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Photodimers of a Soluble Tetracene Derivative. Excimer Fluorescence from the Head-to-Head Isomer

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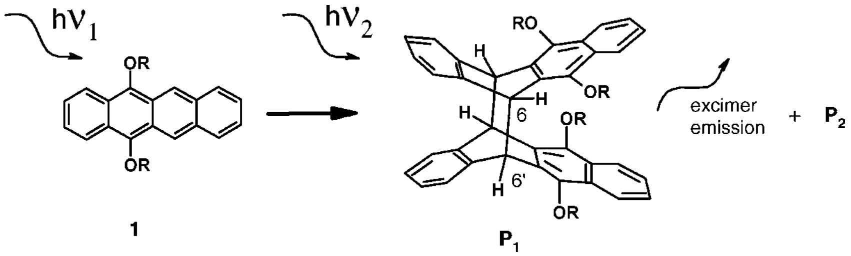
ABSTRACT



Irradiation of 5,12-didecyloxytetracene (1) leads to photodimers P_1 (planosymmetric) and P_2 (centrosymmetric). P_1 is characterized by naphthalene excimer fluorescence, whereas P_2 emits naphthalene monomer fluorescence.

Polycyclic aromatic hydrocarbons, especially tetracene and pentacene, are of current interest for their potential applications in organic electronic devices, due to their optoelectronic properties.[1] They are also known for their photoreactivity.[2] Tetracene was indeed the first photochromic organic compound described in the literature.[3] These acenes display a very low solubility in organic solvents, and the majority of studies were hence performed in the solid state.[4] This low solubility strongly limits their applications (inter alia introduction into matrices, organization on surfaces) and hampers photochemical studies in solution, which are hence less documented than those of anthracene and its derivatives.[5]

Tetracene was found to photodimerize at a lower rate than anthracene.[2d] By irradiation of a suspension in benzene (1 × 10^{-3} M), it was reported to form two photodimers: head-to-head (hh), or planosymmetric, and head-to-tail (ht), or centrosymmetric.[2c] To our knowledge, no photodimer of

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[4] (a) Innone, M.; Scott, G. W. *Chem. Phys. Lett.* **1990**, *171*, 569−574. (b) Katul, J. A.; Zahlan, A.-B. *J. Chem. Phys.* **1967**, *47*, 1012−1014. (c) Müller, H.; Bässler, H.; Vaubel, G. *Chem. Phys. Lett.*, **1974**, *29*, 102−104.

[5] (a) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43−55. (b) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2001**, *30*, 248−263.

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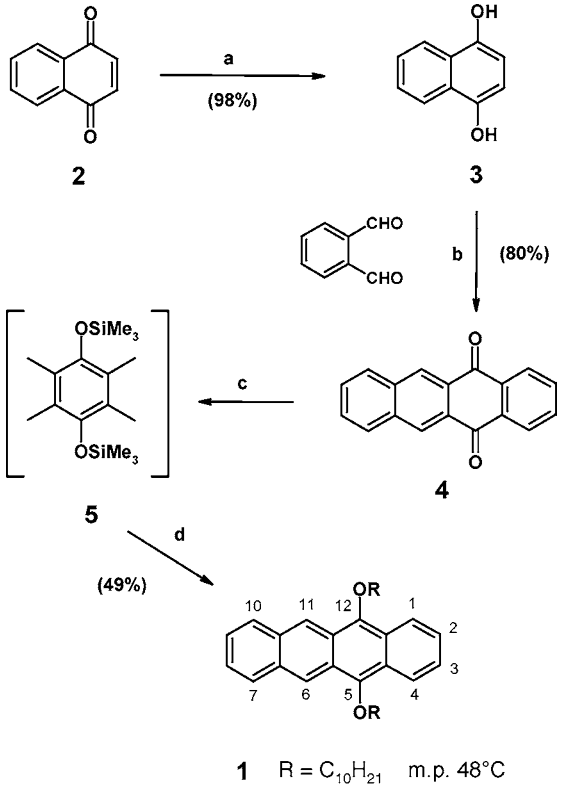
substituted tetracenes has been described. In analogy with anthracenes,[6] it was anticipated that substitution with long-chain alkoxy groups would substantially increase the solubility in common organic solvents and make the photochemical studies easier.

