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Intramolecular photocycloaddition of anthracene and benzene ring systems

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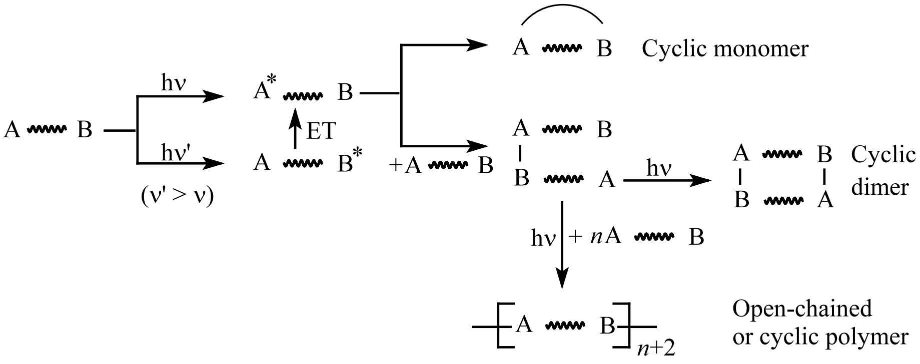
Abstract—The anthracenes **3a**–**c**, substituted in the 9-position with 3,5-dialkoxybenzyloxymethyl groups exhibit, in diluted solutions, intramolecular [4π+4π] photocycloaddition reactions to the polycyclic compounds **4a**–**c**. The quantitative processes are completely reversible by heating, unless acid-catalyzed cleavages lead to thermally stable mono- and diketones: **4a**–**c**→**5a**–**c**→**6**.

Compounds which are suitable for photochemical addition or cycloaddition reactions of the AB type lead to competitive *intra*- and *intermolecular* processes, which depend on the concentration *c* and particularly on the average lifetime τ of the excited species. The prediction of the major route seems to be possible on the basis of the diffusion equation, provided that the values of *c* and τ are known.[1] However, the situation becomes more difficult, if ground-state aggregates are involved, which render the diffusion needless. Scheme 1 summarizes the mono-, bi- and polymolecular reaction routes for AB photo(cyclo)addition reactions. Both reactive sites A and B represent separate chromophores in the same molecule. Due to the energy transfer ET from the energy-higher to the energy-lower excited state, the excitation can take place by irradiation into the absorption of the A or B part.

Recently we published in the dendrimer series[2,3] some antenna systems of anthracenes A substituted in 9,10-position with Fréchet dendrons B.[4] These compounds show in aggregates reversible photocycloaddition reactions to dimers (Scheme 1). We modified the systems and the reaction conditions for the photochemistry, so that a monomolecular switching process became easily feasible. The starting compounds **3a**–**c** were prepared by the reaction of 9-chloromethylanthracene **1** and the 3,5-dialkoxybenzylalcohols **2a**–**c** (Scheme 2).

Irradiation (λ>350 nm) of **3a**–**c** in diluted solutions ($c<3.3\times10^{-3}$ mol L^{-1}) in benzene does not lead to dimers or oligomers;[4] we observed a quantitative *intramolecular* photocycloaddition to **4a**,[8] **4b**[9] and **4c**,[10] respectively, which is completely reversed by heating to 100°C. Consequently, a 1:1 mixture of **3b** and **3c** gave



Scheme 1. Competition between intra- and intermolecular photo(cyclo)addition reactions.

