Substituent-Dependent Reactivity in the Photodimerization of N-Substituted Dibenz[*b*,*f*]azepines

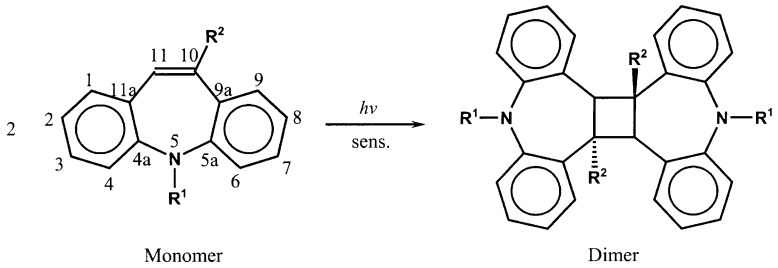
Jens Querner,[a] Thomas Wolff,*[a] and Helmut Görner[b]

Abstract: The photoprocesses of a series of N-substituted dibenz[*b*,*f*]azepines (iminostilbenes) were studied by absorption and emission spectroscopy, by laser flash photolysis, and by preparative irradiation with NMR analysis. In solutions, 2π+2π photodimers of N-cyano and N-acyl dibenzazepines are formed via the triplet state upon acetone- or benzophenone-sensitized energy transfer. T–T absorption spectra were measured and absorption coefficients were determined. The triplet energy transfer is equally efficient for N-alkyl dibenzazepines, which do not dimerize. Excited states of nπ* character in the latter cases are discussed to rationalize the different reactivities. In spite of negligible intersystem crossing of 21 dibenzazepine derivatives, photodimers of N-acyl and N-cyano dibenzazepines are formed upon direct excitation in concentrated solutions (0.01–0.1 mol dm^{-3}) as well as in the solid state. A selective *anti*-configuration of the photodimers was found throughout.

Keywords: photodimerization · photolysis · selectivity · triplet-sensitizing

Introduction

The photochemistry of dibenz[*b*,*f*]azepines (DBA) has been studied mainly with respect to their possible photodimerization[1,2] upon benzophenone sensitization (Scheme 1). It was concluded that the reaction proceeds through the triplet state of the DBA thereby differing from other stilbenes which undergo dimerization upon direct irradiation, that is, through the singlet excited state.[3,4] Moreover, only N-acyl derivatives, such as N-acetyl (**10**) and N-propionyl DBA (**14**)[1,2,5] or the pharmaceutically active N-carbamoyl compound "carbamazepine" (**21**), were found to photodimerize.



Monomer Dimer

Scheme 1. Photodimerization of dibenzazepine derivatives.

Compound **21** is a drug used in the therapy of epilepsy,[6] in which the photochemical dimerization and/or the photochemical addition to DNA bases may cause problems.[7] Upon photodimerization the cyclobutane ring was formed exclusively in the *anti*-configuration;[8–10] in solution isomeric dimers differing in the amide bond configuration were detected for **10** and **14**.[5] For the non-substituted dibenzazepine (**1**) and its N-acetyl (**10**) and N-valeroyl (**15**) derivatives, low quantum yields of intersystem crossing (Φ_{ISC}) were reported.[11] For benzophenone-sensitized excitation of **15**, an *anti*-cyclobutane dimer is formed with a quantum yield of photodimerization of up to $\Phi_d = 0.15$.[11] Non-sensitized photodimerization were reported to be less efficient,[1] a result which was questioned later on by other authors[11] who claimed that direct excitation did not yield dimers at all.

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

 DOI: 10.1002/chem.200305199

A ketone-sensitized triplet population has been applied in other cases.[12–20] The energy level of the triplet state (E_T) of DBA should be comparable to that of *cis*-stilbene, 260 kJ mol^{-1}.[21] Direct and sensitized photoprocesses were recently compared for bis-benzimidazole dyes[17] and sulfur- or carboxy-substituted N-alkylphthalimides.[18] Electron transfer occurs from the sulfur atom in methionine or cysteine derivatives to the triplet state of 4-carboxybenzophenone in alkaline aqueous solution.[13–16] A further example for energy vs. electron transfer is the combination of ketones and DNA bases.[19,20]

Here, the photoprocesses of a series of DBA (**1**–**14**, **16**–**22**, Table 1) were studied by steady-state and time-resolved spectroscopy as well as by preparative irradiations. The role of the sensitizer and the effects of the molecular structure of the DBA were investigated. It will be shown that efficient triplet sensitization takes place in all cases while only N-acyl and N-cyano derivatives are capable of photodimerization. Reasons for the differing triplet reactivity will be discussed. Furthermore, we prove that direct excitation clearly leads to photodimers in considerable yield in a variety of N-acyl DBA, clarifying the equivocal literature situation with regard to non-sensitized photodimerizations.

Experimental Section

General: All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 (^{1}H: 500 MHz; ^{13}C: 126 MHz) spectrometer. NMR shifts refer to the solvent signal as an internal standard ($CDCl_3$, $\delta = 7.25$ for ^{1}H and $\delta = 77.0$ for ^{13}C NMR). UV: polytec x-dap spectrometer. Fluorescence: Shimadzu RF-5000 spectrometer. GC/MS: Hewlett Packard, model 5890 with a HP 5972 detector. Elemental analyses were performed by the Institute of Organic Chemistry of the Technical University of Dresden (Germany). Melting points are uncorrected.

Solvents and chemicals: The solvents (Merck) were of the purest spectroscopic quality available, for example, acetone and acetonitrile: Uvasol; methylcyclohexane (MCH) and 2-methyltetrahydrofuran (MTHF) were purified by distillation. The sensitizers were used as received (acetophenone, Fluka) or purified by recrystallization (benzophenone and benzil). Compound **1** was purchased from Acros Chimica and recrystallized three times from ethanol.

Preparation and characterization of dibenzazepine (DBA) derivatives: The preparation and characterization of dibenzazepine derivatives are described in the Supporting Information.

Characterization of photodimers: The photochemical formation and spectral characterization of the photodimers of **10** and **14** has been described elsewhere.[5] In these and all other photodimers, the *anti*-configuration was concluded from the coupling pattern of the cyclobutane protons in the ^{1}H NMR spectra. For **9**, **16**, **19**–**21** two AA′BB′ spin systems were found in the ^{1}H NMR spectra of the cyclobutane protons. In these cases, two rotamers of the dimers exist which originate from hindered rotations of the amide C–N bonds, see ref. [5]

Photodimer of 8: M.p. 329–332 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (d, 4H, Ar-H), 7.33 (t, ^3J = 7.6 Hz, 4H, Ar-H), 7.17 (t, ^3J = 7.5 Hz, 4H, Ar-H), 7.01 (d, ^3J = 7.4 Hz, 4H, Ar-H), 4.25 (s, 4H, cyclobutane-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.4 (C4a, C4a′, C5a, C5a′), 136.0 (C9a, C9a′, C11a, C11a′), 131.2, 128.9, 128.2, 123.2 (Ar-C), 114.6 (N-*C*N, N-*C*N′); MS (ESI, positive): *m*/*z* (%): 437 (77) $[M]^+$, 391 (100) $[M-46]^+$, 193 (48) $[M-244]^+$, 171 (27) $[M-266]^+$, 149 (31) $[M-288]^+$; elemental analysis calcd (%) for $C_{30}H_{20}N_4$ (M_w = 436.52): C 82.55, H 4.62, N 12.84; found C 82.28, H 4.64, N 12.88.

