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Laser photolysis of 1-(4-nitrophenyl)-3-methylpyrazole and 1-ethyl-3-(4-nitrophenyl)-5-chloropyrazole

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The spectral kinetic characteristics of the triplet states of 1-(4-nitrophenyl)-3-methylpyrazole (**1**) and 1-ethyl-3-(4-nitrophenyl)-5-chloropyrazole (**2**) were studied by the laser nanosecond photolysis technique in different solvents. The triplet lifetimes (τ_T) of molecules **1** and **2** were found to depend strongly on the solvent nature. An increase in τ_T by approximately two orders of magnitude on going from nonpolar and polar aprotic solvents ($\tau_T \leq 15$ ns) to aqueous-acetonitrile solutions ($\tau_T = 1100$ ns for a volume acetonitrile to water ratio of 1 : 3) was analyzed, taking into account the influence of the medium on the relative contribution of the n,π*- and π,π*-configurations to the lowest triplet state.

Key words: 1-(4-nitrophenyl)-3-methylpyrazole, 1-ethyl-3-(4-nitrophenyl)-5-chloropyrazole, nanosecond laser photolysis, triplet states, lifetime, solvent effect.

The reactivity of triplet states of aromatic compounds depends, to a great extent, on the nature of the lowest triplet state (n,π* or π,π*).[1] The deactivation rate constant of the triplet state in the absence of specially introduced quenching agents ($k_T = 1/\tau_T$) is an important parameter, which determines the efficiency of photochemical transformation.[1] Nitroaromatic compounds have a specific feature: their lowest n,π*-triplet states in liquid solutions at room temperature are very short-lived.[2—5] For instance, the nonradiative deactivation rate constant of the ^{3}(n,π*)-state of nitrobenzene is[2] 10^9 s^{-1}. The k_T values of the ^{3}(π,π*)-states are much lower. For example, for nitronaphthalene, whose lowest triplet state has the ππ*-character, $k_T < 4 \cdot 10^5$ s^{-1}.[2] Therefore, we can expect that, in the case of the nitro compounds with close energies of the ^{3}(π,π*)- and ^{3}(n,π*)-configurations, their insignificant mixing would change the reactivity of the lowest triplet state due to a change in its nature and also to a substantial change in its lifetime.

It is known[6,7] that electron-donor substituents stabilize ππ*-triplets and can result, in several cases, in the inversion of the low-energy ^{3}(π,π*)- and ^{3}(n,π*)-levels. One of a few known examples of nitroaromatic compounds with close in energy n,π*- and ππ*-triplet states is 3-nitroanisole, which exhibited a considerable (approximately 100-fold) elongation of the lifetime on going from acetonitrile to aqueous solutions.[8]

In this work, the nanosecond laser photolysis technique was used to study the properties of the triplet states of 1-(4-nitrophenyl)-3-methylpyrazole (**1**) and 1-ethyl-3-(4-nitrophenyl)-5-chloropyrazole (**2**), which have the push-pull structure D—Ar—NO$_2$ bearing the pyrazole fragment as an electron donor. As shown below, the presence of a moderately electron-donor fragment provides a decrease in the energy of the ^{3}(π,π*)- and ^{3}(n,π*)-levels in these molecules and a noticeable influence of the medium nature on the spectral kinetic characteristics of their triplet states.

Experimental

All solvents (99.9%, Merck) were used without additional purification. Water was subjected to two-step distillation.

Spectrophotometric measurements were carried out with a Perkin—Elmer Lambda 35 spectrophotometer.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX-400 instrument (400.6 Mhz) in DMSO (HMDS as an internal standard). IR spectra were obtained with an IFS-25 spectrophotometer in KBr pellets.

A sample was excited in nanosecond laser photolysis experiments with an AIL-3 N$_2$ laser (λ = 337.1 nm, pulse energy 3 mJ, pulse duration at the half-width 7 ns). The experimental setup has been described earlier.[10]

Oxygen was removed from solutions by argon bubbling for 20 min.

