Chemical triggering of dioxetanes derived from 9-adamantylideneacridanes: fluoride- and base-induced chemiluminescence (CIEEL) of siloxy- and acetoxy-substituted dioxetanes

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Photooxygenation of the methoxy-, siloxy- and acetoxy-substituted adamantylideneacridanes 3 afforded the corresponding dioxetanes 4. Thanks to the spiroadamantyl-substitution, these dioxetanes were sufficiently persistent to allow their isolation and full characterization. The activation parameters (E_a, log A, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) of the direct chemiluminescence for the methoxy-substituted derivatives 4a–c were determined by standard isothermal kinetic methods. The fluoride-ion- and base-induced decomposition of the siloxy- and acetoxy-substituted dioxetanes 4g,h,j,k was shown to involve intramolecular CIEEL emission. The CIEEL quantum yields (Φ^{CIEEL}) were independent of the nature of the protective group, but marked differences were observed between the 2- and the 3-substituted derivatives; the latter are about two orders of magnitude more efficient. The difference in the CIEEL quantum yields was attributed to the distinct fluorescence properties of the corresponding emitters 7 since fluorescence from the 2-substituted derivative 7(2) is too small to be measurable, while for the 3-substituted derivative 7(3) the fluorescence quantum yields (Φ^{Fl}) are as much as a few percent. AM1 calculations were conducted on the oxy-substituted acridone emitters 7 to explore the reasons. Presumably, the dominant charge-transfer excitation of the acridone chromophore is not appreciably perturbed by the oxy substituent for both regioisomeric emitters 7(2,3). Thus, the similar singlet excitation yields (Φ^{S}) for the regioisomeric oxy-substituted spiroacridane dioxetanes 6 generated on triggering reveal that they do not follow the odd/even rationale established for the related oxy-substituted benzoates and naphthoates.

Introduction

The chemiluminescence properties of dioxetanes as high-energy molecules are of particular interest for the generation of excited states, *i.e.* without the use of light. The formation of electronically excited products can be induced either thermally or by an electron-transfer mechanism. The latter process was originally discovered by Schuster for the dibenzoyl peroxide[1] and in the meantime abundantly documented for the α-peroxy lactones[2] and appropriate dioxetanes.[3] This phenomenon of light emission has been designated as chemically initiated electron exchange luminescence (CIEEL).

The CIEEL may result from both inter- and intra-molecular electron transfer. The latter case has been postulated to operate in firefly bioluminescence.[4] Also 1,2-dioxetanes with substituents of low oxidation potentials, *e.g.* the aryl-O^- or aryl-RN^- functionalities, display intramolecular CIEEL.[5–8] The most successful design[5,6] utilizes thermally persistent spiroadamantane-substituted dioxetanes with a protected but releasable phenolate ion. The advantage of such dioxetanes is their convenient synthesis through photooxygenation. The CIEEL emission of these dioxetanes can be generated at will on treatment with an appropriate reagent (trigger), which depends on the nature of the protective group, to release the phenolate ion. The chemi-excitation step consists of the cleavage of the intermediate dioxetane phenolate anion. Such cleavage is initiated by the intramolecular electron transfer (ET) from the oxidizable phenolate functionality to the antibonding σ* orbital of the peroxide bond. These phenolate-initiated, intramolecular CIEEL processes provide the basis for numerous commercial applications, most prominently in chemiluminescent immunoassays.[9]

In our search for new, efficient CIEEL systems, we investigated the oxy-substituted spiroadamantane spiroacridane dioxetanes,[10] protected either by silylation or by acetylation. During the triggering process, the acridone phenolates are released, which are expected to possess good fluorescence properties based on the known data of a variety of acridone derivatives.[11] Furthermore, it was of interest to assess the influence of oxy-substitution on the chemiluminescence quantum yields of the regioisomeric dioxetanes.

Results

Synthesis of the starting materials

A convenient two-step synthesis of the adamantylideneacridanes **3a**–**c** by starting from adamantanone and the acridanes **1a**–**c** (Scheme 1) was developed. Addition of the *in situ* formed acridyllithium to adamantanone led to the alcohols **2a**–**c** (step i), which were subsequently dehydrated to afford the methoxy-substituted olefins **3a**–**c** (step ii). Cleavage of the ethers **3a**,**b** by treatment with hydrobromic acid gave the phenolic olefins **3d**,**e** (step iii), which were subsequently either silylated or acetylated to the siloxy (**3g**,**h**) (step iv) and the acetoxy (**3j**,**k**) derivatives (step v).

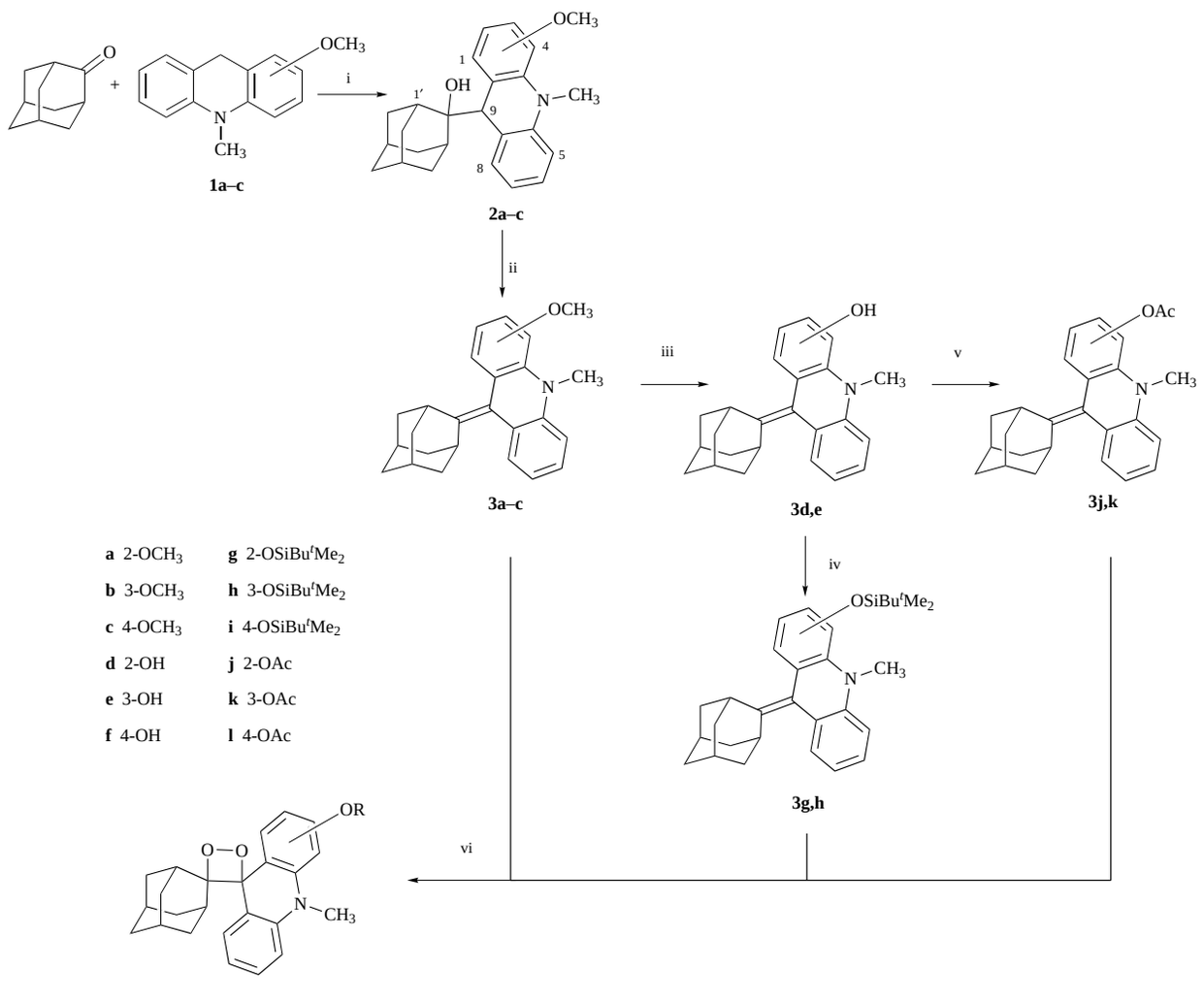
Synthesis of the dioxetanes 4

Upon tetraphenylporphyrin (TPP)-sensitized photooxygenation of the olefins **3a**–**c**,**g**,**h**,**j**,**k**, the hitherto unknown spiroacridane spiroadamantane dioxetanes **4** were readily obtained (step vi). The dioxetanes **4** were isolated by low-temperature, silica-gel chromatography at −10 °C, which was conducted quickly to avoid decomposition of the dioxetanes on the column. Their structure was unequivocally assigned on the basis of their spectral and analytical data and by their chemiluminescence. The ^{13}C NMR chemical shifts of the four-membered ring carbon atoms (δ 86.7–88.6 and 97.5–98.0) are characteristic for the 1,2-dioxetane structure.

Table 1 Rate constants[a] and activation parameters[b] for the thermal decomposition of the dioxetanes **4a–c** in toluene

Dioxetane	T/°C[c]	$k/10^{-4}$ s^{-1}	E_a/kcal mol^{-1}	log A	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
4a[d]	80.0	0.47 ± 0.05	26.0 ± 0.7	11.8 ± 0.4	25.3 ± 0.7	−6.9 ± 1.7
	85.0	0.88 ± 0.05				
	90.0	1.38 ± 0.06				
	95.0	2.17 ± 0.02				
4b[e]	85.0	0.72 ± 0.01	26.4 ± 0.6	12.0 ± 0.4	25.7 ± 0.6	−6.1 ± 1.7
	87.5	0.92 ± 0.06				
	90.0	1.05 ± 0.03				
	92.5	1.54 ± 0.01				
	95.0	1.96 ± 0.06				
4c[f]	80.0	0.44 ± 0.04	25.3 ± 0.6	11.3 ± 0.3	24.6 ± 0.6	−9.0 ± 1.3
	85.0	0.83 ± 0.05				
	90.0	1.25 ± 0.07				
	95.0	1.98 ± 0.05				

[a] Calculated by first-order kinetics. [b] Determined by isothermal kinetics. [c] Temperature control within ±0.1 °C. [d] [**4a**] = 1.10 × 10^{-3} mol dm^{-3}. [e] [**4b**] = 1.38 × 10^{-3} mol dm^{-3}. [f] [**4c**] = 4.78 × 10^{-3} mol dm^{-3}.



Scheme 1 *Reagents and conditions:* i, BuLi, THF, −78 to 20 °C, 24 h; ii, HOAc–H_2SO_4 (4:1), 50 to 70 °C, 30 min; iii, HBr (48%)–HOAc (1:1), 140 °C, 3 h; iv, Bu^{t}Me$_2$SiCl, imidazole, DMF, 40 to 50 °C, 4 h; v, Ac_2O, Et_3N, CH_2Cl_2, 20 °C, 4 h; vi, O_2, TPP, *hν*, $CDCl_3$, −10 °C, 30 to 45 min

Synthesis of the dioxetane decomposition products 5

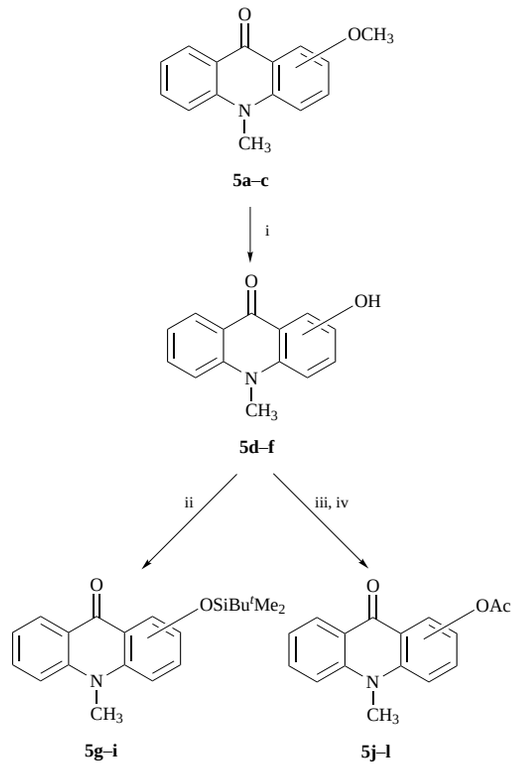
The acridones **5**, formed during the thermally or chemically induced dioxetane decomposition, were independently prepared (Scheme 2). Ether cleavage of the methoxy-substituted acridones **5a–c** with hydrobromic acid led to the corresponding hydroxy-substituted derivatives **5d–f**, which were subsequently either silylated or acetylated to the siloxy (**5g–i**) or the acetoxy (**5j–l**) acridones. These hitherto unknown compounds **5g–l** were characterized on the basis of their spectral and analytical data.

Chemiluminescence measurements

The activation parameters for the thermal decomposition of the dioxetanes **4a–c** were determined by standard isothermal kinetic methods in toluene, by monitoring the direct chemiluminescence decay photometrically. First-order (semilogarithmic) plots of the emitted light intensity *versus* time were perfectly linear. Arrhenius and Eyring treatment of the rate data gave the activation parameters E_a, log A and $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$. These results together with the k values are given in Table 1. The thermal persistence of these spiroadamantane dioxetanes is

clearly manifested by the high activation energies (E_a *ca.* 26 kcal mol^{-1}; 1 cal = 4.184 J).

