Intra- and intermolecular quenching of carbazole photoluminescence by imidazolidine radicals

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Mechanisms of carbazole photoluminescence quenching by the free and chemically bound nitroxyl radicals in the model bound system "carbazole (CBZ)—imidazolidine nitroxyl radical $R^{\cdot}$" were investigated and the photophysical properties of the system were studied and compared with those of free CBZ and $R^{\cdot}$ in solution. The quantum yield and lifetime of fluorescence from the local singlet excited state of the carbazole moiety in the bound CBZ—$R^{\cdot}$ system is three orders of magnitude lower than in free CBZ. The lifetime of the local triplet excited state of the carbazole moiety in the bound system is shorter than 50 ns. The rate constants for intermolecular quenching of the singlet and triplet excited states of free CBZ by $R^{\bullet}$ in acetonitrile were found to be $(1.4\pm0.1)\cdot10^{10}$ and $(1.5\pm0.2)\cdot10^{9}$ L mol^{-1} s^{-1}, respectively. The most plausible mechanisms of both free and covalently bound carbazole luminescence quenching by nitroxyl radicals are exchange energy transfer and acceleration of internal conversion due to electron exchange.

Keywords: spin-labeled luminophores, laser flash photolysis, fluorescence quenching.

Spin catalysis of chemical reactions by paramagnetic species occurs in triads of paramagnetic species where spin conversion in a pair of species is initiated by the third electron spin.[1,2] This phenomenon was experimentally confirmed for a number of photochemical, biochemical, and radiation-chemical systems.[3—5] The third spin plays the role of the source of external magnetic field in which a spin-correlated radical pair created in some (*e.g.*, radiation-chemical) way is placed. Systematic research on spin catalysis requires some model compounds comprising a paramagnetic fragment bound to a partner from the radical pair.

In this connection, spin-labeled luminophores are of particular interest. Theoretical calculations predict a number of interesting effects in radiation processes involving them.[6] However, in most cases the paramagnetic center acts as an efficient quencher of the luminescence of such compounds.[4,7—9] It should be noted that it was proposed to use the reverse effect, *viz.*, the rise of the luminescence of fluorophore—nitroxide radical dyads due to reduction of the nitroxide group, for the design of sensors for the superoxide radical, antioxidants, hydrogen peroxide in biological systems,[10] and for alkyl radicals in polymers.[11]

The accelerated internal conversion proceeding by the electron exchange mechanism is the main quenching mechanism of the fluorescence of chemically bound systems "luminophore—nitroxide radical".[7,8] However, some other mechanisms of quenching in these systems were proposed, *e.g.*, acceleration of intersystem crossing (ISC) from the excited singlet to triplet state.[7] These assumptions are based on the fact that quenching of singlet states of luminophores by free (chemically unbound) nitroxide radicals (this process has been studied in more details) can follow all known channels including energy transfer,[12,13] electron transfer,[14] ISC,[15,16] and internal conversion[14,16,17] (in particular, by the vibrational relaxation mechanism[15]). The contribution of each quenching channel is determined by the properties of particular systems.

In the framework of a program of design of model three-spin systems for spin catalysis, in this work we used the reaction of 4-bromomethyl-2,2,3,5,5-pentamethylimidazolidine 1-oxyl (**1**) with carbazole (CBZ) to synthesize 4-(carbazol-5-yl)methyl-2,2,3,5,5-pentamethylimidazolidine 1-oxyl (**2**, CBZ—$R^{\cdot}$) (Scheme 1). The photophysical properties of system **2** were studied and compared with those of carbazole and a mixture of car-