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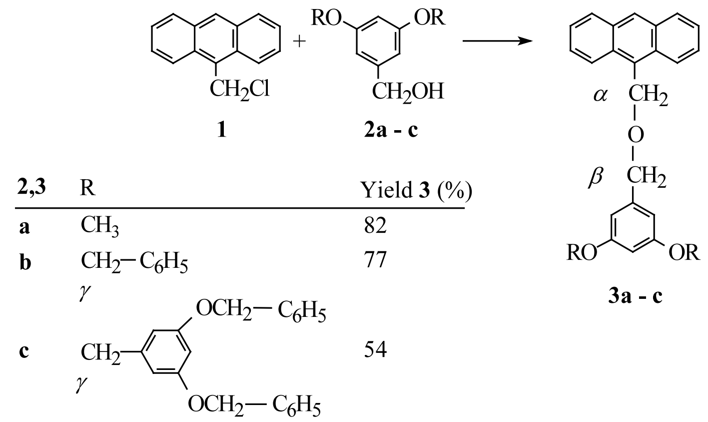
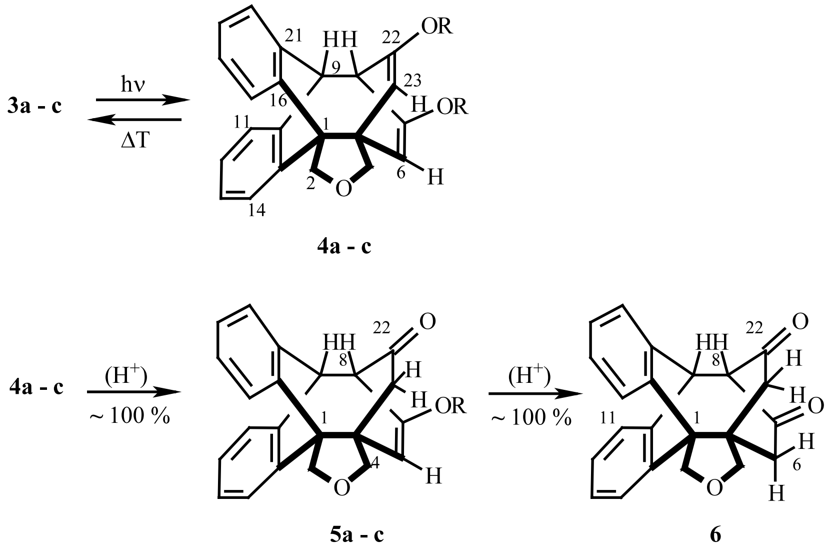


2,3	R	Yield 3 (%)
a	CH_3	82
b	$CH_2-C_6H_5$ γ	77
c	CH_2 γ $OCH_2-C_6H_5$ $OCH_2-C_6H_5$	54

Scheme 2. Preparation of 9-alkoxymethylanthracenes: model compound **3a**,[5] dendrimers **3b**[6] and **3c**.[7] (Phase transfer catalysis: $Bu_4N^+Br^-$, chlorobenzene/water 20:1.)



Scheme 3. Formation of the cycloadducts **4a**–**c** and enol ether cleavage to **5a**–**c** and **6**.

only **4b** and **4c** under these conditions. (Photodimerizations would also yield a mixed product.) The observed [4π+4π] photocycloaddition between an anthracene and a benzene ring system is so far unprecedented[11,12] and corresponds principally to the intermolecular variant that we found recently.[4]

Treatment of **4a**–**c** with formic acid led to a stepwise cleavage of the enol ether moieties yielding the monoketones **5a**,[13] **5b**,[14] **5c**[15] and the diketone **6**.[16] The 1,3-cyclohexanedione system **6** exists in the di-keto form, because the enolization would lead to a double bond on the bridgehead C-8. Moreover, compounds **5** and **6** proved to be stable on heating to 100°C. The thermal retrocycloadditions would not restore the aromatic benzene rings; **5a**–**c**, for example, would lead to energetically high-lying cyclohexa-2,4-dien-1-one substructures (Scheme 3).