The fluoride-ion-triggered decomposition of the siloxy dioxetanes **4g**,**h** was performed with Bu_4NF in methylene chloride or acetonitrile. The base-induced decomposition of the acetoxy-substituted dioxetanes **4j**,**k** was carried out by treatment with Bu_4NOH in acetonitrile or methanol, or alternatively by sodium methanolate in methanol. Both pathways resulted in rapid decomposition with intense light emission and afforded the corresponding above-mentioned hydroxy-substituted acridones **5d**,**e**. For the chemically triggered decompositions a relatively short light emission up to one minute was observed, while the thermolysis of the methoxy-substituted dioxetanes **4a–c** led at elevated temperatures (T > 80 °C) to direct chemiluminescence with a continuous glow over several hours. The spectra of the chemically induced chemiluminescence matched the fluorescence spectra of the corresponding acridones **5g**,**h**,**j**,**k** under the same conditions.



Scheme 2 *Reagents and conditions:* i, HBr (48%), 140 °C, 2 h; ii, Bu^tMe_2SiCl, imidazole, DMF, 40 to 50 °C, 45 h; iii, NaH, DMF, 20 °C, 1 h; iv, Ac_2O, DMF, 20 °C, 30 min

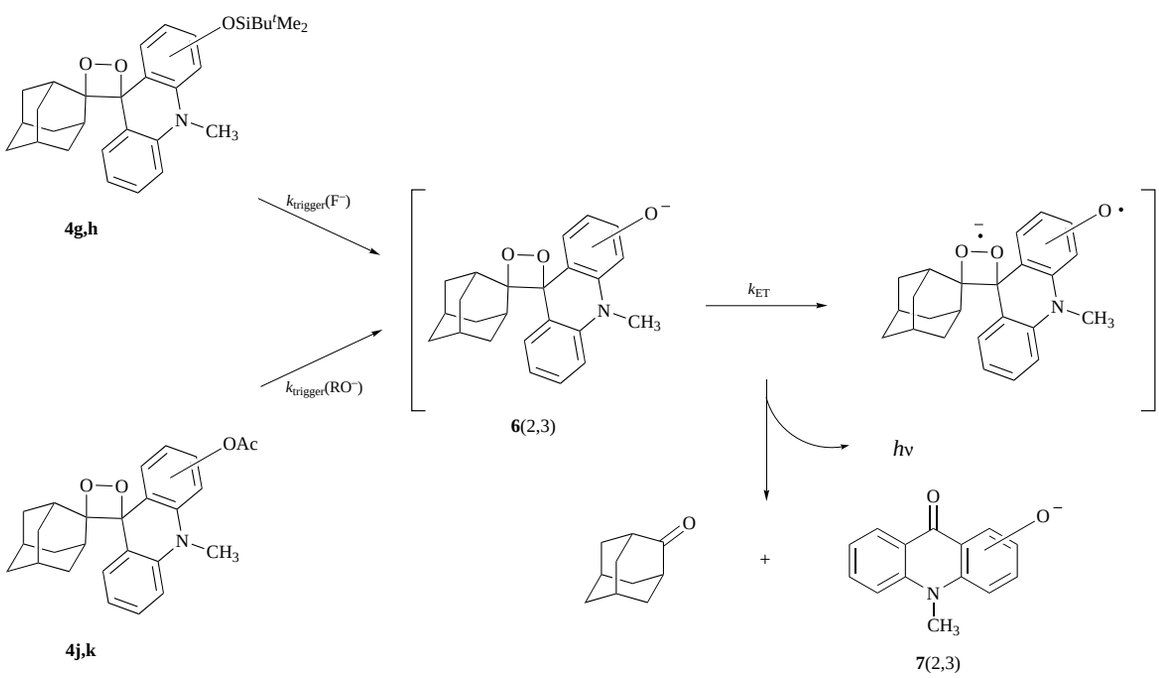
The intensity–time profiles were evaluated by using first-order kinetics and the chemiluminescence yields were determined therefrom as described previously.[12] The results are collected in Table 2. The reactions of the dioxetanes **4g**,**h**,**j**,**k** with fluoride ions or with base reveal different kinetic regimes, which are dependent on the ammonium fluoride or base concentrations. With increasing concentration of the triggering agent, the CIEEL decay obeys pseudo-first-order kinetics, while at relatively low concentrations (*i.e* up to tenfold excess of fluoride or base) the intensity–time profiles do not fit well monoexponentially. Therefore, for proper evaluation of the kinetics, a large excess (at least twentyfold) of triggering agent is necessary since $k_{trigger}$ $[trigger]_0 \gg k_{ET}$ applies, *i.e.* the rate-determining step is the electron-transfer-induced (k_{ET}) cleavage of the dioxetane phenolate ion, while deprotection by the trigger ($k_{trigger}[trigger]_0$) is fast (Scheme 3). Then, the CIEEL decay follows pseudo-first-order kinetics. A similar behaviour was observed with other CIEEL systems, *e.g.* the fluoride-induced decomposition of siloxyaryl-substituted spiroadamantyl dioxetanes.[13]

The base-induced decomposition of the acetoxydioxetanes **4j**,**k** was solvent dependent. For example, in methanol, somewhat smaller rate constants were obtained than in methylene chloride (*cf.* Table 2). The reason for this observation is found in the saponification kinetics of the ester functionality, *i.e.* $k_{trigger}(RO^-)[RO^-]_0 \ll k_{ET}$ applies and the triggering step $k_{trigger}(RO^-)[RO^-]_0$ is slow and, therefore, rate-determining.

The siloxy and acetoxy dioxetanes with the same substitution pattern possess similar chemiluminescence quantum yields. A marked difference is observed between the 2- *versus* the 3-substituted derivatives, *i.e.* Φ^{CIEEL}(**4g**,**j**) ≈ 10^{-5} E mol^{-1} *versus* Φ^{CIEEL}(**4h**,**k**) ≈ 10^{-3} E mol^{-1}.

Determination of fluorescence quantum yields of the acridones 5g–l

To determine the fluorescence quantum yields of the acridone phenolate ions **7**, the siloxy-substituted acridones **5g–i** were



Scheme 3 CIEEL mechanism of the chemically induced decomposition of the siloxy- and acetoxy-dioxetanes **4g**,**h**,**j**,**k**

Table 2 CIEEL for the dioxetanes **4g**,**h**,**j**,**k** and fluorescence data for the cleavage products **5g**,**h**,**j**,**k** and the oxoacridanolates **7**(2,3)

Dioxetane	Solvent	Triggering agent[a]	$k/10^{-3}$ s^{-1}[b]	$\Phi^{CIEEL}/10^{-5}$ E mol^{-1}[c]	Φ^{Fl} (**5**)$/10^{-2}$[d]	Φ^{Fl} (**7**)$/10^{-2}$[d]	$\Phi^{S}/10^{-2}$[e]
4g[f]	CH_2Cl_2	Bu_4NF	29.9 ± 0.3	7.2 ± 0.4	95 ± 5	<0.1	>7
	CH_3CN	Bu_4NF	360 ± 100	0.10 ± 0.03	50 ± 5	<0.1	>0.1
4h[g]	CH_2Cl_2	Bu_4NF	22.6 ± 3.2	350 ± 20	1.0 ± 0.1	2.0 ± 0.2	18 ± 3
	CH_3CN	Bu_4NF	25.6 ± 3.4	510 ± 50	3.0 ± 0.3	1.0 ± 0.1	52 ± 10
4j[h]	CH_2Cl_2	Bu_4NOH	17.6 ± 2.8	0.62 ± 0.09	14 ± 1	<0.1	>0.5
	CH_3OH	Bu_4NOH	7.0 ± 0.7	7.5 ± 0.8	3.0 ± 0.3	<0.1	>7
	CH_3OH	NaOMe	4.4 ± 0.7	5.9 ± 0.9		<0.1	>5
4k[i]	CH_2Cl_2	Bu_4NOH	21.5 ± 2.5	120 ± 10	4.0 ± 0.4	0.7 ± 0.1	18 ± 4
	CH_3OH	Bu_4NOH	8.8 ± 1.3	480 ± 70	2.0 ± 0.2	1.0 ± 0.1	49 ± 12
	CH_3OH	NaOMe	5.4 ± 0.8	380 ± 60		0.9 ± 0.1	44 ± 12

[a] 20-fold excess of triggering agent. [b] k at 25 °C. [c] Chemiluminescence quantum yield. [d] Fluorescence quantum yield, relative to quinine bisulfate (Φ^{Fl} = 0.56, *cf.* ref. 26). [e] Quantum yield for the formation of the singlet-excited state of the free **7** derived from the acridone **5** by triggering. [f] [**4g**] = 3.28 × 10^{-4} mol dm^{-3}. [g] [**4h**] = 6.75 × 10^{-8} mol dm^{-3}. [h] [**4j**] = 1.68 × 10^{-4} mol dm^{-3}. [i] [**4k**] = 1.20 × 10^{-6} mol dm^{-3}.

desilylated with the help of fluoride ions, and the acetoxy-substituted ones **5j–l** saponified by means of a base (Bu_4NOH or NaOMe). The acridone **5** solutions as well as the resulting oxoacridanolate **7** solutions were submitted to fluorescence analysis. The fluorescence quantum yield data for the acridones **5g**,**h**,**j**,**k** [Φ^{Fl} (**5**)] and their corresponding oxoacridanolates **7**(2,3) [Φ^{Fl} (**7**)] are given in Table 2, together with the estimated quantum yields for the formation of singlet-excited states (Φ^{S}).

The acridones **5** showed moderate to excellent fluorescence quantum yields. While the 2-substituted derivative **7**(2) derived from the acridones **5g**,**j** displayed a dramatic decrease in the fluorescence intensity (Φ^{Fl} < 0.1%), the 3-substituted derivative **7**(3) derived from **5h**,**k** remained essentially constant with moderate fluorescence yields (Φ^{Fl} *ca.* 1%). Since the 4-substituted derivative **7**(4) from the acridones **5i**,**l** showed no fluorescence at all, the synthesis of the corresponding dioxetanes was not further pursued.

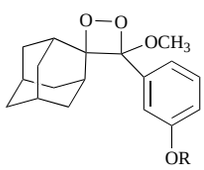
Discussion

Spiroadamantane substitution[14] stabilizes sufficiently the labile enamine-type dioxetanes **4** to permit their isolation and characterization. The activation parameters for the dioxetanes **4a–c** (Table 1) show clearly that the introduction of only one spiroadamantane moiety is enough to stabilize the dioxetane ring system against thermal decomposition. As expected, the introduction of a methoxy substituent on the acridane moiety shows no influence on the kinetics compared to the unsubstituted system.[10] The somewhat negative activation entropies obtained with the isothermal kinetic method suggest some participation of dark catalytic decomposition,[15] a problem which is difficult to avoid for such enamine-type and, therefore, easily oxidizable, dioxetanes. Presumably, this chemically induced electron-exchange-type decomposition is also the reason for the observed lability of these dioxetanes during the silica gel chromatographic work-up. Apparently, contact with solid surfaces promotes ion formation and catalyses electron-transfer-type decomposition.[16]

The siloxy- and acetoxy-substituted dioxetanes **4g**,**h**,**j**,**k** served the purpose for chemically triggered CIEEL emission. Treatment of the siloxy derivatives with fluoride ions and the acetyl ones with base induced rapid decomposition of the dioxetanes with appreciable chemiluminescence, which was considerably higher than the light emission derived from their direct thermal decomposition. This speaks for an intramolecular electron-exchange mechanism of the CIEEL type,[1–3] which yields a higher proportion of singlet-excited carbonyl products and, hence, the more intense fluorescence. In the proposed mechanism (Scheme 3), first the dioxetane phenolate ion **6** is formed, either by desilylation or by saponification, in which subsequently the electron-rich oxy anion acts as an intramolecular electron donor. After electron transfer (ET) with cleavage of the dioxetane ring, an electronically excited singlet state is generated, which manifests itself through fluorescence emission.

The intensity–time profiles of the emission decay obey strict first-order kinetics in accordance with the proposed mechanism. Only the short bursts of light emission, which were obtained in the fluoride-ion-induced decomposition of dioxetane **4g** in acetonitrile (*cf.* Table 2), are an exception. Presumably, both the deprotection as well as the electron-transfer steps are too fast for proper kinetic evaluation without time-resolved, spectral analysis.

The CIEEL quantum yields in Table 2 reveal that the protecting group, *i.e.* whether silyl or acetyl, has no dramatic influence on the chemiluminescence efficiency. A comparison with the established spiroadamantane dioxetanes of the AMPPD type



R = $SiBu^tMe_2$, Ac, PO_3Na_2, sugar

AMPPD-type dioxetanes

(Φ^{CIEEL} up to 25%) demonstrates that the spiroacridane dioxetanes **4** are, indeed, rather inefficient CIEEL systems, especially the 2-substituted regioisomers **4g**,**j** with chemiluminescence quantum yields in the range of 10^{-6} to 10^{-5} E mol^{-1}. Nevertheless, the 3-substituted derivatives **4h**,**k** are far more effective than the 2-substituted ones. For these systems, quantum yields of up to 0.5% were obtained, which compare quite well with other CIEEL systems of the spiroadamantane type.[9a]

The overall chemiluminescence quantum yield Φ^{CIEEL}, *i.e.* the total number of photons emitted per number of molecules triggered, is described by eqn. (1), in which Φ^{S} gives the yield of

$$\Phi^{CIEEL} = \Phi^{S} \cdot \Phi^{Fl} \quad (1)$$

the singlet-excited-state molecules that result from the intramolecular electron-transfer pathway and Φ^{Fl} the fluorescence quantum yield of the oxoacridanolate **7** emitter. From this equation it is apparent that the fluorescence properties of the oxoacridanolates **7** derived from the acridones **5** (Scheme 3) may play an important role in determining the efficiency of triggered chemiluminescence (Φ^{CIEEL}) of the dioxetanes **4**.

