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Selectivity in the Photodimerization of 6-Alkylcoumarins

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Coumarin and 6-alkylcoumarins (alkyl = C_1 to C_{16}) were photodimerized in homogeneous solvents differing in polarity and in aqueous micellar solutions. The four possible photodimers, syn head-to-head (hh), anti head-to-head, syn head-to-tail (ht), and anti head-to-tail, were identified through a combination of X-ray analysis and NMR spectroscopy. In 6-methylcoumarin the concentration-corrected dimerization (quantum) yield increases with decreasing concentration of the educt; anti-hh was formed exclusively in nonpolar solvents and upon triplet sensitization and was the main product under all conditions except for ionic micellar systems, which direct to preferred syn-hh dimerization. Long alkyl substituents, however, lead to anti-hh in polar solvents and in micelles, too. Predominating ht dimer formation was observed for nonsubstituted coumarin in polar solvents only. Thus, syn/anti and hh/ht selectivity can be steered by varying the 6-alkyl substituent. Syn-hh photodimers of 6-methylcoumarin can be photochemically split into the monomers; they partly proved thermally unstable against acids, bases, methanol, and on SiO_2 surfaces.

Introduction

The photochemical $2\pi + 2\pi$ dimerization of unsaturated organic molecules is a well-known process in organic photochemistry.[1] Among the compounds investigated, coumarin[2a] (**1**) and its derivatives have attracted considerable interest, in part because of their biological and photobiological importance.[2b] Head-to-head dimers (hh, **2**,**3**), head-to-tail dimers (ht, **4**,**5**) as well as syn- (**2**,**4**) and anti dimers (**3**,**5**) may be formed, as shown in Scheme 1. About 1990, the knowledge on the coumarin photodimerization was summarized in textbooks and reviews as follows:[3] in nonpolar solvents nonreactive self-quenching (process f in Scheme 1) widely suppresses the formation of dimers; the syn-head-to-head (**2**, R = H) dimer is formed in polar solvents from the singlet excited ^{1}**1*** state (process d, perhaps via an excimer intermediate); the anti-head-to-head dimer (**3**, R = H) was found after benzophenone-sensitized population of the triplet ^{3}**1*** state in both polar and nonpolar solvents (process b) along with trace amounts of the anti-head-to-tail dimer (**5**, R = H, process c), possibly via a triplet diradical intermediate.[4] A variety of coumarin derivatives was investigated in solution[5] as well as in solid systems[6a] or anchored to a surface.[6b] In the derivatives, considerable amounts of head-to-tail dimers may be formed. Anti dimers were found in chloro-substituted coumarins and in heavy atom solvents. Due to the competing nonreactive self-quenching process, the dimerization quantum yield was comparatively poor in most cases; i.e., quite long irradiation times were necessary. Nevertheless, the photo-cross-linking of coumarin side chains in polymers has been applied to induce surface anisotropy in thin films and subsequent liquid crystal alignment for displays.[6c] The photodimerization of coumarins monosubstituted in the 6-position has not yet been investigated so far.

A wealth of publications on the use of micellar systems to direct regio- and stereoselectivities in photoreactions through preorientation can be found in the literature.[7] The influence of micelles on the regioselectivities of ($4\pi + 4\pi$)[8] and ($2\pi + 2\pi$)[9] dimerizations has been studied thoroughly. Several attempts were made by Ramamurthy et al. to employ the micellar preorientation effect in the photodimerization of coumarin derivatives.[10] Although

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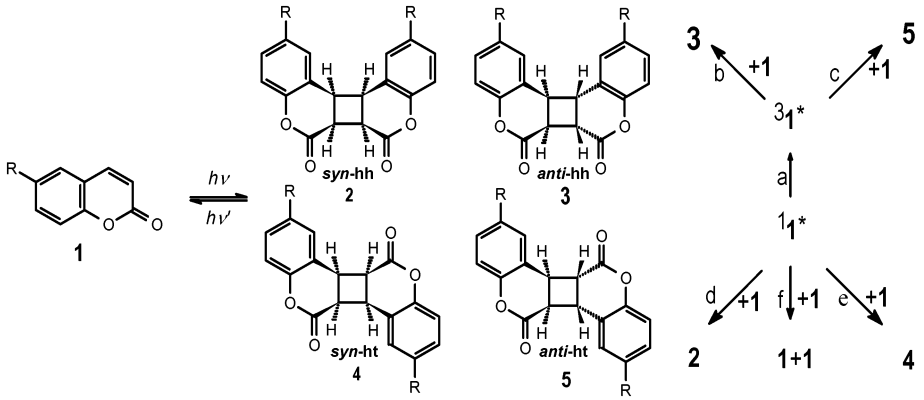
SCHEME 1. Photodimerization of Coumarins (R = H, alkyl) and Reaction Scheme: (a) Intersystem Crossing, (b−e) Dimerization, (f) Nonreactive Self-Quenching



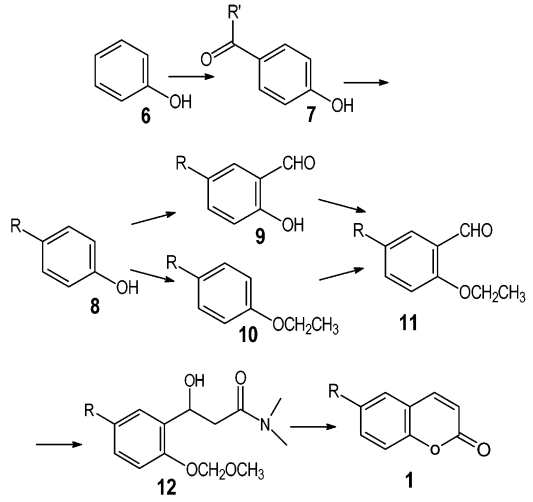
the authors synthesized "surfactant-like" coumarins (long alkyloxy substituents in 7-position), they did not observe effects attributable to preorientation and, consequently, they discussed their results in terms of micropolarity at the reaction site in the microheterogeneous systems.

In this paper, we present our results on the photodimerization of 10 6-alkylcoumarins[11] (**1**, R = methyl, ethyl, 2-propyl, *tert*-butyl, *n*-butyl, *n*-pentyl, *n*-octyl, *n*-dodecyl, *n*-cetyl; 6,8-diethylcoumarin), in which up to four of the possible dimers (Scheme 1) may be formed. The separation of isomeric dimers is complicated by thermal reactions of the dimers in the presence of adsorbents. Therefore, a steering of hh/ht ratios as well as syn/anti ratios (regio and stereoselectivity) is desirable. We will show that this can be widely achieved by the use of micellar systems and by varying the length of the alkyl substituent.

Results

Synthesis. The study required the syntheses of a series of 6-alkylcoumarins. 6-Ethylcoumarin could be prepared analogously to 6-methylcoumarin in a one-step synthesis following a literature procedure.[12] This literature route failed for 6-propyl and larger alkyl substituents. These compounds therefore were prepared as depicted in Scheme 2. The alkyl phenols **8** were commercially available. The rest had to be prepared starting from phenol **6**.[13] The conversion of alkylphenols **8** to methoxymethoxybenzaldehydes **11** was achieved in two ways: (i) by introducing the aldehyde group at the 2-position to form **9**[14] and subsequently **11**[15] or (ii) by formation of 4-alkylmethoxymethoxy phenyl ether (**10**), ortho metalation, and subsequent reaction with dimethylformamide.[16] Better yields resulted from the second way. Finally, the 6-alkylcoumarins **1** were prepared from **11** via **12** by the addition of lithium *N*,*N*-dimethyl acetamide and cyclization in acetic acid.[17]

SCHEME 2. Scheme of the Synthesis of 6-Alkylcoumarins



Spectra. Absorption and emission spectra of coumarin and two 6-alkylcoumarins in methanol are compared in

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(11) While most of the 6-alkylcoumarins have not been studied previously, 6-methylcoumarin was used as a fragrance component. Thus, this compound was investigated with respect to its physiological activities. Recently its use in fragrances was questioned because of its photoallergic and hepatic effects and its tendency to sensitize singlet oxygen: (a) DeLeo, V. A.; Suarez, S. M.; Maso, M. J. *Arch. Dermatol.* **1992**, *128*, 1513. (b) Lake, B. G.; Evans, J. G.; Lewis, D. F.; Price, R. J. *Food Chem. Toxicol.* **1994**, *32*, 743. (c) Allen, S. K.; Todd, A.; Allen, J. M. *Biochem. Biophys. Res. Commun.* **1997**, *235*, 615.

(12) (a) Fries, K.; Klostermann, W. *Ber.* **1906**, *39*, 871. (b) Thompson, T. J.; Edee, R. H. *J. Am. Chem. Soc.* **1925**, *47*, 2556. (c) De Benneville, P. L.; Conner, R. *J. Am. Chem. Soc.* **1940**, *62*, 3067.

(13) (a) Buu-Hoi, Ng. Ph.; Séailles, J. *J. Org. Chem.* **1955**, *20*, 606−607. (b) Read, R. R.; Wood, J., Jr. *Org. Synth. Collective* **1955**, *3*, 444.

(14) Stepniak-Biniakiewicz, D. *Pol. J. Chem.* **1980**, *54*, 1567−1571.

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(16) (a) Christensen, H. *Synth. Commun.* **1975**, *5*, 65−78. (b) Townsend, C. A.; Bloom, L. M. *Tetrahedron Lett.* **1981**, *22*, 3923−3924.

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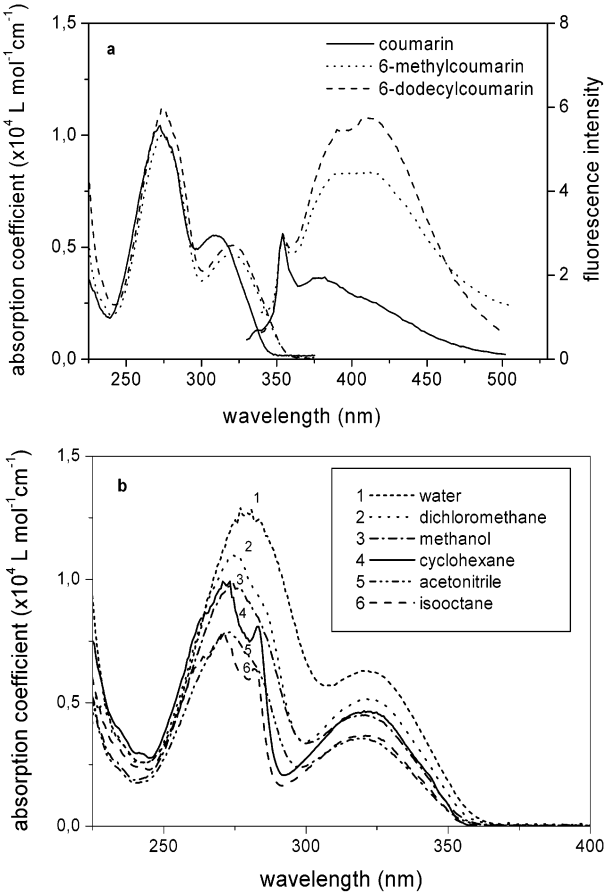

FIGURE 1. (a) Absorption and emission spectra of 6-alkylcoumarins in methanol; (b) absorption spectra of 6-methylcoumarin (**1**, R = methyl) in various solvents.

