo-t, $H_{2,7,14}$, *J* 7.5), 7.04 (3H, pseudo-t, $H_{3,6,15}$, *J* 7.0), 5.48 (1H, s, H_{10}), 4.36 (CH_2, s, H_{23}); δ_C (125 MHz, CD_2Cl_2): 146.9 ($C_{4a,10a,11}$), 146.4 ($C_{8a,9a,12}$), 143.9 (C_{18a}), 143.3 (C_{17}), 143.3 (C_{22a}), 136.1 (C_{18}), 126.6 (C_{20}), 125.3 ($C_{2,7,14}$), 125.0 (C_{21}), 124.8 ($C_{3,6,15}$), 123.8 ($_{C4,5,16}$), 121.1 (C_{19}), 59.0 (C_9), 54.8 (C_{10}), 42.9 (C_{23}).

13a-Phenyl-13,13a-dihydro-8b*H*-indeno-[1,2-*l*]-phenanthrene (22), and 13*H*-indeno[1,2-*l*]-phenanthrene (21)

To a hot stirred solution of **8** (96 mg, 0.5 mmol) and isopentyl nitrite (234 mg, 2 mmol) in dichloroethane (4 mL) was added a solution of anthranilic acid (274 mg, 2 mmol) in dioxane (1.5 mL) over a period of 30 min. The reaction mixture was extracted with dichloromethane and separated eluting with 3% dichloromethane in cyclohexane to give **8** (84 mg, 88%), **21** (5 mg, 3.7%) and **22** (10 mg, 6%); **21** as a white solid (Found C, 94.54; H, 5.40. $C_{21}H_{14}$ requires: C, 94.70; H, 5.30); mp 158 °C;[27] δ_H (500 MHz, $CDCl_3$, numbering in accord with Scheme 7) 8.85 (1H, d, H_8, *J* 8.0), 8.79 (1H, d, H_5, *J* 8.2), 8.75 (1H, m), 8.39 (1H, d, H_9, *J* 7.8), 8.07 (1H, m, H_1), 7.74 (1H, pseudo-t, H_7, *J* 8.0), 7.68 (1H, pseudo-t, H_6, *J* 8.0), 7.67 (1H, d, H_{12}, *J* 8.0), 7.63 (2H, m, H_2, H_3), 7.49 (1H, pseudo-t, H_{10}, *J* 8), 7.35 (1H, pseudo-t, H_{11}, *J* 8.0), 4.23 (CH_2, s, H_{13}); δ_C (125 MHz, $CDCl_3$): 142.8 (C_{8c}), 142.2 (C_{12a}), 139.0 (C_{13a}), 133.6 (C_{8b}), 129.9 (C_{4b}), 128.9 (C_{4a}), 128.7 (C_{13b}), 128.3 (C_{8a}), 126.0 (C_2), 126.0 (C_7), 126.0 (C_{10}), 125.5 (C_3), 124.9 (C_6), 124.7 (C_{11}), 123.8 (C_{12}), 123.7 (C_1), 123.5 (C_8), 122.7 (C_5), 122.4 (C_4), 36.8 (C_{13}). **22** as a white solid (Found: C, 93.80; H, 6.15. $C_{27}H_{20}$ requires: C, 94.15; H, 5.85); mp 145 °C; δ_H (500 MHz, $CDCl_3$, numbering in accord with Scheme 7) 7.84 (1H, d, H_4, *J* 9.2), 7.74 (1H, d, H_5, *J* 9.2), 7.56 (1H, d, H_8, *J* 7.6), 7.40 (1H, d, H_1, *J* 8.8), 7.37 (2H, m, $H_{2,3}$), 7.27 (2H, d, $H_{15,19}$, *J* 7.2), 7.20–7.10 (6H, m, H_7, H_6, H_9, H_{16}, H_{18}, H_{17}) 7.06 (1H, pseudo-t, H_{10}, *J* 7.8), 7.00 (1H, pseudo-t, H_{11}, *J* 7.6), 6.82 (1H, d, H_{12}, *J* 7.6), 4.04 and 3.85 (CH_2, each 1H, d, H_{14}, *J* 15.2); δ_C (125 MHz, $CDCl_3$): 146.9 (C_{19a}), 144.5 (C_{12a}), 141.1 (C_{12b}), 139.8 (C_{8a}), 134.8 (C_{13b}), 133.4 (C_{4b}), 132.9 (C_{4a}), 129.8 (C_1), 128.3 ($C_{16,18}$), 128.1 (C_8), 127.7 ($C_{2,3}$), 127.0 (C_6), 126.8 (C_{10}), 126.6 ($C_{15,19}$), 126.5 (C_{11}), 126.3 (C_{17}), 124.2 (C_4), 123.6 (C_5), 123.5 (C_{12}), 123.5 (C_9), 56.6 (C_{13a}), 56.4 (C_{13}), 46.2 (C_{14}).

Crystal data

Crystallographic data were collected using a Bruker SMART APEX CCD area detector diffractometer. A full sphere of the reciprocal space was scanned by phi-omega scans. A semi-empirical absorption correction, based on redundant reflections, was performed by the program SADABS.[31a] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 for all data using the program library SHELXTL.[31b,c] In **16**, all hydrogen atoms were located in the difference Fourier map and allowed to refine freely. In **2** and **7a**, all hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to.†

Acknowledgements

We thank Science Foundation Ireland and University College Dublin for generous financial support.

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