ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 53-57

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photophysical and photochemical deactivation behaviour of streptopolymethines

J. Bendig [a], U. Schedler [a], T. Harder [a], P. Wessig [a], J. Lobedank [a], W. Grahn [b]

[a] *Institut für Chemie, Humboldt-Universität, Hessische Str. 1-2, D-10115 Berlin, Germany*
[b] *Institut für Organische Chemie, Technische Universität, Hagenring 30, D-38106 Braunschweig, Germany*

Received 24 March 1995; accepted 3 May 1995

Abstract

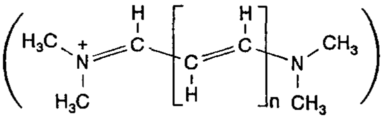
The photophysical and photochemical deactivation behaviour of the homologous series of streptopolymethines 1,3-bis(dimethylamino)-tri-, -penta-, -hepta- and -nonamethine has been investigated and is discussed on the basis of an energy scheme. The deactivation of the S_1-states occurs by fluorescence and thermally activated photochemistry (E–Z isomerization). With the exception of the trimethine the fluorescence dominates at low temperature. The ab initio calculated potential curves of the S_1 states indicate an increase in the rotation barrier with increasing length of the molecule. In the case of the nonamethine a multiple E–Z isomerization is discussed.

Keywords: Polymethine dye; Fluorescence; Excited state; Photoisomerization; Quantum chemical calculation

1. Introduction

Polymethine dyes are functional colorants par excellence; they are used as silver halide sensitizers [1] in photography, as laser dyes [2] and as potential components of data storage media [3] and of non-linear optical materials [4]. Within a single vinylogous series such as the "pure" open-chained polymethines (streptopolymethines **1a**–**4a**, Scheme 1) the absorption wavelength changes over a wide range [5].

The wavelength of fluorescence of polymethine dyes also varies strongly in vinylogous series. In contrast with the wavelength dependence, the fluorescence intensity may be strong, very weak or absent [6], but without an understandable correlation to the molecular structure. The quantum yields of fluorescence and the fluorescence lifetimes differ extremely between comparable dyes of vinylogous series (polymethine dyes with different heterocyclic end groups and/or different substitution pattern) and, within a vinylogous series, between members of different chain length [7].



X = Cl, Br, I, BF_4, N_3, ClO_4

n	1	2	3	4
	1a	**2a**	**3a**	**4a**

Scheme 1.

Additionally, most of the few investigated quantum yields depend on temperature, viscosity and polarity of the solvent. These are the reasons why a comparison is so difficult.

The fluorescence kinetic properties are strongly influenced by radiationless deactivation processes, especially internal conversion and photoisomerization. Intersystem crossing is generally a less efficient deactivation path of polymethine dyes [8] provided that heavy atoms are absent and the triplet state is of minor importance for the photochemistry (see Fig. 1 below). The Z isomers are unstable at room temperature; their lifetimes are limited to nanoseconds or microseconds. In no case could a detailed structure be proved experimentally [9–11]. The results of experimental and theoretical investigations of the photoisomerization are often contradictory; no general theory of the mechanism of photoisomerization exists for the interpretation of the dependence of the fluorescence and/or photoisomerization rate on the molecular structure. Adiabatic and diabatic models and the participation of TICT states have been discussed [7,12].

In this paper the photophysical and photochemical deactivation behaviour of the streptopolymethines **1a**–**4a** (**1a**, $n=1$, 1,3-bis(dimethylamino)trimethine; **2a**, $n=2$, 1,5-bis(dimethylamino)pentamethine; **3a**, $n=3$, 1,7-bis(dimethylamino)heptamethine; **4a**, $n=4$, 1,9-bis(dimethylamino)nonamethine) is discussed on the basis of a proposed energy scheme. These compounds possess substituents of small size and of negligible electronic effects. The absorption

1010-6030/95/$09.50
SSDI 1010-6030(95)04108-7

and emission spectra are characterized by only one band and, in contrast with the end groups of other polymethines, the methyl groups do not contribute qualitatively to the UV–visible spectra in the long wavelength region.

It is generally accepted that the different deactivation behaviour of streptopolymethines corresponds with their rotation barriers in ground and excited states. To estimate these rotation barriers, the structures of compounds **1a**–**4a** were optimized by an ab initio calculation at the HF/3-21G* level for the first time.

2. Experimental details

2.1. Synthesis

Dyes **1a**–**3a** were prepared by known methods [13]. The perchlorates were used for the investigations. In ethanolic solutions ($c = 10^{-3}$–10^{-6} mol l^{-1}) the salts are completely dissociated [14].

