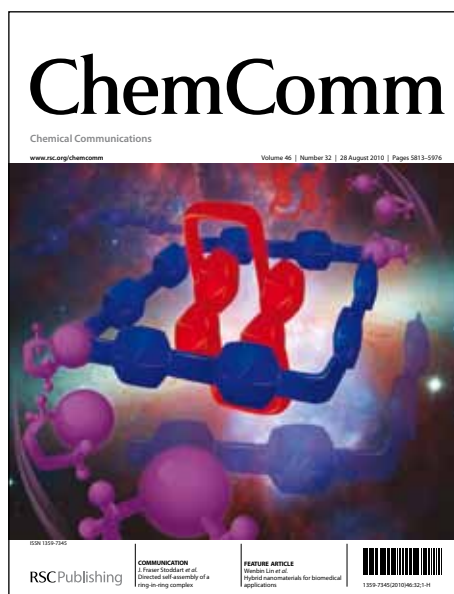


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ARTICLE TYPE

Intriguing Diels-Alder products: Chiral Centres with an added twist.

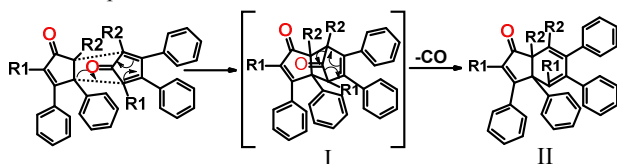
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Two chiral fluoranthene-based polyaromatics were isolated from a Diels-Alder cycloaddition between two molecules of 7,9-diphenylcyclopenta[*a*]acenaphthylene-8-one. The two highly coloured, novel compounds were characterized by a combination of spectroscopic techniques and single crystal X-ray diffraction. Structural differences between the unexpected products included the nature of their conjugated fluoranthene portions and the position, strain and handedness of their chiral centres.

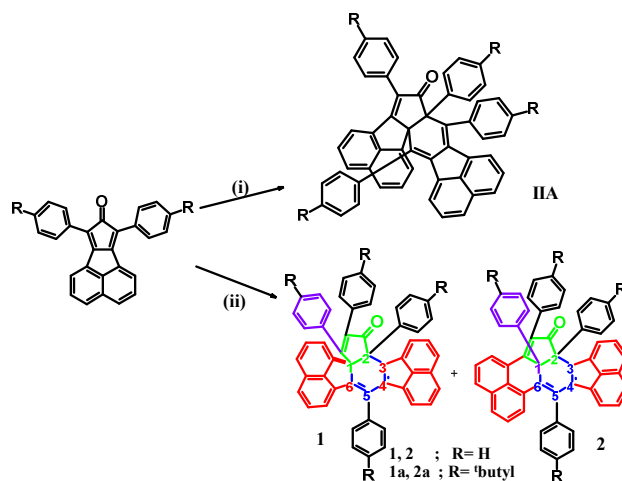
Current understanding of the dimerisation products that result from the cycloaddition of polyaromatic cyclopentadienones stems from the seminal work of Allen and Van Allan.^{1,2} In 1950 they were the first to observe Diels-Alder generated dimerisations of 2,5-substituted diphenylcyclopentadienones. They postulated that a transition state dimer (I) (shown in Scheme 1) was formed upon the lateral approach of the two reactant molecules when R₁, R₂ = H and that the reactants and dimer were in equilibrium. This idea was subsequently supported in publications by Fuchs *et al.*^{3,4} and Becker *et al.*⁵ When bulkier substituents were used (e.g. R₂ = methyl, propyl, phenyl in Scheme 1) only the monomeric starting materials were observed. This drew them to the conclusion that steric congestion in the six-member ring of the transition state could prevent the reaction from occurring.



Scheme 1: Representation of the Allen and Van Allan inspired mechanism for the dimerisation of 7,9-diphenylcyclopenta[*a*]acenaphthylene-8-one.

