Photochemistry of heterocycles
XXIII.* Photophysical properties of substituted condensed isoxazolines

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Photophysical measurements of phenyl-, cyano-, and methoxycarbonyl--substituted condensed isoxazolines aimed at learning the properties of triplet states by quenching experiments with selected sensitizers and kinetics measurements of the quenching process are described. Phosphorescence spectra of some isoxazolines were measured ($E_T = 307—315 \, \mathrm{kJ \, mol^{-1}}$) and lifetimes ($\tau_T = 2—5 \, \mu s$) of probably $n_N—\pi^*$ triplet states determined.

В работе описаны фотофизические измерения R-замещенных конденсированных изоксазолинов, где R — фенил, циано или метоксикарбонилгруппа, с целью изучения свойств триплетных состояний и исследования процессов гашения в смеси с некоторыми сенсибилизаторами, а также кинетики процесса гашения. Были измерены фосфоресцентные спектры некоторых изоксазолинов ($E_T = 307—315 \, \mathrm{кДж \, моль^{-1}}$) и времена жизни триплетных, вероятнее всего, $n_N—\pi^*$ состояний ($\tau_T = 2—5 \, \mathrm{мкс}$).

Isoxazolines became recently increasingly popular as precursors of novel compounds, some of which even possessed biological activity [1]. Photochemical studies of isoxazolines revealed the importance of singlet excited state [2—5]. We have devoted this study to the so far rather neglected triplet state, addressing two principal questions — lifetime of the triplet state and its possible photochemical reactions. The studied nine isoxazolines possessed three different condensed skeletons, namely that of 7-R-3,4-bis(methoxycarbonyl)-9,10-dioxa--8-azatricyclo[4,3,0,1²,⁵]-7-decene (*I*), 3-R-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*II*), and 8-R-3,5,10-trioxa-9-azabicyclo[5,3,0]-8-decene (*III*), substituted in turn by phenyl (*a*), cyano (*b*), and methoxycarbonyl (*c*) group. Their preparation has been described in [6—9].

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* For Part *XXII* see Ref. [9].

Ia—Ic

E = COOCH₃

IIa—IIc

IIIa—IIIc

	a	b	c
R =	Ph	CN	COOCH₃
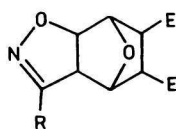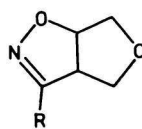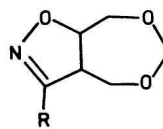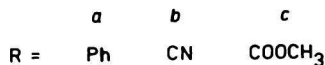
Experimental

Phosphorescence spectra of the isoxazolines prepared according to Ref. [6—9] were taken with the spectrometer, designed and built at the Technical University in Merseburg [10], and having an XBO 200 light source and SEV photomultiplier, of 1×10^{-2} M acetonitrile solutions. The home-made flash photolysis device used 7 kV flash voltage and was connected on line to the MC 80 computer of VEB Gera Elektronik, operated with BLIFO software for the first-order reactions. All measurements were performed in acetonitrile (Apolda, GDR), purified by a distillation with, in turn, P_2O_5, $KMnO_4$, and Na_2CO_3 and by subsequent rectification. For measurements only the fraction, having at $\lambda = 220$ nm more than 90 % transmittance, was used. Commercial sensitizers were twice crystallized before use.

Measurements of rate constants of phosphorescence quenching

The possible effect of isoxazolines *Ib*, *Ic*, *IIb*, and *IIIb* on the triplet state of benzophenone was examined under the following experimental conditions:

a) (0.5—10) $\times$ 10^{-5} M solutions in an acetonitrile—acetone mixture ($\varphi_r = 9:1$) kept under argon atmosphere, furnished $I_0/I = f$(isoxazoline concentration) plots (Fig. 1), when irradiated by the light with $\lambda = 350$ nm;