Figure 1a. The figure reveals a red shift of the long wavelength absorption peak by ca. 10 nm upon alkylation and an according shift of the emission. In all three cases the emission yield is very low, as can be seen by the appearance of the sharp peak at 354 nm, which is due to Raman lines of the solvent. This is in keeping with a literature value for the fluorescence quantum yield of $\Phi_{fl} < 10^{-4}$.[18a] In Figure 1b the influence of the solvent polarity on the absorption of 6-methylcoumarin is shown. In nonpolar solvents some vibrational structure of the peak around 270 nm appears, whose maximum shifts to lower wavelengths compared to polar solvents, as expected for $\pi-\pi^*$-transitions. The weaker long wavelength peak—perhaps of n$-\pi^*$-character (cf. ref 18b)—however, does not shift strongly upon changing the solvent polarity. In the concentration range of $10^{-5}-10^{-2}$ mol dm^{-3} we did not observe significant changes in the absorption spectra. In Figure 2 the absorption spectra in chloroform of 6-methylcoumarin and two of its photodimers (syn-hh and anti-hh) are compared. It can be seen that upon irradiation at $\lambda > 305$ nm the photodimers cannot be excited, i.e., secondary photochemical processes originating from the irradiation of dimers need not be discussed.

Assignment of 6-Methylcoumarin Photodimers. In Figure 3 the structural formulas of the four possible

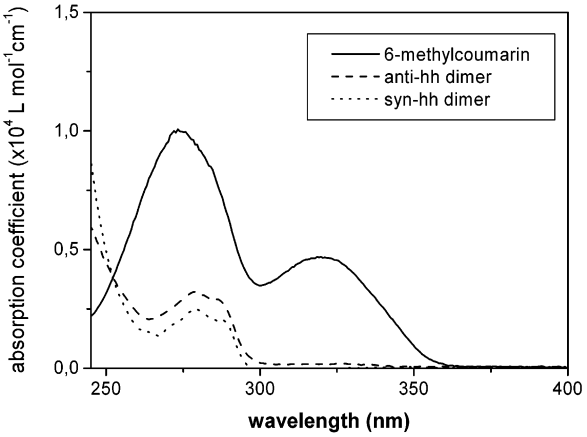

FIGURE 2. Absorption spectra of 6-methylcoumarin (**1**, R = methyl) and its syn-hh (**2**) and anti-hh (**3**) dimers in $CHCl_3$.

photodimers of 6-methylcoumarin (**1**, R = methyl) are depicted, as revealed from force field calculations (COSMOS (PRO) 4.5 for WINDOWS). The ^{1}H NMR spectrum of the cyclobutane protons resulting from the irradiation of 6-methylcoumarin (Figure 4) shows a mixture of all four possible dimers. Two of the dimers were isolated in pure form, so that their spectra could be taken separately. For one of them the crystal structure was determined via an X-ray investigation. As shown in Figure 5, this isomer exhibits syn-hh geometry (**2**, R = methyl).

Therefore, the ^{1}H NMR spectrum of this isomer served as reference for the assignment of the other dimers. The other three isomers were assigned according to the following arguments: the aromatic protons of syn dimers appear at higher field as compared to anti dimers. The cyclobutane protons behave oppositely. Because of negligible interactions with other parts of the molecule, the signals of the aromatic protons of anti-hh and anti-ht dimers appear at very similar chemical shifts. The cyclobutane protons (at C-8, C-8′, C-9, C-9′) of the syn-hh configuration exhibit an AA′XX′ coupling pattern. The coupling constants $^3J_{AX}$ and $^3J_{A'X'}$ are identical at 8.5 Hz as well as the coupling constants $^3J_{AA'}$ and $^3J_{XX'}$ at 8.2 Hz. From the A_2B_2 pattern of the analogous part of the syn-ht spectrum, these couplings are calculated by simulation as $^3J_{AB} = 8.6$ Hz. These comparatively large values are to be expected for cyclobutane protons in "cis" configuration. In fact, the dihedral angles are 30°−32° according to the COSMOS-optimized geometries shown in Figure 3 (i.e. deviating from 60°, the true cis dihedral angle). In the anti dimers both, "cis" and "trans" protons are present. The "cis" protons show coupling constants of $^3J_{AX}$ and $^3J_{A'X'}$ at 8.6 Hz (similar to the cyclobutane protons of the syn dimers above), while the coupling constants of the "trans" protons are smaller, i.e., $^3J_{AA'} = {}^3J_{XX'} = 5.4$ Hz (or 6.1 Hz, respectively). The smaller coupling constants are corroborated by the COSMOS geometry optimizing, which delivers dihedral angles of 135° (to be compared with 180° for true trans). In Table 1 the ^{1}H NMR data are compiled.

For the two isolated isomers syn-hh (**2**, R = methyl) and anti-hh (**3**, R = methyl) as well as for the ht isomers **4** and **5**, the assignment of the ^{1}H NMR signals of the cyclobutane protons is further supported by simulations of the spectra, which are shown and compared with

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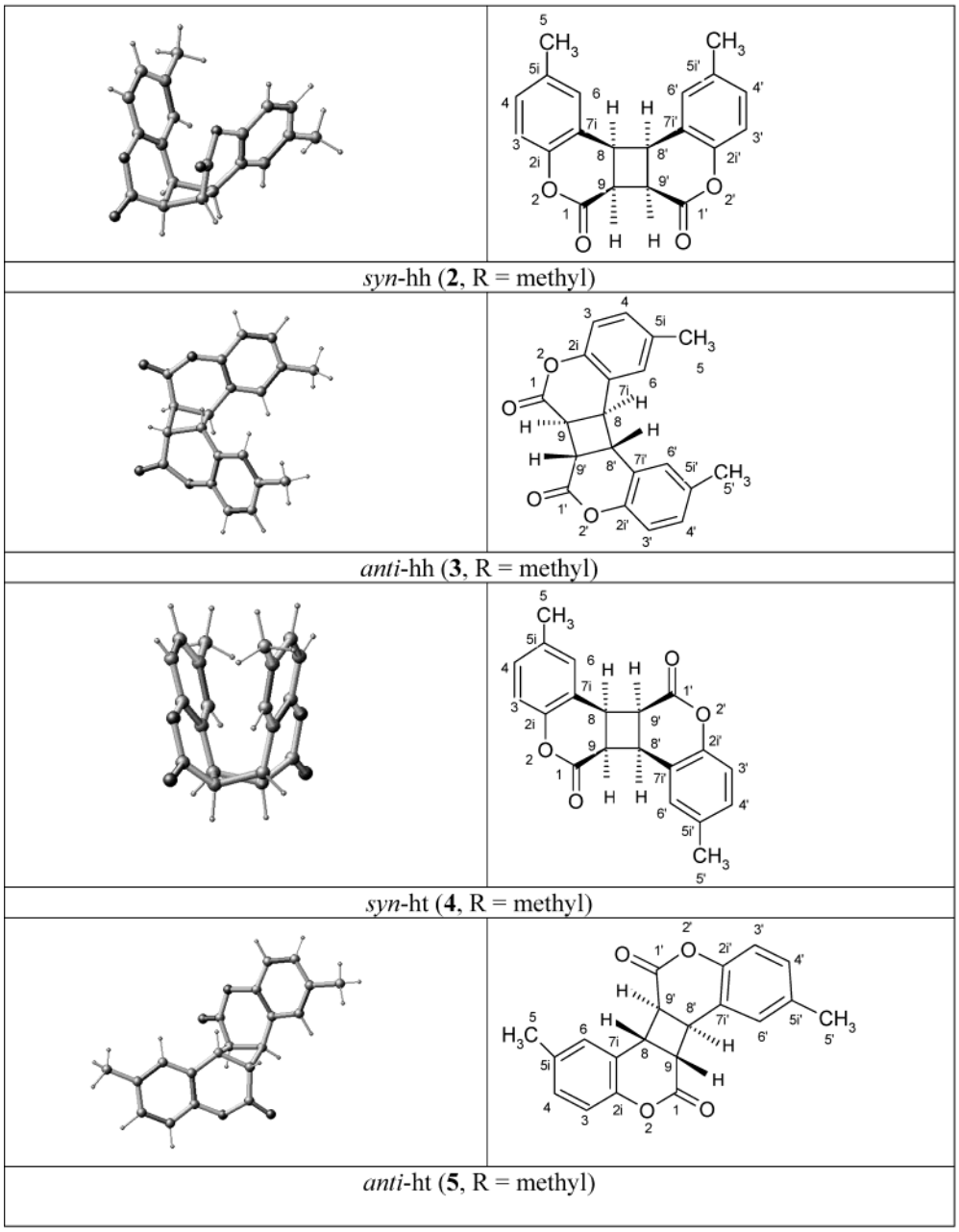

FIGURE 3. Structures of 6-methylcoumarin dimers (**2**−**5**, R = methyl) and numbering of C-atoms.

experimental spectra in Figure 6. An interesting distinction appears when the two ht simulations are compared: for syn-ht the spectrum was simulated as an A_2X_2 pattern, for anti-ht a satisfying simulation was possible using an AA′XX′ pattern. ^{13}C NMR spectral data of **2**−**5** (R = methyl) are given in the experimental part.

In analogy to the analysis above, the dimers of the other 6-alkyl coumarins were assigned.

Irradiations. Influence of the Solvent on the Product Distribution in 6-Methylcoumarin. 6-Methylcoumarin (**1**, R = methyl) was irradiated in a variety of homogeneous solvents differing in polarity and in micellar solutions of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate. For comparison, a solid film of **1** (R = methyl) was included in the investigation. The distribution of products as revealed by integrals of ^1H NMR spectra is comprised in Table 2.

