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2,3-Di-*n*-undecylanthracene and 2,3-Di-*n*-decyloxyanthracene (DDOA) – on the Connecting Link between the Aromatic Substrate and the Aliphatic Chain in Self-Assembling Systems

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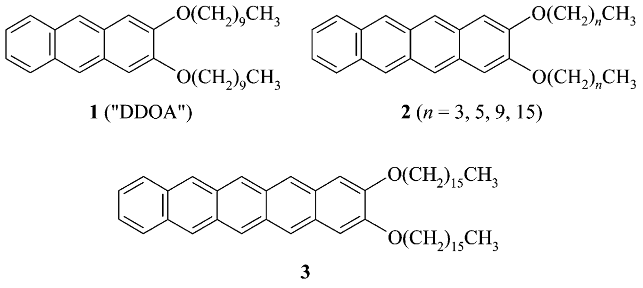
In contrast to its bis(oxa) analog **1** (DDOA), the hydrocarbon **11** was not found to form organogels with linear alcohols, alkanes, toluene, acetonitrile and other solvents. Whereas the photoreactivity of **1** did not follow the usual behaviour of anthracene derivatives, compound **11**, irradiated in cyclohexane, produced the two expected [4+4]cycloadducts **12** and **13** (*anti* and *syn* photodimers, respectively). These facts point to the role of the connecting link between the rigid core and the flexible chain for some self-assembled systems.

Introduction

Linear [*n*]acenes substituted at C-2 and C-3 by long alkoxy chains, like the anthracene, tetracene, and pentacene derivatives **1**–**3** shown in Scheme 1, are very efficient organogelators yielding soft three-dimensional architectural materials imprisoning the isotropic fluid by intertwined nanofibers. These self-assembled fibers, which can be also organized by mechanical and magnetic stimuli, were found to be efficient light-harvesting systems.[1,2] The gelling effectiveness depends on a subtle balance between the length[3] of the alkoxy chains, which confer solubility, and that of the aromatic moiety of these derivatives, which favours crystallization.

Such a balance was also observed to be important in other self-assembled systems such as discotic liquid crystals.[4] Of special interest, in this respect, is the role of the connecting link between the aromatic core and the aliphatic chain. For disc-shaped liquid crystals, it was noted that the alkoxy-substituted mesogens show an increase in both the clearing and the melting temperatures compared to those of the alkyl counterparts. It is argued that the introduction of oxygen atoms in the linking group results in an enhanced electron density in the aromatic core, hence of attractive π–π interactions, leading to higher transition temperatures.[5]



Scheme 1. Gel-forming linear acenes.

To investigate the influence of the ether oxygen atoms connecting the two hydrocarbon halves of these compounds on their gelating and other properties, we decided to prepare the all-carbon analog of DDOA (**1**), the hydrocarbon 2,3-di-*n*-decylanthracene (**11**) which holds two 11-atom chains.

Preparation

To prepare hydrocarbon **11**, we adopted a route described 20 years ago by Bender and Müllen for the preparation of various 2,3-disubstituted dialkylanthracenes.[6] Towards this end, 2,3-dimethyl-1,3-butadiene (**4**) was metalated with the Schlosser-Lochmann base *tert*-butylOK/*n*BuLi[7,8] (in a glove box under argon) to provide the bis(anion) **5**. When this was quenched at 0 °C with *n*-decyl bromide in THF, the diene **6** was produced in 30% yield (Scheme 2).