Here, we describe the synthesis and the photodimerization of 5,12-di-*n*-decyloxytetracene (**1**) as well as the determination of the structure of photodimers $\mathbf{P_1}$ and $\mathbf{P_2}$.

The synthesis of compound **1** is outlined in Scheme 1. Although 5,12-tetracenequinone **4** is a commercial product, the preparation described here is straightforward and allows scaling up to multigram quantities. The two-step formation of 5,12-dialkoxytetracenes follows a route that has been employed successfully for anthracene derivatives.[7] The use of Zn powder as a reductant and the ultrasound technique were found to be more convenient than the published procedures.[7] The yields are limited by the back-reaction of **5** to **4** during the alkylation step.

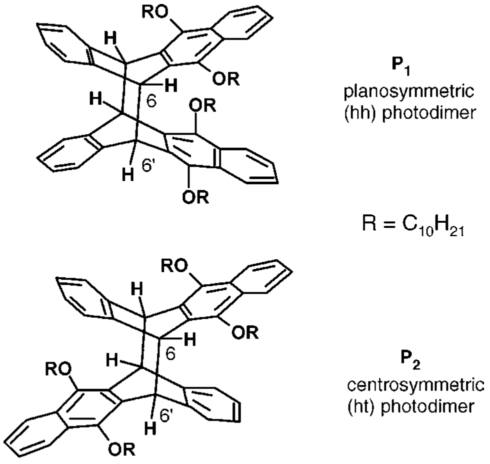
Scheme 1[a]



[a] Conditions: (a) Zn, HOAc, ultrasound; (b) Na_2CO_3, CF_3CH_2OH; (c) Zn, Me_3SiCl, THF, ultrasound; (d) K_2CO_3, DMF, $C_nH_{2n+1}Br$; compound **5** was not isolated. Overall yield 38%.

The preparative irradiation was carried out on 500 mg of **1** (5×10^{-2} M) in argon-purged cyclohexane with a 1000 W halogen lamp in a glass (Duran: transmittance 5% at 285 nm, 10% at 290 nm) vessel for 5 days at ambient temperature. Two photoproducts, $\mathbf{P_1}$ and $\mathbf{P_2}$ (Scheme 2, ratio 1:1, 104 mg each, 0.092 mmol, 20%), were isolated as white powders by silica gel column chromatography. $\mathbf{P_1}$, eluting first, was also found to be more soluble in cyclohexane than $\mathbf{P_2}$. The ^1H NMR spectra ($CDCl_3$) revealed the presence of signals characteristic of four bridgehead protons (6,11- and 6′,11′-positions) at δ 5.35 ($\mathbf{P_1}$) and 5.32 ($\mathbf{P_2}$).[5,6c]

Scheme 2



Attempts to obtain single crystals suitable for X-ray structure determination did not meet with success. Compelling evidence of the hh structure of $\mathbf{P_1}$ (and hence ht structure of $\mathbf{P_2}$) came from fluorescence spectroscopy. The absorption (**1**, $\mathbf{P_1}$, $\mathbf{P_2}$) and fluorescence ($\mathbf{P_1}$, $\mathbf{P_2}$) spectra are represented in Figures 1 and 2, respectively. $\mathbf{P_1}$ and $\mathbf{P_2}$ exhibit