From inspection of the table one recognizes the following:

(i) The hh-dimers always prevail; the anti-ht dimer is formed in the irradiation of the solid and in benzene only (process c in Scheme 1).

(ii) Anti dimers prevail in homogeneous solvents; in ionic surfactant solutions as well as in the solid the opposite is observed.

(iii) in nonpolar solvents (cyclohexane, benzene) and in ketones (acetone, cyclohexanone), anti-hh dimers are formed almost exclusively. In polar solvents syn-dimers also form.

(iv) In pure dichloromethane the anti-hh dimer is formed selectively; in the presence of BF_3 the selectivity is reduced while the (quantum) yield rises strongly.

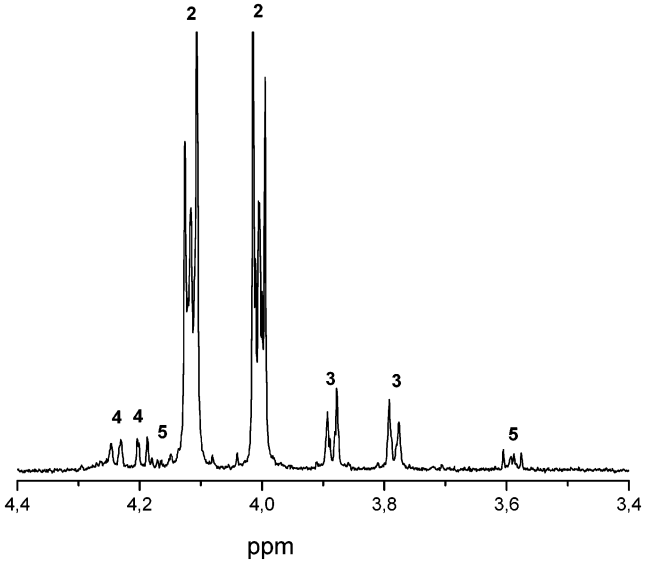

FIGURE 4. ^{1}H NMR spectrum of the cyclobutane proton region showing all four dimers.

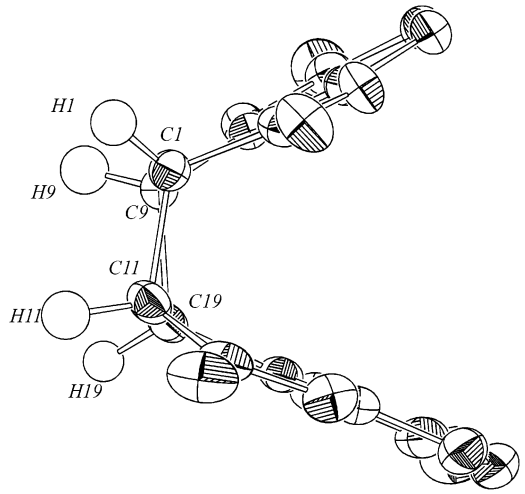

FIGURE 5. X-ray structure of the syn-hh dimer (**2**, R = methyl) of 6-methylcoumarin. (The numbering of atoms differs from Figure 5.)

(v) The presence of a triplet sensitizer (benzophenone) generally increases the overall yield; the selectivity for the anti-hh product rises in methanol but not in acetonitrile.

The largely differing results in water and in aqueous CTAB (at 0.004 molar educt) indicate that 6-methylcoumarin is associated with the micelles, so the photodimerization takes place in a micellar environment. As a consequence, the high local concentration leads to an increased conversion rate. A heavy atom effect of the bromide counterions[19] directing to anti-hh cannot be observed. Despite some variation of the intensity of the lamp (±15% throughout the study due to aging and exchanges), the degree of photochemical conversion related to the irradiation time reflects differences in (relative) quantum yields. A higher quantum yield in polar solvents as compared to nonpolar ones (as reported for the nonsubstituted coumarin[4a]) cannot be clearly distinguished at all concentrations.

Photodimerization of 6-Methylcoumarin at Different Concentrations. The dependence of the product distribution on the concentration of the educt was studied in methanol, acetonitrile, water, and 0.25 M aqueous CTAB. Table 3 displays the results.

At very low concentrations side products may form at quite high quantum yields (as revealed by the pc′ values), which were not investigated further. If we inspect irradiations not producing side products, it is obvious that the concentration-corrected relative quantum yields increase at decreasing concentration in all the solvents investigated. Among the photodimers, the anti-hh isomer (triplet product) always prevails at low concentrations. At higher concentrations, the selectivity is reduced (i.e., the process d competes more favorably with the processes a in Scheme 1). Acetonitrile and methanol give similar results with respect to the pc′ values, while considerable amounts of syn dimers at low concentrations are absent in acetonitrile.

In water, the educt (**1**, R = methyl) is not soluble at 0.01 mol/dm^3 and above. As might have been expected because of the close vicinity of the reaction partners, the relative quantum yields (pc/*t*) in suspensions are much higher as compared to homogeneous solutions of, for example, methanol at comparable concentrations. In CTAB again, the possible heavy atom effect[19c] does not work, which should lead to an increased anti-hh formation.

Photodimerization of 6-Methylcoumarin at Different Temperatures. The temperature dependence of the product distribution was investigated in water and in cyclohexane as solvents. As shown in Table 4 the overall product yield strongly decreases with increasing temperature in both the solvents. The product distribution does not change between 0 and 40 °C in cyclohexane (anti-hh being the only product), while in water the yield of syn dimers rises at the expense of anti-hh (**3**, R = methyl).

Photodimerization of 6-Methylcoumarin at Various Irradiation Times. Like in benzene and in acetonitrile (cf. Tables 2 and 3) the product distribution in water (presented in Table 5) does not vary much with the irradiation time. The nonproportional increase of pc as well as a slight increase of the anti-hh (triplet product) is reasonable, since at longer irradiation times both the educt concentration and the probability of encounters of singlet excited and ground-state molecules lower.

Photochemical Back Reaction. A 10^{-4} M solution of the syn-hh photodimer of 6-methylcoumarin (**3**, R = methyl) in $CHCl_3$ was irradiated with quartz-filtered light of a high-pressure mercury lamp. A clean reformation of 6-methylcoumarin was observed according to the UV spectrum. Due to the low concentration, a photostationary equilibrium was not established, and a subsequent reirradiation at $\lambda > 305$ nm (using a cutoff filter) had no effect.

Photodimerization of Nonsubstituted Coumarin in Various Solvents. For comparison, the product

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TABLE 1. ^{1}H NMR Data of the Four Isomeric Dimers (2, 3, 4, 5, R = methyl) of 6-Methylcoumarin (1, R = methyl) in $CDCl_3$[a]

	H-3, H-3′		H-4, H-4′	H-5, H-5′	H-6, H-6′	H-8, H-8′, H-9, H-9′				
dimer	d	$^3J_{3,4} = {}^3J_{3,4}$	d	d	d	$\delta_8 = \delta_{8'}$	$\delta_9 = \delta_{9'}$	$^3J_{8,9} = {}^3J_{8',9'}$	$^4J_{8,9'} = {}^4J_{8',9'}$	$^3J_{8,8'} = {}^3J_{9,9'}$
syn-hh (**2**)	6.97	8.3	6.74	2.12	6.56	4.12	4.01	8.5	1.6	8.2
anti-hh (**3**)	6.99	8.3	7.12	2.34	6.95	3.78	3.88	8.6	−1.3	5.4
syn-ht (**4**)	6.49	8.9	6.89	2.26	6.90	4.23	4.19	8.6	0	8,6
anti-ht (**5**)	6.98	8.3	7.12	2.33	7.09	3.59	4.13	8.6	0.8	6.1

[a] Chemical shifts, δ, in ppm and coupling constants, J, in hertz.

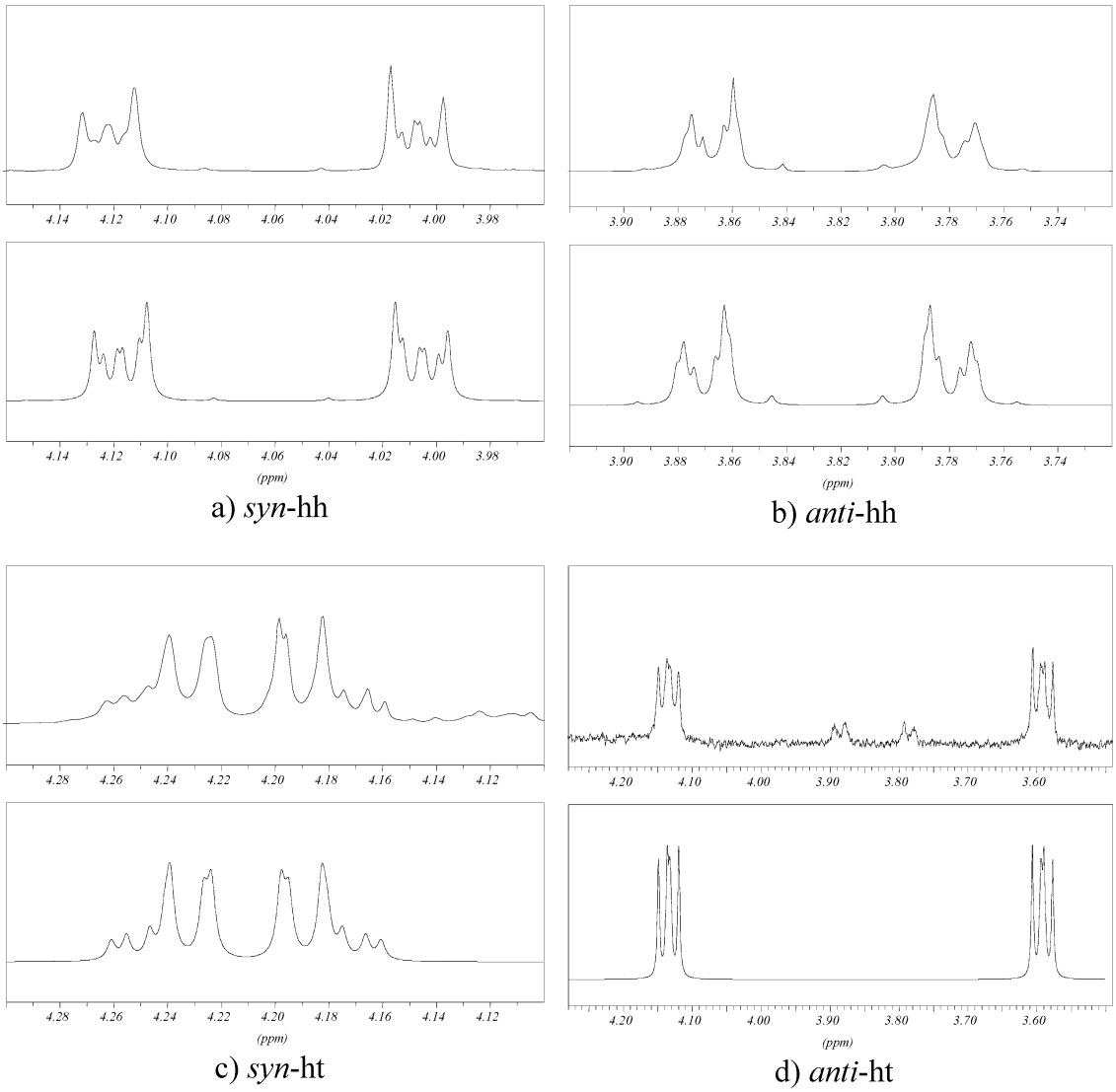


FIGURE 6. Simulated and experimental ^{1}H NMR spectra for (a) syn-hh (**2**, R = methyl), (b) anti-hh (**3**, R = methyl), (c) syn-ht (**4**, R = methyl), and (d) anti-ht (**5**, R = methyl), with some **3** present. Top, experimental; bottom, simulated.