Photodimer of 9: M.p. 339–340 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.85 (s, 2H, C*H*O), 7.44–7.41 (2d, ^3J = 7.6 Hz, 2H, Ar-H), 7.38–7.30 (m, 6H, Ar-H), 7.23–7.19 (m, 2H, Ar-H), 7.17–7.14 (m, 2H, Ar-H), 7.00 (2d, ^3J = 7.6 Hz, 2H, Ar-H), 6.93–6.91 (2d, ^3J = 7.5 Hz, 2H, Ar-H), 4.03–3.83 (2AA′BB′ spin systems, 4H, cyclobutane-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.4, 162.3 (*C*HO, *C*HO′), 139.5, 139.4, 138.9, 138.8, 138.1, 138.0, 137.1, 137.0 (C4a, C4a′, C5a, C5a′, C9a, C9a′, C11a, C11a′), 131.5, 131.3, 131.1, 130.9, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.2, 127.9, 127.5, 127.3 (Ar-C), 49.4, 49.3, 48.5, 48.3 (C10, C10′, C11, C11′); MS (ESI, positive): *m*/*z* (%): 443 (100) $[M]^+$, 391 (2) $[M-52]^+$, 221 (3) $[M-222]^+$; elemental analysis calcd (%) for $C_{30}H_{22}N_2O_2$ (M_w = 442.52): C 81.43, H 5.01, N 6.33; found C 81.14, H 4.99, N 6.35.

Photodimer of 16: M.p. 304 °C (lit. [8] 300–304 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (2d, ^3J = 7.7 Hz, 4H, Ar-H), 7.59 (2d, ^3J = 7.7 Hz, 2H, Ar-H), 7.43 (m, 2H, Ar-H), 7.34 (m, 6H, Ar-H), 7.18–7.01 (m, 10H, Ar-H), 6.85 (2d, 2H, Ar-H), 4.75–4.14 (m, 2AA′BB′ spin systems, 4H, cyclobutane-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.9, 168.3 (N*C*O, N*C*O′), 142.6, 141.9, 141.4, 137.7, 137.6, 137.2, 137.1, 135.1, 134.1, 133.9 (C4a, C4a′, C5a, C5a′, C9a, C9a′, C11a, C11a′, NCO-*C*, NCO-*C*′), 132.1, 131.6, 131.1, 130.8, 130.5, 130.4, 130.3, 130.2, 130.1, 129.5, 129.3, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.3 (Ar-C), 48.8, 48.7, 46.4, 46.4 (C10, C10′, C11, C11′); MS (ESI, positive): *m*/*z* (%): 653 (6) $[M+58]^+$, 595 (100) $[M]^+$; elemental analysis calcd (%) for $C_{42}H_{30}N_2O_2$ (M_w = 594.71): C 84.82, H 5.08, N 4.71; found C 84.51, H 5.12, N 4.75.

Photodimer of 17: M.p. > 365 °C; MS (ESI, positive): *m*/*z* (%): 753 (13) $[M+58]^+$, 695 (100) $[M]^+$; elemental analysis (%) calcd for: $C_{50}H_{34}N_2O_2$ (M_w = 694.83): C 86.43, H 4.93, N 4.03; found C 86.60, H 4.90, N 4.07.

Photodimer of 18: M.p. 305–311 °C; MS (ESI, positive): *m*/*z* (%): 717 (20) $[M+22]^+$, 695 (100) $[M]^+$, 579 (12) $[M-116]^+$; elemental analysis (%) calcd for: $C_{50}H_{34}N_2O_2$ (M_w = 694.83): C 86.43, H 4.93, N 4.03; found C 86.05, H 4.96, N 4.04.

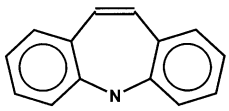
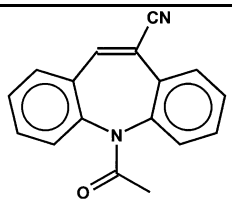
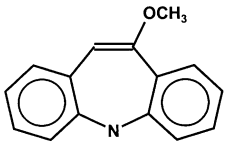
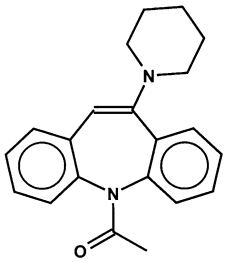
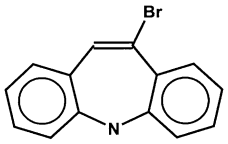
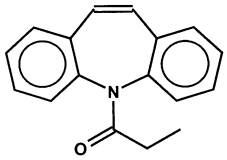
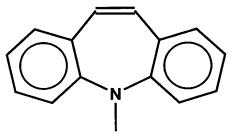
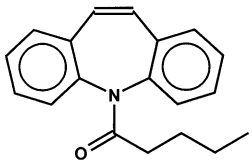
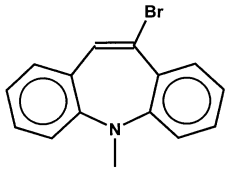
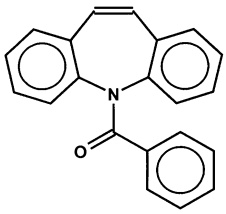
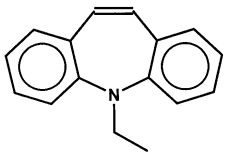
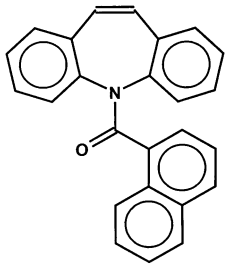
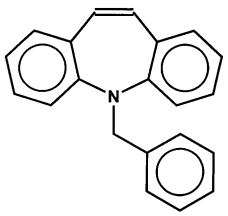
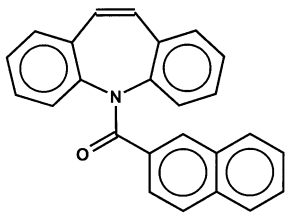
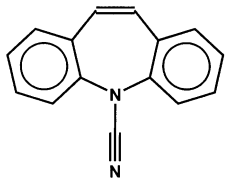
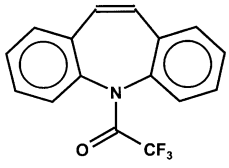
Photodimer of 19: M.p. 327–329 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.41 (m, 4H, Ar-H), 7.39–7.29 (m, 4H, Ar-H), 7.28–7.16 (m, 4H, Ar-H), 7.02 (2d, ^3J = 7.9 Hz, Ar-H), 6.92 (2d, 2H, ^3J = 7.8 Hz, Ar-H), 4.22–3.91 (m, 2AA′BB′ spin systems, 4H, cyclobutane-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.3 (2d, N*C*O, N*C*O′), 139.4, 139.2, 138.4, 138.2, 137.0, 136.9, 136.8, 136.6 (C4a, C4a′, C5a, C5a′, C9a, C9a′, C11a, C11a′), 132.1, 131.8, 131.5, 131.3, 129.8, 129.1, 128.9, 128.8, 128.7, 128.6, 127.7, 127.5, 127.4, 127.3 (Ar-C), 116.7 (q, J(C,F) = 289 Hz, CO-*C*F$_3$, CO-*C*F$_3$′), 48.4, 48.0, 46.8, 46.4 (C10, C10′, C11, C11′); elemental analysis calcd (%) for $C_{32}H_{20}N_2O_2F_6$ (M_w = 578.51): C 66.44, H 3.48, N 4.84; found C 66.23, H 3.49, N 4.86.