Its subsequent Diels–Alder addition to 1,4-naphthoquinone (**7**) furnished the expected adduct **8** (44%), which was oxidized under oxygen in ethanolic KOH solution. The desired anellated quinone **9** was obtained in a satisfactory

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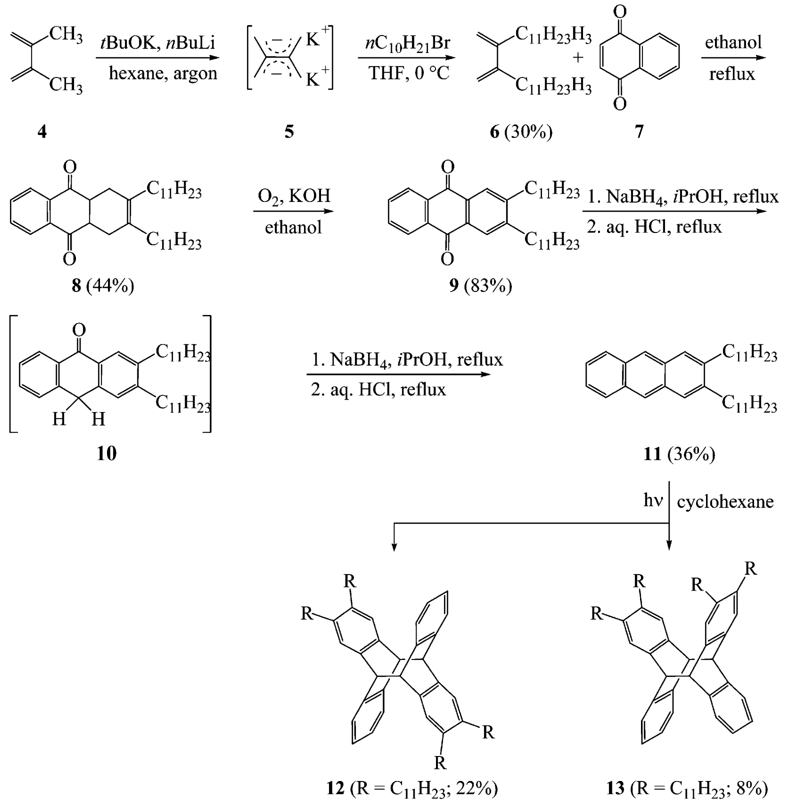

Scheme 2. Preparation and photochemistry of 2,3-bis(*n*-undecyl)anthracene (**11**).

yield of 83%. Reduction of **9** to **11** was accomplished by treating it with sodium borohydride in 2-propanol followed by acidic workup in a two-step procedure. This process probably takes place via the anthrone intermediate **10**, which was not characterized but directly subjected, after isolation as a crude solid, to a second reduction step. Hydrocarbon **11**, formed in 36% yield, was – like its precursors – characterized by the usual spectroscopic methods (see Supporting Information).

Photoreactivity

Irradiation of a degassed benzene solution (10^{-3} M) of DDOA at ambient temperature with a medium-pressure mercury lamp, using a Pyrex filter, led to the slow disappearance (14 h) of the typical anthracene UV absorption (300–400 nm) and the growing-in of a new band at $\lambda \leq 300$ nm tailing down to 450 nm. The UV spectrum was recovered after allowing the solution to stand for ca. 12 h. Attempts to isolate and characterize the photoproducts failed.

In contrast, a degassed cyclohexane solution of **11** (10^{-4} M) irradiated under the same experimental conditions through a < 320 nm cut-off filter (ca. 12 h) provided two photoproducts identified as the expected head-to-tail **12** (*anti*; 22%) and head-to-head **13** (*syn*; 8%) photodimers (Scheme 2). Evidence of their structure stems from the following spectral characteristics:[9] (a) ^{1}H NMR spectrum: $\delta = 4.30$ (s, 4 H) ppm corresponding to the four protons 9, 10, 9′, and 10′; (b) UV spectrum: absorption bands peaking at 280–290 nm (see Figure 1); (c) IR spectrum: the 1450 (**13**) and 1455 cm^{-1} (**12**) absorption bands (s and m-s) corre-