distribution in the photodimerization of nonsubstituted coumarin (**1**, R = H) was reinvestigated under our conditions. In Table 6 the results are displayed, which mainly corroborate the literature findings. The compilation, however, reveals that low concentrations direct to anti-hh, while at high concentrations (or at high local concentrations in the micellar systems) syn-dimers also form and may become the main products. Two significant differences to 6-methylcoumarin (Tables 2 and 3) arise: (i) while in benzene the results are similar, the catalytic BF_3-induced formation of syn-ht in CH_2Cl_2 is much more efficient for coumarin; i.e., syn-ht becomes the main product; (ii) in H_2O the syn-hh fraction is more than 50% and it increases with the educt concentration. The pc′ values for the literature data were not calculated because of differing irradiation conditions.

Photodimerization of 6-Dodecylcoumarin in Various Solvents. In contrast to the coumarin and 6-methylcoumarin results, of the anti-hh dimer (**4**, R = *n*-dodecyl) is the main product in methanol and in two micellar

TABLE 2. Product Distribution (fractions of dimers 2−5) in the Photodimerization of 6-Methylcoumarin (1, R = methyl) in Various Solvents[g]

					fraction of dimers (%)					
solvent	c (mol/dm^3)	t (h)	pc (%)	pc′	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht
benzene	0.2	15	22	5.4×10^{-4}	0	100	0	0	0	∞
benzene	0.2	50	56.4	4.1×10^{-4}	1.7	95.4	1.0	1.9	3/97	97/3
cyclohexane	0.025	2	7.4	0.011	0	100	0	0	0	∞
dichloromethane	0.2	15	9.6	2.3×10^{-4}	0	100	0	0	0	∞
dichloromethane[a]	0.2	7.5	43	2.1×10^{-3}	trace	79.6	20.4	trace	20/80	80/20
dichloromethane[a,b]	0.2	7.5	30.7	1.5×10^{-3}	trace	24.9	63.3	11.8	63/37	25/75
cyclohexanone	0.2	15	26	6.3×10^{-4}	0	100	0	0	0	∞
acetone	0.2	15	2.3	$<1 \times 10^{-5}$	0	100	0	0	0	∞
acetonitrile[c]	0.01	3	46.1	0.11	11.6	88.4	0	0	12/88	∞
acetonitrile[d]	0.01	3	82.5	0.20	13.1	87.1	0	0	13/87	∞
acetonitrile	0.2	15	2	$<1 \times 10^{-5}$	23	77	0	0	23/77	∞
methanol	0.2	15	22.7	5.9×10^{-4}	20.1	69.7	10.2	0	30/70	90/10
methanol[d]	0.2	15	83.3	2.0×10^{-3}	6.9	91.3	1.8	0	9/91	98/2
water	0.004	0.5	23.6	0.86	25.7	74.3	0	0	26/74	∞
CTAB[e]	0.004	2	71	0.65	63.5	26.4	10.1	0	74/26	90/10
CTAB[f]	0.1	13	49.7	2.8×10^{-3}	68.2	17.8	14	0	84/18	86/14
SDS[e]	0.15	11.5	43.8	1.9×10^{-3}	58.9	31	10.1	0	69/31	90/10
without solvent	20 mg	15	86.8		75.1	12.1	8.1	4.6	83/17	87/13

[a] In the presence of a Lewis acid catalyst: BF_3/Et_2O (0.2 mol/dm^3). [b] Carefully dried CH_2Cl_2. [c] Considerable amounts of side products are formed. [d] Sensitized by benzophenone (0.1 mol/dm^3). [e] Surfactant concentration 0.015 mol/dm^3. [f] Surfactant concentration 0.25mol/dm^3. [g] c = concentration, t = irradiation time, pc = photochemical conversion, pc′ = pc/(tc) relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3 in Table 4; see the text.

TABLE 3. Product Distribution in the Photodimerization of 6-Methylcoumarin (1, R = methyl) at 25 °C in Four Argon-Saturated Solvents at Various Educt Concentrations c[d]

			photodimer (%)						
c (mol/dm^3)	pc (%)	pc′	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht	remark
acetonitrile, irradiation time t = 11 h									
0.001	55	0.36	0	100	0	0	0	∞	mainly side products
0.01	87	0.058	trace	100	0	0	0	∞	side products
0.05	10.1	1.3×10^{-3}	trace	100	0	0	0	∞	
0.1	9.7	6.4×10^{-4}	12.6	87.5	0	0	13/87	∞	
0.2	5.4	1.9×10^{-4}	21.3	78.7	0	0	21/79	∞	
0.2[a]	13	1.4×10^{-4}	20.8	79.2	0	0	21/79	∞	
0.2[b]	18.2	6.1×10^{-4}	trace	100	0	0	0	∞	
methanol, irradiation time t = 15 h									
0.001	95	0.46							decomposition
0.01	34.8	0.017	11.9	75.7	12.4	0	24/76	88/12	side products
0.1	12.8	6.2×10^{-4}	15.2	80	4.8	0	20/80	95/5	
0.2	22.7	5.5×10^{-4}	20.1	69.7	10.2	0	30/70	90/10	
0.3	27.5	4.5×10^{-4}	19.9	66.5	13.6	0	44/66	86/14	
0.2[b]	83.3	2.0×10^{-3}	6.9	91.3	1.8	0	9/91	98/2	
H_2O, irradiation time 2 h									
0.004	57.1	0.53	21.7	75.9	2.4	0	24/76	98/2	
0.01[c]	73.2	0.27	29.4	64	6.6	0	36/64	93/7	
0.1[c]	62.7	0.025	92	8	trace	0	92/8	∞	
0.25 M aq CTAB, irradiation time t = 13 h, 27 °C									
0.02	50	0.014	51.7	34.3	14	0	66/34	86/14	
0.05	64.5	7.4×10^{-3}	73.4	14.5	12.1	0	86/14	88/12	
0.1	49.7	2.8×10^{-3}	68.2	17.8	14	0	82/18	86/14	

[a] Irradiation time 33 h. [b] In the presence of benzophenone at 0.1mol/dm^3. [c] Suspension. [d] t and pc as in Table 2, pc′ = pc/t/c relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3 in Table 4.

environments, i.e., under all conditions investigated; see Table 7. Head-to-tail dimers formed in the suspension only. The low solubility of 6-dodecyl coumarin in nonpolar homogeneous solvents did not allow comparative irradiations.

Photodimerization of Various 6-Alkylcoumarins in CTAB. A series of 6-alkylcoumarins with alkyl substituents varying from methyl to hexadecyl (=cetyl) was irradiated in 0.25 M aqueous CTAB. The product distribution was analyzed and the results are collected in Table 8.

With increasing weight of the substituents, (i) the syn:anti ratio is almost reverted from ca. 9:1 to ca. 2:8, (ii) the hh:ht ratio rises from ca. 6:4 to infinity, (iii) the syn-ht content in the product mixture diminishes from 40% to zero, and (iv) the photochemical conversion increases from 20% to 90%, reflecting an according rise in the dimerization quantum yield.

Thermal Reactions of 6-Methylcoumarin Dimers. During attempts to chromatographically separate dimers of 6-methylcoumarin from their reaction mixture, it turned out that some of them were not stable on the silica

TABLE 4. Product Distribution in the Photodimerization of 6-Methylcoumarin (1, R = methyl) in Argon-Saturated Water and Cyclohexane at Various Temperatures[d]

			dimer (%)					
T (°C)	pc (%)	pc	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht
			H_2O, educt concentration $c = 0.0035$ mol/dm^3					
1	95.7	1	16.6	74.1	6.7	2.6	24/76	91/9
10	91.8	0.96	18.7	70.3	8.6	2.4	27/73	89/11
20	79.4	0.83	22.9	68.1	9.0	0	32/68	91/9
30	73.3	0.77	27.6	63.2	9.2	0	37/63	91/9
40	56.6	0.59	31.0	59.2	9.8	0	41/59	90/10
50	52.8	0.55	34.4	53.4	12.2	0	47/53	88/12
			cyclohexane, educt concentration $c = 0.02$ mol/dm^3					
0[b]	19.1	0.035	0	99	0	1	0	99/1
10	14.6	0.027	0	100	0	0	0	∞
20	8.6	0.016	0	100	0	0	0	∞
25[c]	7.4	0.011	0	100	0	0	0	∞
30	7.1	0.013	0	100	0	0	0	∞
40	5.4	0.010	0	100	0	0	0	∞

[a] At 0.004 mol/dm^3. [b] Solid solution. [c] $c = 0.025$ mol/dm^3 (less efficient lamp). [d] Irradiation time $t = 2$ h, pc as in Table 2, pc′ = pc/(tc) relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3.

TABLE 5. Product Distribution in the Photodimerization of 6-Methylcoumarin (c = 0.004 mol/dm^3) at 25 °C in Argon-Saturated Water at Various Irradiation Times[a]

			dimer (%)					
t (h)	pc (%)	pc′	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht
0.5	23.6	0.86	25.7	74.3	0	0	26/74	∞
1	47.1	0.86	23.5	74.5	2.0	0	26/74	98/2
2	57.1	0.53	21.7	75.9	2.4	0	24/76	98/2
3	64.6	0.39	21.8	75.8	2.4	0	24/76	98/2
4.2	79	0.35	21.1	75.6	3.3	0	24/76	97/3

[a] pc′ = pc/(tc) relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3 in Table 4.

gel column employed. To identify the decomposition processes, we treated the two isolated photodimers (syn-hh and anti-hh) with HCl, NaOH, water, and methanol, respectively, and we studied their behavior in the presence of SiO_2 and Al_2O_3. The reactions with 10% aqueous HCl, 10% aqueous NaOH, and with methanol are summarized in the Schemes 3 and 4. One or both of the lactone rings open and form acids or methyl esters, respectively. The syn-hh dimer is stable against 10% HCl. Both the dimers do not react with water under reflux for 3 h. In all these reactions the cyclobutane ring was not attacked.