Dye **4a** was synthesized by a Vilsmeier reaction [13] starting with 0.1 mol octatrienal, prepared from 0.15 mol crotonic aldehyde and purified by vacuum distillation and multiple recrystallization of the sodium bisulphite adduct, and 0.15 mol of the Vilsmeier reagent (dimethylformamide–$POCl_3$). The obtained dimethylamino-nonatetraenal was isolated and dissolved in ethanol. An aqueous solution of dimethylamine (25%) was added to adjust the pH to 7.5. Subsequently the solution was acidified immediately with perchloric acid (1%) to pH 6. Compound **4a** was purified by column chromatography (silica gel, 1:1 methanol–ethanol) and recrystallization from dichloromethane; m.p. 106 °C (dec.). Yield of spectroscopically pure material, 1%. ^{1}H NMR (d_6-DMSO) δ: 3.11 (s, 12H, CH_3), 5.85 (dd, J 11.7 Hz, 2H, 2,8-H), 6.18 (dd, J 11.7 Hz, 2H, 4,6-H), 7.15 (t, J 11.7 Hz, 1H, 5-H), 7.21 (dd, J 11.7 Hz, 2H, 3,7-H), 7.58 (dd, J 11.7 Hz, 2H, 1,9-H). ^{13}C NMR (d_6-DMSO) δ: 39.6 (CH_3), 106.5 (C-2,8), 120.5 (C-4,6), 155.5 (C-5), 156.5 (C-3,7), 159.6 (C-1,9). UV–visible (ethanol) λ_{abs}^{max}: 614 nm (lg ϵ 5.36).

2.2. Instrumentation and spectroscopy

The UV–visible spectra were recorded on a U-3410 (Hitachi) spectrophotometer. For recording the fluorescence spectra, an MPF-2A (Hitachi–Perkin–Elmer) fluorescence spectrophotometer was used. The temperature was varied in the range 77–350 K using a cryostat. The NMR spectra were recorded on a Bruker AM 400 spectrometer. The degree of substitution of the carbon atoms was determined by DEPT 135° experiments.

The absolute fluorescence quantum yields φ_f were determined at 298 K by the relative method [15] using various standards (**2a**, anthracene, $\varphi_f = 0.27$; **3a**, IC 580, $\varphi_f = 0.94$; **4a**, cresyl violet, $\varphi_f = 0.54$). Taking into account the change in refractive index and concentration, the temperature-dependent quantum yields were referred to these values ϕ_f (298 K) [16].

The determination of the fluorescence decay times τ_f is described in Ref. [17]. For all linear plots (Arrhenius), least-squares adjustments were carried out.

2.3. Quantum chemical calculations

The rotation barriers were estimated by the rigid rotor approximation. In each case the double bond beside the symmetry centre was chosen. Points of the rotation curve were calculated from 0° to 90° in steps of 15°. The curves of excited streptopolymethines were ascertained by a CIS calculation at the 3-21G* level [18] and C_1 symmetry of the cations was used.

The optimization of Z isomers (**2b**, **2c**, **3b**–**3d**; see Table 2 below) was carried out at the HF/3-21G* level; the energy values were determined by MP2/6-31G* single-point calculations.

All structures were pre-optimized by semiempirical methods (PM3). All ab initio calculations were done with the GAUSSIAN 92 programme package [19].

3. Results

The streptopolymethines **1a**–**4a** show only one very strong absorption band in the UV–visible range (Fig. 1). The band maxima are described by a typical Koenig equation (Table 1, footnote a). The fluorescence band position (**2a**–**4a**) follows a Koenig equation too (Table 1, footnote b). The fluorescence of **1a** could not be detected, so the quantum yield must be lower than 10^{-4}. There is only a small influence of the solvent on the absorption and fluorescence maxima caused by dispersion interactions [5b].

The fluorescence quantum yields display a remarkable dependence on the temperature (Fig. 2) and it was shown that the respective values reach unity at low temperature (in all cases φ_f (77 K) ≈ 1, apart from the non-fluorescent **1a**).