Compound **1** was synthesized as described earlier.[9] Found (%): C, 59.15; H, 4.43; N, 20.70. $C_{10}H_9N_3O_2$. Calculated (%): C, 59.11; H, 4.46; N, 20.68. IR, ν/cm^{-1}: 3145, 3120, 3085, 3055 (=C—H); 1600 (C=N); 1595 (C=C); 1535, 1320 (NO$_2$). ^{1}H NMR, δ: 8.62 (d, 1 H, C(5)H, *J* = 2.3 Hz); 8.36 (d, 2 H, C(3´)H, C(5´)H, *J* = 7.9 Hz); 8.08 (d, 2 H, C(2´)H, C(6´)H, *J* = 7.9 Hz); 6.50 (s, 1 H, C(4)H, *J* = 2.3 Hz).

Compound **2** was synthesized from 2,2-dichlorovinyl 4-nitrophenyl ketone (2.46 g, 0.01 mol) and ethylhydrazine

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(0.6 g, 0.01 mol) in the presence of Et_3N (1.01 g, 0.01 mol) in EtOH (15 mL). After the end of the exothermic reaction, the reaction mixture was stirred for 4 h and poured into water. The precipitate formed was filtered off, washed with water, dried, and recrystallized from EtOH. The yield was 2.15 g (91%), m.p. 116—117 °C. Found (%): C, 52.50; H, 4.00; Cl, 14.09; N, 16.70. $C_{11}H_{10}ClN_3O_2$. Calculated (%): C, 52.03; H, 4.20; Cl, 14.05; N, 16.65. IR, ν/cm^{-1}: 3140, 3070 (=CH); 2990, 2960, 2940 (C_2H_5); 1600 (C=N); 1490 (C=C); 1510, 1340 (NO_2); 770 (C—Cl). ^{1}H NMR, δ: 8.26 (d, 2 H, C(3´)H, C(5´)H, J = 8.1 Hz); 8.04 (d, 2 H, C(2´)H, C(6´)H, J = 8.1 Hz); 7.13 (s, 1 H, C(4)H); 4.24 (d, 2 H, NCH_2, J = 7.2 Hz); 1.38 (t, 3 H, Me, J = 7.2 Hz). ^{13}C NMR, δ: 147.63 (C(4´)); 146.63 (C(3)); 138.64 (C(4)); 127.10 (C(5´)); 125.62 (C(3´)); 124.00 (C(2´)); 103.22 (C(1)); 44.21 (CH_2); 14.62 (CH_3).

Results and Discussion

The electronic absorption spectra of compounds **1** and **2** in *n*-hexane and acetonitrile are shown in Fig. 1. The longest-wave absorption bands in the spectra of **1** and **2** (ε ~20000 L mol^{-1} cm^{-1}) undergo bathochromic shifts with an increase in the solvent polarity (Table 1). The change in the shape, character, and value of the shift of the solvatochromic band confirm the polar structure of the compounds under study and indicate that their dipolar moments increase upon excitation.

Table 1. Solvent effect on the position of the solvatochromic absorption band of compounds **1** and **2**

Solvent	λ_{max}/nm	
	1	**2**
n-Hexane	321.0*	304.4*
Dibutyl ether	322.6	310.6
BuOH	325.7	314.5
EtOH	325.2	314.5
AcOEt	327.9	314.5
MeOH	322.6	315.5
MeCN	330.6	319.5
DMSO	337.8	325.7
MeCN—H_2O (1 : 1)	327.9	317.5

* The absorption band has a vibrational structure.