Upon stirring with silica gel in ethyl acetate for 1 week in the dark, syn-hh remained unchanged while anti-hh disappeared almost completely, the mono acid **16** and some diacid **17** being the main products. The same experiment using Al_2O_3 instead of SiO_2 led to a complete decomposition of both of the dimers under formation of unknown products. Thus, the chromatographic methods using SiO_2 and Al_2O_3 are problematic in separating coumarin dimers: only the syn-hh dimer (**2**, R = methyl) can be separated and purified (and used for X-ray analysis after crystallization).

Discussion

Spectra. From the minor effects that the substituents have on the UV and fluorescence spectra, we conclude that the influence of the 6-alkyl substituents on the geometry of the molecule or on the electronic structure (in the ground and excited state) is minor and should not account for different reactivities and selectivities. Also, the changes of solvent polarity do not lead to effects that are obviously important for the reactivity (such as changes in the order of transitions). The observed differences in reactivity, therefore, have to be rationalized in other terms.

A remark is required concerning the differing coupling patterns of the cyclobutane protons in the ^{1}H NMR spectra of syn-ht (**4**, R = methyl) and anti-ht (**5**, R = methyl), as revealed by the simulations. The AA′XX′ pattern indicates a reduced flexibility of the cyclobutane ring in the anti-ht isomer. This contradicts our expectation (A_2B_2 pattern), since intramolecular interactions of the coumarin moieties (affecting the flexibility) should be larger in the syn compound. Differing interactions of solvent molecules with the syn and the anti isomer, respectively, might cause the observation.

pc′ Values. According to Scheme 1, dimerization quantum yields as well as relative dimerization quantum yields are concentration dependent, regardless of whether the dimerization originates from the singlet or triplet excited state. Therefore, pc′ values are included in Table 2 and the following tables. These were gained by dividing pc by the irradiation time and further by the initial concentration in order to (widely) eliminate the concentration dependence of quantum yields, and the data were normalized to the highest value, which was obtained in water at 1 °C (Table 4). Inspecting Table 2 in this respect, we note that (i) pc′ in sensitized irradiations is higher than upon direct irradiation, (ii) the concentration-corrected relative quantum yields (pc′) at low concentrations evidently exceed those at 0.2 mol/dm^3.

Coumarin. Apparent discrepancies in the literature result from the strong concentration dependence of the product distribution (cf. methanol or ethanol values in Table 6), which in terms of Scheme 1 is a consequence of singlet nonreactive self-quenching: the concentration-corrected relative quantum yield (pc′) decreases with increasing concentration; anti products (i.e. triplet products via processes a and b or c) are formed exclusively at low concentrations because of the long lifetime of the

TABLE 6. Product Distribution after Photodimerization of Nonsubstituted Coumarin (1, R = H) in Various Solvents[m]

					photodimer (%)					
solvent	c (mol/dm^3)	t (h)	pc (%)	pc′	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht
benzene	0.2	15	8.6	2.2×10^{-4}	2.3	91.2	2.3	4.2	5/95	94/6
CH_2Cl_2[a]	0.2	7.5	79.8	3.9×10^{-3}	0	9.2	90.8	0	91/9	9/91
H_2O	0.004	2	23.2	0.21	52	24	24	0	76/24	76/24
H_2O	0.02	3	22	0.027	70	12	18	0	88/12	82/18
CTAB[b]	0.02	4	20.6	0.019	50.8	12.2	37	0	88/12	63/37
CTAB[b]	0.1	4	2.6	5.2×10^{-4}	53.2	6.7	40.1	0	93/7	60/40
				literature data						
benzene[c]	0.01	40[d]	17.2			main				
benzene[c]	0.5	60[d]	4.7		4.5	92.5	3.0	0	7/93	97/3
benzene[e]	0.02	22[f]	2			main				
dioxane[c]	0.5	60[d]	4.4		4.8	90.4	4.8	0	10/90	95/5
dioxane[g]	0.31	68[f]	5			main				
dioxane[g,h]	0.31	68[f]	71			main				
$CHCl_3$[c]	0.5	60[d]	10.5		3.9	91.5	4.6	0	8/92	95/5
CH_2Cl_2[a,i]	0.2	28[f]	>85				100			
CH_2Cl_2[j]	0.2	5	20			20	80			
methanol[e]	0.02	22[f]	2			main				
methanol[g]	0.31	68[f]			main					
ethanol[d]	0.01	40[d]	7.8			main				
ethanol[c]	0.5	60[d]	8.4		54.0	23.8	22.1	0	76/24	78/22
2-propanol[c]	0.5	60[d]	7.1		41.3	33.7	25.0	0	66/44	75/25
1,2-ethanediol[c]	0.5	60[d]	38.6		59.0	21.8	19.2	0	78/22	81/90
formic acid[c]	0.5	60[d]	60.8		64.3	16.0	19.7	0	84/16	80/20
acetic acid[c]	0.01	40[d]	35.1			main				
acetic acid[c]	0.5	60[d]	15.2		25.2	46.9	27.9	0	53/47	72/28
H_2O[e]	0.02	22[f]	20		main					
SDS[e,k]	0.02	22[f]	21		main					
CTAB[e,l]	0.02	22[f]	3		main					
Triton X-100[e,m]	0.02	22[f]	11		main					

[a] In the presence of a Lewis acid catalyst: BF_3/Et_2O (0.2 mol/dm^3). [b] CTAB concentration 0.25mol/dm^3. [c] From ref 20. [d] 125 W mercury. [e] From ref 10a. [f] 450 W mercury. [g] From ref 23. [h] In the presence of benzophenone (10%). [i] From ref 22a. [j] In the presence of BF_3/Et_2O (0.15 mol/dm^3), from ref 22b. [k] Sodium dodecyl sulfate (aqueous solution, 0.02 mol/dm^3). [l] Cetyltrimethylammonium bromide (aqueous solution, 0.02 mol/dm^3); aqueous solution, 0.02 mol/dm^3. [m] c, t, and pc as in Table 2; pc′ = pc/(tc) relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3 in Table 4.

TABLE 7. Photodimerization of 6-Dodecylcoumarin in Various Solvents[b]

					photodimer (%)					
solvent	c (mol/dm^3)	t (h)	pc (%)	pc′	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht
CH_3OH	0.02	8	95	0.049	1	99	0	0	1/99	∞
CH_3OH[a]	0.2	8	30	1.5×10^{-3}	8.8	83.1	2.2	5.9	11/89	92/8
CTAB	0.02	4	90.8	0.93	20.1	79.9	0	0	20/80	∞
SDS	0.02	8	44.9	0.023	29.2	70.8	0	0	29/71	∞

[a] Suspension. [b] c, t, and pc as in Table 1; pc′ = pc/(tc) relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3 in Table 4.

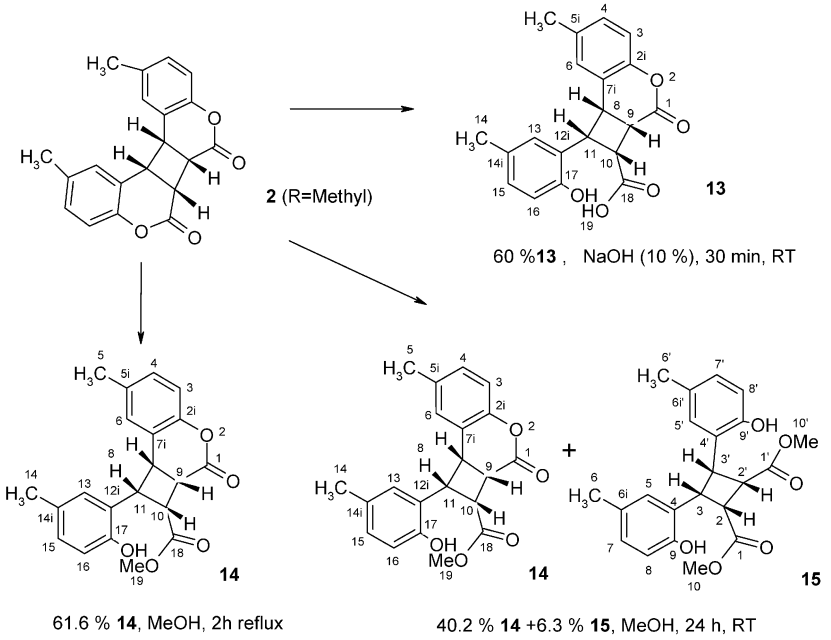
TABLE 8. Photodimerization of 6-Alkylcoumarins in 0.25 mol/dm^3 CTAB[b]

			photodimer (%)					
coumarin derivatives	pc (%)	pc	syn-hh	anti-hh	syn-ht	anti-ht	syn/anti	hh/ht
coumarin	20.6	0.022	50.8	12.2	37	0	88/12	63/37
6-methylcoumarin[a]	50	0.051	51.7	34.3	14	0	66/34	86/14
6-ethylcoumarin	90	0.092	12.6	81.8	5.6	0	18/82	94/6
6-isopropylcoumarin	89.6	0.092	7.6	82.7	9.7	0	17/83	90/10
6,8-diethylcoumarin	95	0.098	10.6	81.6	7.8	0	18/82	92/8
6-*tert*-butylcoumarin[a]	77.3	0.082	20.5	69.9	9.6	0	30/70	90/10
6-*n*-butylcoumarin	89.3	0.092	17.4	72.4	10.2	0	28/72	90/10
6-*n*-pentylcoumarin	88.7	0.091	13.4	81.8	4.9	0	18/82	95/5
6-*n*-octylcoumarin	85.5	0.088	24.2	71.1	4.7	0	29/71	95/5
6-*n*-dodecylcoumarin	90.8	0.092	20.1	79.9	0	0	20/80	∞
6-*n*-cetylcoumarin	80.9	0.083	23.3	76.7	0	0	23/77	∞

