183(2) K. Enraf-Nonius CAD4, graphite monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, ω scans, $\Delta\omega = 0.8°$, $((\sin\theta)/\lambda)_{max} = 0.592$ Å^{-1}, *hkl* range: $+37$, $+18$, $-39 - +35$. Of a total of 13282 measured reflexions, 13008 were unique ($R_{int} = 0.027$) and 7920 were "observed" with $I > 2\sigma(I)$. Refinement of 797 parameters was done on F^2 of all unique reflexions leading to $R(F)/wR(F^2) = 0.064/0.190$, $GoF = 1.06$, $w = 1/(\sigma^2(F_o^2) + (0.1086\,P)^2)$, $P = (\max(F_o^2,0) + 2F_c^2)/3$. $\Delta\rho_{fin}$ (max/min) $= 0.62/-0.69$ e Å^{-3}. In the refinement all non-H atoms were refined anisotropically, except the C atoms of the coordinated molecule Et_2O which were treated in a split atom model. H11, H21, H31 were refined freely with individual isotropic displacement parameters. While one of the interstitial hexane molecules could be refined satisfactorily, the second one was found to be severly disordered, thereby impeding any meaningful refinement. Therefore, it was excluded from structure factor calculations with the routine SQUEEZE[8] as included in PLATON.[9] Restraints were applied to the bonds between the disordered ether and hexane atoms. Programs used: SHELXS-97 (structure solution),[10] SHELXL-97 (structure refinement),[10] ORTEP-III (molecular drawings).[11]

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[20] Crystal structure data of **4**: $C_{100}H_{108}Ca_4O_8P_4$, $M_r = 1722.06$, tetragonal, space group $I4_1/a$ (No. 88), $a = b = 25.091(9)$, $c = 14.050(9)$ Å, $V = 8845(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.293$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.74$ cm^{-1}, $F(000) = 3648$, $T = 183(2)$ K. Enraf-Nonius CAD4, graphite monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71069$ Å, ω-scans, $\Delta\omega = 0.8°$, $((\sin\theta)/\lambda)_{max} = 0.50$ Å^{-1}, *hkl* range: ± 25, ± 25, $+14$. Of a total of 10451 measured reflexions, 2369 were unique ($R_{int} = 0.122$) and 1380 were "observed" with $I > 2\sigma(I)$. Refinement of 302 parameters on F^2 of all unique reflexions leading to $R(F)/wR(F^2) = 0.046/0.104$, $GoF = 1.01$, $w = 1/(\sigma^2(F_o^2) + (0.0456\,P)^2 + (10.2187\,P))$, $P = (\max(F_o^2,0) + 2F_c^2)/3$. $\Delta\rho_{fin}$ (max/min) $= 0.22/-0.26$ e Å^{-3}. In the refinement all non-H atoms were refined anisotropically. Some of the H atoms including that at C1 were refined freely with individual isotropic displacement parameters.

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The Unusual Photochemistry of Dendrimers with an Anthracene Core[**]

Derong Cao and Herbert Meier[*]

Monodisperse dendrimers represent a link between organic compounds with low molecular masses and polymers, and are distinguished by a number of special properties.[1] The objective of the present work was to study the photochemistry and the photophysics of anthracene when used as a core of a dendritic structure. Thus, dendrons of the Fréchet type[2] were attached in the 9 and 10 positions of anthracene. The nucleophilic substitution of the halogen atoms in 9,10-bis(chloromethyl)- or 9,10-bis(bromomethyl)anthracene (**2**) with 3,5-dialkoxy-substituted benzyl alcohols **1a–c** in an alkaline medium under phase-transfer conditions provided yields between 66 and 30% (Scheme 1). An increase in the branching makes the reaction less effective.[3] For comparitive purposes the methoxy compound **3d** was prepared by an analogous procedure.

The ^1H and ^{13}C NMR data of the dendrimers **3a–c** are summarized in Table 1; they differ little from the model compound **3d**, apart from the presence of methoxy groups in

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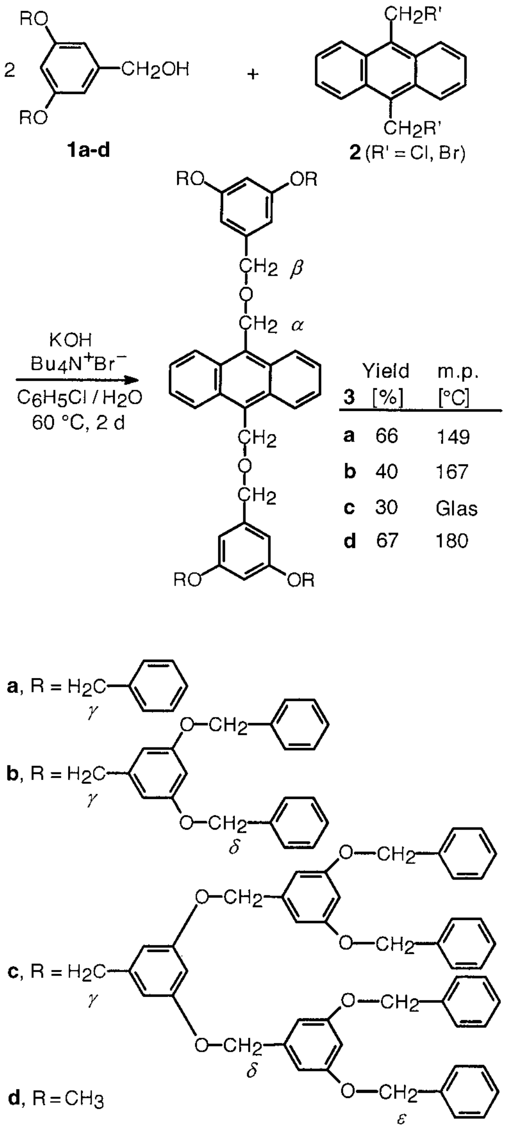