Acknowledgements

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5. Compound **3a**, mp 100°C; ^{1}H NMR (CDCl$_3$): $\delta = 3.76$ (s, 6H, OCH$_3$), 4.65 (s, 2H, β-CH$_2$), 5.48 (s, 2H, α-CH$_2$), 6.43 (t, 1H, *p*-H, benzene), 6.57 (d, 2H, *o*-H, benzene), 7.48 (m, 4H, anthracene), 8.00 (m, 2H, anthracene), 8.32 (m, 2H, anthracene), 8.45 (s, 1H, anthracene); ^{13}C NMR (CDCl$_3$): $\delta = 55.3$ (OCH$_3$), 64.0 (α-CH$_2$), 72.3 (β-CH$_2$), 100.1 (*p*-CH, benzene), 105.5 (*o*-CH, benzene), 124.3, 124.9, 126.1, 128.5, 129.0 (CH, anthracene), 128.7, 131.1, 131.5 (C$_q$, anthracene), 140.9, 160.9 (C$_q$, benzene).
6. Compound **3b**, mp 108°C; ^{1}H NMR (CDCl$_3$): $\delta = 4.64$ (s, 2H, β-CH$_2$), 4.97 (s, 4H, γ-CH$_2$), 5.48 (s, 2H, α-CH$_2$), 6.57 (t, 1H, *p*-H, benzene), 6.65 (d, 2H, *o*-H, benzene), 7.38 (m, 10H, benzene), 7.48, m, 4H/8.01, m, 2H/8.33, m, 2H/8.46, s, 1H (anthracene).
7. Compound **3c**, mp 132°C; ^{1}H NMR (CDCl$_3$): $\delta = 4.62$ (s, 2H, β-CH$_2$), 4.90 (s, 4H, γ-CH$_2$), 4.99 (s, 8H, δ-CH$_2$), 5.47 (s, 2H, α-CH$_2$), 6.54, t, 3H/6.61, d, 2H/6.65, d, 4H/7.36, m, 20H (benzene), 7.38, m, 4H/7.99, m, 2H/8.30, m, 2H/8.44, s, 1H (anthracene).
8. Compound **4a**, mp 98°C; ^{1}H NMR (C$_6$D$_6$): $\delta = 2.82$ (s, 6H, OCH$_3$), 3.42 (dt, $^3J = 10.7$ Hz, $^4J = 2.4$ Hz, 1H, 8-H), 3.90 (s, 2H, 4-H), 4.20 (d, $^3J = 10.7$ Hz, 9-H), 4.34 (d, $^4J = 2.4$ Hz, 2H, 6-H, 23-H), 4.70 (s, 2H, 2-H), 7.09, m, 6H/7.30, m, 2H (benzene rings); ^{13}C NMR (C$_6$D$_6$): $\delta = 51.3$ (C-9), 53.3 (C-8), 54.8 (OCH$_3$), 56.9, 65.7 (C-1, C-5), 71.2 (C-2), 81.1 (C-4), 105.8 (C-6, C-23), 122.8, 125.2, 125.8, 127.7 (C-11, 12, 13, 14, 17, 18, 19, 20), 145.0, 146.8 (C-10, 15, 16, 21), 163.7 (C-7, 22).
9. Compound **4b**, mp 70°C; ^{1}H NMR (CDCl$_3$): $\delta = 3.24$ (m, 1H, 8-H), 3.59/4.25 (AB, $^2J = -10.6$ Hz, γ-CH$_2$), 3.90 (s, 2H, 4-H), 4.28 (d, $^3J = 11.4$ Hz, 1H, 9-H), 4.48 (d, $^4J = 2.0$ Hz, 6-H, 23-H), 4.75 (s, 2H, 2-H), 7.07–7.36 (m, 18H, aromat. H).
10. Compound **4c**, mp 74°C; ^{1}H NMR (CDCl$_3$): $\delta = 3.22$ (dt, $^3J = 10.6$ Hz, $^4J = 1.9$ Hz, 1H, 8-H), 3.48/4.14 (AB, $^2J = -11.0$ Hz, 4H, γ-CH$_2$), 3.85 (s, 2H, 4-H), 4.23 (d, $^3J = 10.6$ Hz, 1H, 9-H), 4.41 (d, $^4J = 1.9$ Hz, 2H, 6-H, 23-H), 4.71 (s, 2H, 2-H), 5.01 (s, 8H, δ-CH$_2$), 6.44 (d, 4H, aromat. H), 6.53 (t, 2H, aromat. H), 6.97–7.42 (m, 28H, aromat. H).