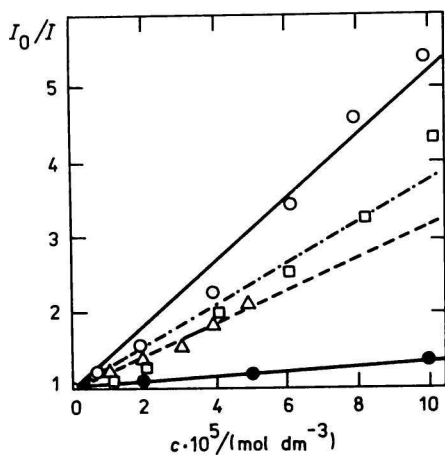Fig. 1. Quenching of the benzophenone phosphorescence. ○ Compound *Ib*, △ *Ic*, ● *IIb*, □ *IIIb*.

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b) benzophenone concentration was held constant at 5×10^{-3} mol dm^{-3};

c) the decrease of the intensity of the benzophenone phosphorescence was observed at the 0—0 transition.

Measurements of the rate constants of quenching k_q by means of flash photolysis

The effect of isoxazolines on the quenching of triplet states of a series of sensitizers (xanthone, benzophenone, Michler ketone, 4-phenylbenzophenone, and benzil) has been examined under the following conditions:

a) solutions were irradiated by a flash, generated by 7 kV voltage, WG-2 and UG-11 filters were used;

b) the following wavelengths were selected for the irradiation: 510 nm (benzophenone), 560 nm (xanthone), 500 nm (4-phenylbenzophenone), 475 nm (benzil), and 500 nm (Michler ketone);

c) $(0.5—10) \times 10^{-5}$ M solutions of isoxazoline in acetonitrile were irradiated under argon atmosphere;

d) concentrations of sensitizers were $c/(\text{mol dm}^{-3})$: 5×10^{-3} (benzophenone), 1×10^{-4} (xanthone), 5×10^{-3} (4-phenylbenzophenone), 1×10^{-4} (Michler ketone), 5×10^{-5} (benzil).

Calculated k_q values are given in Table 1.

Table 1

Measured constants of compounds *I—III*

Compound	λ^p_{max} nm	E_T kJ mol^{-1}	k_q 10^{-9a}	k_q 10^{-9b} dm^3 mol^{-1} s^{-1}	k_q 10^{-9c}	τ_T μs
Ia	387	309		0.52	0.11	5 ± 1
Ib	385	311	4.1	1.4		
Ic	*d*		1.7		1.1	2 ± 1
IIb	385	311	0.40			
IIc	387	309				
IIIa	385	311				5 ± 1
IIIb	380	315	3.3		0.89	2 ± 1
IIIc	390	307				

a) Values obtained from experiments with the quenching of benzophenone triplet state; *b*) values obtained from the quenching of benzophenone triplet state; *c*) values obtained from the quenching of xanthone triplet state; *d*) no phosphorescence observed.

Measurements of lifetime of isoxazoline triplet states τ_T

a) Measured were 0.01 M acetonitrile solutions of isoxazolines, kept under argon;

b) E_0 and τ_T values were determined at wavelengths of 400—600 nm and for the triplet state lifetime the τ_T value at maximal E_0 was taken (Fig. 2).

Measured triplet lifetime values are given in Table 1.

Results and discussion

As can be seen from the measured phosphorescence spectra (Table 1) of isoxazolines *I—III*, they lack the vibronic structure but indicate clearly an observable, probably an n_N—π^*, triplet state. Triplet states of compounds *Ic—IIIc*, containing a carbonyl group, can also have an n_0—π^* character, those of phenyl-substituted derivatives *Ia—IIIa* a π—π^* character. Emission bands representing the transitions from the respective triplet states have been observed in the region of $\lambda = 380$—390 nm. Triplet energies, determined from the phosphorescence emissions measured in acetonitrile at 25 °C, were approximately $E_T = 307$—315 kJ mol^{-1} The intensity, but not the position, of the phosphorescence emission bands was influenced by either substituents or character of the condensed skeleton (Table 1). Under experimental conditions compounds *Ic* and *IIa* showed no phosphorescence at all.
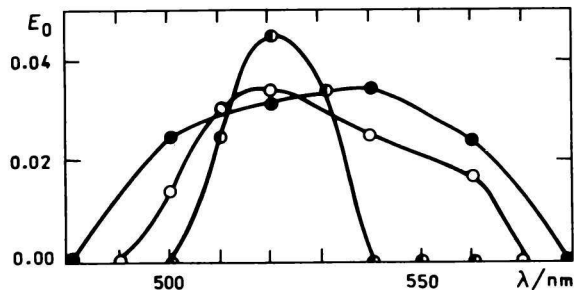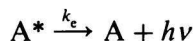