Pulse photoexcitation (λ = 337.1 nm) of compounds **1** and **2** in organic solvents in the region of their long-wave absorption bands induces short-lived products, whose spectra contain broad bands at 400—650 nm (Figs 2 and 3). In the case of solutions of **2** in EtOH and MeOH, the decay kinetics of these products obeys a law of the first order with rate constants of $3.37 \cdot 10^7$ and $1.42 \cdot 10^7$ s^{-1}, respectively. The character of the decay kinetics and the k_T value are independent of the wavelength of a probing light, which indicates that absorbing species of only one type are generated in each solvent. Under similar conditions, the lifetimes of the products formed by the photoexcitation of **1** are close to the apparatus time resolution (~15 ns) and, hence, their precision measurement is impossible. The products formed by laser photolysis of solutions of **1** and **2** in aprotic inert and aprotic protophilic media also have very short lifetimes ($\leq$15 ns). The k_T values (except those in MeOH) remain unchanged when oxygen

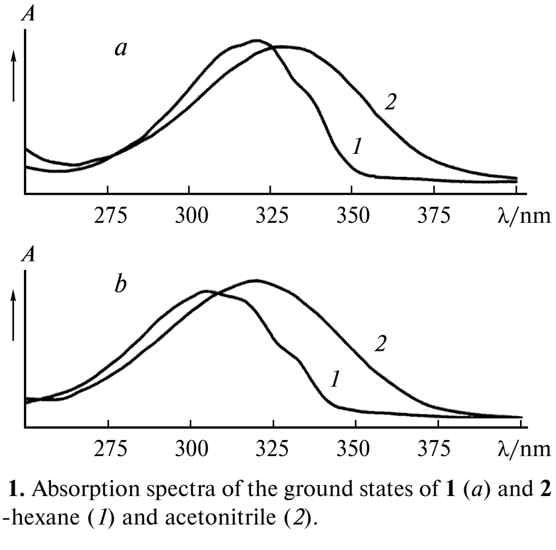

Fig. 1. Absorption spectra of the ground states of **1** (*a*) and **2** (*b*) in *n*-hexane (*1*) and acetonitrile (*2*).

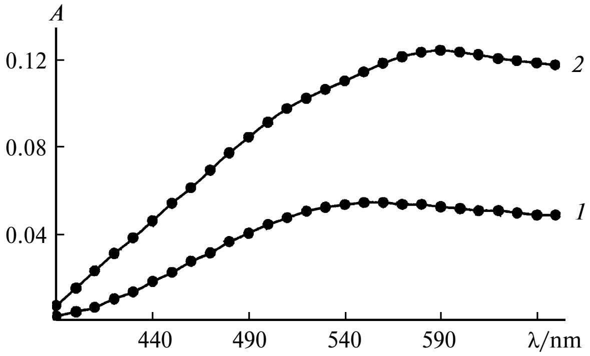

Fig. 2. Absorption spectra of the short-lived products measured immediately after the photoexcitation of solutions of **1** (~10^{-4} mol L^{-1}) in acetonitrile (*1*) and ethanol (*2*).

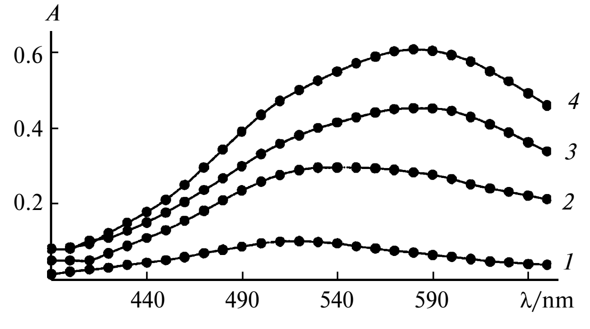

Fig. 3. Absorption spectra of the short-lived products measured immediately after the photoexcitation of solutions of **2** (~10^{-4} mol L^{-1}) in ethyl acetate (*1*), acetonitrile (*2*), ethanol (*3*), and methanol (*4*).