While the acridones **5** themselves showed moderate to excellent fluorescence quantum yields [*cf.* Table 2, Φ^{Fl} (**5**) 1–95%], which is expected on the basis of the known fluorescence data of acridone derivatives,[11] drastic differences were encountered for the regioisomeric ions **7** generated from the dioxetanes **4** during the triggering process. Thus, in the case of the 2-substituted oxoacridanolate **7**(2), the fluorescence quantum yields Φ^{Fl} [**7**(2)] dropped dramatically below the detection limit of our fluorescence spectrophotometer (Φ^{Fl} < 0.1%), whereas

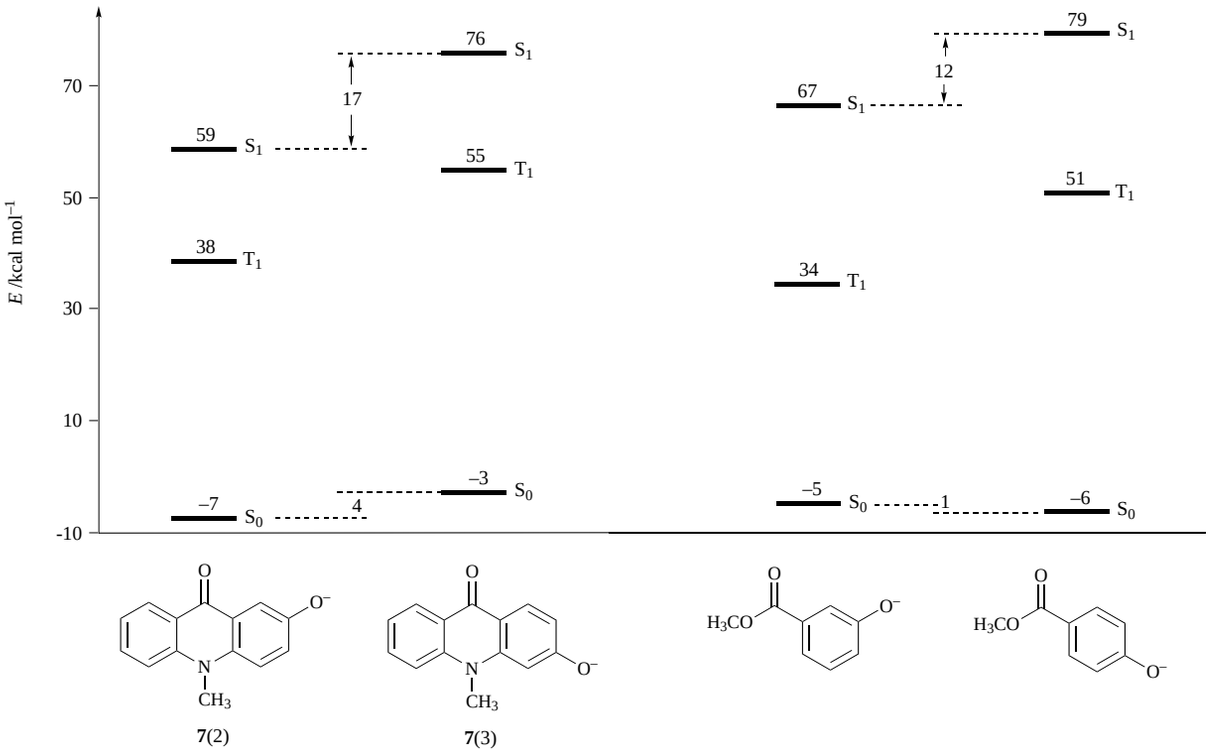
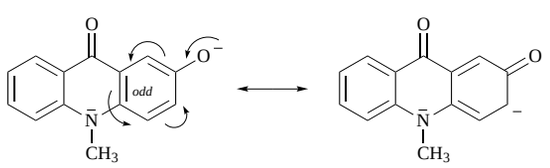


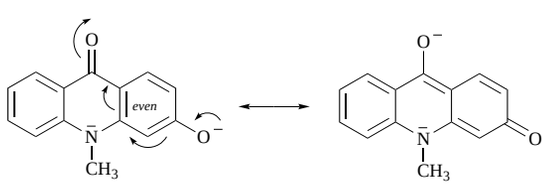
Fig. 1 Energies of the ground (S_0) and the first excited singlet (S_1) and triplet (T_1) states as calculated by the AM1 method implemented in the VAMP 5.0 software package

the values for the 3-substituted regioisomer **7**(3) remained essentially constant (Φ^{Fl} *ca.* 1%). Apparently, in the cross-conjugated derivative **7**(2), the strong electron-donating 2-oxy



7(2)

Crossed conjugation
(*odd* substitution)



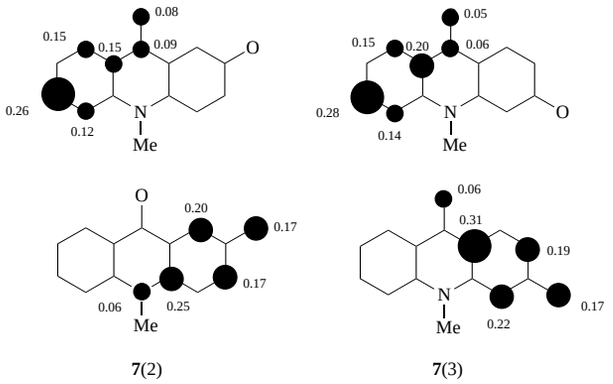
7(3)

Extended conjugation
(*even* substitution)

anion seriously disturbs the fluorescence properties of the acridone chromophore, while for the extended-conjugated **7**(3) regioisomer the relatively efficient fluorescence ability is retained. Thus, in view of eqn. (1), a direct response exists between the poor triggered-chemiluminescence efficiencies (Φ^{CIEEL}) and the essentially non-fluorescent 2-substituted emitter **7**(2), on the one hand, and the quite good triggered-chemiluminescence quantum yields and the moderate fluorescent 3-substituted emitter **7**(3), on the other hand.

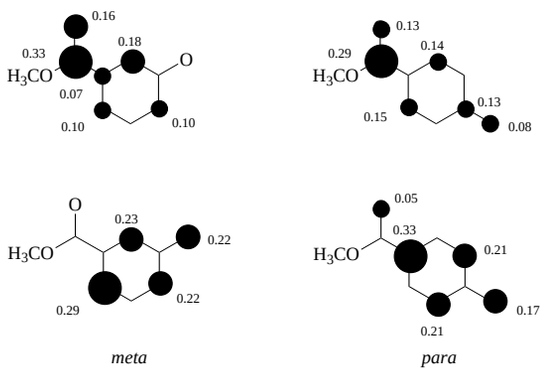
With the fluorescence quantum yields of the emitters **7** available, according to eqn. (1), the singlet excitation yields (Φ^{S}) for the chemically induced decomposition of the dioxetanes **4g**,**h**,**j**,**k** may be estimated. For the 3-substituted dioxetanes **4h**,**k**, the singlet excitation yields were found to range between 18 and 52% (*cf.* Table 2). As already pointed out, for the 2-substituted dioxetanes **4g**,**j** only upper limits (fluorescence detection limit *ca.* 0.1%) for the fluorescence yields of the corresponding oxoacridanolate **7**(2) have been established, such that for these dioxetanes only lower limiting values of Φ^{S} may be obtained in Table 2. These estimated Φ^{S} data suggest that the yield of singlet-excited molecules is about an order of magnitude lower for the cross-conjugated 2-substituted **4g**,**j** *versus* the extended-conjugated 3-substituted **4h**,**k** regioisomers. However, this constitutes the maximum difference in the Φ^{S} values for these two sets of regioisomers since the Φ^{Fl} values may very well be substantially lower than the upper limit taken at *ca.* 0.1%, our detection limit. Consequently, it may very well be that the 2- and 3-substituted regioisomeric acridone dioxetanes **4** possess a similar capacity to generate singlet-excited states on CIEEL triggering.

During the development of the first efficient CIEEL-active spiroadamantane dioxetanes,[5,6] a significant dependence of the chemiluminescence quantum yields (Φ^{CIEEL}) on the substitution pattern was established. In the case of acetoxynaphthyl spiroadamantyl dioxetanes, Bronstein *et al.*[17] observed empirically that extended-conjugated carbonyl chromophores derived from dioxetanes during triggered decomposition gave rise to flash-like emission, accompanied by low chemiexcitation efficiencies, whereas cross-conjugated carbonyl compounds exhibited a steady glow with higher quantum yields. The authors[17] postulated a so-called odd/even rationale to explain this empirical phenomenon: charge transfer from the donor (phenolate) to the acceptor (carbonyl group) occurs more effectively when the two groups are cross-conjugated (an odd number of carbon atoms between the interacting groups), as substantiated by semiempirical MO calculation. Presumably, charge transfer enhances excited-state formation, ensures high chemiexcitation efficiencies and provides a persistent glow through stabilization of the incipient excited state. In contrast, extended conjugation stabilizes the ground state through dipolar resonance, which disfavours excited-state formation and, consequently, low efficiencies and short flashes are observed.[17,18]



7(2) **7**(3)

Fig. 2 Charge-density distributions for the ground (bottom) and the first excited states (top) of the regioisomeric oxoacridanolates **7**

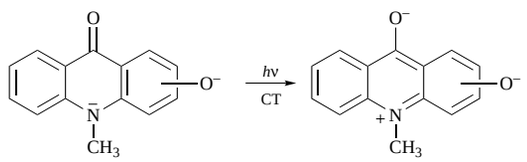


meta *para*

Fig. 3 Charge-density distributions for the ground (bottom) and the first excited states (top) of the regioisomeric oxybenzoates

Application of this odd/even rationale on our spiroacridane system **4** and, if as a first approximation, the electronic influence of the methylamino functionality is neglected, one would expect the cross-conjugated 2-regioisomer to be more efficient in its light emission than the extended-conjugated 3-regioisomer; however, experimentally quite the contrary is observed (Table 2). Therefore, to assess how the oxy-anion substituent affects the ground and excited states of the regioisomeric ions **7**(2,3), AM1 calculations were conducted. The computed energies of the ground and the first excited singlet and triplet states of the regioisomeric ions **7**(2,3) are shown in Fig. 1, and for comparison also the oxybenzoate regioisomers. Analogous to the latter reference system, the energy gap between the first excited singlet states of **7**(2) and **7**(3) was computed to be 17 kcal mol^{-1} lower for the **7**(2) regioisomer, which elucidates that the first excited singlet state is stabilized by 2-oxy more effectively than by 3-oxy substitution. However, in contrast to the oxybenzoate reference system, the ground state is also stabilized by the 2-oxy substituent since the energy gap between **7**(2) and **7**(3) was calculated to be *ca.* 4 kcal mol^{-1} again in favour of the **7**(2) regioisomer. Therefore, the odd/even rationale is not valid for this particular acridone system, which establishes that the singlet-excited state of the cross-conjugated regioisomer **7**(2) is stabilized while it is the ground state for the extended-conjugated **7**(3) regioisomer. The calculated singlet energies for the two regioisomers of **7** are in good agreement with the experimental UV absorption spectra, *i.e.* the observed absorption maxima (λ_{max}) are located at *ca.* 435 for **7**(2) and *ca.* 370 nm for **7**(3), while the AM1-calculated ones are at 437 and 361 nm. Furthermore, the calculations revealed that the amount of charge transfer from the donor (phenolate) to the acceptor (benzoyl group) is more or less independent of the substitution pattern, which was confirmed by configuration-interaction calculations. The charge density distributions for the excitation of the oxoacridanolates **7** are shown in Fig. 2, and for comparison also the oxybenzoate regioisomers in Fig. 3.

The first excited singlet as well as triplet state wave functions are mainly composed of HOMO and LUMO contributions, which are both of the π-type. In the excitation step of the acridone system, charge is transferred from the phenolate to the benzoyl moiety. The amount of charge transfer is essentially independent of the oxy-substitution (Fig. 2). In comparison, the charge distributions for the regioisomeric oxybenzoates show a definite dependence on the substitution pattern, *i.e.* charge transfer occurs more effectively for the *meta* regioisomer (Fig. 3), as it was proposed in the odd/even rationale.[17] Therefore, as already pointed out, this rationale is not valid for the oxoacridinolates **7**. Apparently, the charge-transfer character of the excited oxoacridinolate **7*** chromophore,[19] as expected for a vinylogous amide, is the main electronic characteristic of **7** [eqn. (2)]. Thus, the introduction of an additional oxy sub-



7(2,3) **7***(2,3) (2)

stituent, whether in the 2- or 3-positions of the excited oxoacridanolates **7**(2,3), does not perturb significantly this charge-transfer transition.