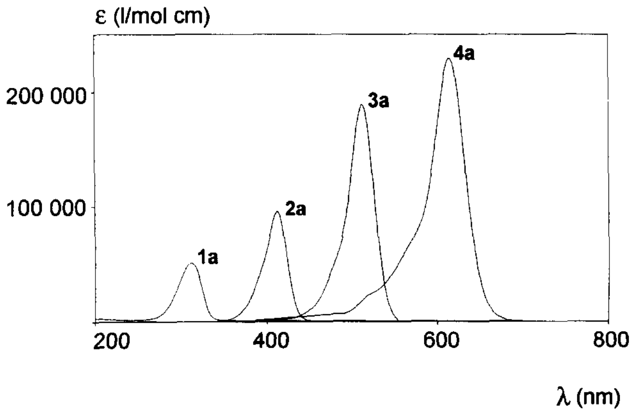


Fig. 1. UV–visible spectra of **1a**–**4a** in ethanol.

Table 1
Data of photophysical and photochemical deactivation (solvent ethanol)

	1a	**2a**	**3a**	**4a**
λ_{abs}^{max} (nm) [a]	310.5	411	512	614
λ_f^{max} (nm) [b]	365	440	543	656
$\Delta\tilde{\nu}$ (cm^{-1})	4809	1604	1115	1043
φ_f (298 K)	$<10^{-4}$	0.0028 ± 0.0004	0.020 ± 0.005	0.13 ± 0.02
φ_f (77 K)	$\ll 0.01$	≈ 1	≈ 1	≈ 1
τ_f (298 K) (ps)	[c]	10	36	320
k_f (298 K) (s^{-1})	[c]	2.8×10^8	5.6×10^8	4.1×10^8
E_A* (kJ mol^{-1})	[c]	10.5 ± 1	15 ± 2 [e]	7 ± 2
$k_d^{\neq}$ (s^{-1})	[c]	7×10^{12}	11×10^{12}	5×10^{10}
E–Z isomerization [d]	One isomer $\lambda_{abs} = 340$ nm	One isomer $\lambda_{abs} = 444$ nm	One isomer [e] $\lambda_{abs} = 542$ nm	Isomers between 77 and 298 K not observed

[a] $\lambda_{abs}^{max} = (210 + n \times 100.5)$ nm; 1,11-bis(dimethylamino)undecamethine, 716 nm.
[b] $\lambda_f^{max} = (222 + n \times 108)$ nm; without **1a** [c].
[c] Fluorescence intensity too low.
[d] 160 K.
[e] 2,3-Mono-cis (**3b**) [7], 3,4-mono-cis (**3c**) [8].

According to the equation

$$\ln(\varphi_f^{-1} - 1) = \ln\left(\frac{k_d^{\neq}}{k_f}\right) - \frac{E_A^*}{RT} \qquad (1)$$

the Arrhenius plots of $\ln(\varphi_f^{-1} - 1)$ vs. T^{-1} show straight lines (Fig. 2). The resulting values of E_A* and $k_d^{\neq}$ are listed in Table 1.

At room temperature the decay times of the fluorescence are in the picosecond range. The lifetimes increase with decreasing temperature. The rate constant of fluorescence, k_f, was calculated from

$$k_f = \varphi_f \tau_f^{-1} \qquad (2)$$

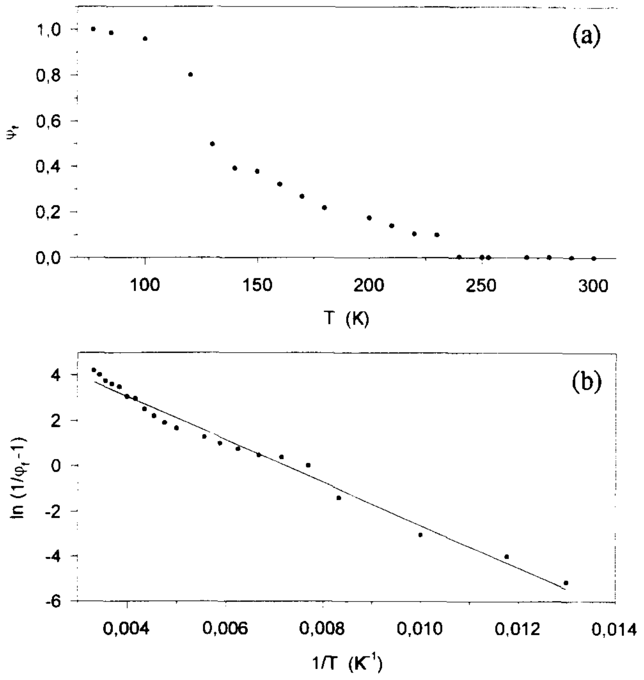


Fig. 2. (a) Temperature-dependent fluorescence quantum yield and (b) Arrhenius plot of **3a** in ethanol.