In an interesting twist, our investigations into [2+4] Diels-Alder cycloadditions between appropriately substituted alkynes and fluoranthene-based cyclopentadienones led us to revisit these earlier dimerisation conclusions. On heating 7,9-diphenylcyclopenta[*a*]acenaphthylene-8-one in benzophenone a reaction occurred. Based on an adaptation of the earlier findings we anticipated that product (IIA) in Scheme 2 might have been formed, however as we report here the reaction had proceeded very differently.

Under high-temperature Diels-Alder conditions, as outlined previously,⁶⁻⁹ the intermolecular cycloaddition actually generated two isomeric products (**1** and **2**) which differed from that predicted, particularly in the para arrangement of their fluoranthenes. No evidence for the formation of **IIA** was obtained, but it is possible that a two-step process, involving a phenyl rearrangement could have generated **1** from **IIA**. The major structural difference between products **1** and **2** is in the arrangement of the pendant phenyl rings on their fused cyclopentenones: the phenyl ring outlined in purple, now protrudes from the fused aromatic platform of **2** in position '1' of the central ring. The structural consequences of this change are manifested in the twisting of the central six-membered ring and are evident in the crystal structure of **2a** shown in Fig. 1.



Scheme 2: (i) Proposed dimerisation to form **IIA**, as extrapolated from Allen and Van Allan (ii) Actual formation of **1** and **2** (maximum yields 15% and 10% respectively using benzophenone, 200 °C and 40% and 30% respectively under microwave conditions)).

1a crystallized from methanol and dichloromethane in the P21/c space group, with one dimer molecule (S,R) in the unit cell. One dichloromethane solvent molecule was also present. The solvent molecules within the crystal lattice exhibited weak H-bonding interactions between the aromatic extremities of adjacent dimers. Nishio *et al.*¹⁰ have previously observed this. The cyclopentenone ring (shown in green), protrudes from the central six-member ring at an angle of 104.6° from the central plane of the molecule. The central ring, shown in

blue possesses three typical aliphatic bonds; 1.59 Å, 1.53 Å, 1.56 Å, reflecting its highly strained nature. **2a** was found to crystallise in the monoclinic C2/c space group, also showing two molecules in the unit cell in addition to two molecules of methanol. The fluoranthene moiety (shown in red in Scheme 2) is now directly bonded to the cyclopentene ring (green) and the C1-C6 bond of the central six-member ring forms the hinge of a 101.4° dihedral angle (Figure 1 inset). The isostructural (**2**), synthesised without the cumbersome *tert*-butyl groups, is seen to crystallise in the P-1 space group with a unit cell containing 4 molecules of R,R or S,S handedness. This implies that the generation of **2** from **1** which involves a phenyl migration necessitates a change in the handedness of one of the chiral centres.

Contrary to expectation, the absence of the *tert*-butyl groups in **2** leads to less-efficient crystal packing. The *tert*-butyl groups actually serve to open up the pendant phenyls thus allowing each molecule to pack more closely with its intermolecular neighbour. The overall orientation of the molecule however remains unchanged, as seen in Fig. 1.

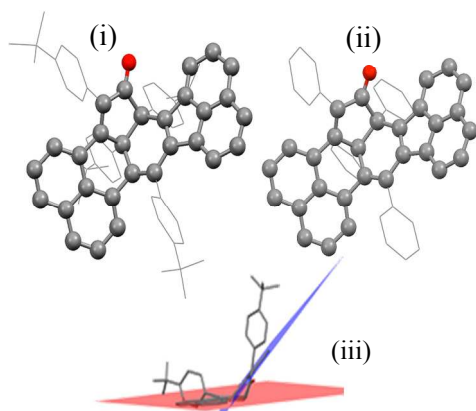


Figure 1. Single-Crystal XRD structures of **2a** (ii) and **2** (ii) (H atoms removed). (iii) Two planes through the fused core of the molecules forming an obtuse dihedral-angle, as quantified in the text.

The NMR assignment of such complex systems proved challenging. Through the use of selective NOESY experiments assignment of the pendant phenyl rings was successfully achieved. Through-space experiments then made the fused core accessible for full assignment, (Figure 2). Full assignment of **2** is presented in Figure S4.