In summary, we have demonstrated that the CIEEL-active spiroacridane spiroadamantane 1,2-dioxetanes undergo fluoride-ion- or base-triggered decomposition with appreciable chemiluminescence. The substitution pattern plays a significant role in regard to the relative Φ^{CIEEL} values, as exhibited by the chemiluminescence quantum data in Table 2. The efficiency of the chemically induced chemiluminescence is dictated by the markedly different fluorescence properties of the corresponding oxoacridanolate emitters (Table 2), with high fluorescence yields for the 3-oxy- **7**(3) and unexpectedly low ones for the 2-oxy-substituted **7**(2) regioisomers. This unusual fluorescence behaviour requires further elucidation.

Experimental

General

^{1}H and ^{13}C NMR spectra were measured on a Bruker AC 200 (^{1}H: 200 MHz, ^{13}C: 50 MHz) or a Bruker QF 600 spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz) with deuteriochloroform, [$^2H_6$]dimethyl sulfoxide or [$^2H_4$]methanol as internal standards. *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1420 Ratio Recording IR spectrophotometer, UV spectra on a Hitachi U-3200 spectrophotometer, and fluorescence spectra on a Perkin-Elmer LS50 spectrofluorimeter. Elemental analyses were carried out by the Microanalytic Division of the Institute of Inorganic Chemistry, University of Würzburg. Melting points were taken on a Büchi apparatus B-545 and are not corrected. TLC analysis was conducted on precoated silica gel foils Polygram SIL G/UV_{254} (40 × 80 mm) from Macherey and Nagel. Spots were identified under a UV lamp and dioxetanes additionally by heating (short flash). Silica gel (63–200 μm; Woelm) was used for column chromatography, the adsorbance : substrate ratio was *ca.* 100 : 1. Low-temperature chromatography was performed on a column equipped with a vacuum-jacketed cooling mantle through which refrigerant was circulated from a RK 20 Lauda Cryomat.

All kinetic measurements were performed on a Mitchell-Hastings photometer[20] equipped with a RCA 926 B photomultiplier and a Lauda thermostat K 20 for temperature control of the cell compartment. Beckmann scintillation vials were used as reaction vessels. A Servogor Z10 recorder registered the output signal of the kinetic run.

Starting materials

The acridanes **1a**–**c**[21] were prepared according to the literature procedure[22] by reduction of the corresponding acridones **5a**–**c**[23,24] with sodium in refluxing isopentyl alcohol. The physical and spectral data of these compounds were consistent with those reported.[21]

General procedure for the synthesis of the adamantanols 2a–c. To a cooled solution (−78 °C) of the acridane **1** (*ca.* 0.01 mmol) in dry tetrahydrofuran (THF) (100 cm^3) was added under nitrogen butyllithium (5 equiv., 1.3–1.6 mol dm^{-3} in hexane). The solution turned red. After stirring at 0 °C for 30 min and subsequent cooling to −78 °C, a solution of adamantanone (1.1 equiv.) in dry THF (50 cm^3) was added, followed by stirring at *ca.* 20 °C for 24 h. The solution was poured into aqueous sodium hydrogen carbonate (100 cm^3) and extracted with THF (3 × 50 cm^3). The extract was dried ($MgSO_4$) and evaporated to dryness. Chromatography on silica gel with methylene chloride as the eluent yielded the adamantanols **2a**–**c**.

2-(2-*Methoxy*-10-*methylacridan*-9-*yl*)*adamantan*-2-*ol* (**2a**).—By following the above procedure, from the acridane **1a** (3.00 g, 13.3 mmol), BuLi (40 cm^3, 64.0 mmol) and adamantanone (2.20 g, 14.6 mmol) the adamantanol **2a** was obtained as pale-yellow needles (3.35 g, 67%), mp 156.0–156.5 °C, $R_f(CH_2Cl_2)$ 0.36 (Found: C, 79.59; H, 8.07; N, 3.87. $C_{25}H_{29}NO_2$ requires C, 79.96; H, 7.78; N, 3.73%); ν_{max}(KBr)/cm^{-1} 3500–3250 (OH), 2940, 2880, 2840, 1470; δ_H(200 MHz; $CDCl_3$) 0.90–2.40 (14 H, m, Ad-H), 3.31 (3 H, s, 10-CH_3), 3.78 (3 H, s, 2-OCH_3), 4.63 (1 H, s, 9-H), 6.79–6.99 (5 H, m, 1-H, 3-H, 4-H, 5-H and 7-H) and 7.19–7.29 (2 H, m, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) 27.0 (d), 27.7 (d), 32.9 (2d), 33.0 (t), 33.2 (t), 33.7 (q), 34.6 (t), 34.9 (t), 38.4 (t), 46.7 (d), 55.7 (q), 80.1 (s), 112.0 (d), 112.5 (d), 113.3 (d), 115.6 (d), 120.3 (d), 123.3 (s), 125.2 (s), 127.3 (d), 129.6 (d), 138.6 (s), 144.8 (s) and 154.1 (s).

2-(3-*Methoxy*-10-*methylacridan*-9-*yl*)*adamantan*-2-*ol* (**2b**).—By following the above procedure, from the acridane **1b** (3.47 g, 15.4 mmol), BuLi (55 cm^3, 77.0 mmol) and adamantanone (2.54 g, 16.9 mmol) the adamantanol **2b** was obtained as a colourless powder (4.26 g, 74%), mp 80–82 °C, $R_f(CH_2Cl_2)$ 0.40 (Found: C, 79.85; H, 8.04; N, 3.64. $C_{25}H_{29}NO_2$ requires C, 79.96; H, 7.78; N, 3.73%); ν_{max}(KBr)/cm^{-1} 3440–3300 (OH), 2930, 2880, 2830, 1580, 1460; δ_H(200 MHz; $CDCl_3$) 0.90–2.40 (14 H, m, Ad-H), 3.33 (3 H, s, 10-CH_3), 3.82 (3 H, s, 3-OCH_3), 4.62 (1 H, s, 9-H), 6.53–6.57 (2 H, m, 2-H and 4-H), 6.94–7.01 (2 H, m, 5-H and 7-H), 7.12 (1 H, m, 1-H) and 7.20–7.29 (2 H, m, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) 27.0 (d), 27.7 (d), 32.9 (2d), 33.2 (2t), 33.6 (q), 34.6 (t), 34.8 (t), 38.3 (t), 45.5 (d), 55.3 (q), 79.8 (s), 99.8 (d), 105.1 (d), 112.8 (d), 116.0 (s), 120.6 (d), 123.9 (s), 127.2 (d), 129.7 (d), 130.2 (d), 144.2 (s), 145.3 (s) and 159.2 (s).

2-(4-*Methoxy*-10-*methylacridan*-9-*yl*)*adamantan*-2-*ol* (**2c**).—By following the above procedure, from the acridane **1c** (3.00 g, 13.3 mmol), BuLi (40 cm^3, 64.0 mmol) and adamantanone (2.20 g, 14.6 mmol) the adamantanol **2c** was obtained as a yellow viscous oil that solidified after some days (3.82 g, 76%), mp 52–54 °C, $R_f(CH_2Cl_2)$ 0.45 (Found: C, 79.72; H, 7.59; N, 3.89. $C_{25}H_{29}NO_2$ requires C, 79.96; H, 7.78; N, 3.73%); ν_{max}(KBr)/cm^{-1} 3500–3300 (OH), 2940, 2900, 2840, 1635, 1595, 1530, 1490; δ_H(200 MHz; $CDCl_3$) 0.90–2.40 (14 H, m, Ad-H), 3.58 (3 H, s, 10-CH_3), 3.83 (3 H, s, 4-OCH_3), 4.58 (1 H, s, 9-H), 6.79–6.83 (2 H, m, 1-H and 3-H), 6.89–6.98 (2 H, m, 2-H and 7-H), 7.08–7.15 (2 H, m, 5-H and 8-H) and 7.19–7.28 (1 H, m, 6-H); δ_C(50 MHz; $CDCl_3$) 27.0 (d), 27.6 (d), 32.9 (t), 33.2 (t), 33.4 (d), 33.7 (d), 34.5 (2t), 38.3 (t), 39.6 (q), 46.3 (d), 55.8 (q), 77.9 (s), 110.9 (d), 115.5 (d), 120.4 (d), 121.5 (d), 122.3 (d), 125.8 (s), 127.0 (d), 128.1 (s), 129.1 (d), 133.9 (s), 146.8 (s) and 150.8 (s).

General procedure for the synthesis of the methoxy olefins 3a–c. A solution of the adamantanol **2a**–**c** (*ca.* 7–8 mmol) in glacial acetic acid–sulfuric acid (4:1) (20 cm^3) was stirred at 50–70 °C for 30 min. After diluting with water (20 cm^3), the solution was extracted with methylene chloride (4 × 10 cm^3). The extract was washed with aqueous sodium hydrogen carbonate (2 × 20 cm^3), dried ($MgSO_4$), and evaporated to dryness at 20 °C and 10 Torr. Chromatography of the residue on silica gel with methylene chloride and, if necessary, other eluents afforded the olefins **3a**–**c**.

9-*Adamantylidene*-2-*methoxy*-10-*methylacridane* (**3a**).—Dehydration of the adamantanol **2a** (2.50 g, 6.66 mmol) yielded the olefin **3a** as colourless needles (1.40 g, 59%), mp 190–191 °C, R_f(light petroleum–diethyl ether, 20:1) 0.50 (Found: C, 84.06; H, 7.60; N, 3.66. $C_{25}H_{27}NO$ requires C, 83.99; H, 7.61; N, 3.92%); ν_{max}(KBr)/cm^{-1} 2880, 2820, 1485, 1455, 1260, 1230; δ_H(200 MHz; $CDCl_3$) 1.50–2.20 (12 H, m, Ad-H), 3.37 (3 H, s, 10-CH_3), 3.46 (1 H, br s, 1′-H), 3.53 (1 H, br s, 1′-H), 3.79 (3 H, s, 2-OCH_3), 6.74–6.99 (5 H, m, 1-H, 3-H, 4-H, 5-H and 7-H) and 7.16–7.24 (2 H, m, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) 28.0 (2d), 32.2 (d), 32.4 (d), 33.4 (q), 37.1 (t), 39.7 (4t), 55.7 (q), 111.2 (d), 111.7 (d), 112.3 (d), 113.3 (d), 119.6 (d), 120.3 (s), 125.6 (s), 126.3 (d), 127.2 (d), 127.3 (s), 139.3 (s), 144.5 (s), 145.2 (s) and 153.7 (s).

9-*Adamantylidene*-3-*methoxy*-10-*methylacridane* (**3b**).—Dehydration of the adamantanol **2b** (3.00 g, 8.00 mmol) yielded the olefin **3b** as colourless needles (1.37 g, 48%), mp 168–169 °C (Found: C, 84.10; H, 7.54; N, 3.59. $C_{25}H_{27}NO$ requires C, 83.99; H, 7.61; N, 3.92%); ν_{max}(KBr)/cm^{-1} 2880, 2820, 1580, 1450; δ_H(200 MHz; $CDCl_3$) 1.60–2.20 (12 H, m, Ad-H), 3.39 (3 H, s, 10-CH_3), 3.46 (2 H, br s, 1′-H), 3.84 (3 H, s, 3-OCH_3), 6.54–6.59 (2 H, m, 2-H and 4-H), 6.95–7.02 (2 H, m, 5-H and 7-H) and 7.13–7.27 (3 H, m, 1-H, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) 28.1 (2d), 32.2 (2d), 33.4 (q), 37.2 (t), 39.2 (4t), 55.3 (q), 99.1 (d), 104.4 (d), 112.0 (d), 119.4 (s), 119.7 (s), 120.0 (d), 126.1 (d), 126.4 (s), 127.1 (d), 127.8 (d), 143.2 (s), 144.7 (s), 146.1 (s) and 158.5 (s).

9-*Adamantylidene*-4-*methoxy*-10-*methylacridane* (**3c**).—Dehydration of the adamantanol **2c** (2.90 g, 7.72 mmol) yielded the olefin **3c** as colourless needles (1.65 g, 60%), mp 172–173 °C, R_f(light petroleum–diethyl ether 5:1) 0.70 (Found: C, 83.90; H, 7.88; N, 3.75. $C_{25}H_{27}NO$ requires C, 83.99; H, 7.61; N, 3.92%); ν_{max}(CCl_4)/cm^{-1} 2880, 2820, 1430, 1250; δ_H(200 MHz; $CDCl_3$) 1.60–2.20 (12 H, m, Ad-H), 3.40 (1 H, br s, 1′-H), 3.46 (1 H, br s, 1′-H), 3.67 (3 H, s, 10-CH_3), 3.82 (3 H, s, 4-OCH_3), 6.76 (1 H, dd, $J_{3,2}$ 7.6 and $J_{3,1}$ 1.7, 3-H), 6.84 (1 H, dd, $J_{1,2}$ 7.6 and $J_{1,3}$ 1.7, 1-H), 6.93 (1 H, dd, $J_{2,1}$ and $J_{2,3}$ 7.6, 2-H), 6.94 (1 H, m, 7-H), 7.07–7.18 (2 H, m, 5-H and 8-H) and 7.19 (1 H, ddd, $J_{6,5}$ 8.3, $J_{6,7}$ 7.0 and $J_{6,8}$ 1.5, 6-H); δ_C(50 MHz; $CDCl_3$) 28.1 (2d), 32.1 (d), 32.5 (d), 37.2 (t), 38.8 (q), 39.2 (4t), 56.1 (q), 110.5 (d), 113.7 (d), 119.8 (d), 120.3 (d), 120.8 (s), 120.9 (d), 126.0 (d), 126.7 (d), 127.9 (s), 130.8 (s), 133.8 (s), 143.6 (s), 146.9 (s) and 150.4 (s).