On irradiation of frozen (160 K) ethanolic solutions of **1a**, **2a** and **3a**, a photoreaction was observed characterized by the formation of a bathochromically absorbing isomer (shoulder in the UV–visible spectra, Table 1). Subsequent warming restores the spectra of the non-photolysed compounds. The behaviour of the irradiation spectra indicates the formation of the corresponding Z isomers. Below 156 K (solid ethanolic matrix) no E–Z isomerization was observed. In the case of **4a** no isomerization could be detected within the investigated temperature range.

4. Discussion

The results of the photophysical investigations show that at room temperature the deactivation of the singlet excited state of **1a**–**4a** occurs by fluorescence and radiationless transitions, including photochemistry (E–Z isomerization) and internal conversion (IC). The dependence of the fluorescence quantum yield on the temperature is a result of the competition between the fluorescence and the thermally activated IC process/isomerization. Apart from the fluorescence, no other temperature-independent deactivation process exists. No indication of the participation of triplet states was observed.

The mechanism of deactivation can be explained by the model of a thermally activated non-adiabatic photoreaction [20]. The potential energy diagram for the lowest electronic states of the investigated streptopolymethines shows the dependence of their energy on the angle of rotation on one C–C bond (Fig. 3). After absorption of a photon the singlet excited polymethine reaches, by twisting, the biradicaloid minimum (orthogonal geometry) on the hypersurface of S_1. Aside from **1a**, the transition from the excited S_1 Franck–Condon state to the 90°-twisted state ($k_d^{\neq}$) requires an activation energy (E_A*). At low temperature the fluorescence dominates; at room temperature the thermally activated change in the molecular structure is the main pathway of

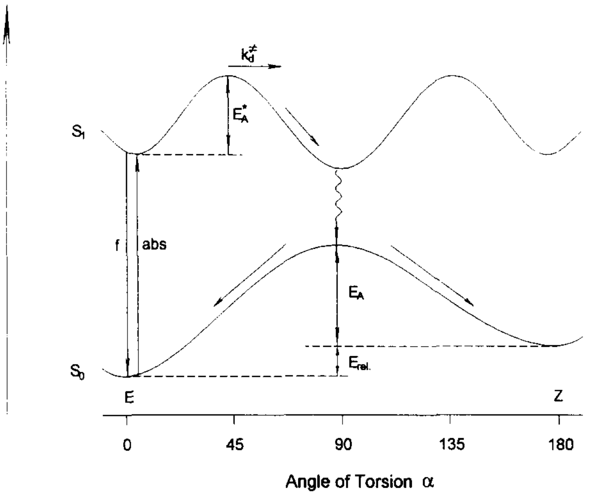


Fig. 3. Schematic energy curves and deactivation process.

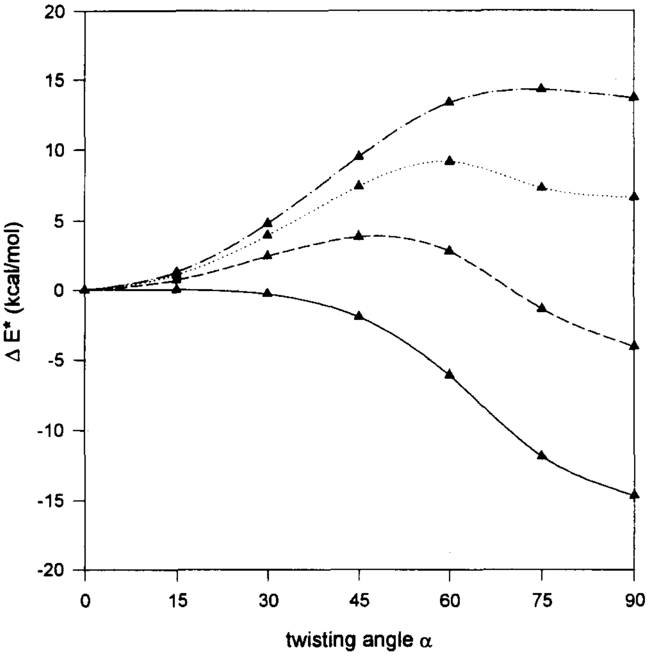


Fig. 4. Twisting energy of excited **1a**–**4a**: ——, **1a**; – – –, **2a**; · · · · ·, **3a**; –·–·–, **4a**.

deactivation. Since singlet–singlet transitions are allowed, the perpendicularly twisted S_1 state can return efficiently to the hypersurface of the S_0 state, forming E and Z isomers. At room temperature the Z isomers are unstable and isomerize to the corresponding E isomers because of the low activation barriers E_A. At low temperature the Z isomers are stable and experimentally detectable (Table 1) provided that the cooled solution is liquid. In a frozen solid matrix, isomerization does not occur.