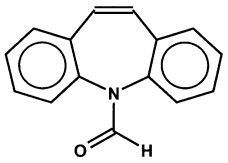
Photodimer of 20: M.p. 331–340 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 4H, Ar-H), 7.36–7.30 (m, 4H, Ar-H), 7.25–7.17 (m, 4H, Ar-H), 6.99 (t, ^3J = 7 Hz, 4H, Ar-H), 4.39–4.05 (2AA′BB′ spin systems, 4H, cyclobutane-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.4, 149.3 (N*C*O, N*C*O′), 140.8, 140.6, 139.9, 139.8 (C4a, C4a′, C5a, C5a′), 137.5, 137.4, 137.4, 137.3 (C9a, C9a′, C11a, C11a′), 131.6, 131.5, 131.4, 131.3, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 127.6, 127.5, (Ar-C), 48.6, 47.5, 47.5 (C10, C10′, C11, C11′); MS (ESI, negative): *m*/*z* (%): 511 (100) $[M]^+$, 465 (63) $[M-46]^+$, 415 (14) $[M-96]^+$, 311 (17) $[M-200]^+$, 227 (23) $[M-284]^+$; elemental analysis calcd (%) for $C_{30}H_{20}N_2O_2Cl_2$ (M_w = 511.41): C 70.46, H 3.94, N 5.48; found C 70.69, H 3.97, N 5.51.

Photodimer of 21: M.p. > 360 °C (lit.[8] 367–370 °C); ^{1}H NMR (500 MHz, TFA + [D$_6$]DMSO ext.): δ = 7.54–7.48 (m, 4H, Ar-H), 7.35–7.34 (2d, ^3J = 7.5 Hz, 2H, Ar-H), 7.26–7.24 (m, 4H, Ar-H), 7.17–7.15 (2d, ^3J = 7.5 Hz, 2H, Ar-H), 7.10 (d, ^3J = 7.1 Hz, 1H, Ar-H), 7.04 (d, ^3J = 7.3 Hz, 1H, Ar-H), 6.99 (d, ^3J = 7.5 Hz, 1H, Ar-H), 6.93 (d, ^3J = 7.1 Hz, 1H, Ar-H), 4.16–4.12 (m, 2AA′BB′ spin systems, 4H, cyclobutane-H); ^{13}C NMR (126 MHz, TFA + [D$_6$]DMSO ext.): δ = 160.1 (N*C*O, N*C*O′), 138.1, 137.9, 137.1, 136.9, 136.7, 136.4, 131.8, 131.6, 130.8, 130.6, 129.7, 128.9, 128.7, 128.1, 128.1, 127.1, 126.9, 125.8, 125.7 (Ar-C), 48.2, 48.1, 47.9, 47.7(C10, C10′, C11, C11′); MS (ESI, positive): *m*/*z* (%): 473 (100) $[M]^+$, 391 (5) $[M-82]^+$, 236 (11) $[M-237]^+$; elemental analysis calcd (%) for $C_{30}H_{24}N_4O_2$ (M_w = 472.55): C 76.25, H 5.12, N 11.86; found C 76.02, H 5.14, N 11.92.

Photodimer of 22: M.p. 311–313 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.77 (d, ^3J = 7.1 Hz, 4H, Ar-H), 7.60 (brs, 4H, Ar-H), 7.58 (t, ^3J = 7.4 Hz, 2H, Ar-H), 7.46 (t, ^3J = 7.5 Hz, 4H, Ar-H), 7.38 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.35 (t, ^3J = 7.4 Hz, 4H, Ar-

Table 1. Structural formulae and numbering of dibenz[*b*,*f*]azepines.

	5H-dibenz[*b*,*f*]azepine (iminostilbene)	**1**		5-acetyl-10-cyano-dibenz[*b*,*f*]azepine	**12**
	10-methoxy-dibenz[*b*,*f*]azepine	**2**		5-acetyl-10-(piperidin-1-yl)-dibenz[*b*,*f*]-azepine	**13**
	10-bromo-dibenz[*b*,*f*]azepine	**3**		5-propionyl-dibenz[*b*,*f*]azepine	**14**
	5-methyl-dibenz[*b*,*f*]azepine	**4**		5-valeroyl-dibenz[*b*,*f*]azepine	**15**[a]
	5-methyl-10-bromo-dibenz-[*b*,*f*]azepine	**5**		5-benzoyl-dibenz[*b*,*f*]azepine	**16**
	5-ethyl-dibenz[*b*,*f*]azepine	**6**		5-(1-naphthoyl)-dibenz[*b*,*f*]azepine	**17**
	5-benzyl-dibenz[*b*,*f*]azepine	**7**		5-(2-naphthoyl)-dibenz[*b*,*f*]azepine	**18**
	5-cyano-dibenz[*b*,*f*]azepine	**8**		5-trifluoroacetyl-dibenz[*b*,*f*]azepine	**19**



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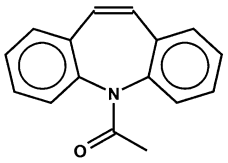

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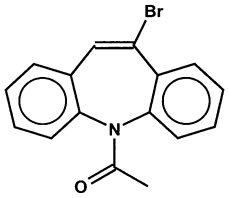
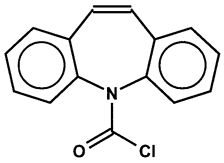
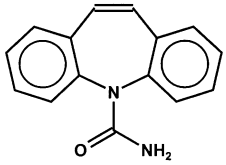


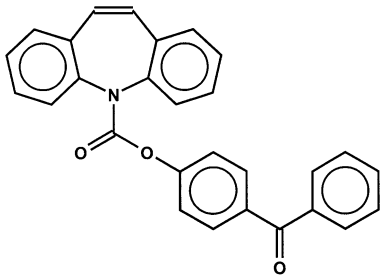
5-acetyl-10-bromo-dibenz[*b*,*f*]-azepine **11**



5-chlorocarbonyl-dibenz[*b*,*f*]azepine **20**



Carbamazepin (5-carbamoyl-dibenz[*b*,*f*]azepine) **21**



5-benzophenoxy-dibenz[*b*,*f*]azepine **22**

[a] Studied in ref. [11].

H), 7.19 (t, ^3J = 7.4 Hz, 4H, Ar-H), 7.03 (brs, 2H, Ar-H), 6.95 (brs, 2H, Ar-H), 4.31 (brs, 2H, cyclobutane-H), 4.23 (brs, 2H, cyclobutane-H); ^{13}C NMR (126 MHz, $CDCl_3$ + TFA): δ = 199.5 (Ph-*C*O-Ph), 154.5, 137.4, 136.2, 134.7, 133.9, 132.7, 131.6, 131.2, 130.6, 129.3, 129.0, 128.7, 128.3, 127.9, 121.6 (Ar-C), 48.8, 48.7, 48.6 (C10, C10′, C11, C11′); MS (ESI, positive): *m*/*z* (%): 835.2 (100) $[M]^+$, 637 (65) $[M-198]^+$, 551.4 (10) $[M-284]^+$; elemental analysis calcd (%) for $C_{56}H_{38}N_2O_6$ (M_w = 834.92): C 80.56, H 4.59, N 3.36; found C 80.25, H 4.58, N 3.35.

Continuous irradiations and analyses: Stirred argon-saturated solutions of appropriate monomer concentrations were thermostatted at 20 °C and irradiated through the gas–liquid interface for the desired time. Precipitated dimers were separated and combined with the residue obtained after evaporation of the solvent. The combined solids were dried in vacuo and dissolved in an appropriate NMR solvent for analysis.