Fig. 2. Visible spectrum of the triplet state of *Ic* (○), *IIIa* (●), *IIIb* (◉).
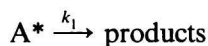
Phosphorescence quenching experiments were evaluated by means of Stern——Volmer plots [11], according to the following equations

$$\frac{\Phi_e^o}{\Phi_e} = \frac{k_e}{k_e + k_1} \frac{k_1 + k_e + k_q[Q]}{k_e} = 1 + k_q \tau_A [Q]$$

for the reaction

$$A^* \xrightarrow{k_e} A + h\nu$$

where k_e is the rate constant of emission from A* and for the reaction

$$A^* \xrightarrow{k_1} \text{products}$$

where k_1 is the rate constant of the conversion of A*, and using the modified formula

$$\frac{I_0}{I} = 1 + k\,[Q]$$

whereby $k = k_q \tau_T$ and [Q] is the concentration of the quencher, k_q quenching rate constant, τ_T lifetime of the quenched triplet state, in our case that of the benzophenone triplet $- (9 \pm 1) \times 10^{-6}$ s, *i.e.* in accordance with the literature [11].

The obtained linear plots $I_0/I = f([Q])$ are depicted in Fig. 1, calculated k_q values of benzophenone phosphorescence quenching are given in Table 1. In an analogous manner, we have calculated k_q values for benzophenone (or xanthone) isoxazoline pairs from the measured values of extinction E_0, obtained by means of flash photolysis. The obtained k_q values fall in the range of 1.1×10^8—4.1×10^9, indicating an energy transfer

$$\text{SENS}(T_1) + \text{ISOX}(S_0) \quad \longrightarrow \quad \text{SENS}(S_0) + \text{ISOX}(T_1)$$
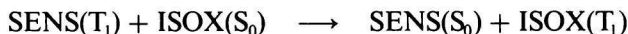
and excluding the possible hydrogen transfer from an isoxazoline radical to the sensitizer, since in such instance the k_q value for the process

$$\text{SENS}(T_1) + \text{ISOX—H} \quad \longrightarrow \quad \cdot\text{SENS—H} + \text{ISOX}\cdot$$
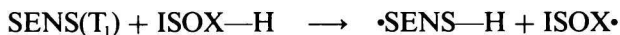
would have been expected to fall in the range of 10^5—10^6 s^{-1}

Quenching experiments with sensitizers, such as benzil ($E_T = 224.7\,\text{kJ mol}^{-1}$), 4-phenylbenzophenone ($E_T = 259\,\text{kJ mol}^{-1}$), Michler ketone ($E_T = 263.6\,\text{kJ mol}^{-1}$) failed to reveal any phosphorescence quenching. These data, combined with those, obtained from quenching with xanthone ($E_T = 309\,\text{kJ mol}^{-1}$) and benzophenone ($E_T = 284\,\text{kJ mol}^{-1}$) allowed us to locate triplet energies of the measured isoxazolines in the range of 270—315 kJ mol^{-1}

Measurements of visible spectra and lifetimes of isoxazoline triplet states indicated a short triplet lifetime on the order of 2—5 µs. Attempts to obtain products from photochemical reactions of triplet states gave only intractable tars, no products known from experiments with singlet states could be obtained [6—9]. We could nevertheless give an affirmative answer to one of our primary questions, concerning observability of the triplet states of the condensed isoxazolines.

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