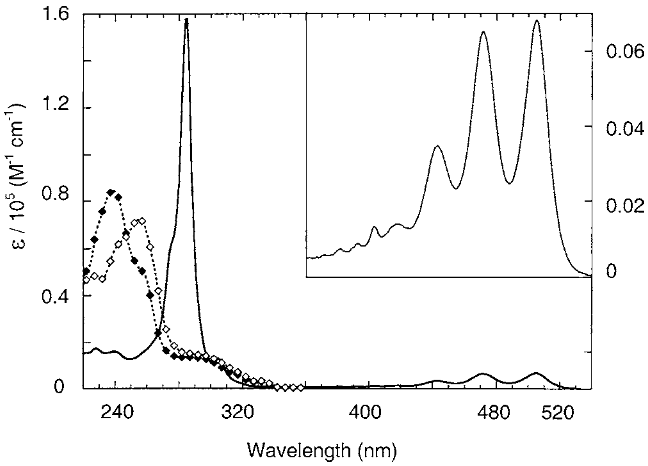


Figure 1. UV−vis absorption coefficients (ε) of (—) **1**, (◆) $\mathbf{P_1}$, and (◇) $\mathbf{P_2}$ in CH_2Cl_2. Inset: **1** from 360 to 540 nm. Concentrations of **1**, 1.6×10^{-5} M; $\mathbf{P_1}$, 1.9×10^{-5} M; $\mathbf{P_2}$, 1.9×10^{-5} M at ambient temperature.

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[6] (a) Fages, F.; Desvergne, J.-P.; Bouas-Laurent, H. *Bull. Soc. Chim. Fr*. **1985**, 959−964. (b) Fages, F.; Desvergne, J.-P.; Frisch, I.; Bouas-Laurent, H. *J. Chem. Soc., Chem. Commun*. **1988**, 1413−1415.(c) Brotin, T. Thèse, Université Bordeaux 1, Talence, France, 1990. The ^1H NMR chemical shift of the bridgehead protons of 1,4-didecyloxyanthracene photodimer was found to be δ ($CDCl_3$) 5.0 ppm.

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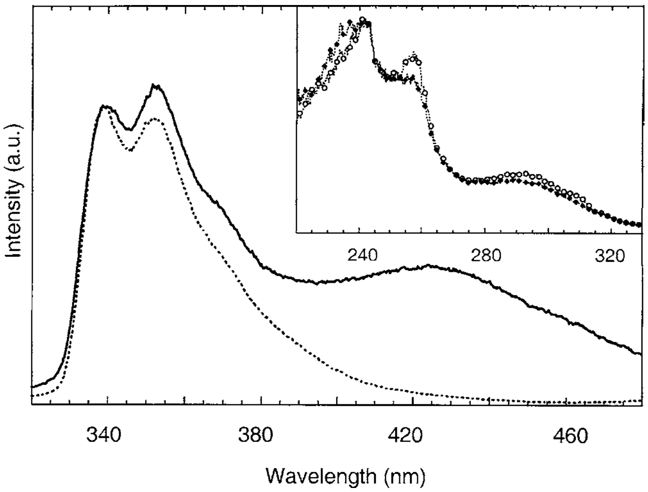


Figure 2. Fluorescence spectra of (—) $\mathbf{P_1}$ and (···) $\mathbf{P_2}$ in hexane. Concentration: 1.5×10^{-5} M at ambient temperature; λ_{exc}, 310 nm (the same spectra are obtained with λ_{exc}, 240 nm).

the normal monomer fluorescence of a substituted naphthalene derivative (emitting between 340 and 425 nm); additionally, and in contrast to $\mathbf{P_2}$, $\mathbf{P_1}$ presents a nonstructured and red-shifted band ($\lambda_{max} = 424$ nm, $\nu_{max} = 23\,585$ cm^{-1}). The shift from the onset emission (29 585 cm^{-1}) is $\Delta\nu \approx 6000$ cm^{-1}, in keeping with known data in the naphthalene series.[8]

That this emission is typical of an excimer is borne out by the kinetic analysis using the single-photon counting technique. The fluorescence decay of $\mathbf{P_1}$ (at ambient temperature) was fitted with the following equations:

at $\lambda = 352$ nm,

$$i(t) \propto 0.50 \exp(-t/1.3 \text{ ns}) + 0.06 \exp(-t/6.3 \text{ ns})$$

at $\lambda = 424$ nm,

$$\mathrm{i(t)} \propto -0.18 \exp(-t/1.6 \text{ ns}) + 0.45 \exp(-t/6.6 \text{ ns})$$