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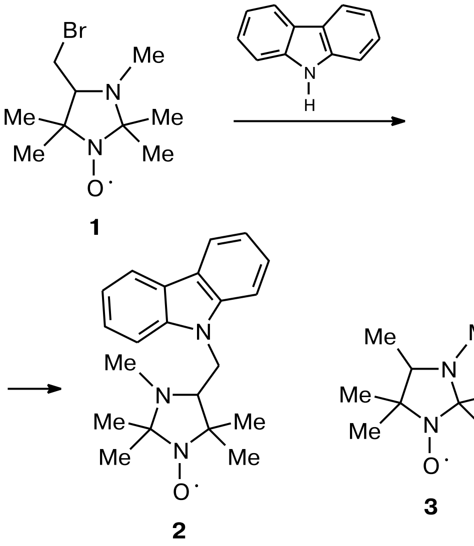
bazole and stable radical **3** (2,2,3,4,5,5-hexamethylimidazolidine 1-oxyl, R$^{\cdot}$).

Scheme 1



Experimental

Electronic absorption spectra were measured on an Agilent 8453 spectrophotometer (Agilent Technologies). Steady-state luminescence spectra were recorded on a Hitachi MPF-4 spectrofluorimeter. Stationary photolysis was carried out using a DRSh-500 high-pressure mercury lamp and a number of glass filters to select light with the necessary wavelengths. Laser flash photolysis experiments were performed with a setup described earlier,[18] with excitation by the fourth harmonic of an YAG laser (excitation wavelength 266 nm, pulse duration 5—6 ns, pulse energy up to 10 mJ). The temporal resolution of the setup was a few hundreds of nanoseconds.

The reactants used were as follows: dioxane ("pure" grade) dried with KOH and distilled over metallic sodium; carbazole ("pure" grade) for photochemical experiments was additionally purified by recrystallization from hexane; acetonitrile ("analytical pure" grade, Cryochrome); silica gel (Merck); ethyl acetate; hexane; and Et_2O ("pure" grade). When needed, oxygen was removed from the samples by bubbling with argon. Radicals **1** (see Ref. 19) and **3** (see Ref. 20) were synthesized following known procedures. The synthesis and physicochemical properties of compound **2** are described below. By and large, the synthetic procedure corresponds to a general approach of base catalysis for hydrogen substitution reactions in a heteroaromatic ring.

Compound 2. A mixture of carbazole (100 mg) and NaH (50 mg) in anhydrous dioxane (5 mL) was stirred for 30 min at about 20 °C and then a solution of bromide **1** (150 mg) in dioxane was added dropwise with stirring over a period of 10 min. Stirring was continued for 24 h, excess NaH was quenched by adding EtOH (3 mL), the reaction mixture was diluted with water (15 mL) and extracted with $CHCl_3$ (3×15 mL). The combined extracts were dried with $MgSO_4$ and the solution was concentrated. Compound **2** was isolated by chromatography on a column with silica gel (hexane—Et_2O, 2 : 1). The yield was 100 mg (40%), m.p. 163—164.5 °C (hexane—ethyl acetate). Found (%): C, 74.57; H, 7.63; N, 12.5. $C_{21}H_{26}N_3O$. Calculated (%): C, 74.97; H, 7.79; N, 12.49. UV spectrum (MeCN), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 236 (60300), 261 (26000), 292 (20600), 329 (4740), 342 (5640). EPR spectrum (hexane): $a_N = 14.04$ G; $a_H = 0.19$ G; $a_{^{13}C} = 5.99$ G; $g = 2.0036$.

Results and Discussion

UV spectra and luminescence spectra of compounds under study. The molecule of compound **2** synthesized in this work contains two relatively weakly interacting fragments of an *N*-substituted carbazole (CBZ) moiety and of the nitroxide radical **3** (R$^{\cdot}$). This follows from a comparison of the UV spectra of CBZ, CBZ—R$^{\cdot}$, and R$^{\cdot}$ (Fig. 1, *a*). The spectral pattern of CBZ—R$^{\cdot}$ is almost identical to that of CBZ; however, all absorption bands undergo a bathochromic shift of 2 to 8 nm; also, they are 20—40%