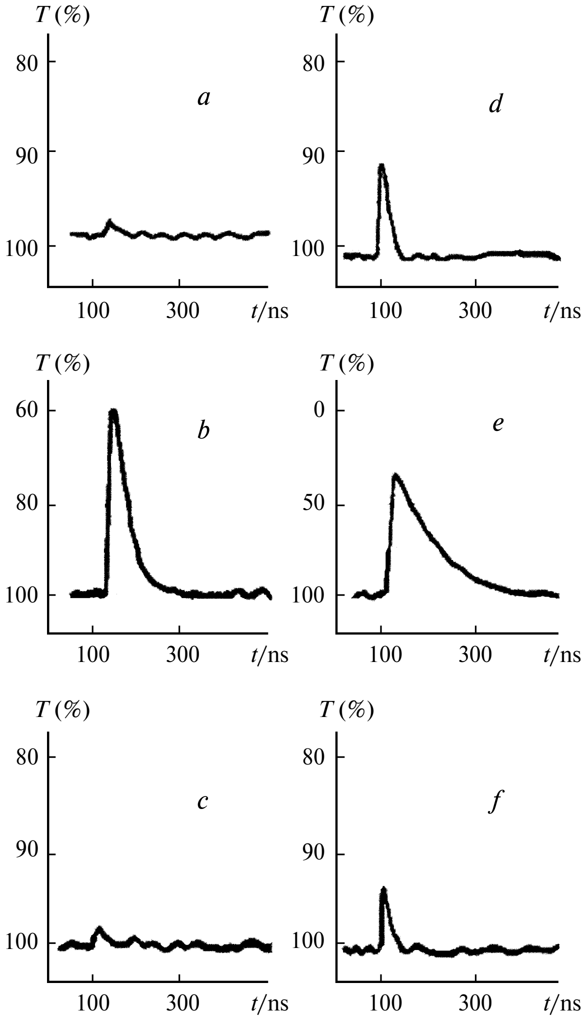

Fig. 4. Oscillograms of transmission changes in maxima of the absorption bands of the short-lived products of **1** (*a—c*) and **2** (*d—f*) in ethyl acetate (*a*, *d*), methanol (*b*, *e*), and DMSO (*c*, *f*).

is removed from solutions. The oscillograms (Fig. 4) demonstrate the influence of the solvent nature on the decay kinetics of the short-lived products of the compounds under study.

The monoexponential decay of the photolysis products of **2** in EtOH and MeOH, a decrease in k_{T} in a methanolic solution of **2** upon air removal, and similarity of the induced absorption spectra of **1** and **2** make it possible to assign (with a high probability) the short-lived products formed by the excitation of **1** and **2** to the triplet states of these compounds. They cannot be assigned to singlet-excited states because of the very short lifetime of the singlet states of the nitroaromatic compounds (~10^{-12} s).[11] At the same time, it is known that the n,π^*-triplet states of the nitro compounds have lifetimes of an order of several nanoseconds.[4] On the contrary, τ_{T} of the π,π^*-triplet states lie in the microsecond time interval.[6,11] Taking into account the obtained short lifetimes of the triplets (29 and 70 ns for **2** and $\leq$15 ns for **1**), we can assume that the latter are mainly of the n,π^*-type but some contribution of the π,π^*-state cannot be excluded completely. This situation is discussed, for example, for the triplet state of 3-nitroanisole in acetonitrile with τ_{T} of 26 ns ($k_{\mathrm{T}} = 3.8 \cdot 10^7$ s^{-1}), since the generation of singlet oxygen by nitroanisoles and nitroveratrole is efficient.[8]

The lifetimes of the triplet states of **1** and **2** obtained from the oscillograms are shown in Table 2. The empirical parameters of solvents π^* (a measure of the ability of a medium to stabilize dipoles) and α (a measure of the ability of a medium to act as a hydrogen bond donor) are used as characteristics of the medium polarity.[12] The absorbances in maxima of the absorption bands reached under the experimental conditions are also presented in Table 2. The starting solutions for all solvents had the same absorbances at the excitation wavelengths in order

Table 2. Influence of the properties of the solvent on τ_{T} and maximally achieved absorbances (*A*) of the triplet states of **1** and **2**