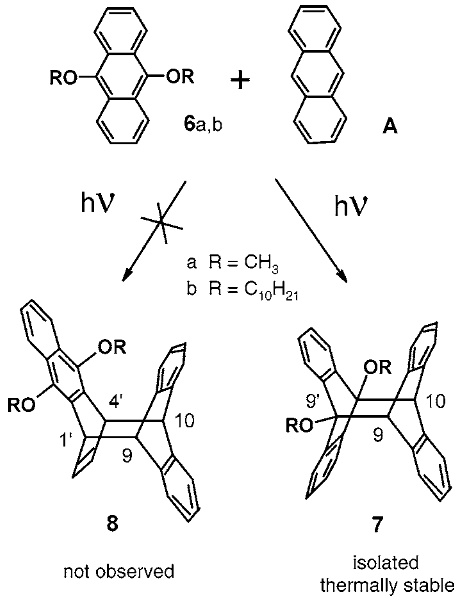
The similarity of the short decay time of the high energy emission (352 nm) and of the rise time of the lower energy emission (424 nm) is a typical signature for excimer states populated by S_1 excited states.[8] The excimer nature of the nonstructured red-shifted emission is corroborated by the excitation spectra, which were found to match the absorption spectrum regardless of the emission wavelength of observation (340 or 424 nm; see inset of Figure 2). The fluorescence decay of $\mathbf{P_2}$ was found to be single-exponential at 352 nm with $\tau = 1.8$ ns. The unusually short lifetimes for naphthalene derivatives fluorescence are presumably related to the dissociation of the photodimers in their excited states.[2h] Intermolecular excimer formation must be discarded for the following reasons: (i) the naphthalene monomer singlet-state lifetime is too short (<2 ns) to allow a bimolecular reaction to compete at ca. 10^{-5}M; (ii) the excimer/monomer ratio was found to be the same at 10^{-6} and 10^{-5} M, respectively; (iii) intermolecular excimer emission should have been observed for $\mathbf{P_2}$ as well under the same conditions.

Although excimer emission is evidence of intermolecular interactions of aromatic hydrocarbons in polymers or aggregates,[9,10] the present example is an interesting case of an intramolecular emission used as a tool to distinguish between two regioisomers.

The reaction quantum yield, measured at 439 nm in freeze and thaw degassed cyclohexane, using the Parker actinometer, was found to be equal to 6.5×10^{-3} (average of two measurements) at a concentration of 8.3×10^{-3} M.

The regioselectivity of photodimerization differs from that observed for the crossed photodimerization between 9,10-dialkoxyanthracenes and anthracene; the only photoproducts obtained (Scheme 3) were the 9,10:9′,10′-photodimers (**7**), which are thermally stable, and some dianthracene ($\mathbf{A_2}$).[6a,11] The 9,10:1′,4′-cycloadduct (**8**), presumably also thermally stable in comparison with other mixed compounds of the same type,[6b] was not observed. The main reason is probably the loss of stabilization energy[12] that is higher to form **8** than

Scheme 3[a]



[a] Crossed photodimerization between 9,10-dialkoxyanthracene (**6**) and anthracene (A). Φ_R ($\mathbf{6_b} + \mathbf{A}$) at 10^{-3} M = 20×10^{-3} in methylcyclohexane;[6a] some dianthracene ($\mathbf{A_2}$) is also formed (not represented).

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to obtain **7**. This factor is absent in the case of the tetracene derivative in which the reactivity of the 6,11-positions is apparently higher than that of the 5,12-positions.

Similarly to Livingston,[2b] we observed that $\mathbf{P_1}$ (mp 70 °C) and $\mathbf{P_2}$ (mp 125 °C) dissociate back to **1** in solution (dissociation after 15 min of $\mathbf{P_1} = 10\%$ at 308 K and 13% at 342 K; $\mathbf{P_2} = 19\%$ at 308 K and 36% at 342 K), but the back-reaction has not been studied in depth so far. It is surprising that the thermal stability of $\mathbf{P_2}$ is lower than that of $\mathbf{P_1}$; this point deserves further investigation. In the solid state, the two photodimers are stable for months, and they dissociate to a small extent at 150 °C in a Schlenck tube.

The results obtained in this work for tetracene will be extended to pentacene. This would pave the way to the introduction of tetracene and pentacene derivatives as components in light-modulated systems.

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Supporting Information Available: ^{1}H and ^{13}C NMR data of **1**, $\mathbf{P_1}$, and $\mathbf{P_2}$ and HRMS of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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