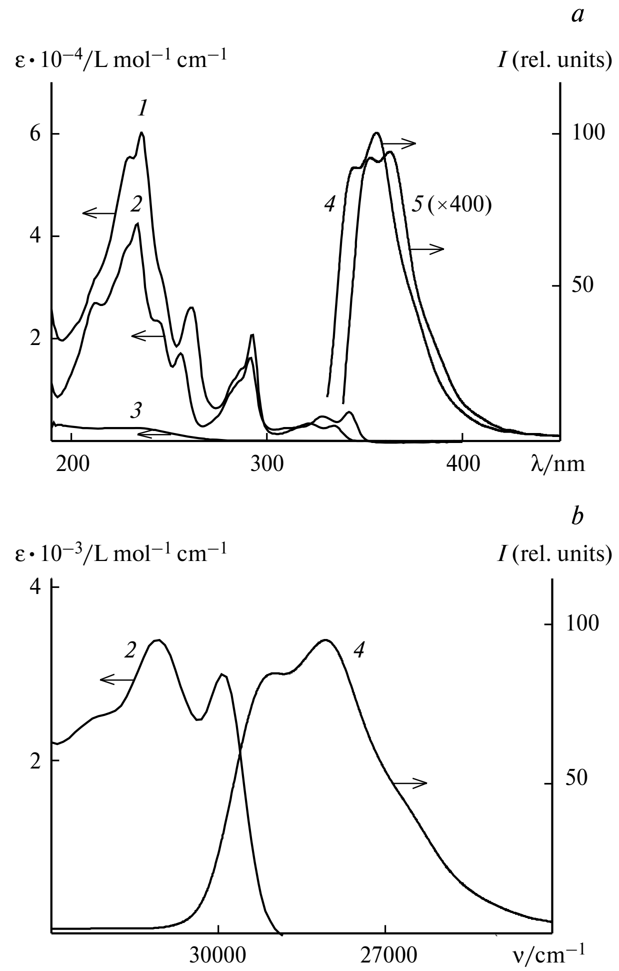


Fig. 1. *a*. Absorption spectra of compound **2** (*1*), CBZ (*2*), **3** (*3*) and luminescence spectra of carbazole (*4*) and **2** (*5*) in MeCN; *b*. Fragments of absorption spectra (*2*) and luminescence spectra (*4*) of carbazole in the crossing region on a commeasurable scale.

more intense. In the near-UV region, the radical R$^{\cdot}$ exhibits a weak absorption band with a maximum near 420 nm ($\varepsilon \approx 10$ L mol^{-1} cm^{-1}). In our laser flash photolysis experiments, this absorption was neglected up to radical concentrations of about 10^{-2} mol L^{-1}. The CBZ spectrum presented in this work exactly matches that reported earlier.[21]

Free carbazole exhibits intense room-temperature fluorescence in the region 340—350 nm with $\varphi_{\text{fl}} = 0.38$ (see Ref. 22) and $\tau_{\text{fl}} = 15$ ns.[23] Like the absorption spectrum of compound **2**, the luminescence spectrum of this system (see Fig. 1, *a*) undergoes a bathochromic shift relative to the spectrum of unsubstituted CBZ (the shift of the most intense band is 7 nm) and its intensity is much lower (by three orders of magnitude). Thus, the radical fragment in molecule **2** causes rapid deactivation of the singlet excited state of the luminophore. Having compared these spectra, one gets the following estimate: $\varphi_{\text{fl}}(\mathbf{2}) = 10^{-3}$; as a consequence, the characteristic time of intramolecular deactivation is a few tens of picoseconds.

To elucidate the mechanisms of the effect of nitroxide radicals on the photophysical properties of carbazole, we carried out two series of experiments involving (1) studies of intermolecular quenching of ^{1*}CBZ by radical **3** and (2) laser flash photolysis studies of the chemically bound system **2** and an unbound system (CBZ in the presence of **3**).

It should be noted that photoirradiation of CBZ and **2** in the region $\lambda \geq 254$ nm does not change their absorption spectra, *i.e.*, the observed photophysical processes are not complicated by additional photochemical reactions.