Spectral features: The absorption spectra were recorded on a diode array (HP 8453). Fluorescence and phosphorescence spectra at 77 K were recorded on a Spex Fluorolog or a Perkin–Elmer (LS-5) fluorimeter. The phosphorescence lifetime (τ_p) was obtained from a first-order decay component with the laser set-up. Fluorescence spectra at room temperature were taken on a Shimadzu (model RF-5000) spectral fluorimeter. The spectra are uncorrected. Spectra of concentrated samples were taken from the surface at an angle of 30° relative to the exciting light. Integrated fluorescence spectra obtained under identical absorption conditions were taken as measures for relative quantum yields with diphenylanthracene (Aldrich, >99+%, recrystallized three times from ethanol, Φ_{fl} = 0.9[22,23] in cyclohexane) as the reference. Measured values were reproducible within ±3%. Lifetimes at room temperature were measured employing an apparatus described elsewhere.[24] Measured lifetimes were reproducible with deviations of ±0.2 ns.

Flash photolysis: For photolysis with UV/Vis detection the third harmonic from a Nd laser (λ_{exc} = 354 nm, rise time 10 ns), two excimer lasers (λ_{exc} = 248 and 308 nm, rise time <20 ns), two transient digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling were used as in previous work.[17,18] The molar absorption coefficient of the benzophenone triplet state at the maximum is $\varepsilon_{520} = 6.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}.[13–16] Those for the DBA were obtained from the height of the T–T absorption maximum with respect to that of benzophenone ($\Delta A_{TT}/\Delta A_{520}$) after extrapolation for 100% quenching and assuming unity for the efficiency of energy transfer. The donor concentrations were adjusted to A_{exc} = 1–3 in 1 cm quartz cells. The molar absorption coefficient of **7** in acetonitrile at the maximum is $\varepsilon_{255} = 3 \times 10^4$ dm^3 mol^{-1} cm^{-1}. The molar absorption coefficient of the acetophenone triplet state at the maximum and 400 nm is $\varepsilon_{320} = 1.3 \times 10^4$ dm^3 mol^{-1} cm^{-1} and <20%, respectively.[13–16]

Results

Spectral properties: The absorption spectra of **1**–**7** in acetonitrile exhibit the maximum at λ = 255–265 nm, a second peak at λ = 285–296 nm as well as a third peak with a small absorption coefficient extending to λ = 380 nm, in methanol to λ > 400 nm. This third peak is not present in **9**–**14** and in **16**–**22** where direct excitation at λ = 354 nm is therefore not reasonable. In the N-cyano compound **8**, the third peak appears as a shoulder at ≈320 nm. In order to understand the results of irradiations in concentrated solutions (≥ 0.01 mol dm^{-3}, see below) the absorption spectra were measured at high concentrations in cuvettes of low optical path length: changes of the spectra attributable to the possible formation of ground state dimers of aggregates were not observed.

At room temperature in most of the DBA, only weak or virtually no emission could be detected. Fluorescence was found for **8** and **9** (Figure 1a) with quantum yields Φ_{fl} = 0.19 and 0.09 and lifetimes of 7.5 ns and <5 ns in methanol, respectively. The fluorescence spectra were identical for concentrations between 10^{-2} and 10^{-5} mol dm^{-3} in methanol or between 10^{-2} and 10^{-6} mol dm^{-3} in cyclohexane, that is, an emission from potential excited-state aggregates was not observed for these two compounds. At −196 °C, an emission as a result of fluorescence (**1**–**14**, **16**, **19**, **20**, **22**) and/or phosphorescence (**4**–**7**) was observed in ethanol. Examples are shown in Figure 1b for **4** and **7**. Mostly both emission yields at −196 °C are weak (except **8** and **9**). The largest values for phosphorescence quantum yields Φ_p = 0.01, 0.02 and 0.05 were measured in ethanol for **4**, **6** and **7**, respectively, to be

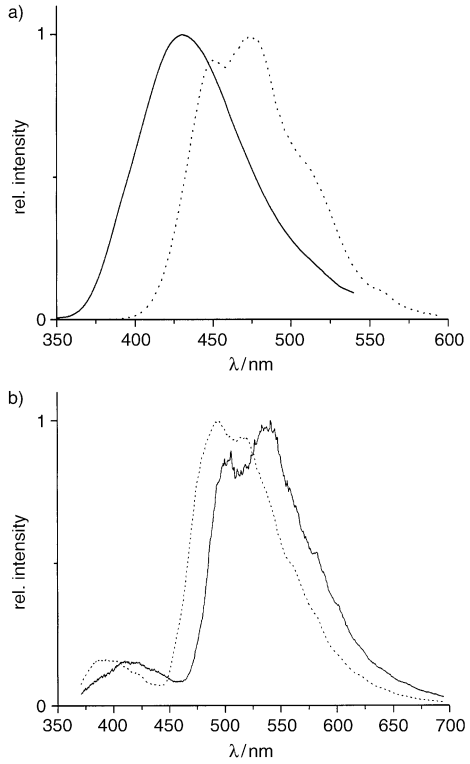


Figure 1. a) Fluorescence spectra of **8** (-----) and **9** (——) in cyclohexane at room temperature, $\lambda_{exc} = 280$ nm. b) Emission spectra of **4** (——) and **7** (-----) in ethanol at 77 K; $\lambda_{exc} = \lambda_{max}$.

compared with the literature value $\Phi_p = 10^{-4}$ for the acetyl derivative **10**.[11] Phosphorescence is concluded i) from the long-wavelength onset of the spectrum for **4**–**7**, and ii) from a first-order decay component with a lifetime of 3–5 ms for **4** and **7**. From the phosphorescence onset and maxima at $\lambda = 500$ and 538 nm for **4**, a triplet energy of $E_T = 254$ kJ mol^{-1} was estimated. For **7**, which exhibits peaks at 485 and 516 nm, we determined $E_T = 266$ kJ mol^{-1}.

In order to test for transient absorption at room temperature upon direct excitation in argon-saturated benzene or acetonitrile, $\lambda_{exc} = 308$ nm was applied. Mostly, the transient absorption is too weak for a kinetic evaluation (tested for **1**, **2**, **4**, **6**–**10**), at least when compared with the sensitized formation of the triplet state of the dibenzazepines (see below). On the other hand, for **8** and **9**, a short-lived (< 10 ns) transient absorption appeared at approximately 340–380 nm, which should be attributed to an $S_1 \rightarrow S_n$ transition as the lifetime of the transient is in satisfactory agreement with the fluorescence lifetimes in methanol. However, for **22** in acetonitrile or ethanol at room temperature ($\lambda_{exc} = 248$ or 308 nm) or in benzene ($\lambda_{exc} = 308$ or 354 nm), the triplet state could be detected (Figure 2). The triplet nature is concluded from the build-up during the pulse, the first-order decay and quenching by oxygen. A weak T–T absorption was also found for **16** and **17** in acetonitrile or ethanol, in contrast to most other DBA. A likely reason for the triplet population is the benzoyl, naphthoyl or benzophenoxy moiety in **16**, **17** and **22**, respectively. No T–T absorption could be detected for any other DBA examined in acetonitrile. The reason is that the Φ_{ISC} value is too low. For **8**, an

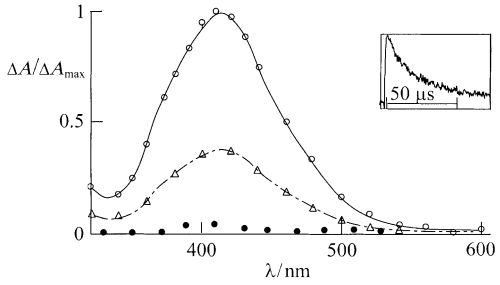


Figure 2. T–T absorption spectra of **22** in argon-saturated acetonitrile at 24 °C at 20 ns (○), 20 µs (△) and 0.1 ms (●) after the 354 nm pulse. Inset: triplet-state decay kinetics at 410 nm.

even weaker transient absorption was observable in the 380–440 nm range ($\lambda_{exc} = 354$ nm), but assignment to a triplet state is unlikely, owing to the lack of quenching by oxygen. However, when an appropriate sensitizer, such as benzophenone, is present, a strong secondary transient absorption was formed for all DBA.