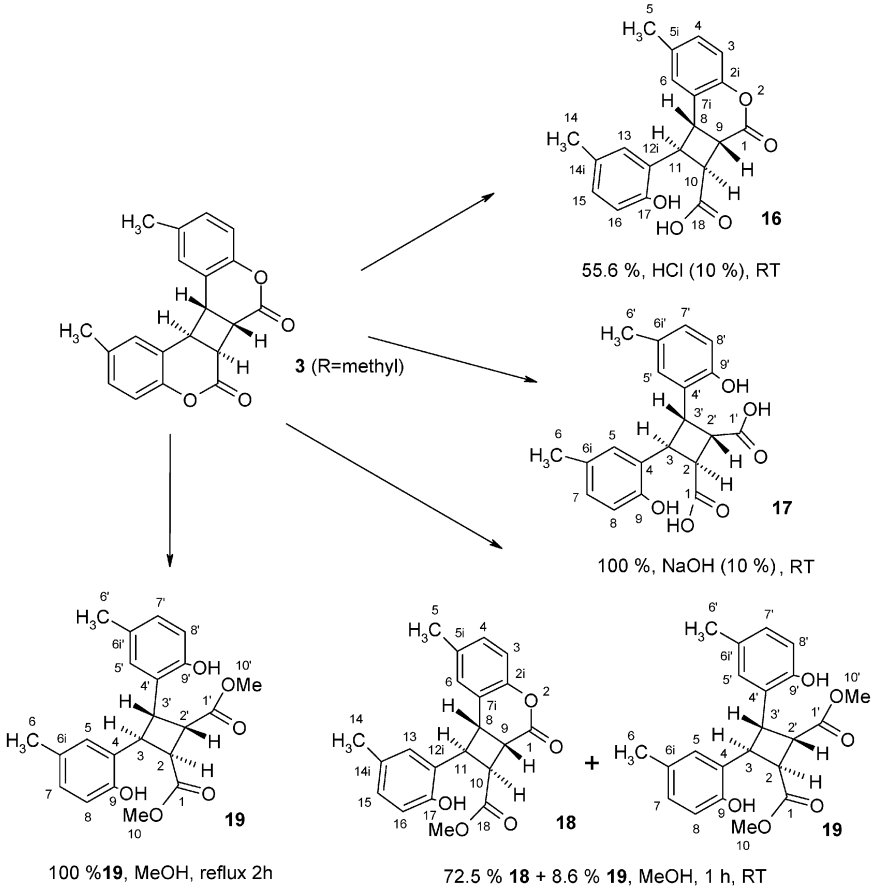
[a] Irradiation time = 6 h. [b] c = 0.02 mol/dm^3, irradiation time = 4 h, T = 27 °C; pc′ = pc/(tc) relative to pc′ = 1 for 6-methylcoumarin in H_2O at 1 °C and 0.0035 mol/dm^3 in Table 4.

triplet state, which allows encounters with ground-state coumarin molecules. Syn dimers, on the other hand, are found at high concentrations when the processes d + e (Scheme 1) can compete effectively with intersystem crossing (process a), always in competition with the nonreactive self-quenching (process f). These effects are

SCHEME 3. Thermal Reactions of the Syn-hh (2, R = methyl) Dimer of 6-Methylcoumarin



SCHEME 4. Thermal Reactions of the Anti-*hh* Dimer (3, R = methyl) of 6-Methylcoumarin



found in all solvents, but they are most pronounced in nonpolar ones.

6-Methylcoumarin. The increase of the anti-hh fraction to 91% in methanol in the presence of a triplet sensitizer and the exclusive formation of anti-hh in the heavy atom solvent dichloromethane indicate that this isomer is the one preferably formed from the triplet state. Accordingly, the fraction of anti-hh (**3**, R = methyl) increases with decreasing educt concentration (Table 5), as at low concentration only encounters of the longer living triplet monomer (^{3}**1*** in Scheme 1) with a ground-state monomer are likely. In this respect, 6-methylcou-

marin behaves similar to the nonsubstituted coumarin.[4,20] If we accept nonreactive self-quenching of singlet states strongly prevailing over dimerization in the nonpolar cyclohexane (as in coumarin, process f),[21] it is in keeping that only the triplet product is formed at all temperatures investigated. Further, the fact that the pc′ values diminish with rising concentrations (in polar and nonpolar solvents) indicate a nonreactive self-quenching of singlet states in all solvents, which may differ in efficiency depending on the manner of solvation as discussed by Krauch et al. for the nonsubstituted coumarin.[20]

An effect attributable to the availability of protons or to the capability of forming hydrogen bridge bonds (cf. refs 4b and 23) might be indicated by the considerable formation of syn products at low concentrations in protic solvents (cf. acetonitrile vs methanol in Table 3, and water in Table 4). The effect becomes evident when the concentration dependence of the pc values are considered, i.e., the values of Table 3 for acetonitrile at between 0.05 and 0.2 mol/dm^3 and for methanol at between 0.1 and 0.3 mol/dm^3 (values in the presence of a sensitizer or connected with the formation of side products are disregarded here): in methanol a plot of 1/pc vs 1/*c* shows the linearity with a positive slope expected for photodimerizations (and pc′ is almost constant), while in acetonitrile the photochemical conversion decreases with increasing concentration. In terms of Scheme 1, this means that in acetonitrile the sum of the rates of the bimolecular ^{1}**1*** decay processes d, e, and (mainly) f exceeds that of process a in this concentration range. It is in keeping that the fraction of the singlet product syn-hh increases accordingly with rising concentration. It is, however, not in keeping that considerable amounts of the singlet product syn-hh are formed in acetonitrile upon sensitized irradiation at low concentrations (Table 1). Thus, some mechanistic details remain to be investigated.

In acetone and cyclohexanone as solvents, the cutoff filter (305 nm) used did not completely prevent the excitation of solvent molecules. Thus, here the solvent molecules can act as triplet sensitizers, so that the exclusive formation of the triplet (anti-hh) product is reasonable.

For the parent coumarin (**1**, R = H), it was found by Lewis et al. that the presence of a Lewis acid, i.e., BF_3, substantially increases the quantum yield of photodimerization and leads to the syn-ht dimer mainly[22b] or even exclusively[22a] depending on the BF_3-content of the solution. In our experiments with 6-methylcoumarin in dichloromethane, this effect appears to compete effectively with the effect of the heavy atom solvent directing to anti-hh, so that the selectivity is reduced. The system is sensitive to the presence of traces of water: when the solvent is not carefully dried, a part of the BF_3 complexes are destroyed by water and the product distribution changes toward the result without BF_3.

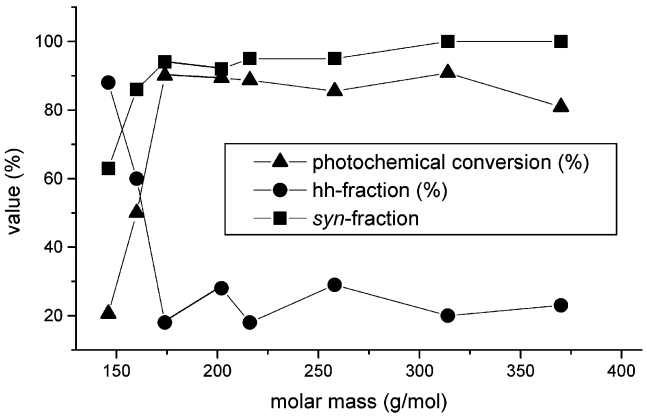


FIGURE 7. Syn fraction (squares) and hh fraction (circles) in product distributions, and photochemical conversion (triangles) as a function of the molecular weight of the educt in the photodimerization of 6-*n*-alkylcoumarins (cf. Table 8) at 0.01 mol/dm^3 after 4 h irradiation at 27 °C in 0.25 M aqueous cetyltrimethylammonium bromide (CTAB).

The temperature dependence of the product distribution in water is such that the amount of the triplet product (anti-hh) diminishes with rising temperature. This can be rationalized when the fluidity of the solvent is considered, which increases with temperature. As a consequence, the probability of the formation of products from the short-lived singlet state can compete more favorably as compared to low temperatures, as diffusion is faster. On the other hand, the obvious decrease of the (relative) dimerization quantum yield with increasing temperature in both water and cyclohexane indicates the involvement of other deactivation routes of the excited states, which require activation energy. A solvation differing with temperature (e.g. partial self-solvation[20]) may also give rise to the observed temperature dependence of yields and product distributions. The fact that dimerization occurs even in a solid solution (cyclohexane at 0 °C, Table 4) clearly points to an aggregation of the solutes (under these conditions), which differs from the crystal: while the irradiation of the pure solid delivers all four isomeric photodimers (Table 2), 99% anti-hh was found in solid cyclohexane.

The poor dependence of the product distribution on the irradiation time observed in water, acetonitrile, and benzene (Tables 2−5) indicates that secondary thermal or photochemical reactions during the long irradiation times are very minor, if not remote.

6-Alkylcoumarins in CTAB. The main features of the irradiations in CTAB micelles are comprised in Figure 7 for the *n*-alkyl substituents (data from Table 8). From inspection of the figure it follows that the syn:anti ratio and the hh:ht ratio strongly depend on the weight (length) of the alkyl substituents. Thus, to a considerable extent, these ratios can be steered by exchanging the substituents in the 6-position and performing the irradiation in CTAB micelles. It is remarkable that we could observe an influence on the regio- and stereoselectivity induced by 6-alkyl substituents while previous attempts with 7-alkoxy- and 4-methyl-7-alkoxycoumarins failed in this respect; i.e., syn-ht products were found under all conditions.[10] The figure further reveals that the observed variations in the syn:anti ratio and in the hh:ht ratio level off at butyl and larger alkyl sub-

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stituents. One is tempted to ascribe the high anti-hh fraction (triplet product via processes a and b) to the heavy atom interaction (accelerating process a) of the surfactant counterions,[19c] which operates best for propyl and longer alkyl chains. This might indicate the preorientation of these heavier coumarins in such a way that the alkyl moiety of the educts points to the micellar center, thereby orienting the coumarin part in head-to-head position within the counterion region. However, the fact that in 6-dodecylcoumarin the anti-hh fraction is always high (Table 7)—even in homogeneous methanol solution—casts doubt on the efficiency of the heavy atom effect, while the preorientation of hh geometry for the larger substituents appears not to be restricted to the presence of micellar matrixes: the increased quantum yield in the larger alkyl substituents might be due to a predominant solubilization in the form of preoriented pairs even in homogeneous solvents (cf. pc for 6-methyl- and 6-dodecylcoumarin in methanol at the respective concentrations). The formation of ground-state aggregates (or any form of self-solvation as suggested by Krauch et al.)[20] might give rise to concentration dependent absorption or emission spectra, which were not observed, however.