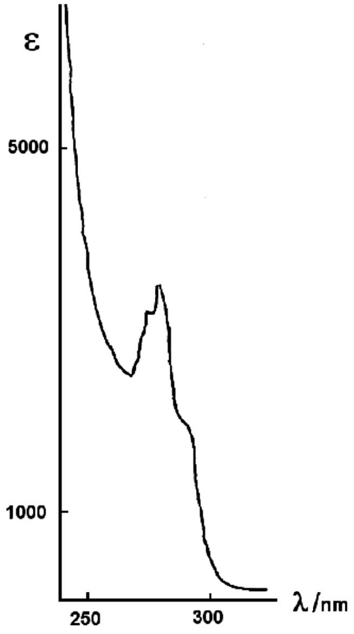

Figure 1. UV spectrum of **12** (*anti*; photodimer of compound **11**); solvent: hexane; concentarion: 7×10^{-5} M.

spond to C–H bending vibrations δCH of benzylic hydrogen atoms resulting from ring closure; this absorption is usually encountered in anthracene photodimers and considered a good indication that [4+4] cycloaddition has actually taken place.[9]

The two photoproducts could be separated by silica gel column chromatography, but, unfortunately, we have so far been unable to obtain crystals of X-ray quality for the two isomers. We assume that the faster moving zone is due to **12** (*anti*) because of its presumably lower dipole moment (centrosymmetric structure).

Solvent Screening for Gel Forming Ability

In contrast to DDOA, which has been recognized as a supergelator[10,11] as it gelifies methanol[3] at a concentration of 6×10^{-4} M (0.03 wt%) at room temperature and a number of other fluids,[12–14] hydrocarbon **11** did not reveal any gelling properties in alcohols, heptane, methylcyclohexane, toluene and acetonitrile, using the inverted tube technique (see Experimental Section, Supporting Information), at concentrations from 10^{-2} M (0.6 wt.-%) to 2×10^{-2} M (1.2 wt%).

Conclusions

Clearly, the two oxygen atoms play a paramount role in inducing the gelling properties of these acenes. The driving force probably originates from the presence of a weak dipole moment induced by the two heteroatoms, which control the intermolecular interaction and in turn the self-assembly.[15] Whether other hetero atoms (sulfur, nitrogen, phosphorus) can take over this role, remains to be established.

Experimental Section

Photodimerization of 11: A degassed solution of **11** (50 mg, 0.1 mmol) in cyclohexane (10 mL) was placed in a Pyrex vial and irradiated with a high-pressure mercury lamp through a ≤ 320 nm cut-off filter. After irradiation at room temperature overnight, TLC analysis showed that most of the substrate had reacted and that two photoproducts had been formed, which were separated by column chromatography (silica gel; pentane). **12** (*anti*): Colorless crystals, m.p. 48 °C (11 mg, 22%). ^{1}H NMR (60 MHz, $CDCl_3$, int. TMS): δ = 0.83 (t, J = 7.4 Hz, 12 H, CH_3), 1.20 (m, 72 H, methylene chain), 2.27 (m, 8 H, Ar-CH_2-), 4.30 (s, 4 H, bridgehead CH), 6.50 (s, 4 H, dialkylated benzene ring), 6.67 (AA′BB′-m, 8 H, Ar-H) ppm. IR (KBr): $\tilde{\nu}$ = 3034 (w), 2900 (vs), 2820 (s), 1455 (m-s), 875 (m), 745 (m), 710 (w) cm^{-1}. UV (cyclohexane): λ_{max} (ε) = 290 (3509) nm. **13** (*syn*): Colorless oil (4 mg, 8%). IR (neat, NaCl plates): $\tilde{\nu}$ = 3040 (w), 2900 (vs), 2830 (s), 1450 (m), 880 (m-w), 795 (m), 725 (w) cm^{-1}. The fluorescence of **11** has been studied in comparison with other disubstituted anthracenes.[16].

Gelling Experiments: They were carried out by using septum-capped test tubes of ca. 4 cm length and 0.7 cm diameter, heating the mixture until dissolution and allowing to cool down to room temperature. A gel is formed if the content does not flow when the tube is turned upside down. The gels obtained in this series were characterized as thermoreversible physical gels.

Supporting Information (see footnote on the first page of this article): Experimental data, full spectroscopic data, gelling experiments.

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