Benzophenone-sensitized triplet energy transfer: The benzophenone triplet state, which is formed within the pulse ($\lambda_{exc} = 354$ nm), has a well-known absorption spectrum with a maximum at $\lambda = 520$ nm.[12] On addition of a given DBA, the decay of the triplet state of the benzophenone donor (^{3}D*) at 520 nm in argon-saturated acetonitrile is faster than in the absence of DBA. Moreover, a longer-lived transient absorption with a maximum (λ_{TT}) in the 390–430 nm range is observable. This second transient is ascribed to the triplet state of the dibenzazepine (^{3}DBA*), produced by energy transfer from ^{3}D*, according to Equation (1). This agrees with findings for the valeroyl derivative **15**.[11]

$$^3D^* + DBA \rightarrow D + {}^3DBA^* \quad (1)$$

Similar T–T absorption maxima of the benzophenone/DBA system were recorded in either acetonitrile or acetone (Table 2). Examples are shown for **1** and **19** (Figure 3). Electron transfer to ^{3}D* as an alternative or competing quenching step can be excluded since the benzophenone radical anion or the conjugate acid with maximum at $\lambda = 660$ and 550 nm, respectively,[12–14] was not detected. Note that the presence of water (1 %, pH > 10), that was added to make the radical anion longer lived, has no marked effect in the case of **1**.

The triplet nature of the observed transient in solution is concluded from i) the similarity of the first-order rate constants of decay of the benzophenone triplet (k_{obs}) and build-up at λ_{TT} (insets of Figure 3), ii) quenching by oxygen and iii) the linear dependence of k_{obs} on the DBA concentration. From the latter dependence, the rate constants of energy transfer (k_1) were determined. For a concentration of 0.3 mmol dm^{-3} **7**, the k_{obs} value is 2×10^6 s^{-1}, resulting in $k_1 = 7 \times 10^9$ dm^3 mol^{-1} s^{-1} (Table 2). The molar absorption coefficients compiled in Table 2 were obtained from the ratio of ΔA values at λ_{TT} of ^{3}DBA* and ^{3}D*, assuming quantitative energy transfer and $\varepsilon_{520} = 6.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}.

The decay of ^{3}DBA* can be fitted by mixed first- and second-order kinetics with a first-order component (k'_{obs} =

Table 2. T–T absorption maximum, triplet lifetime, absorption coefficient and quenching rate constant for various DBA upon sensitized excitation in argon-saturated solution at 24 °C.

DBA	λ_{TT} [nm][a]	τ_T [μs][a]	τ_T [μs][b]	τ_T [μs][c]	ε_{TT} [$\times 10^3$ dm^{3}mol^{-1}cm^{-1}][a]	k_1 [$\times 10^9$ dm^{3}mol^{-1}s^{-1}][a]
1	395	15	5	10	7	18
2	400		5	20	5	18
3	405	0.8		<2	5	>5
4	410	20	10	20	6	14
5	420	0.4		<2	7	>5
6	425	15	5	20	5	9
7	415	15	10	20	6	7
8	400	20	10	20	8	6
9	410	15	10	10	9	7
10	420	15	10	10	8	5
11	420	10				>5
12	420	25		20	7	>5
13	410	15		10	6	>5
14	415	15	10	10	8	7
16	415	15	10	15	7	5
17	415	20		10	12	>5
18	415	15		15	11	>5
19	410	15	15	20	9	7
20	420	10		10	7	>5
21	410	15		15	8	>5
22	415	15	20	30	5	9

[a] Benzophenone in acetonitrile. [b] Benzophenone in acetone. [c] Acetophenone in acetonitrile.

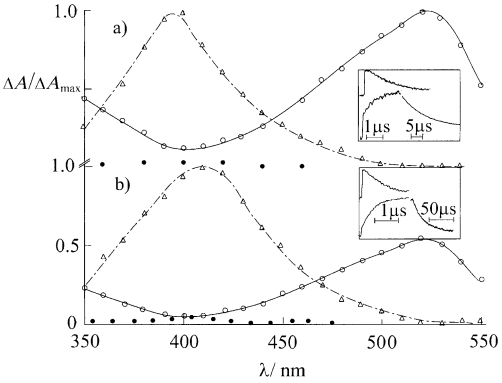


Figure 3. T–T absorption spectra of benzophenone in argon-saturated acetonitrile (24 °C, $\lambda_{exc} = 354$ nm) with a) **1** and b) **19** at 20 ns (○), 2 μs (△) and 0.1 ms (●) after the pulse. Insets: decay kinetics at 520 nm (upper) and build-up and decay at $\lambda_{TT} = 400$ nm (lower).

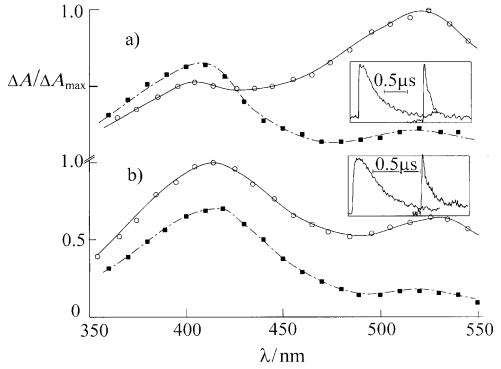


Figure 4. T–T absorption spectra of benzophenone-sensitized excitation in argon-saturated acetone for a) **3** and b) **5** at 20 ns (○) and 0.2 μs (■) after the pulse. Insets: decay kinetics at 520 nm (right) and build-up and decay at $\lambda_{TT} = 400$ nm (left).

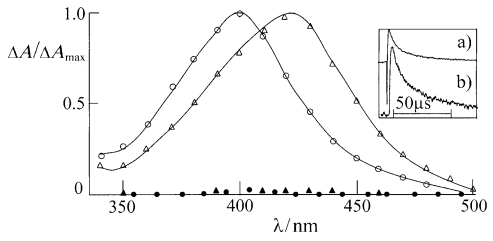


Figure 5. T–T absorption spectra of acetophenone-sensitized excitation of **2** (circles) and **14** (triangles) in argon-saturated acetonitrile at 1 μs (open) and 1 ms (filled) after the 354 nm pulse. Insets: decay kinetics at 400 nm of a) **2** and b) **14**.

$1/\tau_T$) at lower laser intensity; the second-order component results from T–T annihilation. The triplet lifetime of DBA is typically in the 5–20 μs range (Table 2). When acetonitrile was replaced by benzene as a solvent of low polarity, the results were found to be similar. The literature values of the valeroyl derivative **15** in dichloromethane are $\lambda_{TT} = 420$ nm, $\tau_T = 17$ μs and $k_1 = 3\times10^9$ dm^{3}mol^{-1}s^{-1}.[11] A significantly shorter triplet lifetime, $\tau_T < 1$ μs, was obtained for **3** and **5** (Figure 4).

Triplet energy transfer with other donors: When the sensitizing ketone was acetophenone, the ^{3}DBA* state was likewise generated from the triplet state of acetophenone following Equation (1). Examples of the spectra are shown for **2** and **14** (Figure 5). Because the T–T absorption of acetophenone is below 400 nm, the decay kinetics of the donor and acceptor triplet states do not overlap at λ_{TT} and above. The latter decay can be fitted by mixed first-order kinetics with a major first-order component at lower laser intensity. The triplet lifetime is typically in the 10–30 μs range (Table 2). For both donors (benzophenone and acetophenone), the efficiency of the formation of any ^{3}DBA* state is assumed to be substantial or close to unity (60–99 %) since k_1 is relatively large and the donor triplet state is populated with $\Phi_{ISC} = 1$.