Intermolecular quenching of carbazole fluorescence by nitroxide radical. The Stern—Volmer dependence of the ^{1*}CBZ fluorescence intensity on the concentration of **3** described by Eq. (1) is plotted in Fig. 2.

$$I_0/I([\mathrm{Q}]) = 1 + K_{\mathrm{q}}^{\mathrm{s}}[\mathrm{Q}], \qquad (1)$$

where I_0 and $I([\mathrm{Q}])$ are the fluorescence intensities in the absence and in the presence of a quencher, respectively; [Q] is the quencher concentration; and $K_{\mathrm{q}}^{\mathrm{s}}$ is the Stern—Volmer constant equal to the product of the intrinsic fluorescence lifetime of fluorophore by the rate constant for quenching.[24] The slope of the straight line in Fig. 2 is $K_{\mathrm{q}}^{\mathrm{s}} = 210 \pm 20$, which corresponds to the bimolecular rate constant for quenching $k_{\mathrm{q}}^{\mathrm{s}} = (1.4 \pm 0.1) \cdot 10^{10}$ L mol^{-1} s^{-1} provided that $\tau_{\text{fl}}(\text{CBZ}) = 15$ ns (see Ref. 23). This is close to the diffusion rate constant in MeCN ($1.9 \cdot 10^{10}$ L mol^{-1} s^{-1}, see below).

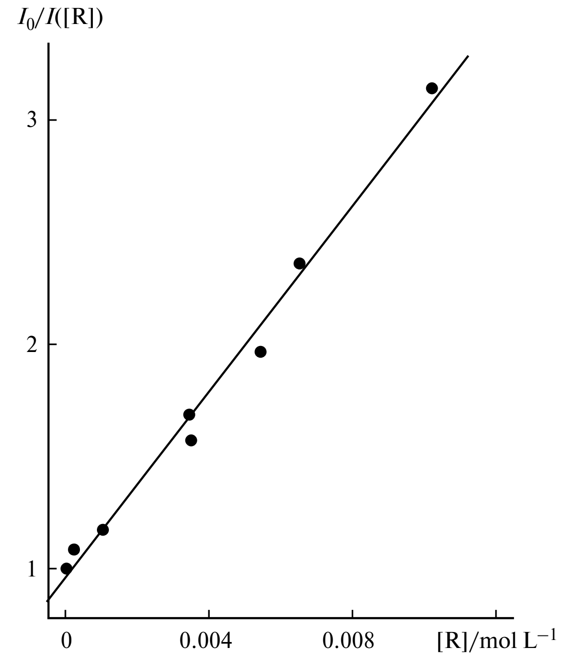


Fig. 2. The Stern—Volmer depndence of the efficiency of CBZ quenching by imidazolidine radical **3** in MeCN; [CBZ] = $6.6 \cdot 10^{-5}$ mol L^{-1}; I_0 and I are the CBZ fluorescence intensities in the absence and in the presence of quencher, respectively.

Short-lived intermediates formed during laser flash photolysis of CBZ (266 nm). To carry out a comparative laser flash photolysis study of the chemically bound system **2** and the unbound system (CBZ in the presence of **3**), we did a preliminary research on photolysis of free CBZ in order to optimize the experimental conditions.