Solvent	α^a	π^{*a}	**1**		**2**	
			τ_{T}/ns	A^b	τ_{T}/ns	A^b
n-Hexane	0.00	−0.08	$\leq$15	$\leq$0.004	$\leq$15	0.016
AcOEt	0.00	0.55	$\leq$15	0.009	$\leq$15	0.170
ДМСО	0.00	1.00	$\leq$15	0.012	$\leq$15	0.053
MeCN	0.19	0.75	$\leq$15	0.127	30	0.513
EtOH	0.83	0.54	$\leq$15	0.371	40	0.786
MeOH	0.93	0.60	30	0.435	70	0.870
MeCN—H_2O (3 : 1, vol/vol)	—	—	120	0.813	260	1.000
MeCN—H_2O (1 : 1, vol/vol)	—	—	560	0.813	630	1.000
MeCN—H_2O (1 : 3, vol/vol)	—	—	1100	0.813	1100	1.000

[a] For the parameter values, see Ref. 12.

[b] The absorbance in the T—T absorption maximum of compound **2** in a MeCN—H_2O (1 : 3, vol/vol) mixture is accepted as unity.

to provide the equal amount of light absorbed by the ground state.

It is seen for compound **2** (see Fig. 4, Table 2) that τ_T increases sharply on going from the group of solvents, which are not hydrogen bond donors (α = 0), *viz.*, *n*-hexane, ethyl acetate, and DMSO, to proton-donor solvents, *viz.*, ethanol (α = 0.83), methanol (α = 0.93), and acetonitrile (α = 0.19), being a weak hydrogen bond donor. For **1** (see Fig. 4), when the time resolution is restricted, this conclusion can be drawn only indirectly, by a comparison of a change in the absorbances on going from aprotic to proton-donor solvents (see Table 2). As in the case of compound **2**, they increase considerably. Therefore, the main factor responsible for the increase in the absorption intensity is, most likely, an increase in the lifetime of the triplet state.

The data on the influence of nonspecific and specific interactions on τ_T of compounds **1** and **2** indicate that the energy gap between the two lowest in energy n,π*- and π,π*-triplet states in these molecules is rather small. The short lifetime in *n*-hexane and, as a consequence, the low T—T-absorption intensity are caused by the n,π*-character of the lowest triplet state in molecules **1** and **2**. Probably, polar aprotic solvents weakly stabilize π,π*-triplets. In protic media, the nature of the lowest triplet state is determined by different abilities of the π,π*- and n,π*-triplets to form hydrogen bonds with a solvent. A strong stabilization of the π,π*-triplet state due to the hydrogen bond formation results in bringing together the π,π*- and n,π*-states and an increase in the degree of their mixing due to the electron-vibrational interaction. An increase in the contribution of the π,π*-triplet state is accompanied by an increase in τ_T on going from aprotic to proton-donating media.

It can be expected that the π,π*-triplet states become the lowest in energy on going from alcohols to more proton-donor media. We obtained the kinetic and spectral characteristics of the triplet states of **1** and **2** in aqueous-acetonitrile solutions at different volume acetonitrile to water ratios (the Kamlet—Taft parameter for H_2O is α = 1.17). Already in an aqueous-acetonitrile (1 : 3, vol/vol) mixture, τ_T tenfold exceeds τ_T for **2** in a methanolic solution. For a volume water to acetonitrile ratio of 3 : 1, τ_T of compound **2** reaches the microsecond range, which is characteristic of the π,π*-triplets of the nitroaromatic compounds (Fig. 5, see Table 2). A considerable increase in τ_T in aqueous-acetonitrile solutions is also observed for **1**, as compared to the lifetimes of its triplet states in organic solvents (see Table 2). The τ_T values obtained for **1** and **2** show that an increase in the volume water content enhances the π,π*-character of the lowest triplet states of these compounds, which becomes predominant in an aqueous-acetonitrile mixture (volume ratio 3 : 1). The T—T-absorption spectra of **1** and **2** in an aqueous-acetonitrile mixture are presented in Fig. 6.