The acetone triplet state has an absorption at 325 nm, which is accessible to laser excitation, and no band in the visible range. The ^{3}DBA* state in argon-saturated acetonitrile is also generated following Equation (1) within 0.5–2 μs for the appropriate DBA concentrations. It can be formed in most cases (except for **3** and **5**), examples are shown in Figure 6 for **1** and **19**. Interestingly, the T–T absorptions of **1**, **2**, **4**, **6**, **7** show a second, stronger band at $\lambda < 320$ nm, which is not accessible with other sensitizers because of their transient and/or ground state absorption. The triplet nature of the observed transient in acetophenone (or benzophenone) is fur-

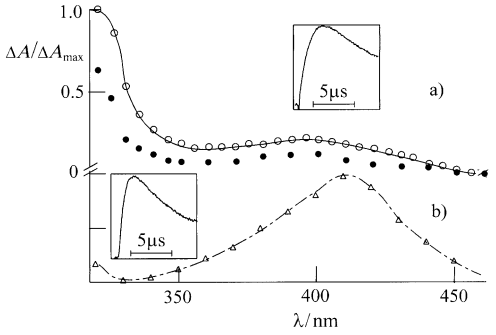


Figure 6. T–T absorption spectra of acetone-sensitized excitation (λ_{exc} = 308 nm) of a) **1** in argon-saturated acetonitrile at 3 μs (○) and 10 μs (●) after the pulse and b) **19** at 3 μs (△). Insets: kinetics of build-up and decay at a) 325 nm and b) 410 nm.

ther supported by the effect of quenching by oxygen. When the oxygen concentration is low, decay of the acceptor triplet becomes faster, while air-saturation also reduces the yield (ΔA_{TT}). Whether or not the ^{3}DBA* state is still observable in air depends on the DBA concentration owing to competition of i) quenching by oxygen of the donor triplet, and ii) Equation (1). With fluorenone and benzil in argon-saturated acetonitrile, the ^{3}DBA* state (e.g. for **1**, **7** or **10**) is likewise generated following Equation (1); however, k_1 is smaller, $(1–3)\times10^9$ dm^3 mol^{-1}s^{-1}. Acridine with E_T = 190 kJ mol^{-1} was found not to generate the ^{3}DBA* state (for **19** the upper limit is $k_1 < 1\times10^7$ dm^3 mol^{-1} s^{-1}).

Continuous sensitized irradiation: The benzophenone-sensitized photodimerization was studied in either acetone or acetonitrile as the solvents. The results are summarised in Table 3. On inspection it is clearly revealed that DBA **1**–**7** do not yield detectable amounts of dimers. As expected from previous results, N-acyl derivatives of the DBA, that is, **9**–**22**, form photodimers. N-cyano DBA **8** belongs to the latter class as it photodimerizes. Side-products were detected in all cases. Possible regioisomers (with respect to R_2 in Scheme 1) in the dimers of **11**–**13** could not be distinguished. In **1** and in the N-acyl derivatives, these side-products are acridine derivatives, at least in part. At irradiation times longer than those given in Table 3, the yield of acridine and other side-products slowly increases while that of the dimers does not change significantly any more. The N-alkyl DBA **2**–**7** slowly produce high molecular-weight products, clearly distinct from photodimers and acridines, which were not investigated in detail.

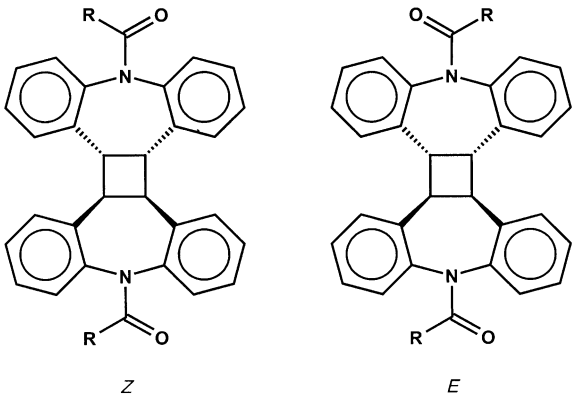
Table 3. Product yields and product distribution in the sensitized irradiation of various DBA in argon-saturated solutions at 20 °C.

DBA	Conditions[a]	c [mol dm^{-3}]	Irradiation time [h]	Dimer [%]	Educt [%]	Side-products (acridines) [%]
1	A	0.02	7	0	85	15
	B	0.1	4.5	0	53	47
2	A	0.02	4	0	91	9
4	A	0.02	7	0	87	13
	B	0.1	5	0	90	10
7	A	0.02	4	0	93	7
	B	0.1	5	0	86	14
8	A	0.2	4	18		
	B	0.1	5	6	75	19
	C	0.01	5	13	22	65
9	A	0.04	11	9		
	B	0.1	4.5	14	69	17
	C	0.01	5	1	23	76
10	A	0.04	4	37		
	B	0.1	5	>80	<15	>10
	C	0.01	5	>60	<15	>25
11	B	0.1	6	0	77	23
14	A	0.04	6	29		
	B	0.1	5	>80	<15	<10
	C	0.01	5	>80	<10	<10
16	A	0.02	7	26	69	5
	B	0.1	5	25	64	11
17	B	0.1	5	5	82	13
18	B	0.1	5	9	79	12
19	A	0.04	4	32		
	B	0.1	5	61	31	8
20	B	0.1	5	29	47	24
21	B	0.1	5	59	33	8
22	B	0.1	5	>85	[b]	<15

[a] A: sensitizer benzophenone (0.04 mol dm^{-3}), solvent acetone, cut-off filter 320 nm, dimers precipitated from the solution; B: sensitizer acetone = solvent, cut-off filter 280 nm; C: sensitizer benzophenone (0.05 mol dm^{-3}), solvent acetonitrile, cut-off filter 280 nm. [b] no signals in the ^{1}H NMR of the crude product.

In principle, the photodimers of **17**, **18** and **22** are expected to form rotamers, too. However, the ^{1}H NMR signals of the cyclobutane protons are too broad for an unequivocal evaluation. Rotamers do not exist in the dimer of the N-cyano compound **8** on account of the lack of amide bonds.

Similar to the photodimers of **10** and **14**,[5] those of **9**, **16**, **19**, **20**, and **21** exist in two rotameric forms, that is, in *Z* and *E* configurations with respect to the amide groups, which result from the restricted rotation of the C–N of the amide bond, see Scheme 2. According to a previous study,[5] the *Z* and *E* rotamers can be best distinguished from the ^{1}H NMR signals of the cyclobutane protons. Table 4 gives the fractions of *Z* and *E* conformers which were obtained from integrals of the NMR signals after photodimerization and dissolving the dimer in the NMR solvent. Also included in Table 4 are the free energies of activation $\Delta G^{\neq}$ of the amide bond rotation obtained from the coalescence temperature of the separated NMR signals either in [D$_7$]DMF or [D$_8$]toluene/[D$_6$]DMSO (9:1).[5] The values agree within the accuracy of the determination. The $\Delta G^{\neq}$ value was not measurable for the dimer of **20**, which decomposed upon heating the NMR tube.



Z E

Scheme 2. Rotamers of dibenzazepine dimers.[5]

Table 4. Fractions of *Z* and *E* rotamers of various photodimers in NMR solvents at room temperature and free energy of activation $\Delta G^{\neq}$ for the amide bond rotation in ([D_7]DMF or [D_8]toluene/[D_6]DMSO (9:1)).

