# The First Intermolecular 9,10–1′,4′ Photodimerization of the Anthracene Ring

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9,10–1′,4′ Unsymmetrical anthracene ring photodimerization is observed upon irradiation of a 2,6-didecyloxyanthracene; this is the first example of anthracene intermolecular photodimerization not restricted to the *meso* positions.

Anthracenes usually photodimerize *via* a singlet state process through formation of 9,10′–10,9′ bonds involving the more reactive sites. Moreover, it has been observed that the reaction, which is concentration dependent, is sensitive to the size and nature of the *meso* substituents.[1] The relatively rare deviations from this rule are only met with linked systems where conformational constraints or triplet states may favour 9,1′–10,4′ or 9,1′–10,2′ bond formation, respectively.[1,2] The tendency to involve the 9,10-positions in the photodimerization process is so strong that even the *syn*-[2.2] (1,4)-anthracenophane yields not the expected 1,4–1′,4′ photocyclomer but the strained 9′9′–10,10′ cycloadduct.[3]

As 1,4-transannular singlet oxygen or benzyne[4] additions to aromatic hydrocarbons have been shown to be accelerated by electron donor groups, we prepared, in order to improve the photodimerization efficiency (for photochromic purposes), several fairly soluble† bis(n-decyloxyanthracenes)($\mathbf{I}_{2,6}$, $\mathbf{I}_{1,4}$, $\mathbf{I}_{1,5}$, and $\mathbf{I}_{1,8}$) which have no *meso* substituents. In contrast to anthracene itself and many of its derivatives, two of these compounds display peculiar spectroscopic properties as shown in Table 1 for fluorescence emission.‡ Indeed, the quantum yields for fluorescence emission (conc. $\leqslant 10^{-5}$ M) are very high ($\phi_F \approx 1$) and the fluorescence lifetimes surprisingly long ($\tau_F$ = 19—20 ns) for compounds $\mathbf{I}_{2,6}$ and $\mathbf{I}_{1,4}$ (suggesting negligible non-radiative deactivation channels, often due, in anthracene,[5a] to intersystem crossing) in comparison with the data obtained for the two other isomers ($\phi_F < 0.3$ and $\tau_F \approx$ 3—4 ns, with anthracene $\phi_F = 0.30$ and $\tau_F = 4.5$ ns; $\mathbf{I}_{9,10}$ behaves like 9,10 di-n-propylanthracene).[5b]

The discrepancy between these values can be rationalized by considering the location of strongly electron donating mesomeric substituents which should modify the electron density distribution in the aromatic substrate.[6] In that connection, we have recently reported[7] that formylation (Vilsmeier Haack) of compound $\mathbf{I}_{2,6}$ mainly provided two

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† The methoxy derivatives are poorly soluble in organic solvents. The new compounds gave satisfactory spectroscopic, analytical, and mass spectral data.

‡ The u.v. spectra are also very sensitive to substitution.

**Table 1.** Fluorescence emission quantum yields of compounds **I** in different solvents at room temperature.[a]

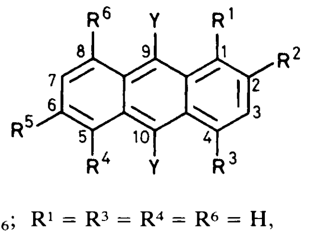
| Solvent | $\phi_F$ $(\tau_F/ns)$[b] **I**$_{2,6}$ | **I**$_{1,4}$ | **I**$_{1,5}$ | **I**$_{1,8}$ | **I**$_{9,10}$ |
|---|---|---|---|---|---|
| Tetrahydrofuran | 0.87 (23.3) | 1.00 (19.4) | 0.26 (3.7) | 0.23 (2.8) | 0.80 (13.8) |
| Methylcyclohexane | 0.99 | 0.90 | 0.28 | 0.17 | 0.86 |
| Benzene | 1.00 | 0.82 | 0.23 | 0.25 | 0.93 |
| Methanol | 1.00 | 0.98 | 0.24 | 0.23 | 0.76 |

[a] Conc. $< 10^{-5}$ M. [b] The fluorescence lifetimes $\tau_F$ were measured in THF using a single photon counting technique as described elsewhere.[10]

**Table 2.** Photodimerization quantum yields ($\phi_R$) of compounds **I**.[a]

| | **II**$_s$ $\phi_R$ | **II**$_s$ M.p. (decomp.)/°C | **II**$_a$ $\phi_R$ | **II**$_a$ M.p./°C |
|---|---|---|---|---|
| **I**$_{1,4}$ | $6.5 \times 10^{-3}$ | 131 | — | |
| **I**$_{1,5}$ | $3.7 \times 10^{-2}$ | 150 | — | |
| **I**$_{1,8}$ | $3.2 \times 10^{-2}$ | 158 | — | |
| **I**$_{2,6}$ | $1.0 \times 10^{-3}$ | 162 | $5.5 \times 10^{-3}$ | 186 |

[a] Degassed THF, room temp., conc. ≈ 2—5 × $10^{-2}$ M.