3	Yield [%]	m.p. [°C]
a	66	149
b	40	167
c	30	Glas
d	67	180

Scheme 1. Synthesis of the dendrimers **3a–c** and the model compound **3d**.

the latter. The chemical shifts of the OCH_2 groups (α to ε, Scheme 1 and Table 1) are most characteristic. Their chemical shifts $\delta(^1H)$ follow the sequence: $\alpha > \varepsilon > \delta > \gamma > \beta$; however, contrary to this, the β-OCH_2 group has the highest and the α-OCH_2 group the lowest chemical shift in the ^{13}C NMR spectra, with the sequence being: $\beta > \varepsilon \approx \delta \approx \gamma > \alpha$.

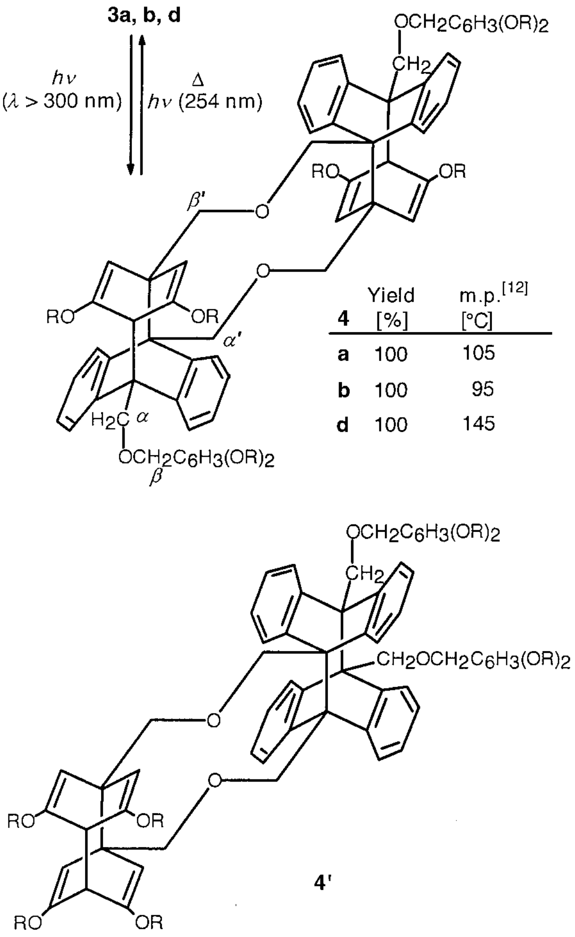
The Fréchet-type dendrons were selected so that the "antenna effect" could be studied.[4, 5] The electronic transitions in the dendrons **3a–c** can be localized, to a first approximation, in separated molecular regions: in the anthracene core A, in the middle benzene rings B_m bearing alkoxy groups, and in the peripheral benzene rings B_p. The corresponding excitation energies $[E(S_1) - E(S_0)]$ decrease from the outside to the inside, and an effective singlet energy transfer $B_p \rightarrow B_m \rightarrow A$ should, therefore, be possible. An impressive proof of this hypothesis was provided by the fluorescence quantum yields: Φ_F increases by a factor of 2.24 for **3a** and by a factor of 2.57 for **3b** relative to unsubstituted anthracene when solutions of the compounds in dichloromethane at room temperature are excited at $\lambda = 260$ nm.[6] Solutions containing equal molar concentrations of anthracene and the "arms" **1a** or **1b** the probes of **3a** and **3b**, respectively, do not indicate an amplification effect at all. Thus, an intermolecular energy transfer under the conditions described can be ruled out.

The photochemistry of anthracene and its derivatives is distinguished by wavelength-dependent dimerization reactions. Apart form the [4π+4π] cyclodimerization of the central rings, some examples of [4π+4π], [4π+2π], and [2π+2π] cyclodimerization reactions are known in which the outer rings are involved.[7, 8] Irradiation in the near-UV region ($\lambda \geq 300$ nm) of an approximately 10^{-3} M solution of **3a**, **b** or **3d** in benzene leads to the quantitative formation of similar dimerization products; the ^1H and ^{13}C NMR spectra of the crude products do not reveal any side reactions occurred. The structures of the photodimers do not fit into the known reaction schemes.[7–9] We established that in each case a benzene ring at the β-OCH_2 group is involved in the dimerization. This finding points to structures **4** and **4'** (Scheme 2). Photocycloadditions between two benzene rings[10] or between an anthracene and a benzene ring system[11] are extremely rare; up to now they were only observed in intramolecular reactions of a few rigid structures.