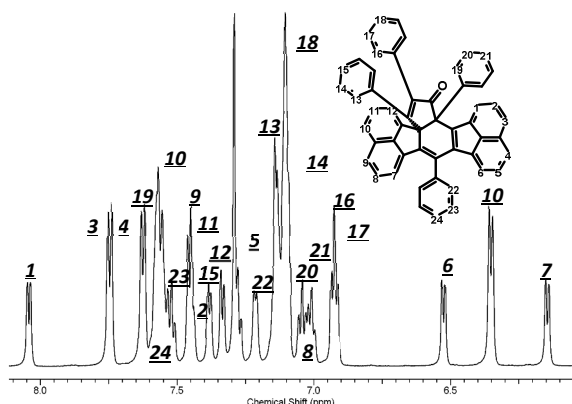


Figure 2: ¹H-NMR (RT, 600 MHz, CDCl₃) spectral assignment of **1**.

The structures presented here are similar to other fused tetraphenylene derivatives in the literature, comprising fused five-membered rings and are of interest in the investigation of curved graphene analogues. The syntheses of these related systems generally use fused moieties (such as 5,6,11,12-tetrahydrodibenzo-[a,e]cycloctene) as masked acetylenes in [2+4] Diels Alder reactions with fluoranthene-based cyclopentadienones.¹¹ These synthetic conditions require high boiling solvents such as benzophenone or diphenylether. In 1995 however, Otto *et al.*¹² correctly predicted the use of microwave irradiation in Diels-Alder synthesis and the topic has been the subject of more recent attention.¹³⁻¹⁵ With this in mind a CEM S-Discover microwave was used to investigate a more streamlined synthetic approach to our dimerisation products. The yields and reaction times to both dimers were successfully optimised. In reaction times <25 min, **1** could be synthesised from 7,9-diphenyl-cyclopenta[a]acenaphthylene-8-one in a 40% isolated yield. Subsequently **1** could be reacted, using benzophenone or diphenylether as solvents, to directly form **2**. This was a considerable improvement on the yields of both products obtained under thermal conditions (under 15%). Given the differences in the molecular and therefore electronic structures of the two isolated products we went on to investigate these properties further.

1a exhibits several maxima and a degree of fine structure in its absorption spectrum; a series of three structured bands in the $\lambda_{\text{abs}}^{\text{max}} = 350\text{-}390$ nm range (most likely corresponding to $\pi\text{-}\pi^*$ transitions) and a wide and low energy shoulder at $\lambda_{\text{abs}}^{\text{max}} = 527$ nm. Increasing the polarity of the solvent results in a bathochromic shift of the structured bands in addition to an increase in their absorption. These observations support the proposition that these bands emanate from $\pi\text{-}\pi^*$ transitions within **1a**. The lower energy shoulder at $\lambda_{\text{abs}}^{\text{max}} = 527$ nm, visible in Fig. 3 shows negligible solvent dependency and remains unchanged, even upon the addition of acid. For **2a**, a similar absorption spectrum is observed but hypsochromically shifted. This is most likely caused by the new orientation of the pendent phenyl rings, bringing them into closer proximity, reducing the planarity and raising the energy of the π^* orbital. In the $\lambda_{\text{max}}^{\text{abs}} = 340 - 370$ nm range the blue-shifted $\pi\text{-}\pi^*$ transitions appear with considerably less fine-structure than for **1a**, most likely as a result of the less hindered rotation. The presence of a six membered ring in **2a** decreases the degree of unsaturation within the molecule and therefore reduces the extent of planarity compared to **1a**.