Another explanation for the preferred anti-hh formation of coumarins with longer 6-alkyl substituents might be an intersystem crossing rate increasing with the length or weight of the substituents, which is unlikely, as the UV and fluorescence spectra as well as the poor fluorescence quantum yield do not indicate a perturbation of states by the substituents (Figure 1, cf. ref 24). Nevertheless, the triplet quantum yields should be measured in a future mechanistic investigation aimed to complete or correct the simplifying reaction scheme based on literature results (Scheme 1).

The data for the branched 6-alkylcoumarins from Table 8 (R = isopropyl, *tert*-butyl) as well as for the disubstituted 6,8-diethylcoumarin fit fairly well into the diagram in Figure 7. It is therefore justified to plot the molar mass rather than the alkyl chain length in Figure 7.

Conclusions

As compared to nonsubstituted coumarin, the 6-alkyl substituents increase the dimerization quantum yield. In aqueous CTAB alkane chain substituents in the 6-position exceeding propyl in weight (length) direct to anti-hh, while short chains favor syn products and reduce the hh fraction. Considerable ht fractions[25] are possible in nonsubstituted coumarin and in the presence of BF_3. In 6-methylcoumarin the dimerization quantum yield increases with decreasing temperature, and low concentrations direct to the triplet product, i.e., anti-hh (**3**), while ionic micelles favor the formation of syn-hh (**2**).

Experimental Section

Irradiations. Argon-saturated solutions (typically 50 cm^3) thermostated at 25 °C (otherwise indicated) were irradiated through a 305 nm cutoff filter (Schott) and through the gas−liquid interface using a 100 W mercury lamp (Osram XBO, housing from Amko). The filter prohibited the photochemical splitting of the dimers (cf. Figure 2). For the study of the photochemical back reaction, a 254 nm interference filter was used. For solid film irradiation, a solution of the educt in CH_2Cl_2 was placed in the reaction vessel and the solvent was removed by bubbling with argon.

Analyses of Reaction Mixtures. The photochemical conversion (pc) was determined from the decrease of the UV absorption at the long wavelength absorption maximum around 320 nm, cf. Figure 2 after appropriate dilution (if necessary). After the pc determination in homogeneous solutions, the solvent was evaporated at temperatures below 40 °C and the remaining solid was dried in vacuo. Unconverted educt was removed by sublimation. The reaction products were dissolved in deuterated chloroform for NMR analysis. Surfactant solutions were strongly diluted and extracted several times with diethyl ether. The combined ether fraction were dried over Na_2SO_4 and treated as described for homogeneous solvents. Irradiated solid films were directly dissolved in deuterated chloroform. Values determined for repeated irradiations vary within ±5% (relative).

Isolation of the Syn-hh and Anti-hh Dimer of 6-Methylcoumarin. The anti-hh dimer **3** (R = methyl) was produced exclusively on irradiation in acetone, benzene, or cyclohexane (Tables 2 and 3). A noncrystalline solid melting at 196 °C was obtained whose ^{1}H NMR data are collected in Table 1; ^{13}C NMR ($CDCl_3$) δ/ppm 166.0 (CO, C-1, 1′), 149.0 (Cq, C-2i, 2i′), 135.1 (Cq, C-5i, 5i′), 130.2 (CH, C-4, 4′), 128.1 (CH, C-6, 6′), 119.9 (Cq, C-7i, 7i′), 117.5 (CH, C-3, 3′), 43.7 (CH, C-8, 8′), 39.9 (CH, C-9, 9′), 20.7 (CH_3, C-5, 5′); ESI-MS (50.0 V) *m/e* 321.0 [M + H^+]. Anal. Calcd for $C_{20}H_{17}O_4$ (M = 320.33): C, 74.99; H, 5.35. Found: C, 75.23; H, 5.51.

The syn-hh dimer **2** (R = methyl) was separated from a reaction mixture after irradiation in H_2O via chromatography on SiO_2 using ethyl acetate as the eluent (the anti-hh fraction decomposed thereby). Recrystallization of the syn-hh dimer from chloroform yielded transparent colorless plates: mp 263 °C; for ^{1}H NMR, see Table 1; ^{13}C NMR ($CDCl_3$) δ 164.6 (CO, C-1, 1′), 149.9 (Cq, C-2i, 2i′), 133.9 (Cq, C-5i, 5i′), 130.1 (CH, C-4, 4′), 129.2 (CH, C-6, 6′), 117.0 (CH, C-3, 3′), 116.5 (Cq, C-7i, 7i′), 40.0 (CH, C-8, 8′), 39.7 (CH, C-9, 9′), 20.4 (CH_3, C-5, 5′); ESI-MS (50.0 V) *m/e* 321.0 [M +H^+]. Anal. Calcd for $C_{20}H_{17}O_4$ (M = 320.33): C, 74.99; H, 5.35. Found: C, 74.49; H, 5.56.

^{13}C NMR of 4 (R= methyl): ($CDCl_3$) δ 164.1 (CO, C-1, 1′), 148.4 (Cq, C-2i, 2i′), 134.8 (Cq, C-5i, 5i′), 130.3 (CH, C-4, 4′), 128.8 (CH, C-6, 6′), 116.7 (CH, C-3, 3′), 116.5 (Cq, C-7i, 7i′), 40.5 (CH, C-9, 9′), 37.4 (CH, C-8, 8′), 20.7 (CH_3, C-5, 5′).

^{13}C NMR of 5 (R = methyl): ($CDCl_3$) δ 166.3 (CO, C-1, 1′), 148.6 (Cq, C-2i, 2i′), 135.4 (Cq, C-5i, 5i′), 130.3 (CH, C-4, 4′), 128.6 (CH, C-6, 6′), 119.4 (Cq, C-7i, 7i′), 117.2 (CH, C-3, 3′), 43.6 (CH, C-9, 9′), 38.8 (CH, C-8, 8′), 20.6 (CH_3, C-5, 5′).

Thermal Reaction of Photodimers. Reactions of 2 (R = methyl). In a 30 mL flask the syn-hh dimer **2** (R = methyl) (30 mg) was suspended in aqueous NaOH (10% w/w, 10 cm^3). Upon stirring for 30 min the suspension did not change. After heating to 60 °C and stirring for 30 min the solution cleared. It was allowed to cool to room temperature and then cooled to 0 °C and slowly neutralized at this temperature (to avoid relactonization[26]) using aqueous HCl (10% w/w). A white solid precipitated. After 20 min at 0 °C the suspension was extracted three times with diethyl ether, and the combined extracts were washed with NaCl aqueous solution and dried over Na_2SO_4. A white solid was obtained. The ^{1}H NMR spectrum revealed the presence of two substances in a ratio of 2:3, which were identified as starting material and the monoacid **13** of the dimer via 2D-NMR. The cyclobutane ring was unchanged. Compound **13**: ^{1}H NMR (DMSO) δ 12.29 (1H, s, 18-COOH), 9.33 (1H, s, 17-OH), 7.00 (1H, d, $J_{4,3}$ = 8. 2 Hz, H-4), 6.90 (1H, d, $J_{3,4}$ = 8.2 Hz, H-3), 6.78 (1H, dd, $J_{15,16}$ = 8.2 Hz, $J_{15,13}$ = 1.8

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Hz, H-15), 6.68 (1H, d, $J_{16,15}$ = 8.2 Hz, H-16), 6.10 (1H, d, $J_{13,15}$ = 1.8 Hz, H-13), 5.98 (1H, s, H-6), 4.95−4.99 (1H, m, H-11), 4.03−4.07 (1H, m, H-8), 3.97−4.00 (1H, m, H-10), 3.93−3.97 (1H, m, H-9), 1.97 (3H, s, H-5), 1.83 (3H, s, H-14); ^{13}C NMR (DMSO) δ 172.8 (COOH, C-18), 167.1 (CO, C-1), 152.8 (Cq, C-17), 149.6 (Cq, C-2i), 131.6 (CH, C-13), 131.4 (Cq, C-5i), 131.4 (CH, C-6), 128.3 (CH, C-4), 127.9 (CH, C-15), 125.4 (Cq, C-14i), 122.1 (Cq, C-12i), 118.4 (Cq, C-7i), 116.1 (CH, C-3), 114.2 (CH, C-16), 48.7 (CH, C-10), 37.7 (CH, C-8), 33,6 (CH, C-11), 32.8-(CH, C-9), 20,2 (CH_3, C-14), 20.0 (CH_3,C-5).

In a 30 mL flask the syn-hh dimer **2** (R = methyl) (30 mg) was suspended in aqueous HCl (10% w/w, 10 cm^3) and stirred overnight without visible changes. The suspension was refluxed for 30 min and then stirred at 60 °C for 2 h. Two liquid phases formed containing some suspended solid. After cooling to room temperature the mixture was extracted with ether (15 cm^3) three times. The extracts were washed with saturated NaCl (until the aqueous phase was neutral). The extracts were combined and dried over Na_2SO_4, and the solvent was evaporated at room temperature. A white solid was obtained that was identified as the starting dimer **2** (R = methyl).

Refluxing **2** in water for several hours did not lead to reactions.