General procedure for the synthesis of the hydroxy olefins 3d,e. A solution of methoxy olefin **3a**,**b** (*ca.* 0.2–0.6 mmol) in hydrobromic acid (48%)–glacial acetic acid (1:1) (20 cm^3) was kept at reflux for 3 h. By addition of water (20 cm^3), the hydroxy olefins **3d**,**e** precipitated and were dried over P_2O_5 at 20 °C and 10 Torr.

9-*Adamantylidene*-2-*hydroxy*-10-*methylacridane* (**3d**).—Demethylation of the methoxy olefin **3a** (207 mg, 0.579 mmol) yielded the hydroxy olefin **3d** as an orange powder (82.0 mg, 41%), mp 184 °C (Found: C, 84.03; H, 7.46; N, 3.98. $C_{24}H_{25}NO$ requires C, 83.93; H, 7.34; N, 4.08%); ν_{max}(KBr)/cm^{-1} 3600–3000 (OH), 2920, 2870, 1635, 1565, 1495, 1260; δ_H(200 MHz; CD_3OD) 1.66–1.82 (10 H, m, Ad-H), 2.11 (2 H, m, Ad-H), 2.43 (1 H, m, Ad-H), 2.80 (1 H, m, Ad-H), 4.77 (3 H, s, 10-CH_3), 7.84 (1 H, ddd, $J_{7,8}$ 9.0, $J_{7,6}$ 6.7 and $J_{7,5}$ 1.0, 7-H), 7.89 (1 H, dd, $J_{3,4}$ 9.7 and $J_{3,1}$ 2.6, 3-H), 7.99 (1 H, d, $J_{1,3}$ 2.6, 1-H), 8.18 (1 H, ddd, $J_{6,5}$ 9.2, $J_{6,7}$ 6.7 and $J_{6,8}$ 1.2, 6-H), 8.53 (1 H, dd, $J_{5,6}$ 9.2 and $J_{5,7}$ 1.0, 5-H), 8.54 (1 H, d, $J_{4,3}$ 9.7, 4-H) and 8.79 (1 H, dd, $J_{8,7}$ 9.0 and $J_{8,6}$ 1.2, 8-H); δ_C(50 MHz; CD_3OD) 28.8 (d), 28.9 (d), 34.4 (2d), 37.8 (t), 38.2 (2t), 40.2 (t), 40.8 (t), 52.4 (q), 108.3 (d), 119.6 (d), 121.5 (d), 127.6 (d), 128.2 (s), 128.8 (d), 128.8 (s), 130.1 (s), 131.9 (d), 137.0 (d), 138.1 (s), 140.8 (s), 157.3 (s) and 166.0 (s).

9-*Adamantylidene*-3-*hydroxy*-10-*methylacridane* (**3e**).—Demethylation of the methoxy olefin **3b** (72.0 mg, 0.201 mmol) yielded the hydroxy olefin **3e** as a yellow powder (66.0 mg, 96%), mp 160–161 °C (Found: C, 83.61; H, 6.98; N, 3.99. $C_{24}H_{25}NO$ requires C, 83.93; H, 7.34; N, 4.08%); ν_{max}(KBr)/cm^{-1} 3480–3280 (OH), 2900, 2830, 1610, 1590, 1450, 1225; δ_H(200 MHz; CD_3OD) 1.66–1.82 (10 H, m, Ad-H), 2.08 (2 H, m, Ad-H), 2.43 (1 H, m, Ad-H), 2.77 (1 H, m, Ad-H), 4.54 (3 H, s, 10-CH_3), 7.42 (1 H, dd, $J_{2,1}$ 9.8 and $J_{2,4}$ 2.3, 2-H), 7.50 (1 H, d, $J_{4,2}$ 2.3, 4-H), 7.79 (1 H, ddd, $J_{7,8}$ 8.8, $J_{7,6}$ 6.9 and $J_{7,5}$ 1.0, 7-H), 8.16 (1 H, ddd, $J_{6,5}$ 9.1, $J_{6,7}$ 6.9 and $J_{6,8}$ 1.2, 6-H), 8.42 (1 H, dd, $J_{5,6}$ 9.1 and $J_{5,7}$ 1.0, 5-H), 8.69 (1 H, dd, $J_{8,7}$ 8.8 and $J_{8,6}$ 1.2, 8-H) and 8.77 (1 H, d, $J_{1,2}$ 9.8, 1-H); δ_C(50 MHz; CD_3OD) 28.8 (d), 29.1 (d), 34.3 (2d), 37.8 (t), 38.4 (t), 38.7 (t), 40.7 (2t), 52.1 (q), 100.2 (d), 100.6 (d), 119.1 (d), 121.4 (d), 123.2 (s), 126.5 (s), 127.6 (s), 129.1 (d), 132.9 (d), 137.1 (d), 141.9 (s), 146.3 (s), 154.6 (s) and 168.3 (s).

General procedure for the synthesis of the siloxy olefins 3g,h. A solution of the hydroxy olefin **3d**,**e** (*ca.* 0.1 mmol), *tert*-butyldimethylchlorosilane (1.5 equiv.) and imidazole (2.0 equiv.) in dry dimethylformamide (DMF) (5 cm^3) was stirred at 40–50 °C for 4 h. Subsequently, the solution was poured into water (5 cm^3) and extracted with diethyl ether (2 × 5 cm^3) and methylene chloride (5 cm^3). The extract was washed with water (5 cm^3), dried ($MgSO_4$), and evaporated to dryness at 20 °C and 10 Torr. Chromatography of the residue with methylene chloride and light petroleum–diethyl ether (20:1) as the eluents afforded the siloxy olefins **3g**,**h**.

9-*Adamantylidene*-2-(tert-*butyldimethylsiloxy*)-10-*methylacridane* (**3g**).—By following the above procedure, from the hydroxy olefin **3d** (36.0 mg, 0.105 mmol), *tert*-butyldimethylchlorosilane (24.0 mg, 0.159 mmol) and imidazole (14.0 mg, 0.206 mmol) the siloxy olefin **3g** was obtained as a colourless powder (34.0 mg, 71%), mp 129–130 °C, R_f(light petroleum–diethyl ether 20:1) 0.70 (Found: C, 78.88; H, 8.13; N, 2.98. $C_{30}H_{39}NOSi$ requires C, 78.72; H, 8.59; N, 3.06%); ν_{max}(KBr)/cm^{-1} 2930, 2910, 2880, 2830, 1450, 1260; δ_H(200 MHz; $CDCl_3$) 0.18 (6 H, s, $SiMe_2$), 0.98 (9 H, s, $SiCMe_3$), 1.40–2.20 (12 H, m, Ad-H), 3.36 (3 H, s, 10-CH_3), 3.45 (1 H, br s, 1′-H), 3.52 (1 H, br s, 1′-H), 6.69 (1 H, dd, $J_{3,4}$ 8.6 and $J_{3,1}$ 2.6, 3-H), 6.74 (1 H, d, $J_{1,3}$ 2.6, 1-H), 6.81 (1 H, d, $J_{4,3}$ 8.6, 4-H), 6.92–7.00 (2 H, m, 5-H and 7-H) and 7.15–7.25 (2 H, m, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) −4.4 (2q), 18.2 (s), 25.8 (3q), 27.9 (2d), 32.2 (2d), 33.3 (q), 37.1 (t), 38.2 (4t), 111.7 (d), 112.3 (d), 117.6 (d), 118.5 (d), 119.5 (d), 120.2 (s), 120.6 (s), 125.7 (s), 126.2 (d), 127.2 (d), 139.4 (s), 144.1 (s), 145.2 (s) and 149.2 (s).

9-*Adamantylidene*-3-(tert-*butyldimethylsiloxy*)-10-*methylacridane* (**3h**).—By following the above procedure, from the hydroxy olefin **3e** (30.0 mg, 87.3 μmol), *tert*-butyldimethylchlorosilane (20.0 mg, 0.133 mmol) and imidazole (12.0 mg, 0.176 mmol) the siloxy olefin **3h** was obtained as a colourless powder (15.0 mg, 38%), mp 114–115 °C, R_f(light petroleum–diethyl ether 20:1) 0.30 (Found: C, 79.17; H, 8.57; N, 2.76. $C_{30}H_{39}NOSi$ requires C, 78.72; H, 8.59; N, 3.06%); ν_{max}(KBr)/cm^{-1} 2940, 2900, 2830, 1580, 1450; δ_H(200 MHz; $CDCl_3$) 0.21 (6 H, s, $SiMe_2$), 0.99 (9 H, s, $SiCMe_3$), 1.50–2.20 (12 H, m, Ad-H), 3.35 (3 H, s, 10-CH_3), 3.43 (2 H, br s, 1′-H), 6.44–6.49 (2 H, m, 2-H and 4-H), 6.93–7.07 (3 H, m, 1-H, 5-H and 7-H) and 7.15–7.23 (2 H, m, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) −4.3 (2q), 18.2 (s), 25.7 (3q), 28.1 (2d), 32.1 (2d), 33.3 (q), 37.1 (t), 39.2 (4t), 104.3 (d), 111.3 (d), 111.9 (d), 119.6 (s), 119.8 (s), 119.9 (d), 126.1 (d), 126.4 (s), 127.2 (d), 127.7 (d), 143.1 (s), 144.7 (s), 146.0 (s) and 154.3 (s).

General procedure for the synthesis of the acetoxy olefins 3j,k. The hydroxy olefin **3d**,**e** (1 equiv.) was suspended in methylene chloride (10 cm^3), triethylamine (1.1 equiv.) and, subsequently, acetic anhydride (1.1 equiv.) were added and the solution was stirred for 24 h. After the addition of water (10 cm^3), the solution was extracted with diethyl ether (2 × 10 cm^3), the extract was washed with 10% HCl (10 cm^3), aqueous sodium hydrogen carbonate (10 cm^3) and water (10 cm^3), dried ($MgSO_4$), and evaporated to dryness at 20 °C and 10 Torr. Chromatography of the residue with methylene chloride and light petroleum–diethyl ether as the eluents afforded the acetoxy olefins **3j**,**k**.

2-*Acetoxy*-9-*adamantylidene*-10-*methylacridane* (**3j**).—By following the above procedure, from the hydroxy olefin **3d** (279 mg, 0.812 mmol), triethylamine (130 mm^3, 0.938 mmol) and acetic anhydride (90.0 mm^3, 0.952 mmol) the acetoxy olefin **3j** was obtained as a colourless powder (184 mg, 59%), mp 85–87 °C, R_f(light petroleum–diethyl ether 5:1) 0.30 (Found: C, 81.08; H, 6.92; N, 3.24. $C_{26}H_{27}NO_2$ requires C, 81.01; H, 7.06; N, 3.63%); ν_{max}(KBr)/cm^{-1} 2880, 2820, 1740 (CO), 1200, 1185; δ_H(200 MHz; $CDCl_3$) 1.50–2.20 (12 H, m, Ad-H), 2.30 (3 H, s, $COCH_3$), 3.39 (3 H, s, 10-CH_3), 3.44 (2 H, br s, 1′-H), 6.92–7.01 (5 H, m, 1-H, 3-H, 4-H, 5-H and 7-H) and 7.16–7.26 (2 H, m, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) 21.2 (q), 27.4 (2d), 32.1 (d), 32.2 (d), 33.4 (q), 37.1 (t), 39.2 (4t), 111.9 (d), 112.2 (d), 118.9 (d), 119.7 (s), 120.0 (d), 120.1 (d), 125.6 (s), 126.4 (d), 126.9 (s), 127.2 (d), 142.8 (s), 144.1 (s), 144.7 (s), 145.1 (s) and 170.0 (s).

3-*Acetoxy*-9-*adamantylidene*-10-*methylacridane* (**3k**).—By following the above procedure, from the hydroxy olefin **3e** (20.0 mg, 58.2 μmol), triethylamine (10.0 mm^3, 72.1 μmol) and acetic anhydride (7.00 mm^3, 74.0 μmol) the acetoxy olefin **3k** was obtained as a colourless powder (17.0 mg, 76%), mp 150–152 °C, R_f(light petroleum–diethyl ether 20:1) 0.20 (Found: C, 81.23; H, 6.76; N, 3.56. $C_{26}H_{27}NO_2$ requires C, 81.01; H, 7.06; N, 3.63%); ν_{max}(KBr)/cm^{-1} 2880, 2820, 1730 (CO), 1450, 1200, 1180; δ_H(200 MHz; $CDCl_3$) 1.60–2.20 (12 H, m, Ad-H), 2.31 (3 H, s, $COCH_3$), 3.37 (3 H, s, 10-CH_3), 3.43 (2 H, br s, 1′-H), 6.68–6.73 (2 H, m, 2-H and 4-H), 6.94–7.02 (2 H, m, 5-H and 7-H) and 7.16–7.24 (3 H, m, 1-H, 6-H and 8-H); δ_C(50 MHz; $CDCl_3$) 21.2 (q), 27.4 (2d), 32.2 (2d), 33.4 (q), 37.1 (t), 39.2 (4t), 105.6 (d), 112.0 (d), 112.8 (d), 119.5 (s), 120.3 (d), 123.8 (s), 126.0 (s), 126.3 (d), 127.2 (d), 127.6 (d), 144.5 (s), 144.6 (s), 145.9 (s), 149.2 (s) and 169.7 (s).