Photodimer of	NMR solvent	*Z* Rotamer [%]	*E* Rotamer [%]	$\Delta G^{\neq}$ [kJ mol^{-1}]
9	$CDCl_3$	38	62	n.m.[b]
10[a]	$CDCl_3$	32	68	74±2
14[a]	$CDCl_3$	40	60	70±2
16	$CDCl_3$	44	56	n.m.[b]
19	$CDCl_3$	47	53	72±2
20	$CDCl_3$	48	52	–
21	TFA[c]	43	57	n.m.[b]

[a] Data from ref. [5]. [b] n.m. = Not measured. [c] TFA = trifluoroacetic acid.

Continuous direct irradiation: In concentrated ($\geq$0.01 mol dm^{-3}) solutions, the photodimerization of several N-acylated DBA was observed upon direct excitation. Considerable yields of the dimers were obtained in the cases of **10**, **14** and **22** (Table 5). This is trivial only for **22**, as the compound bears an attached benzophenone moiety, which can act as an intramolecular sensitizer (cf. flash experiments). As in the sensitized reaction, only dimers with *anti*-configuration were formed. The N-alkyl DBA did not dimerize. Similar results were found on irradiating crystalline dibenzazepines (Table 6).

Calculations: Semiempirical (PM3) calculations[25] reveal an energy difference of 15 kcal mol^{-1} between the hypothetical *syn*-dimer and the corresponding *anti*-dimer of **10** (Scheme 3). In principle, both *syn*- and *anti*-dimers might exist in different conformations with respect to the orientation of i) the seven-membered ring, and ii) to the amide bond,[5] and which would have higher energies according to the calculations.

Discussion

The relationship between emission properties and structure is complex. While in most cases both fluorescence and phosphorescence yields in glassy ethanol at −196 °C are weak, the reason for enhanced fluorescence (found in the N-cyano DBA **8** and N-acyl DBA **9**) and phosphorescence (found in the N-alkyl DBA **4**–**7**) should arise from a more efficient competition with thermal deactivation, even in the glassy environment. Bear in mind that only N-alkyl DBA exhibit phosphorescence, which—compared to N-acyl DBA—already indicates a different nature of the excited states, as will be discussed below.

In all cases, the triplet state of a given dibenzazepine as the acceptor is produced in fluid solutions at 24 °C by energy transfer from that of the benzophenone (E_T = 290 kJ mol^{-1}), acetophenone (310 kJ mol^{-1}), and acetone (343 kJ mol^{-1}) donors. For benzophenone in inert organic solvents, the reactive state of all DBA examined is characterized by T–T absorption with slightly differing λ_{TT} and ε_{TT}. The results for benzophenone in acetone or acetonitrile and also for acetophenone are comparable (Table 2). Note that acetone is not involved in the time-resolved energy-transfer here, since a shorter λ_{exc} is needed for the excitation of acetone itself (as used in the experiments collected in Table 3). The values of E_T = 250–270 kJ mol^{-1} for dibenzazepines determined from phosphorescence spectra in ethanol at −196 °C are in keeping with the fact that slow energy transfer (k_1) is observed when fluorenone (E_T = 224 kJ mol^{-1})

Table 5. Product yields and product distribution in the non-sensitized irradiation of various DBA in argon-saturated acetonitrile at 20 °C.

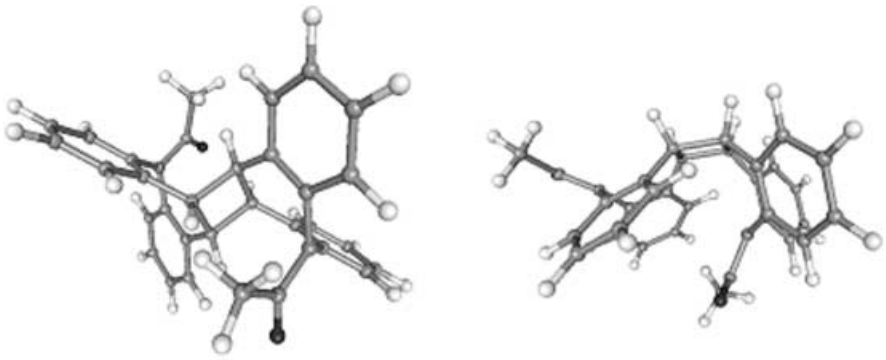
DBA	Cut-off filter [nm]	*c* [mol dm^{-3}]	Irradiation time [h]	Dimer [%]	Educt [%]	Side-products (acridines) [%]
1	<320	0.1	5	0	69	31
2	<320	0.1	5	0	38	62
3	<320	0.1	5	0	93	7
4	<320	0.1	5	0	96	4
5	<320	0.1	5	0	95	5
7	<320	0.1	5	0	97	3
8	<280	0.01	5	0	38	62
	<280	0.1	5	3	89	8
9	<280	0.01	5	traces	69	31
	<320	0.1	4.5	<1	87	12
10	<280	0.01	5	54	18	28
	<280	0.1	5	>80	<10	<10
11	<280	0.1	5.5	0	89	11
14	<280	0.01	5	56	35	9
	<280	0.1	4.5	>90	[a]	<10
16	<280	0.01	5	5	91	4
	<280	0.1	5	9	87	4
17	<280	0.1	5	1	89	10
18	<280	0.1	5	3	94	3
19	<280	0.1	5	10	75	15
20	<280	0.1	5	2	71	27
21	<280	0.1	5	7	88	5
22	<320	0.1	4.5	>90	[a]	<10

[a] No signals in the ^{1}H NMR of the crude product.

Table 6. Product yields and product distribution in the irradiation of various DBA in the solid state under air.

DBA	Cut-off filter [nm]	Irradiation time [h]	Dimer [%]	Educt [%]	Side-products (acridines) [%]
1	< 320	5	0	93	7
2	< 320	5	0	87	13
3	< 280	5	0	92	8
4	< 280	5	0	97	3
5	< 320	5	0	96	4
6	< 320	5	0	96	4
7	< 320	5	0	95	5
8	< 280	5	22	73	5
9	< 280	5	2	92	6
10	< 280	5	14	84	2
11	< 280	5	0	94	6
12	< 280	5	traces[a,b]	96	4
13	< 280	5	10[a,b]	87	3
14	< 280	5	54	38	8
16	< 280	7	7	89	4
17	< 280	5	traces[a]	94	6
18	< 280	5	3	92	5
19	< 280	5	39	59	2
20	< 280	5	0	89	11
21	< 280	5	11	83	6
22	< 280	5	77	19	4

[a] Products not isolated, but signals pertaining to cyclobutane protons present in the ^{1}H NMR spectra. [b] No indication of regioisomers.



Scheme 3. Geometry-optimized[25] structures of *anti* (left) and the hypothetical *syn* (right) dimer of **10**.

or benzil are used as sensitizers and that acridine (E_T = 188 kJ mol^{-1} [26]) does not sensitize.