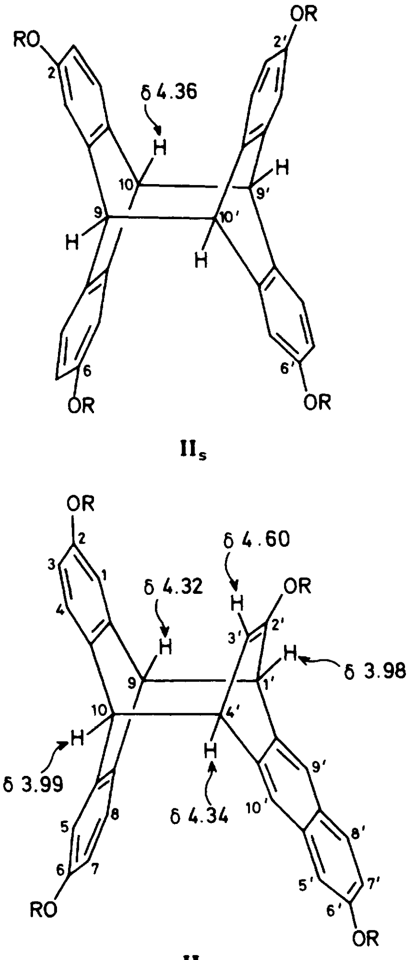


**I**$_{2,6}$; $R^1 = R^3 = R^4 = R^6 = H$,
$R^2 = R^5 = O\text{-}n\text{-}C_{10}H_{21}$, Y = H
**I**$_{1,4}$; $R^2 = R^4 = R^5 = R^6 = H$,
$R^1 = R^3 = O\text{-}n\text{-}C_{10}H_{21}$, Y = H
**I**$_{1,5}$; $R^2 = R^3 = R^5 = R^6 = H$,
$R^1 = R^4 = O\text{-}n\text{-}C_{10}H_{21}$, Y = H
**I**$_{1,8}$; $R^2 = R^3 = R^4 = R^5 = H$,
$R^1 = R^6 = O\text{-}n\text{-}C_{10}H_{21}$, Y = H
**I**$_{9,10}$; $R^1$—$R^6$ = H, Y = $O\text{-}n\text{-}C_{10}H_{21}$

different aldehydes, the 9-monosubstituted (24%) and the 1,5-disubstituted (45%) derivatives, in contrast to anthracene which yields only anthracene-9-carbaldehyde.[8]

Irradiation of compounds **I** (except **I**$_{9,10}$ which is very poorly photoreactive) with a 400 W medium pressure mercury lamp through Pyrex, in carefully purified and freeze and thaw degassed tetrahydrofuran (THF) (100 ml, 2 × $10^{-2}$ M), gave the colourless dimeric products **II**$_s$ (Table 2) which were fully identified by u.v. and 250 MHz $^1$H n.m.r. spectroscopy. The u.v. spectra of photocyclomers **II**$_s$, exclusively obtained from **I**$_{1,4}$, **I**$_{1,5}$, and **I**$_{1,8}$, do not show any naphthalene absorption and the n.m.r. spectra are typical of the structure of 'normal' anthracene photodimer as no naphthalene or vinyl protons are detected.[1,9] In contrast to the preceding compounds, **I**$_{2,6}$ was found to produce two different kinds of photodimers **II**$_s$ and **II**$_a$ ([**II**$_a$]/[**II**$_s$] > 5) which were isolated by fractional crystallisation followed by silica gel column chromatography, eluting with dichloromethane–ligroin (10 : 90—50 : 50).