Photooxygenation of the olefins 3a–c,g,h,j,k. Into a 10 cm^3 test tube, equipped with gas inlet and outlet tubes and a UV filter, was placed a solution of the corresponding olefin **3** (26.0–117 μmol) and a few crystals of tetraphenylporphyrin (TPP) in $CDCl_3$ (0.7–3.0 cm^3). The solution was cooled to −10 °C and a gentle stream of dry oxygen gas was passed through the solution while irradiating with two 150 W sodium lamps (Philips G/98/2-SON). The reaction progress was monitored by TLC and ^{1}H NMR spectroscopy. After complete consumption of the starting material, the dioxetanes **4** were isolated by low-temperature chromatography on silica gel at −10 °C with light petroleum–diethyl ether (5:1) as the eluent. At temperatures higher than 60 °C, decomposition of all dioxetanes took place (*cf.* below: determination of the activation parameters for the thermal decomposition of the dioxetanes **4a**–**c**).

2-*Methoxy*-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4a**).—Photooxygenation of the olefin **3a** (10.0 mg, 28.0 μmol) in $CDCl_3$ (0.7 cm^3) for 30 min gave the dioxetane **4a** as a yellow, amorphous powder (4.90 mg, 45%), R_f(light petroleum–diethyl ether 5:1) 0.52 (Found: C, 77.01; H, 6.49; N, 3.33. $C_{25}H_{27}NO_3$ requires C, 77.09; H, 6.99; N, 3.60%); ν_{max}($CDCl_3$)/cm^{-1} 2910, 2890, 2840, 1585, 1490, 1460, 1265; δ_H(200 MHz; $CDCl_3$) 0.90–2.00 (12 H, m, Ad-H), 2.27 (1 H, br s, 1′-H), 2.32 (1 H, br s, 1′-H), 3.44 (3 H, s, 10-CH_3), 3.89 (3 H, s, 2-OCH_3), 6.97 (3 H, m, 3-H, 4-H and 5-H), 7.14 (1 H, ddd, $J_{7,8}$ and $J_{7,6}$ 7.6 and $J_{7,5}$ 1.0, 7-H), 7.38 (1 H, ddd, $J_{6,5}$ 7.7, $J_{6,7}$ 7.6 and $J_{6,8}$ 1.6, 6-H), 7.75 (1 H, d, $J_{1,3}$ 2.5, 1-H) and 8.15 (1 H, dd, $J_{8,7}$ 7.6 and $J_{8,6}$ 1.6, 8-H); δ_C(50 MHz; $CDCl_3$) 25.5 (d), 25.7 (d), 30.9 (2t), 31.7 (2d), 32.9 (2t), 33.0 (q), 36.2 (t), 55.9 (q), 87.6 (s), 98.0 (s), 111.4 (d), 112.1 (d), 112.7 (d), 115.7 (d), 119.8 (d), 120.9 (s), 124.5 (s), 127.9 (d), 129.0 (d), 133.5 (s), 140.8 (s) and 153.9 (s).

3-*Methoxy*-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4b**).—Photooxygenation of the olefin **3b** (12.3 mg, 24.4 μmol) in $CDCl_3$ (0.7 cm^3) for 30 min gave the

dioxetane **4b** as a yellow, amorphous powder (9.00 mg, 67%), R_f(light petroleum–diethyl ether 5:1) 0.33 (Found: C, 77.01; H, 7.20; N, 3.85. $C_{25}H_{27}NO_3$ requires C, 77.09; H, 6.99; N, 3.60%); $\nu_{max}(CCl_4)/cm^{-1}$ 2910, 2890, 2830, 1585, 1460, 1270, 1210; δ_H(200 MHz; $CDCl_3$) 1.30–1.90 (12 H, m, Ad-H), 2.25 (1 H, br s, 1′-H), 2.31 (1 H, br s, 1′-H), 3.44 (3 H, s, 10-CH_3), 3.88 (3 H, s, 3-OCH_3), 6.53 (1 H, d, $J_{4,2}$ 2.3, 4-H), 6.72 (1 H, dd, $J_{2,1}$ 8.6 and $J_{2,4}$ 2.3, 2-H), 7.00 (1 H, br d, $J_{5,6}$ 8.2, 5-H), 7.17 (1 H, ddd, $J_{7,8}$ 7.7, $J_{7,6}$ 7.3 and $J_{7,5}$ 0.9, 7-H), 7.39 (1 H, ddd, $J_{6,5}$ 8.2, $J_{6,7}$ 7.3 and $J_{6,8}$ 1.5, 6-H), 8.07 (1 H, d, $J_{1,2}$ 8.6, 1-H) and 8.18 (1 H, dd, $J_{8,7}$ 7.7 and $J_{8,6}$ 1.5, 8-H); δ_C(50 MHz; $CDCl_3$) 25.2 (d), 25.4 (d), 31.4 (t), 31.5 (t), 32.6 (d), 32.7 (d), 32.7 (2t), 33.2 (q), 35.9 (t), 55.3 (q), 86.8 (s), 97.8 (s), 98.3 (d), 104.5 (d), 111.7 (d), 114.1 (s), 120.2 (d), 121.5 (s), 127.7 (d), 128.8 (d), 129.0 (d), 140.1 (s), 141.3 (s) and 160.1 (s).

4-*Methoxy*-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4c**).—Photooxygenation of the olefin **3c** (42.0 mg, 117 μmol) in $CDCl_3$ (3.0 cm^3) for 20 min gave the dioxetane **4c** as a yellow, amorphous powder (29.0 mg, 64%), R_f(light petroleum–diethyl ether 5:1) 0.55 (Found: C, 76.68; H, 6.92; N, 3.24. $C_{25}H_{27}NO_3$ requires C, 77.09; H, 6.99; N, 3.60%); $\nu_{max}(CCl_4)/cm^{-1}$ 2910, 2890, 2830, 1475, 1455, 1440, 1335, 1240, 1085, 1015; δ_H(200 MHz; $CDCl_3$) 1.10–2.10 (12 H, m, Ad-H), 2.26 (1 H, br s, 1′-H), 2.38 (1 H, br s, 1′-H), 3.64 (3 H, s, 10-CH_3), 3.85 (3 H, s, 4-OCH_3), 6.94 (1 H, dd, $J_{3,2}$ 7.9 and $J_{3,1}$ 1.4, 3-H), 7.06–7.16 (2 H, m, 5-H and 7-H), 7.13 (1 H, dd, $J_{2,1}$ and $J_{2,3}$ 7.9, 2-H), 7.38 (1 H, m, 6-H), 7.82 (1 H, dd, $J_{1,2}$ 7.9 and $J_{1,3}$ 1.4, 1-H) and 8.08 (1 H, dd, $J_{8,7}$ 7.7 and $J_{8,6}$ 1.5, 8-H); δ_C(50 MHz; $CDCl_3$) 25.5 (d), 25.8 (d), 31.7 (t), 31.8 (t), 33.0 (2d), 33.0 (2t), 36.2 (t), 39.2 (q), 56.2 (q), 87.4 (s), 97.5 (s), 112.4 (d), 113.4 (d), 120.1 (d), 120.2 (d), 121.3 (d), 123.0 (s), 126.3 (s), 127.4 (d), 128.9 (d), 130.8 (s), 143.1 (s) and 149.2 (s).

2-(tert-*Butyldimethylsiloxy*)-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4g**).—Photooxygenation of the olefin **3g** (34.0 mg, 74.3 μmol) in $CDCl_3$ (1.0 cm^3) for 30 min gave the dioxetane **4g** as a yellow, amorphous powder (20.0 mg, 55%), R_f(light petroleum–diethyl ether 5:1) 0.67 (Found: C, 73.62; H, 8.07; N, 2.73. $C_{30}H_{39}NO_3Si$ requires C, 73.58; H, 8.03; N, 2.86%); $\nu_{max}(CDCl_3)/cm^{-1}$ 2910, 2890, 2840, 1590, 1490, 1460, 1265, 1250, 835; δ_H(200 MHz; $CDCl_3$) 0.16 (3 H, s, SiMe), 0.18 (3 H, s, SiMe), 0.98 (9 H, s, $SiCMe_3$), 1.20–1.90 (12 H, m, Ad-H), 2.24 (1 H, br s, 1′-H), 2.38 (1 H, br s, 1′-H), 3.43 (3 H, s, 10-CH_3), 6.89 (2 H, m, 3-H and 5-H), 6.99 (1 H, d, $J_{4,3}$ 8.0, 4-H), 7.15 (1 H, ddm, $J_{7,8}$ 7.5 and $J_{7,6}$ 7.3, 7-H), 7.40 (1 H, m, 6-H), 7.65 (1 H, d, $J_{1,3}$ 1.2, 1-H) and 8.15 (1 H, dm, $J_{8,7}$ 7.5, 8-H); δ_C(50 MHz; $CDCl_3$) −4.4 (2q), 18.2 (s), 25.5 (d), 25.7 (3q), 25.8 (d), 31.7 (2t), 32.9 (2d), 32.9 (2t), 33.1 (q), 36.2 (t), 87.1 (s), 97.9 (s), 111.4 (d), 112.4 (d), 119.2 (d), 119.8 (d), 120.9 (d), 121.0 (s), 122.6 (s), 134.8 (s), 127.9 (d), 128.9 (d), 140.6 (s) and 152.3 (s).

3-(tert-*Butyldimethylsiloxy*)-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4h**).—Photooxygenation of the olefin **3h** (12.0 mg, 26.2 μmol) in $CDCl_3$ (0.7 cm^3) for 30 min gave the dioxetane **4h** as a yellow, amorphous powder (10.0 mg, 78%), R_f(light petroleum–diethyl ether 5:1) 0.70 (Found: C, 73.62; H, 7.75; N, 2.96. $C_{30}H_{39}NO_3Si$ requires C, 73.58; H, 8.03; N, 2.86%); $\nu_{max}(CDCl_3)/cm^{-1}$ 2930, 2860, 1620, 1530, 1510, 1310, 1290, 880; δ_H(200 MHz; $CDCl_3$) 0.20 (3 H, s, SiMe), 0.22 (3 H, s, SiMe), 0.98 (9 H, s, $SiCMe_3$), 1.10–1.90 (12 H, m, Ad-H), 2.19 (1 H, br s, 1′-H), 2.31 (1 H, br s, 1′-H), 3.42 (3 H, s, 10-CH_3), 6.48 (1 H, d, $J_{4,2}$ 2.1, 4-H), 6.65 (1 H, dd, $J_{2,1}$ 8.3 and $J_{2,4}$ 2.1, 2-H), 7.02 (1 H, br d, $J_{5,6}$ 8.3, 5-H), 7.17 (1 H, ddm, $J_{7,8}$ 7.6 and $J_{7,6}$ 7.3, 7-H), 7.40 (1 H, ddd, $J_{6,5}$ 8.3, $J_{6,7}$ 7.3 and $J_{6,8}$ 1.3, 6-H), 7.98 (1 H, d, $J_{1,2}$ 8.3, 1-H) and 8.17 (1 H, dd, $J_{8,7}$ 7.6 and $J_{8,6}$ 1.3, 8-H); δ_C(50 MHz; $CDCl_3$) −4.5 (q), −4.3 (q), 18.2 (s), 25.2 (d), 25.4 (d), 25.6 (3q), 31.4 (t), 31.6 (t), 32.6 (2d), 32.7 (2t), 33.1 (q), 35.9 (t), 88.6 (s), 98.0 (s), 103.8 (d), 111.7 (d), 112.0 (d), 120.2 (s), 120.2 (d), 121.5 (s), 126.6 (d), 127.8 (d), 128.8 (d), 140.1 (s), 141.9 (s) and 154.8 (s).

2-*Acetoxy*-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4j**).—Photooxygenation of the olefin **3j** (28.0 mg, 72.6 μmol) in $CDCl_3$ (2.0 cm^3) for 45 min gave the dioxetane **4j** as a yellow, amorphous powder (12.0 mg, 40%), R_f(light petroleum–diethyl ether 5:1) 0.23 (Found: C, 74.62; H, 6.92; N, 3.24. $C_{26}H_{27}NO_4$ requires C, 74.80; H, 6.52; N, 3.35%); $\nu_{max}(CCl_4)/cm^{-1}$ 2900, 2840, 1705 (CO), 1590, 1495, 1460, 1200; δ_H(200 MHz; $CDCl_3$) 1.10–2.10 (12 H, m, Ad-H), 2.30 (2 H, br s, 1′-H), 2.32 (3 H, s, $COCH_3$), 3.46 (3 H, s, 10-CH_3), 6.97–7.03 (2 H, m, 4-H and 5-H), 7.12–7.21 (2 H, m, 3-H and 7-H), 7.41 (1 H, ddd, $J_{6,5}$ 8.4, $J_{6,7}$ 7.1 and $J_{6,8}$ 1.3, 6-H), 7.90 (1 H, d, $J_{1,3}$ 2.7, 1-H) and 8.15 (1 H, dd, $J_{8,7}$ 8.7 and $J_{8,6}$ 1.3, 8-H); δ_C(50 MHz; $CDCl_3$) 21.1 (q), 25.5 (d), 25.7 (d), 31.6 (t), 31.7 (t), 32.9 (2d), 32.9 (t), 33.0 (t), 33.3 (q), 36.1 (t), 86.9 (s), 97.9 (s), 111.7 (d), 112.3 (d), 120.5 (d), 120.9 (s), 121.0 (d), 122.2 (d), 122.6 (s), 128.0 (d), 129.2 (d), 138.2 (s), 140.2 (s), 144.4 (s) and 169.9 (s).