The syn-hh dimer **2** (R = methyl) (30 mg) was suspended in methanol (10 cm^3) and refluxed for 2 h (prolonged reflux times did not lead to different results). The methanol was evaporated at room temperature. According to the NMR analysis the remaining white solid consisted of unchanged **2** (R = methyl) and the methyl ester **14** (61.6%) of the monoacid **13**. Compound **14**: ^{1}H NMR ($CDCl_3$) δ 7.02 (1H, s, H-3), 7.02 (1H, s, H-4), 6.83 (1H, dd, $J_{15,16}$ = 8,3 Hz, $J_{15,13}$ = 2.1 Hz, H-15), 6.60 (1H, d, $J_{16,15}$ = 8.3 Hz, H-16), 6.10 (1H, s, H-6), 6.03 (1H, d, $J_{13,15}$ = 2.1 Hz, H-13), 5.04−5.09 (1H, m, H-11), 4.71 (1H, s, 17-OH), 4.16−4.19 (1H, m, H-8), 4.14−4.15 (1H, m, H-10), 3.96−3.92 (1H, m, H-9), 3.34 (3H, s, H-19, OCH_3), 2.04 (3H, s, H-5), 1.92 (3H, s H-14); ^{13}C NMR ($CDCl_3$) δ 171.5 (COOMe, C-18), 167.3 (CO, C-1), 150.6 (Cq, C-17), 149.8 (Cq, C-2i), 133.1 (Cq, C-5i), 131.5 (CH, C-13), 131.3 (CH, C-6), 129.2 (CH, C-4), 128.5 (CH, C-15), 121.5 (Cq, C-12i), 117.3(Cq, C-7i), 117.0 (CH, C-3), 114.5 (CH, C-16), 51.5 (OCH_3, C-19), 49.2 (CH, C-10), 38.3 (CH, C-8), 34.6 (CH, C-11), 33.7 (CH, C-9), 20.4 (CH_3, C-14), 20.2 (CH_3, C-5). When the syn-hh dimer was not refluxed but just suspended in methanol (24 h, rt), the diester **15** (6.3%) was formed besides **14** (40.2%) while the rest of the material was unchanged **2** (R = methyl). Compound **15**: ^{1}H NMR ($CDCl_3$) δ 6.85 (2H, d, $J_{7,8}$ = $J_{7',8'}$ = 8.0 Hz, H-7,7′), 6.83 (2H, s, H-5,5′), 6.69 (2H, d, $J_{8,7}$ = $J_{8',7'}$ = 8.0 Hz, H-8,8′), 5.40 (2H, s, 9,9′-OH), 4.82−4.85 (2H, m, H-3,3′), 3.95−3.97 (2H, m, H-2, 2′), 3.36 (6H, s, H-10, 10′, OCH_3), 2.17 (6H, s, H-6, 6′).

Stirring of syn-hh **2** (R = methyl) (20 mg) in ethyl acetate (20 cm^3) in the presence of silica gel (5 g) for 1 week in the dark did not change the starting compound. When Al_2O_3 was used instead of SiO_2, the dimer decomposed completely.

Reactions of 3 (R = methyl). In a 50 cm^3 flask the anti-hh dimer **3** (R = methyl) (30 mg) was mixed with aqueous NaOH (10% w/w, 10 cm^3). Upon stirring for 5 min a clear solution formed that was allowed to rest for 30 min. Then the solution was neutralized using aqueous HCl (10% w/w). After 20 min at room temperature the solution became cloudy. It was extracted three times with diethyl ether, and the combined extracts were washed with aqueous NaCl solution and dried over Na_2SO_4. The ether was evaporated at room temperature to yield a white solid. Aside from starting material, the analysis (2D-NMR and ESI-MS) revealed that both the lactone rings had hydrolyzed to form the diacid **17** while the cyclobutane ring had survived. 3,4-Bis-(2-hydroxy-5-methylphenyl)-cyclobutane-1,2-dicarboxylic acid (**17**): ^{1}H NMR (DMSO) δ 11.90 (2H, s, 1,1′-COOH), 9.26 (2H, s, 9,9′-OH), 7.78 (2H, dd, $J_{7,8}$ = $J_{7'8'}$ = 8.0 Hz, $J_{7,5}$ = $J_{7',5'}$= 1.7 Hz, H-7, 7′), 6.75 (2H, $J_{5,7}$ = $J_{5',7'}$ = 1.7 Hz, H-5, 5′), 6.65 (2H,d, $J_{8,7}$ = $J_{8',7'}$ = 8.0 Hz, H-8, 8′), 4.66−4.68 (2H, m, H-3, 3′), 3.51−3.52 (2H, m, H-2, 2′), 2.10-(6H, s, H-6, 6′); ^{13}C NMR (DMSO) δ 173.6 (Cq, C-1, 1′), 153.2 (Cq, C-9, 9′), 127.7 (CH, C-7, 7′), 127.6 (CH, C-5, 5′), 126.5 (Cq, C-6i, 6i′), 125.4 (Cq, C-4, 4′), 114.3 (CH, C-8, 8′), 43.6 (CH, C-2, 2′), 37.5 (CH, C-3, 3′), 20.4 (CH_3, C-6, 6′); ESI-MS (10.0V) *m/e* 730.2 [2M+NH_4^+].

The anti-hh dimer **3** (R = methyl) (30 mg) was suspended in aqueous HCl (10% w/w, 10 mL) and stirred overnight at room temperature without visually observable changes. Then the suspension was refluxed for 30 min and further stirred at 60 °C for 2 h. Two liquid phases formed containing some suspended solid. After cooling to room temperature the mixture was extracted with ether (15 mL) three times. The extracts were combined and washed with saturated NaCl (until the aqueous phase was neutral). The extracts were combined and dried over Na_2SO_4, and the solvent was evaporated at room temperature. A white solid was obtained consisting of starting **3** (R = methyl) and the monoacid **16** (55.6%): ^{1}H NMR (DMSO) δ 12.24 (1H, s, 18-COOH), 9.23 (1H, s, 17-OH), 7.23 (1H, d, $J_{13,15}$ = 1.6 Hz, H-13), 7.08 (1H, dd, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 1.7 Hz, H-4), 6.98 (1H, d, $J_{3,4}$ = 8.3 Hz, H-3), 6.94 (1H, d, $J_{6,4}$ = 1.7 Hz, H-6), 6.86 (1H, dd, $J_{15,16}$ = 8.8 Hz, $J_{15,13}$ = 1.6 Hz, H-15), 6.65 (1H, dm, $J_{16,15}$ = 8.8 Hz, H-16), 4.30−4.34 (1H, m, H-8), 4.06−4.10 (1H, m, H-11), 3.79−3.82 (1H, m, H-9), 3.62−3.65 (1H, m, H-109, 2.25 (3H, s, H-14), 2.21 (3H, s, H-5); ^{13}C NMR (DMSO) δ 172.1 (Cq, C-18), 168.7 (Cq, C-1), 153.0 (Cq, C-17), 149.2 (Cq, C-2i), 133.8 (Cq, C-5i), 129.1 (CH, C-4), 128.5 (CH, C-15), 128.0 (CH, C-6), 127.0 (Cq, C-14i), 123.7 (Cq, C-12i), 122.6 Cq, C-7i), 116.7 (CH, C-3), 114.6 (CH, C-16), 48.8 (CH, C-10), 44.8 (CH, C-11), 36.1 (CH, C-8), 35.7 (CH, C-9), 20.5 (CH_3, C-14), 20.3 (CH_3, C-5).

Anti-hh **3** (R = methyl) (100 mg) was suspended in methanol (30 cm^3) and refluxed for 2 h (alternatively the suspension was kept at room temperature overnight instead of refluxing, which did not change the result). The solution cleared. After removal of the solvent, a white solid was obtained melting at 173−175 °C, which was identified via NMR and MS analysis as a pure substance, i.e., the diester **19** (100%): ^{1}H NMR ($CDCl_3$) δ 6.88 (2H, dd, $J_{7,8}$ = $J_{7',8'}$ = 8.0 Hz, $J_{7,5}$ = $J_{7',5'}$ = 1.5 Hz, H-7,7′), 6.85 (2H, d, $J_{5,7}$ = $J_{5',7'}$ = 1.5 Hz, H-5,5′), 6.68 (2H, d, $J_{7,8}$ = $J_{8',7'}$ = 8.0 Hz, H-8,8′), 5.03 (2H, s, 9,9′-OH), 4.82−4.84 (2H, m, H-3, 3′), 3.95−3.97 (2H, m, H-2, 2′), 3.37 (6H, s, H-10, 10′, OCH_3), 2.17 (6H, s, H-6, 6′); ^{13}C NMR ($CDCl_3$) δ 172.8 (Cq, C-1,1′), 151.4 (Cq, C-9,9′), 130.1 (Cq, C-6i,6i′), 128.5 (CH, C-7,7′), 127.9 (CH, C-8,8′), 125.4 (Cq, C-4,4′), 115.5 (CH, d, C-5,5′), 51.7 (OCH3, C-10,10′), 43.8 (CH, C-2,2′), 38.5 (CH, C-3,3′), 20.6 (CH_3, C-6,6′); ESI-MS (10.0 V) *m/e* 385.0 [M + H^+], 401.9 [M + NH_4^+]. When the starting suspension was stirred for 1 h at room temperature, an almost clear solution was formed. After evaporating the solvent at low temperature, a mixture of three compounds was obtained: **3** (R = methyl) (18.9%), **19** (8.6%), and 72.5% of the monoester **18**. Spectral data for **18**: ^{1}H NMR ($CDCl_3$) δ 7.14 (1H, d, $J_{13,15}$ = 2.4 Hz, H-13), 7.03 (1H, dd, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.4 Hz, H-4), 6.95 (1H, dd, $J_{15,16}$ = 8.0 Hz, $J_{15,13}$ = 2.4 Hz, H-15), 6.95 (1H, d, $J_{3,4}$ = 8.3 Hz, H-3), 6.86 (1H, d, $J_{6,4}$ = 2.4 Hz, H-6), 6.64 (1H, d, $J_{16,15}$ = 8.0 Hz, H-16,), 4.76 (1H, s, 17-OH), 4.37−4.41 (1H, m, H-8), 4.25−4.29 (1H, m, H-11), 3.93−3.96 (1H, m, H-10), 3.90−3.92 (1H, m, H-9), 3.35 (3H, s, H-19, OCH_3), 2.34 (3H, s, H-14), 2.25 (3H, s, H-5); ^{13}C NMR ($CDCl_3$) δ 171.5 (COOMe, C-18), 168.9 (CO, C-1), 151.0 (Cq, C-17), 149.3 (Cq, C-2i), 134.2 (Cq, C-5i), 130.0 (Cq, C-14i), 129.4 (CH, C-4), 129.0 (CH, C-15), 128.1 (CH, C-6), 127.8 (CH, C-13), 123.9 (Cq, C-12i), 121.6 (Cq, C-7i), 117.1 (CH, C-3), 115.5 (CH, C-16), 51.7 (OCH_3, C-19), 49.0 (CH, C-10), 45.2 (CH, C-11), 36.1 (CH, C-8), 35.5 (CH, C-9), 21.0 (CH_3, C-14), 20.7 (CH_3, C-5).

Stirring of anti-hh **3** (R = methyl) (20 mg) in ethyl acetate (20 cm^3) in the presence of silica gel (5 g) for 1 week in the dark and removal of the solvent led to an almost complete decomposition of the anti-hh dimer. According to NMR analysis, the main product was the monoacid **16** accompanied by some diacid **17** and further unidentified products. When Al_2O_3 was used instead of SiO_2, the dimer decomposed completely.

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Supporting Information Available: Commercial apparatus and chemicals; syntheses and characterizations of **1** and **6**−**12**; X-ray analysis of **2** (R = methyl). This material is available free of charge via the Internet at http://pubs.acs.org.

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