While the minor photoproduct **II**$_s$ displayed the classical anthracenic photodimer geometry[1] (9,10′–10,9′ bond formation, $\lambda_{max.}$ < 300 nm; $H_9$, $H_{10}$, $H_{9'}$, and $H_{10'}$ gave a single resonance singlet at δ 4.36; **II**$_{s(2,6)}$ smoothly reverts to **I**$_{2,6}$ on heating), the major photoproduct **II**$_a$ was found to have a dissymmetrical structure (Figure 1). Its u.v. spectrum exhibits a naphthalene pattern which implies[9] that the cycloaddition is likely to occur between the 9,10-positions of one ring and the 1′,4′-positions of the other ring [$\lambda_{max.}$ ($\varepsilon_{max.}$) : 336 (1 560); 322 (975), 299 (2 790), 281 (5 200), 272 (6 100), 260 (8 830), and 239 (31 400)]. This dissymmetrical geometry is fully confirmed by the $^1$H n.m.r. analysis§ (CDCl$_3$). Bonding with the vertices



R = n-$C_{10}H_{21}$
**Figure 1**

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§ $H_{1'}$ and $H_{4'}$ are coupled with the bridgehead protons $H_9$ [δ 4.32 ($J_{1'-9}$ 10 Hz)] and $H_{10}$ [δ 3.99 ($J_{4'-10}$ 11 Hz)], respectively. The naphthalene protons $H_{9'}$ and $H_{10'}$ gave a single peak at δ 7.13, $H_{7'}$ (δ 6.10) and $H_{8'}$ (6.64) form an AB pattern with $J_{7'-8'}$ 8.1 Hz, $H_{7'}$ being coupled with $H_{5'}$ [δ 6.42 ($J_{7'-5'}$ 2,2 Hz)]. The benzene protons gave two sets of signals due to the dissymmetry of the molecule [$H_3$ : δ 6.94 and $H_4$ : δ7.46 ($J_{3-4}$ 8.9 Hz), $H_1$ : δ 6.89 ($J_{1-3}$ 2.2 Hz), $H_7$ : δ 6.64 and $H_8$ : δ 6.99 ($J_{7-8}$ 8 Hz), $H_5$ : δ 6.90 ($J_{5-7}$ 2.2 Hz)].

1′ and 4′ leads to the formation of a double bond characterised by the typical chemical shift of the ethylenic proton $H_{3'}$ (δ 4.60) which is coupled with $H_{4'}$ (δ 4.34, $J_{3'-4'}$ = 6 Hz) and $H_{1'}$ [δ 3.98 ($J_{1'-3'}$ 1.7 Hz)].

Consideration of the chemical shifts displayed by the protons of the $CH_2$–O groups shows that photoproduct $\mathbf{II}_a$ is in fact a 1 : 1 mixture of two isomers¶ ('*syn*' and '*anti*' forms). Indeed, the protons in the vicinity of position 2′, which undergo the most important effect due to their proximity to the non-symmetrical substituted benzenic ring, gave two distinct triplets (δ 2.77 and 3.32). The protons of the other O–$CH_2$ groups exhibit a moderate splitting for their respective n.m.r. signals.

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¶ Photodimers $\mathbf{II}_s$ also exhibit two isomers (the '*syn*' and '*anti*' forms).

## References

1 H. Bouas-Laurent, A. Castellan, and J.-P. Desvergne, *Pure Appl. Chem.*, 1980, **52**, 2633, and references therein.
2 M. Daney, C. Vanucci, J.-P. Desvergne, A. Castellan, and H. Bouas-Laurent, *Tetrahedron Lett.*, 1985, **26**, 1505; H. D. Becker and K. Sandros, *ibid.*, 1983, **24**, 3273.
3 A. Iwama, T. Toyoda, M. Yoshida, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2988.
4 J. Rigaudy, J. Guillaume, and D. Maurette, *Bull. Soc. Chim. Fr.*, 1971, 144, and references therein; H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.*, 1972, 254; B. H. Klanderman, *J. Am. Chem. Soc.*, 1965, **87**, 4649.
5 J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley Interscience, London, 1970, (a) p. 251, (b) pp. 121 and 352.
6 R. P. Steiner and J. Michl, *J. Am. Chem. Soc.*, 1978, **100**, 6861.
7 F. Fages, J.-P. Desvergne, and H. Bouas-Laurent, *Bull. Soc. Chim. Fr.*, 1985, 959.
8 L. F. Fieser, J. L. Hartwell, and J. E. Jones, *Org. Synth.*, Coll. Vol. III, p. 98.
9 A. Castellan, J.-P. Desvergne, and H. Bouas-Laurent, *Nouv. J. Chim.*, 1979, **3**, 231.
10 J.-P. Desvergne, N. Bitit, A. Castellan, H. Bouas-Laurent, and J.-C. Soulignac, *J. Lumin.*, 1987, **37**, 175.