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13. Compound **5a**, mp 105°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.90/2.04$ (AB, $^2J = -18.4$ Hz, 2H, 23-H), 2.93 (s, 3H, OCH$_3$), 3.44 (dd, $^3J = 11.7$ Hz, $^4J = 1.6$ Hz, 1H, 8-H), 3.70/3.95 (AB, $^2J = -9.0$ Hz, 2H, 4-H), 4.37 ('s', 1H, 6-H), 4.38 (d, $^3J = 11.7$ Hz, 1H, 9-H), 4.68/4.88 (AB, $^2J = -10.6$ Hz, 2H, 2-H), 7.20 (m, 7H, aromat. H), 7.48 (m, 1H, aromat. H); ^{13}C NMR (CDCl$_3$): $\delta = 45.5$ (C-23), 49.4 (C-9), 51.6, 60.4 (C-1, C-5), 54.6 (OCH$_3$), 60.6 (C-8), 72.0 (C-2), 81.0 (C-4), 105.9 (C-6), 122.9, 123.9, 125.9, 126.4, 127.0, 127.1, 127.5, 128.8 (aromat. CH), 140.2, 141.0, 141.6, 144.9 (aromat. C$_q$), 158.8 (C$_q$O), 209.7 (CO).
14. Compound **5b**, mp 72°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.91/2.09$ (AB, $^2J = -18.5$ Hz, 2H, 23-H), 3.52 (dd, $^3J = 11.7$ Hz, $^4J = 1.8$ Hz, 1H, 8-H), 3.67/4.21 (AB, $^2J = -10.7$ Hz, 2H, 4-H), 3.71/3.96 (AB, $^2J = -8.8$ Hz, 2H, γ-CH$_2$), 4.41 (d, $^3J = 11.7$ Hz, 1H, 9-H), 4.51 (d, $^4J = 1.8$ Hz, 1H, 6-H), 4.68/4.90 (AB, $^2J = -10.2$ Hz, 2-H), 7.23 (m, 12H, aromat. H), 7.52 (m, 1H, aromat. H).
15. Compound **5c**, mp 68°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.91/2.08$ (AB, $^2J = -19.0$ Hz, 2H, 23-H), 3.52 (m, 1H, 8-H), 3.57/4.11 (AB, $^2J = -10.7$ Hz, 2H, γ-CH$_2$), 3.70/3.95 (AB, $^2J = -9.3$ Hz, 2H, 4-H), 4.40 (d, $^3J = 11.2$ Hz, 1H, 9-H), 4.48 ('s', 1H, 6-H), 4.68/4.89 (AB, $^2J = -10.3$ Hz, 2H, 2-H), 5.01 (s, 4H, δ-CH$_2$), 6.39 (d, 2H, aromat. H), 6.54 (t, 1H, aromat. H), 7.31 (m, 18H, aromat. H).
16. Compound **6**, mp 207°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.92/2.14$ (AB, $^2J = -18.5$ Hz, 4H, 6-H, 23-H), 3.80 (s, 2H, 4-H), 3.96 (d, $^3J = 12.2$ Hz, 1H, 8-H), 4.61 (d, $^3J = 12.2$ Hz, 1H, 9-H), 4.89 (s, 2H, 2-H), 7.28 (m, 6H, aromat. H), 7.50 (m, 2H, aromat. H); ^{13}C NMR (CDCl$_3$): $\delta = 47.7$ (C-6, C-23), 47.7 (C-9), 48.3, 56.7 (C-1, C-5), 72.5 (C-8), 73.5 (C-2), 81.2 (C-4), 124.5, 127.7, 127.9, 128.9 (aromat. CH), 138.4, 141.8 (aromat. C$_q$), 205.6 (CO).