3-*Acetoxy*-10-*methyldispiro*[*acridane*-9,3′-[1,2]*dioxetane*-4′,2″-*adamantane*] (**4k**).—Photooxygenation of the olefin **3k** (12.0 mg, 31.1 μmol) in $CDCl_3$ (0.7 cm^3) for 30 min gave the dioxetane **4k** as a yellow, amorphous powder (5.00 mg, 39%), R_f(light petroleum–diethyl ether 5:1) 0.15 (Found: C, 74.40; H, 6.42; N, 2.94. $C_{26}H_{27}NO_4$ requires C, 74.80; H, 6.52; N, 3.35%); $\nu_{max}(CCl_4)/cm^{-1}$ 2920, 2900, 2840, 1755 (CO), 1585, 1530, 1455, 1200, 1170, 905; δ_H(200 MHz; $CDCl_3$) 1.20–2.00 (12 H, m, Ad-H), 2.23 (2 H, br s, 1′-H), 2.35 (3 H, s, $COCH_3$), 3.44 (3 H, s, 10-CH_3), 6.75 (1 H, br s, 4-H), 6.90 (1 H, dm, $J_{2,1}$ 8.3, 2-H), 7.02 (1 H, br d, $J_{5,6}$ 8.3, 5-H), 7.19 (1 H, m, 7-H), 7.41 (1 H, m, 6-H), 8.16 (1 H, d, $J_{1,2}$ 8.3, 1-H) and 8.16 (1 H, m, 8-H); δ_C(50 MHz; $CDCl_3$) 21.3 (q), 25.1 (d), 25.4 (d), 31.4 (2t), 32.6 (2d), 32.7 (2t), 33.2 (q), 35.9 (t), 86.7 (s), 97.7 (s), 105.2 (d), 111.7 (d), 113.3 (d), 119.0 (s), 120.6 (d), 124.2 (s), 127.8 (d), 128.9 (d), 129.0 (d), 139.8 (s), 141.1 (s), 151.1 (s) and 169.8 (s).

Synthesis of the dioxetane decomposition products 5

The known *N*-methyl acridones **5a–c**[23,24] were prepared according to the literature procedure[25] by methylation of the corresponding acridones.[23] The hydroxy acridones **5d–f**[24] were synthesized by ether cleavage of the methoxy acridones **5a–c** in hydrobromic acid. The physical and spectral data of these compounds are consistent with those reported.[23–25]

General procedure for the silylation of the hydroxyacridones 5d–f. To a solution of the hydroxyacridone **5d–f** (1.0 equiv.) and *tert*-butyldimethylchlorosilane (1.4 equiv.) in dry DMF (5–10 cm^3) was added a solution of imidazole (2.0 equiv.) in dry DMF (2.5–5 cm^3). After stirring at 40–50 °C for 4 h, more silane (0.7 equiv.) and imidazole (1.0 equiv.) were added and the stirring was continued for 20 h. The solution was poured into water (15 cm^3), the precipitate was collected, dried over P_2O_5 at 20 °C and 10 Torr and purified by recrystallization from ethanol or by chromatography on silica gel.

2-(tert-*Butyldimethylsiloxy*)-10-*methylacridone* (**5g**).—By following the above procedure, from the hydroxyacridone **5d** (900 mg, 4.00 mmol), *tert*-butyldimethylchlorosilane (1.23 g, 8.00 mmol) and imidazole (816 mg, 12.0 mmol) the siloxy acridone **5g** was obtained as a yellow powder (750 mg, 55%), mp 109–110 °C (from EtOH), R_f(light petroleum–ethyl acetate 1:1) 0.75 (Found: C, 71.01; H, 7.74; N, 3.87. $C_{20}H_{25}NO_2Si$ requires C, 70.76; H, 7.42; N, 4.13%); ν_{max}(KBr)/cm^{-1} 2930, 2900, 2860, 2830, 1615 (CO), 1580, 1490, 1450, 1270, 1230, 910, 825, 745; $\lambda_{max}(CH_3CN)$/nm 251 (log ε 4.64), 270 (4.51), 397 (3.88), 416 (3.95); δ_H[600 MHz; $(CD_3)_2SO$] 0.23 (6 H, s, $SiMe_2$), 0.98 (9 H, s, $SiCMe_3$), 3.92 (3 H, s, 10-CH_3), 7.30 (1 H, ddd, $J_{7,8}$ 7.9, $J_{7,6}$ 6.6 and $J_{7,5}$ 1.2, 7-H), 7.39 (1 H, dd, $J_{3,4}$ 9.4 and $J_{3,1}$ 3.1, 3-H), 7.71 (1 H, d, $J_{3,1}$ 3.1, 1-H), 7.78–7.83 (2 H, m, 5-H and 7-H), 7.81 (1 H, d, $J_{4,3}$ 9.1, 4-H) and 8.31 (1 H, dd, $J_{8,7}$ 7.9 and $J_{8,6}$ 1.5, 8-H); δ_C[151 MHz; $(CD_3)_2SO$] −4.7 (2q), 17.9 (s), 25.5 (3q), 33.6 (q), 114.1 (d), 115.8 (d), 117.9 (d), 120.6 (s), 120.7 (d), 122.4 (s), 126.3 (d), 127.5 (d), 133.7 (d), 137.4 (s), 141.9 (s), 149.4 (s) and 175.8 (s).

3-(tert-*Butyldimethylsiloxy*)-10-*methylacridone* (**5h**).—By following the above procedure, from the hydroxyacridone **5e** (433

mg, 1.92 mmol), *tert*-butyldimethylchlorosilane (597 mg, 3.96 mmol) and imidazole (394 mg, 5.78 mmol) the siloxy acridone **5h** was obtained as colourless needles (201 mg, 31%), mp 125.5–126.5 °C (from EtOH), R_f(light petroleum–ethyl acetate 1:1) 0.30 (Found: C, 70.84; H, 7.88; N, 4.06. $C_{20}H_{25}NO_2Si$ requires C, 70.76; H, 7.42; N, 4.13%); ν_{max}(KBr)/cm^{-1} 2930, 2900, 2830, 1615 (CO), 1580, 1450, 1330, 1280, 1210, 980, 860, 750; λ_{max}(CH_3CN)/nm 256 (log ε 4.74), 268 (4.72), 277 (4.71), 372 (3.99), 388 (4.09); δ_H[200 MHz; $(CD_3)_2SO$] 0.30 (6 H, s, $SiMe_2$), 1.00 (9 H, s, $SiCMe_3$), 3.86 (3 H, s, 10-CH_3), 6.87 (1 H, dd, $J_{2,1}$ 8.7 and $J_{2,4}$ 2.0, 2-H), 7.10 (1 H, d, $J_{4,2}$ 2.0, 4-H), 7.32 (1 H, ddd, $J_{7,8}$ 7.7, $J_{7,6}$ 5.1 and $J_{7,5}$ 2.8, 7-H), 7.80 (2 H, m, 5-H and 6-H), 8.26 (1 H, d, $J_{1,2}$ 8.7, 1-H) and 8.31 (1 H, dm, $J_{8,7}$ 7.7, 8-H); δ_C[50 MHz; $(CD_3)_2SO$] −4.5 (2q), 18.0 (s), 25.5 (3q), 33.7 (q), 105.2 (d), 114.9 (d), 115.9 (d), 116.7 (s), 121.0 (d), 121.6 (s), 126.4 (d), 128.8 (d), 133.6 (d), 142.4 (s), 144.1 (s), 160.2 (s) and 175.6 (s).

4-(tert-*Butyldimethylsiloxy*)-10-*methylacridone* (**5i**).—By following the above procedure, from the hydroxyacridone **5f** (340 mg, 1.51 mmol), *tert*-butyldimethylchlorosilane (464 mg, 3.08 mmol) and imidazole (306 mg, 4.50 mmol) the siloxy acridone **5i** was obtained as yellow needles (392 mg, 77%), mp 97–98 °C, R_f(light petroleum–ethyl acetate 2:1) 0.74 (Found: C, 70.41; H, 7.67; N, 4.06. $C_{20}H_{25}NO_2Si$ requires C, 70.76; H, 7.42; N, 4.13%); ν_{max}(KBr)/cm^{-1} 2940, 2910, 2830, 1615 (CO), 1590, 1580, 1490, 1450, 1350, 1255, 1190, 915, 825, 750; λ_{max}(CH_3CN)/nm 259 (log ε 4.59), 299 (3.65), 312 (3.69), 393 (3.90), 406 (3.89); δ_H[200 MHz; $(CD_3)_2SO$] 0.24 (6 H, s, $SiMe_2$), 0.96 (9 H, s, $SiCMe_3$), 3.97 (3 H, s, 10-CH_3), 7.23 (1 H, dd, $J_{2,1}$ and $J_{2,3}$ 7.7, 2-H), 7.26–7.36 (2 H, m, 3-H and 7-H), 7.74–7.82 (2 H, m, 5-H and 6-H), 7.92 (1 H, dd, $J_{1,2}$ 7.7 and $J_{1,3}$ 2.0, 1-H) and 8.23 (1 H, dm, $J_{8,7}$ 8.0, 8-H); δ_C[50 MHz; $(CD_3)_2SO$] −4.4 (2q), 18.2 (s), 25.7 (3q), 41.2 (q), 116.9 (d), 119.0 (d), 121.4 (d), 121.7 (s), 122.1 (d), 124.3 (d), 125.2 (s), 126.0 (d), 133.8 (s), 134.0 (d), 137.0 (s), 145.2 (s) and 176.9 (s).

General procedure for the acetylation of the hydroxyacridones 5d–f. To a suspension of sodium hydride (60% dispersion in mineral oil, 2.0 equiv.) in dry DMF (5 cm^3) was added the hydroxyacridone **5d–f** (1.0 equiv.). The mixture was stirred for 30 min and then acetic anhydride (1.1–2.0 equiv.) was added. Stirring was continued for a further 30 min, then water (10 cm^3) was added, the precipitate was collected, dried over P_2O_5 at 20 °C and 10 Torr and purified, if necessary, by chromatography on silica gel. Thereby, the impurities were removed by eluting with methylene chloride and the acridone was subsequently recovered by washing with ethyl acetate.

2-*Acetoxy*-10-*methylacridone* (**5j**).—By following the above procedure, from the hydroxyacridone **5d** (355 mg, 1.58 mmol), sodium hydride (126 mg, 3.16 mmol) and acetic anhydride (300 μl, 3.17 mmol) the acetoxy acridone **5j** was obtained as a yellow powder (311 mg, 74%), mp 202–203 °C (Found: C, 71.97; H, 4.70; N, 5.11. $C_{16}H_{13}NO_3$ requires C, 71.90; H, 4.90; N, 5.24%); ν_{max}(KBr)/cm^{-1} 2900, 2830, 1725 (CO), 1620 (CO), 1590, 1490, 1230, 745; λ_{max}(CH_3OH)/nm 247 (log ε 4.48), 267 (4.52), 391 (4.00), 409 (4.05); δ_H[600 MHz; $(CD_3)_2SO$] 2.32 (3 H, s, $COCH_3$), 3.96 (3 H, s, 10-CH_3), 7.36 (1 H, ddd, $J_{7,8}$ 8.0, $J_{7,6}$ 5.6 and $J_{7,5}$ 2.3, 7-H), 7.63 (1 H, dd, $J_{3,4}$ 9.4 and $J_{3,1}$ 2.9, 3-H), 7.86 (2 H, m, 5-H and 6-H), 7.93 (1 H, d, $J_{4,3}$ 9.4, 4-H), 8.02 (1 H, d, $J_{1,3}$ 2.9, 1-H) and 8.34 (1 H, dm, $J_{8,7}$ 8.0, 8-H); δ_C[151 MHz; $(CD_3)_2SO$] 20.8 (q), 33.9 (q), 116.2 (d), 117.9 (d), 117.9 (d), 121.1 (s), 121.3 (d), 121.8 (s), 126.4 (d), 128.3 (d), 134.2 (d), 140.1 (s), 142.2 (s), 144.5 (s), 169.5 (s) and 175.8 (s).