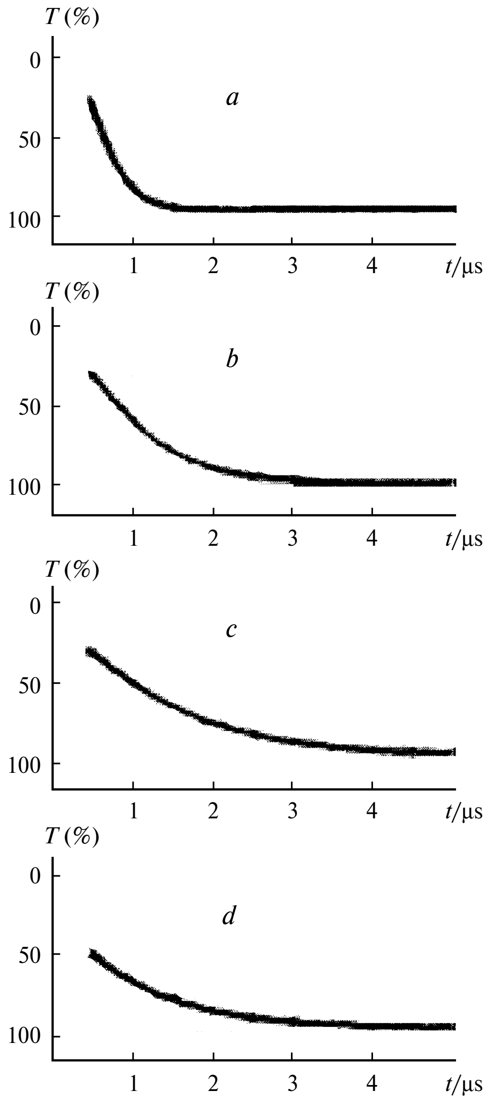

Fig. 5. Oscillograms of transmission changes in maxima of the absorption bands of the short-lived products of **2** (*a*—*c*) in aqueous-acetonitrile solutions with the volume ratio 1 : 3 (*a*), 1 : 1 (*b*), and 3 : 1 (*c*) and an aqueous-acetonitrile (3 : 1, vol/vol) solution of **1** (*d*).

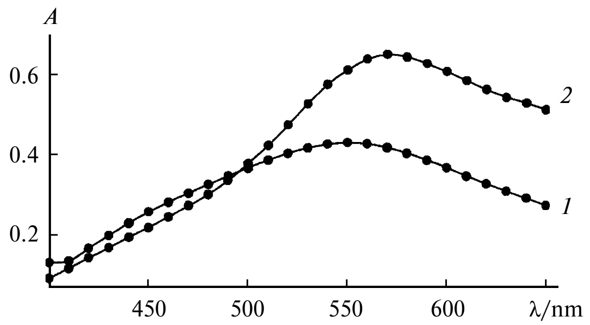

Fig. 6. Absorption spectra of the short-lived products measured immediately after the photoexcitation of ~10^{-4} *M* aqueous-acetonitrile (1 : 1, vol/vol) solutions of **1** (*1*) and **2** (*2*).

Thus, the elongation of the lifetime of the triplet states of the compounds under study by approximately two orders of magnitude on going from nonpolar and polar aprotic media ($\tau_T \le 15$ ns) to proton-donor solvents ($\tau_T \approx$ 1 μs) indicates a change in the nature of their lowest triplet state from predominantly n,π* to predominantly π,π*. These results enable one to predict a relatively low efficiency of the photoreduction of compounds **1** and **2** in both nonpolar and polar aprotic solvents and in media with a significant ability to act as hydrogen bond donors (in the first case, due to the short lifetime of the reactive n,π*-triplet state, while in the second case, because of the nonreactive lowest π,π*-triplet state). The highest efficiency of photoreduction of **1** and **2** should be expected in solvents with an optimum ratio between the orbital nature of the lowest triplet state and its lifetime.

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