To understand the differences between the deactivation parameters of the streptopolymethines **1a**–**4a**, the specific curves of the S_0 and S_1 states are calculated using an ab initio method. The potential curves of excited **1a**–**4a** (energy curves of S_1), shown in Fig. 4, indicate an increase in the rotation barrier with increasing length of the molecules. ΔE and ΔE^* describe the energy of the twisted state in relation to the planar S_0 and S_1 ($\alpha = 0°$) states respectively. In the case of excited **1a** the ab initio calculations demonstrate no activation barrier, in contrast with the longer vinylogous cations. This result corresponds well with experimental observation. Obviously **1a** relaxes very fast to the twisted state. There is no deactivation by fluorescence within the temperature range from 77 to 298 K. Just like in the case of **1a**, the calculated energy curves of **2a** and **3a** agree well with the experimental data. However, the activation energy $E_A{}^*$ of **4a** is lower than the experimentally determined value. For the ab initio calculation of $E_A{}^*$ (Fig. 4) the torsion of only one C–C bond was considered. Especially in the case of the longest vinylogous cation **4a** the activation energy of rotation of the different bonds will be very similar and a multiple E–Z isomerization [21] is probable. In this case at single excitation the simultaneous change in more than one twisting angle results in an energetically lower saddle point on the energy surface compared with the transition state of the energy curve shown in Fig. 4. The ab initio activation barriers of the ground states (E_A) show no significant dependence on the chain length (Fig. 5).

On low temperature photochemistry of the E isomers the formation of Z isomers was observed with the exception of **4a**. A discussion of the structure of these Z isomers is impossible on the basis of the experimental data. The reported analytical results [5a,9,10] are inconsistent. The calculation of the relative ab initio ground state energy of the possible Z isomers shows that different mono-Z isomers of very similar energy exist in the cases of the longer cations **3a** (presented in Table 2) and **4a**. The description of a thermodynamically favoured Z isomer is only possible for **2b**: 2,3-cis.

On irradiation of **4a** down to 160 K, Z isomers were not observed. For the explanation of this finding, two points are

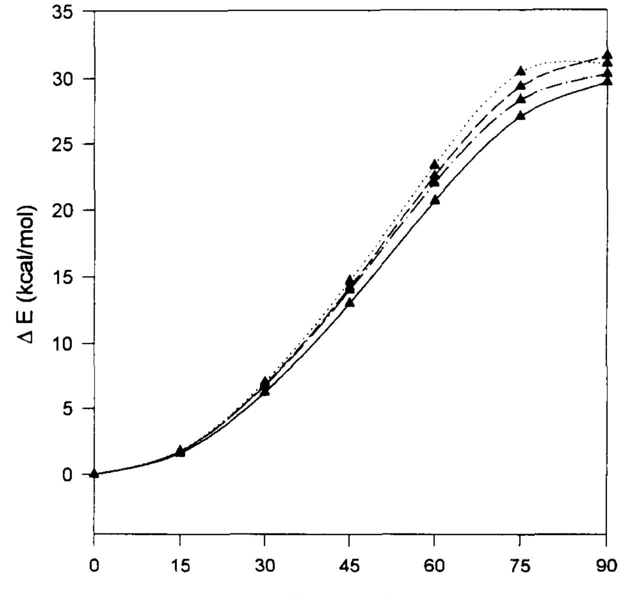
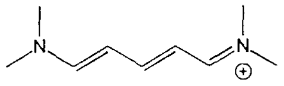
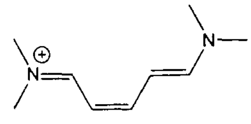
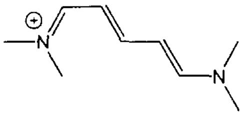
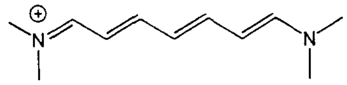
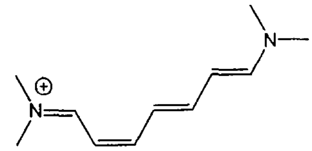
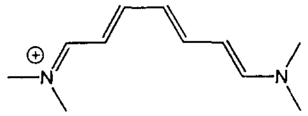
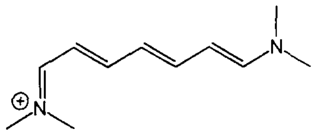


Fig. 5. Twisting energy of ground state **1a**–**4a**: ——, **1a**; – – –, **2a**; · · · · ·, **3a**; –·–·–, **4a**.