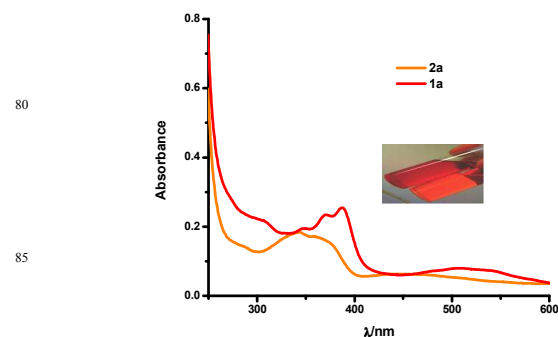


Figure 3: UV-vis absorption spectra of **1** and **2** in dichloromethane.

The electrochemical data obtained for the two isomers correlates well with their optical properties (Table 1). For instance the greater aromaticity and planarity of **1**, gives rise to red shifted π - π^* transitions and manifests itself in a higher first oxidation potential.

Table 1. Redox potentials for **1** and **2** vs Ag/AgCl. Supporting electrolyte: (TBA)PF₆ (0.1 M) in CH₃CN.

	1	2
$E_{1/2 \text{ ox}}$	1.17 V $\Delta E_p = 340 \text{ mV}$	1.08 V $\Delta E_p = 190 \text{ mV}$
$E_{1/2 \text{ Red}}$	-1.56 V $\Delta E_p = 190 \text{ mV}$	-1.46 V $\Delta E_p = 160 \text{ mV}$

In addition, the stabilisation of the LUMO in **1** due to the increased conjugation meant that its reversible single electron reduction occurred more readily than **2** (Fig. 4), with reversible single electron reduction observed at $E_{1/2 \text{ red}} = -1.56$ ($\Delta E_p = 190 \text{ mV}$).

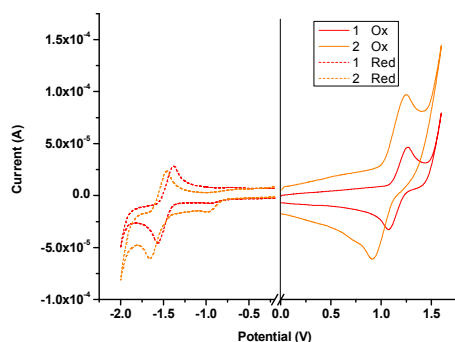


Figure 4: Cyclic Voltammogram of **1** and **2** in 0.1 M TBAPF₆.

The dimerisation of 7,9-diphenylcyclopenta[a]acenaphthylene-8-one is an interesting process and offers an efficient one-pot methodology for the total synthesis of two chemically different chiral isomers. The resulting curved aromatics comprising several fused five-membered rings are structurally similar to those found in non-planar PAHs with parabolic, twisted and bowl-shaped structures such as fullerene end-caps and extended molecular clips.¹⁶⁻¹⁸ The structures presented here offer an alternative to 60 years of well-documented thinking on the reactivity of cyclopentadienones and the manner in which they might dimerise. Supported by ample evidence; in the form of mass spectrometry, full NMR assignment, good quality single-crystal XRD data, UV-vis and cyclic voltammetry studies, these compounds reveal a fascinating twist in a generally accepted tale of reactivity.

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[†]Electronic Supplementary Information (ESI) available. For experimental procedures, selected ¹H-NMR spectra and crystallographic pictures see DOI:..

[‡]Crystal data for **1a**: C₇₀H₆₄Cl₂O, M = 992.11, monoclinic, spacegroup P21/c, a = 14.7164(10), b = 17.2279(12), c = 22.4826(16) Å, α = 90.00, β = 103.120(2), γ = 90.00 μ, V = 5551.3(7) Å³, Z = 4, F(000) = 2104, 2θ max = 25.12, wR2 = 0.2083, R1=0.077). CCDC 969865. Crystal data for **2**: C₅₃H₃₂O, M = 684.79, triclinic, spacegroup P-1, a = 11.797(2), b = 17.099(3), c = 18.309(3) Å, α = 72.282(4), β = 89.938(4), γ = 85.625(4) μ, V = 3506.9(7) Å³, Z = 4, F(000) = 1432, 2θ max = 25.00, wR2 = 0.11, R1=0.0499). CCDC 969866.

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