Provided that the inversion of the central 1,6-dioxacyclodecane ring in **4** and **4'** is fast, **4** will show a C_{2h} and **4'** a C_{2v} symmetry; accordingly one can not distinguish between these two structures on the basis of the number and the splitting of the signals in the ^1H and ^{13}C NMR spectra. A decision in favor of **4a**, **b**, **d** was possible with the help of nuclear Overhauser effect (NOE) measurements. Irradiation into the signal of the methine protons on the cyclohexadiene rings produces a positive NOE in the signal corresponding to the α-OCH_2 groups (and simultaneously an INDOR effect in the signal of the olefinic protons). This result is compatible with structure **4** but not with **4'**. The photodimerization **3**→**4** consists of an intermolecular and an intramolecular [4π+4π] process. The UV spectra measured during the reaction do not reveal an intermediate. Whereas aggregation seems to be relevant for the intermolecular step, the two 4π components of the intramolecular step are already fixed in a spatial proximity.

Table 1. ^1H and ^{13}C NMR data of **3a–c** (δ values in $CDCl_3$, TMS as an internal standard).

Anthracene core				Benzene rings								Oxymethylene groups				
AA'	BB'			A_2	B			AA'	BB'	C		α-H	β-H	γ-H	δ-H	ε-H
C-1	C-2	C-4a	C-9	CH	CH	C_q	C_qO	CH	CH	CH	C_q	α-CH_2	β-CH_2	γ-CH_2	δ-H_2	ε-CH_2
8.35	7.47	–	–	6.64	6.55	–	–	7.32	7.32	7.32	–	5.47	4.62	4.91	4.95	4.98
± 0.02	± 0.02			± 0.01	± 0.02			± 0.04	± 0.04	± 0.04		± 0.02	± 0.03	± 0.06	± 0.05	
125.1	125.7	130.9	130.4	106.6	101.7	140.1	160.1	127.5	128.6	128.0	136.8	64.1	72.3	70.0	70.1	70.1
± 0.1	± 0.1	± 0.1	± 0.1	± 0.2	± 0.1	± 0.9	± 0.1	± 0.1	± 0.1	± 0.1	± 0.1	± 0.1	± 0.1	± 0.1	± 0.1	



4	Yield [%]	m.p.[12] [°C]
a	100	105
b	100	95
d	100	145

Scheme 2. Reversible photodimerization of **3a**, **b**, **d**.

As a result of the loss of aromaticity in the central ring of the anthracene and in the benzene ring which is involved in the cycloaddition the ^{1}H NMR spectra of **4a**, **b**, **d** show numerous changes relative to those of the starting compounds **3a**, **b**, **d**.[13] The methylene groups in the ten-membered ring give singlet signals at $\delta = 4.75 \pm 0.05$ (α') and $\delta = 3.84 \pm 0.05$ (β') in CD_2Cl_2. The protons on the cyclohexadiene ring resonanate at very high field, namely at $\delta = 4.37 \pm 0.10$ (olefinic H) and $\delta = 2.19 \pm 0.20$ (methine group). The AA′BB′ spin system of the original anthracene unit is also shifted to high field: $\delta = 7.29 \pm 0.10$ and 7.12 ± 0.05. Even the signals of the side chains, which are not involved in the dimerization, are affected and have δ values of 4.29 ± 0.15 (α H), 4.60 ± 0.05 (β H), 6.53 ± 0.15 (aromatic H), 7.35 ± 0.10 and 5.02 ± 0.04 (benzyloxy), and 3.77 (methoxy). The AB spin pattern of the benzyloxy groups attached to the cyclohexadiene rings ($\delta = 4.18 \pm 0.03$ and 3.55 ± 0.03, $^2J = -(10.8 \pm 0.3)$ Hz) are particularly striking in the ^{1}H NMR spectra of **4a**, **b**; the corresponding methoxy groups in **4d** lead to a singlet at $\delta = 2.86$.

The molecular ions $[M+H]^+$ of the monomeric and the dimeric structures can be obtained in the mass spectra using field-desorption (FD) conditions. Electron-impact measurements induce a dissociation of the photodimers in the ionization chamber.

The unusual photodimerization of **3a**, **b**, **d** can be explained by an aggregation of the dendrimers and the model compound in solution. Presumably, a π-π interaction of the anthracene unit and the electron-rich, alkoxy-substituted benzene rings is more favorable than the anthracene–anthracene interaction. Until now, cycloadducts of anthracene and benzene rings could only be obtained by multistep procedures.[14, 15] Irradiation of **4a**, **b**, **d** with UV light of short wavelengths[16] or heating above 100 °C leads to a quantitative reverse reaction.

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