Table 2
Relative ab initio energies of **2a–2c** and **3a–3d**

	Formula	E_{rel} (kcal mol^{-1}) (MP2/6-31G*)/(HF-6-31G*)
2a		0
2b		3.96
2c		6.9
3a		0
3b		3.2
3c		3.5
3d		6.7

important: (i) the activation energy E_A of **4a** is too small for the generation of a detectable steady state concentration at $T \geq 160$ K; (ii) below 160 K the formation of Z isomers is hindered by the frozen solvent matrix. The reason for the small activation energy E_A of **4a** (ground state saddle point of low energy) is the multiple isomerization under the existence of some twistable bonds as discussed for the excited state behaviour and described generally by Sundahl et al. [21].

Acknowledgement

Support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

[1] S. Dähne, *Photogr. Sci. Eng.*, *23* (1979) 219; *J. Imag. Sci.*, *38* (1994) 101.

[2] M. Maeda, *Laser Dyes*, Academic, New York, 1984, p. 19.

[3] M. Emmelius, G. Pawlowski and H.W. Vollmann, *Angew. Chem., Int. Edn. Engl.*, *28* (1989) 1445.

[4] Y. Wang, *Chem. Phys. Lett.*, *128* (1986) 209; P.N. Prasad and D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991, Chap. 7; S. Kobayashi, *Mol. Cryst. Liquid Cryst.*, *217* (1992) 77.

[5] (a) J. Fabian and H. Hartmann, *Light Absorption of Organic Colorants*, Springer, Berlin, 1980, Chap. XII; (b) T. Harder and J. Bendig, *Chem. Phys. Lett.*, *228* (1994) 621.

[6] N.J.L. Roth and A.C. Craig, *J. Phys. Chem.*, *78* (1974) 1154.

[7] N. Tyutyulkov, J. Fabian, A. Mehlhorn, F. Dietz and A. Tadjer, *Polymethine Dyes — Structure and Properties*, St. Kliment Ohridski University Press, Sofia, 1991, Chap. VI.

[8] A.K. Chibisov, *J. Photochem.*, *6* (1977) 199.

[9] A. Werncke, A. Lau, M. Pfeiffer, H.-J. Weigmann, W. Freyer, J.T. Tschö and M.B. Kim, *Chem. Phys. Lett.*, *118* (1987) 133.

[10] H. Hartmann and P. Wähner, *Proc. 4th Symp. on Optical Spectroscopy, Reinhardsbrunn, 1986.*

[11] S. Rentsch, R.A. Gadonas and A. Piskarskos, *Chem. Phys. Lett.*, *104* (1984) 235.

[12] H. Ephardt and P. Fromherz, *J. Phys. Chem.*, *95* (1991) 6792; W. Rettig, *Top. Curr. Chem.*, *169* (1994) 253.

[13] W. König and W. Regner, *Ber. Dt. Chem. Ges.*, *63* (1930) 2813; W.T. Simpson, *J. Am. Chem. Soc.*, *71* (1949) 754; H.E. Nikolajewski, S. Dähne and B. Hirsch, *Chem. Ber.*, *100* (1967) 2616.

[14] J. Dale, R.G. Lichtenthaler and G. Teien, *Acta Chem. Scand.*, *33* (1979) 141.

[15] J.N. Demas and C.A. Crosby, *J. Phys. Chem.*, *75* (1971) 991.

[16] J. Bendig and M. Siegmund, *Z. Phys. Chem. (Lpz.)*, *262* (1981) 834.

[17] W. Becker, S. Dähne, K. Teuchner and K. Seliger, *Exp. Tech. Phys.*, *23* (1975) 297.

[18] J.J.P. Stewart, MOPAC v. 6.0, USAF Academy, Serena Software, Bloomington, IN.

[19] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart and J.A. Pople, GAUSSIAN 92, REVISION G.2, Gaussian, Inc., Pittsburgh, PA, 1992.

[20] P. Bruckmann and L. Salem, *J. Am. Chem. Soc.*, *98* (1976) 5073.

[21] M. Sundahl, O. Wennerström, K. Sandros and U. Norinder, *Tetrahedron Lett.*, *27* (1986) 106.