3-*Acetoxy*-10-*methylacridone* (**5k**).—By following the above procedure, from the hydroxyacridone **5e** (17.0 mg, 75.5 μmol), sodium hydride (6.00 mg, 150 μmol) and acetic anhydride (15.0 μl, 159 μmol) the acetoxy acridone **5k** was obtained as a pale-yellow powder (20.0 mg, 98%), mp 165–166 °C (Found: C, 71.61; H, 4.76; N, 5.10. $C_{16}H_{13}NO_3$ requires C, 71.90; H, 4.90; N, 5.24%); ν_{max}(KBr)/cm^{-1} 2900, 1735 (CO), 1620 (CO), 1585, 1455, 1205, 1180, 755; λ_{max}(CH_2Cl_2)/nm 293 (log ε 3.68), 376 (3.85), 394 (4.00); δ_H[200 MHz; $(CD_3)_2SO$] 2.35 (3 H, s, $COCH_3$), 3.90 (3 H, s, 10-CH_3), 7.13 (1 H, dd, $J_{2,1}$ 8.7 and $J_{2,4}$ 1.9, 2-H), 7.37 (1 H, ddd, $J_{7,8}$ 8.0, $J_{7,6}$ 5.0 and $J_{7,5}$ 2.9, 7-H), 7.66 (1 H, d, $J_{4,2}$ 1.9, 4-H), 7.87 (2 H, m, 5-H and 6-H), 8.35 (1 H, dm, $J_{8,7}$ 8.0, 8-H) and 8.37 (1 H, d, $J_{1,2}$ 8.7, 1-H); δ_C[50 MHz; $(CD_3)_2SO$] 20.9 (q), 33.9 (q), 109.0 (d), 116.0 (d), 116.2 (d), 119.4 (s), 121.5 (d), 121.6 (s), 126.4 (d), 128.3 (d), 134.1 (d), 142.4 (s), 143.4 (s), 155.0 (s), 168.9 (s) and 175.6 (s).

4-*Acetoxy*-10-*methylacridone* (**5l**).—By following the above procedure, from the hydroxyacridone **5f** (150 mg, 0.666 mmol), sodium hydride (60.0 mg, 1.50 mmol) and acetic anhydride (150 μl, 1.59 mmol) the acetoxy acridone **5l** was obtained as yellow needles (148 mg, 83%), mp 132–133 °C (Found: C, 71.69; H, 5.05; N, 5.31. $C_{16}H_{13}NO_3$ requires C, 71.90; H, 4.90; N, 5.24%); ν_{max}(KBr)/cm^{-1} 2900, 1750 (CO), 1620 (CO), 1585, 1490, 1180, 1160, 750; λ_{max}(CH_2Cl_2)/nm 257 (log ε 4.55), 292 (3.67), 305 (3.52), 383 (3.92), 400 (3.99); δ_H[600 MHz; $(CD_3)_2SO$] 2.45 (3 H, s, $COCH_3$), 3.90 (3 H, s, 10-CH_3), 7.35 (1 H, dd, $J_{2,1}$ and $J_{2,3}$ 7.8, 2-H), 7.36 (1 H, ddd, $J_{7,8}$ 7.9, $J_{7,6}$ 7.0 and $J_{7,5}$ 0.9, 7-H), 7.58 (1 H, dd, $J_{3,2}$ 7.8 and $J_{3,1}$ 1.6, 3-H), 7.70 (1 H, br d, $J_{5,6}$ 8.6, 5-H), 7.85 (1 H, ddd, $J_{6,5}$ 8.6, $J_{6,7}$ 7.0 and $J_{6,8}$ 1.7, 6-H), 8.21 (1 H, dd, $J_{1,2}$ 7.8 and $J_{1,3}$ 1.6, 1-H) and 8.25 (1 H, dd, $J_{8,7}$ 7.9 and $J_{8,6}$ 1.7, 8-H); δ_C[50 MHz; $(CD_3)_2SO$] 20.9 (q), 40.2 (q), 116.9 (d), 121.6 (d), 121.8 (d), 121.8 (s), 124.2 (d), 124.8 (s), 126.0 (d), 129.1 (d), 134.3 (d), 137.4 (s), 139.2 (s), 144.6 (s), 169.0 (s) and 176.5 (s).

Chemiluminescence measurements

Determination of the activation parameters for the thermal decomposition of the dioxetanes 4a–c. A glass vial was charged with toluene (2.70–2.90 cm^3), placed in the cell compartment of the Mitchell–Hastings photometer[20] and allowed to equilibrate thermally for *ca.* 5 min. An aliquot of dioxetane solution (*ca.* 10^{-3} mol dm^{-3} in toluene; 100–300 mm^3) was introduced so that the total final volume was adjusted to 3.0 cm^3 and the concentration was *ca.* 10^{-5}–10^{-4} mol dm^{-3}. The emitted light intensity was continuously recorded.

For the determination of activation parameters, runs at several temperatures (80–95 °C) were carried out by direct chemiluminescence measurements under isothermal conditions. The rate data were processed according to first-order kinetics and from the set of *k* values the activation parameters were calculated by Arrhenius and Eyring methods. The data are collected in Table 1.

Determination of CIEEL quantum yields for the fluoride- and base-induced decomposition of the dioxetanes 4g,h,j,k. A glass vial was charged with the dioxetane solution (*ca.* 10^{-7}–10^{-4} mol dm^{-3} in methylene chloride, acetonitrile or methanol; 3.00 cm^3) and placed in the cell compartment of the Mitchell–Hastings photometer.[20] After 5 min of thermal equilibration at 25 °C, an appropriate amount of triggering agent [tetrabutylammonium fluoride (0.1 mol dm^{-3} in methylene chloride or acetonitrile), tetrabutylammonium hydroxide (0.1 mol dm^{-3} in acetonitrile or water) or sodium methanolate (0.1 mol dm^{-3} in methanol)] was added by means of a syringe through the rubber septum into the above glass vial under rigorous exclusion of external light, with the photomultiplier open for immediate measurement of the light emission. The rate data were processed according to first-order kinetics and from the set of *k* values the CIEEL quantum yields were calculated as described.[12] The results are collected in Table 2.

Determination of the fluorescence quantum yields of the acridones 5g–l. To a sample of the acridones **5g–l** (10^{-7}–10^{-4} mol dm^{-3} in methylene chloride, acetonitrile or methanol) was added a solution of triggering agent [tetrabutylammonium fluoride (0.1 mol dm^{-3} in methylene chloride or acetonitrile), tetrabutylammonium hydroxide (0.1 mol dm^{-3} in acetonitrile or water) or sodium methanolate (0.1 mol dm^{-3} in methanol)]. UV–VIS absorption as well as fluorescence spectra were recorded and from them the fluorescence quantum yields were calculated according to the literature procedure.[26] Quinine

bisulfate (1.47×10^{-6} mol dm^{-3} in 1 M $HClO_4$) was used as the standard (Φ^{FI} 0.56) for calibration.

Computational methods

The calculations are based on the AM1 theory as implemented in the VAMP 5.0 software package[27] and run on a Silicon Graphics Indigo workstation. The excited-state calculations were performed by using the singles-plus-pair excitation configuration interaction (PECI)[28] approach with an active space of ten molecular orbitals (MO).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 172 'Molekulare Mechanismen kanzerogener Primärveränderungen') and the Fonds der Chemischen Industrie for generous financial support.

References

1 J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, 1977, **99**, 6107; G. B. Schuster, *Acc. Chem. Res.*, 1979, **12**, 366.
2 W. Adam and O. Cueto, *J. Am. Chem. Soc.*, 1979, **101**, 6511; S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, 1980, **102**, 306.
3 K. A. Zaklika, A. L. Thayer and A. P. Schaap, *J. Am. Chem. Soc.*, 1978, **100**, 4916; K. A. Zaklika, T. Kissel, A. L. Thayer, P. A. Burns and A. P. Schaap, *Photochem. Photobiol.*, 1979, **30**, 35; A. P. Schaap and S. D. Gagnon, *J. Am. Chem. Soc.*, 1982, **104**, 3504.
4 J.-Y. Koo, S. P. Schmidt and G. B. Schuster, *Proc. Natl. Acad. Sci. USA*, 1978, **75**, 30.
5 A. P. Schaap, R. S. Handley and B. P. Giri, *Tetrahedron Lett.*, 1987, **28**, 935; A. P. Schaap, T.-S. Chen, R. S. Handley, R. DeSilva and B. P. Giri, *Tetrahedron Lett.*, 1987, **28**, 1155; A. P. Schaap, M. D. Sandison and R. S. Handley, *Tetrahedron Lett.*, 1987, **28**, 1159.
6 I. Bronstein, B. Edwards and J. C. Voyta, *J. Biolumin. Chemilumin.*, 1989, **4**, 99; I. Bronstein, J. C. Voyta, G. H. G. Thorpe, L. J. Kricka and G. Armstrong, *Clin. Chem.*, 1989, **35**, 1441; G. H. G. Thorpe, I. Bronstein, L. J. Kricka, B. Edwards and J. C. Voyta, *Clin. Chem.*, 1989, **35**, 2319; I. Bronstein, J. C. Voyta and B. Edwards, *Anal. Biochem.*, 1989, **180**, 95; R. Tizard, R. L. Cate, K. L. Ramachandran, M. Wysk, J. C. Voyta, O. J. Murphy and I. Bronstein, *Proc. Natl. Acad. Sci. USA*, 1990, **87**, 4514.
7 W. Adam and M. H. Schulz, *Chem. Ber.*, 1992, **125**, 2455; W. Adam, R. Fell and M. H. Schulz, *Tetrahedron*, 1993, **49**, 2227; W. Adam and D. Reinhardt, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1503.
8 M. Matsumoto, H. Suganuma, Y. Katao and H. Mutoh, *J. Chem. Soc., Chem. Commun.*, 1995, 431; M. Matsumoto, H. Suganuma, M. Azami, N. Aoshima and H. Mutoh, *Heterocycles*, 1995, **41**, 2419; M. Matsumoto, N. Watanabe, H. Kobayashi, H. Suganuma, J. Matsubara, Y. Kitano and H. Ikawa, *Tetrahedron Lett.*, 1996, **37**, 5939; M. Matsumoto, N. Watanabe, H. Kobayashi, M. Azami and H. Ikawa, *Tetrahedron Lett.*, 1997, **38**, 411.
9 (*a*) S. Beck and H. Köster, *Anal. Chem.*, 1990, **62**, 2258; (*b*) A. Mayer and S. Neuenhofer, *Angew. Chem.*, 1994, **106**, 1097; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1044; (*c*) *Bioluminescence & Chemiluminescence, Current Status*, ed. P. E. Stanley and L. J. Kricka, Wiley, Chichester, 1991.
10 F. McCapra, I. Beheshti, A. Burford, R. A. Hann and K. A. Zaklika, *J. Chem. Soc., Chem. Commun.*, 1977, 944; F. McCapra and D. Watmore, *Tetrahedron Lett.*, 1982, **23**, 5225.
11 M. Siegmund, J. Bendig and K. Teuchner, *Z. Chem.*, 1985, **25**, 372; M. Siegmund, J. Bendig, M. von Löwis of Menar and J. Wilda, *Monatsh. Chem.*, 1986, **117**, 1113.
12 W. Adam, in *Chemical and Biological Generation of Excited States*, ed. W. Adam and G. Cilento, Academic Press, New York, 1982, ch. 4.
13 A. Trofimov, K. Mielke, R. F. Vasil'ev and W. Adam, *Photochem. Photobiol.*, 1996, **63**, 463.
14 G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam and J. C. Liu, *J. Am. Chem. Soc.*, 1975, **97**, 7110; W. Adam and L. A. Arias Encarnación, *Chem. Ber.*, 1982, **115**, 2592; W. Adam, L. A. Arias Encarnación and K. Zinner, *Chem. Ber.*, 1983, **116**, 839.
15 T. Wilson, M. E. Landis, A. L. Baumstark and P. D. Bartlett, *J. Am. Chem. Soc.*, 1973, **95**, 4765.
16 F. McCapra, *J. Chem. Soc., Chem. Commun.*, 1977, 946; T. Wilson, *Photochem. Photobiol.*, 1995, **62**, 601.
17 B. Edwards, A. Sparks, J. C. Voyta and I. Bronstein, *J. Biolumin. Chemilumin.*, 1990, **5**, 1.
18 F. McCapra, *Tetrahedron Lett.*, 1993, **34**, 6941; W. Adam, D. Reinhardt and C. R. Saha-Möller, *Analyst*, 1996, **121**, 1527.
19 M. Kupfer and W. Abraham, *J. Prakt. Chem.*, 1983, **325**, 95; K.-P. Kronfeld and H.-J. Timpe, *J. Prakt. Chem.*, 1988, **330**, 571.
20 J. W. Hastings and G. Weber, *J. Opt. Am. Soc.*, 1963, **53**, 1410; G. W. Mitchell and J. W. Hastings, *Anal. Biochem.*, 1971, **39**, 243.
21 E. Bergmann, O. Blum-Bergmann and A. Freiherr von Christiani, *Liebigs Ann. Chem.*, 1930, **483**, 80; A. K. Colter, P. Plank, J. P. Bergsma, R. Lahti, A. A. Quesnel and A. G. Parsons, *Can. J. Chem.*, 1984, **62**, 1780.
22 R. A. Reed, *J. Chem. Soc.*, 1944, 679.
23 K. Gleu and S. Nitzsche, *J. Prakt. Chem.*, 1939, **153**, 200.
24 G. K. Hughes, N. K. Matheson, A. T. Norman and E. Ritchie, *Austr. J. Sci. Res.*, 1952, **A5**, 206.
25 I. B. Taraporewala and J. M. Kauffman, *J. Pharm. Sci.*, 1990, **79**, 173.
26 W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, **72**, 3251.
27 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902; G. Rauhut, A. Alex, J. Chandrasekhar, T. Steinke and T. Clark, VAMP 5.0, 1993, University of Erlangen-Nürnberg, Germany.
28 T. Clark, in *Recent Experimental and Computational Advances in Molecular Spectroscopy*, ed. R. Fausto, Kluwer Academic Publishers, Norwell, MA, 1993, p. 369.

Paper 7/01189J
Received 19*th February* 1997
Accepted 25*th March* 1997