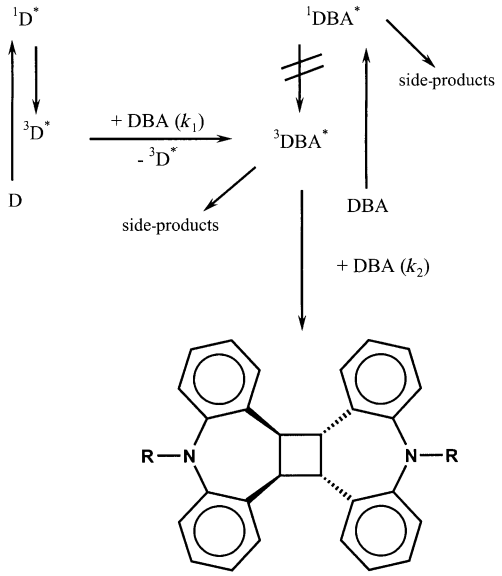
The proposed mechanism of the benzophenone-sensitized dimerization is given in Scheme 4. Since further (e.g. biradical) intermediates could not be detected in the flash experiments, essentially a reaction of ^{3}DBA* with a ground state molecule [Eq. (2)] occurs.

$$^3\mathrm{DBA}^* + \mathrm{DBA} \rightarrow \text{dimer} \qquad (2)$$

The literature value for the rate constant of the valeroyl derivative **15** is $k_2 = 2.4\times10^7$ dm^3 mol^{-1} s^{-1}.[11] The self-quenching reaction in Equation (2) is difficult to measure with nanosecond flash photolysis and $\lambda_{exc} = 354$ nm since low signals are necessary to reduce T–T annihilation of ^{3}DBA*, the required concentration of DBA is rather high and direct excitation cannot be ignored for **1**–**7**. Several attempts gave only a lower limit, typically $k_2 < 3\times10^7$ dm^3 mol^{-1} s^{-1}, for example, for **4** or **7**. While T–T annihilation upon pulsed laser excitation is feasible, this reaction can be excluded for continuous irradiation because of the small triplet concentration. Involvement of radicals in the accessible time window (0.1–10 μs) is unlikely, in fact another longer-lived intermediate than ^{3}DBA* could not be detected.

The dependence of Φ_d on the concentration of DBA follows inherently from the described facts: the dimer yields given in Table 3 do not increase further at longer irradiation times; instead, the amounts of side-products slowly increase. This indicates that, at concentrations below $\approx10^{-3}$ mol dm^{-3}, the possibility of encountering triplet excited and ground state DBA vanishes.

The drastically reduced triplet lifetimes in **3** and **5** (Table 2 and Figure 4) originate from the internal heavy atom effect of the bromine atom. This effect is less pronounced in the decay of **11** and for the chlorine-containing DBA **20** (Tables 1 and 2). Nevertheless, it is sufficient to completely suppress the formation of dimers in the case of **11** and to reduce the dimer yield in the case of **20** (Tables 3, 5, 6), while **3** and **5** are not expected to dimerize because of the missing acyl group. Steric hindrance by the bromine substituents is unlikely in the formation of *anti*-dimers.



Scheme 4. Reaction scheme for the sensitized photodimerization of N-acyl dibenzazepines.

This study clearly establishes the formation of dimers from several dibenzazepines upon direct irradiation, provided the concentration is high or the solid is irradiated (Tables 5, 6). A non-sensitized photodimerization was denied in a previous publication,[11] while another study[1] favors less efficient dimerization without a sensitizer; one paper on carbamazepine **21** is equivocal in this respect:[7] the authors might have irradiated a suspension. Since the brominated compound **11** does not yield photodimers under all conditions, and since the dimeric products are again exclusively *anti*-dimers, we have to regard them as triplet products, in spite of the low intersystem crossing rates upon direct excitation (according to the flash experiments in dilute solutions). The possibility that an acridine derivative formed in a side-reaction might act as a sensitizer for triplet DBA is remote because the acridine triplet energy is too low, as proven by the flash experiments. Since we did not observe indications of ground state aggregates (as suggested previously in a different context[27]), we propose that (non-emitting) excited aggregates of DBA are formed in concentrated solutions, which are capable of intersystem crossing and subsequent dimerization. Unfortunately, the high concentrations (and the laser flash wavelength) prevent corresponding flash experiments.

Some ideas of the mechanism of photochemical acridine formation have been presented previously,[28,29] but mechanistic details are still lacking. The flash photolysis results (Table 2) do not indicate any change in mechanism for either **1**–**7** or for the acylated compounds **9**–**22**. However, since the formation of dimers becomes slow at longer irradiation times (owing to the depletion of monomers) while the formation of acridines continues, we can exclude a bimolecular reaction mechanism involving two DBA molecules. Thus the formation of acridines is a monomolecular side-reaction originating from either ^{3}DBA* or ^{1}DBA*.

As to the question why N-H and N-alkyl derivatives do not dimerize: **3**, **5**, and **11** bear a bromine substituent in the 10-position at the double bond. The different efficiencies of heavy atom interactions on the triplet lifetime of **3** and **5** on the one hand and of **11** on the other (Table 2) may indicate a distinction in the nature of the excited triplet states of N-alkyl and N-acyl DBA. The low absorption coefficient of the long wavelength absorption in **1**–**7** (not present in **8**–**22**) suggests different characters of the lowest excited (singlet) states for the two groups of dibenzazepines. We can assign $n\pi^*$ character to the $S_0 \rightarrow S_1$ transition in **1**–**7** and $\pi\pi^*$ character in the N-acyl and N cyano derivatives. The difference may be rationalized when the +I effect of alkyl substituents and the −M effect of acyl and cyano groups on the electron density at the nitrogen atom are considered. As a consequence (provided these distinctions also apply to the triplet state), the former alkyl-substituted compounds behave more like diphenylamines and the latter more like *cis*-stilbene (= *Z*-stilbene). The chemical reactivity of triplet diphenylamines has been studied in depth:[30] flash photolytic and preparative investigations revealed strictly conrotatory ring closure reactions yielding 4a,4b-dihydrocarbazoles with the 4a and 4b substituents in *trans* conformation. Because of the ethene bridge, such a conformation appears extremely unlikely for our systems, so that only side-routes are possible reactions for these compounds. On the other hand, stilbenes are known to form photodimers through both singlet and triplet excited states,[31] a particularly related system being 2,3,6,7-dibenzocycloheptatriene,[3,32] namely, **1** with the NH-group exchanged by CH_2. This compound undergoes a triplet reaction to form an *anti*-cyclobutane ring.

One question remains open: if dimerization takes place, why is the *anti* configuration formed exclusively? While, in principle, triplet dimerization allows both the formation of *syn* and *anti* cyclobutanes (e.g. in the photodimerization of acenaphthylene[33,34]), steric reasons connected with the repulsion of N-acyl groups and/or the more strained cyclobutane ring in the *syn* isomer (Scheme 3) may lead to the selective formation of *anti* dimers. This view is corroborated by the calculation of energy differences between *anti* and *syn* dimers, which suggest *syn* dimers to be less stable.

Conclusions

Generally, intersystem crossing rates are low for dibenzazepines while triplet energy transfer from suitable sensitizers is efficient. N-H and N-alkyl DBA do not photodimerize under all conditions investigated, while N-cyano and N-acylated DBA form dimers with an *anti* configuration both with sensitization and upon direct excitation (in concentrated solution and in the solid state). The differing reactivities are not a consequence of distinct intersystem crossing rates or triplet energy transfer efficiency, but can be related to the nature of the excited state, which is $n\pi^*$ for the former and $\pi\pi^*$ for the latter class.

Acknowledgement

J.Q. thanks the Deutsche Forschungsgemeinschaft for a grant in the Graduiertenkolleg "Struktur-Eigenschafts-Beziehungen bei Heterocyclen". J.Q. and T.W. are grateful to Mrs. A. Rudolf for measuring NMR spectra, to Dr. R. Müller (former Arzneimittelwerk Dresden AWD) for providing three dibenzazepine derivatives, and to Mr. W. Thiessen for assistance in the use of the graphic programs. H.G. thanks Professor W. Lubitz for his support as well as Mr. Leslie J. Currell and Mrs. A. Keil-Block for technical assistance.

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Received: June 3, 2003 [F5199]