The transient absorption spectrum of CBZ in a deoxygenated solution in MeCN observed upon excitation in the region 266 nm is shown in Fig. 3, *a*. The spectrum is obtained immediately after the laser pulse. An example of the kinetic curve is presented in Fig. 3, *b*. In solutions with normal concentration of oxygen (concentration of dissolved oxygen in air-saturated MeCN is $2.4 \cdot 10^{-3}$ mol L^{-1} at 298 K)[25] the characteristic decay time of transient absorption is shortened to less than 100 ns. Quenching by oxygen indicates that the spectrum in Fig. 3, *a* belongs to ^{3*}CBZ. Indeed, this spectrum matches the T—T-absorption spectrum of carbazole.[26] At the same time, investigations of the photophysical properties of ^{3*}CBZ can be complicated by two-photon reactions leading to either formation of carbazolyl radical or ionization of the starting compound. Two-photon excitation caused by simultaneous irradiation with light at $\lambda_{\max} = 266$ and 530 nm gives rise[27–29] to an absorption maximum of carbazolyl radical (CBZ$^{\cdot}$) at 620 nm ($\varepsilon_{\max} = 5500$ L mol^{-1} cm^{-1})[28] formed as a result of homolytic dissociation of the N—H bond:

$$\text{CBZ} + 2\,h\nu \longrightarrow \text{CBZ}^{\cdot} + \text{H}^{\cdot}. \qquad (2)$$

Photodissociation with the formation of the radical CBZ$^{\cdot}$ can occur from both the triplet and the lowest singlet excited states of CBZ.[28]

One should keep in mind that not only photodissociation, but also two-photon ionization is possible:

$$\text{CBZ} + 2\,h\nu \longrightarrow \text{CBZ}^{\cdot+} + \text{e}^{-}_{\text{solv}}. \qquad (3)$$

According to published data,[30] the radical cation CBZ$^{\cdot+}$ in solution is characterized by an absorption max-

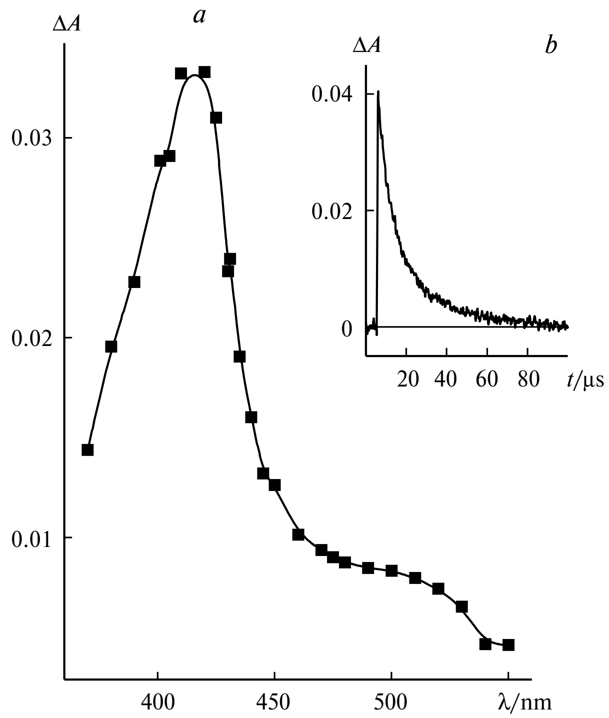


Fig. 3. Laser flash photolysis (266 nm) of carbazole ($1.26 \cdot 10^{-4}$ mol L^{-1}) in MeCN (1-cm cell, solution was bubbled with argon for 15 min): transient absorption spectrum recorded immediately after laser pulse (*a*) and a typical kinetic curve (420 nm) (*b*).

imum in the region 780 nm and a charge resonance band in the IR region (~1600 nm). Stabilized radical cations $CBZ^{\cdot+}$ were also detected in low-temperature polymer matrices[31] and in zeolites.[32] The position of the maximum and the widths of spectral bands are strongly dependent on the environment.

Localization of the excess electron in acetonitrile has been an intensively debatable issue (see Ref. 33 and references cited therein). Experiments on pulsed radiolysis of liquid MeCN revealed two types of anions being in equilibrium, *viz.*, anion **I** characterized by an absorption maximum in the IR region (1450 nm) and anion **II** characterized by absorption in the region 550 nm.[34] It was assumed that anion **I** is a solvated electron while anion **II** is a radical anion of acetonitrile dimer $(MeCN)_2^{\cdot-}$.[35]

In our experiments, a considerable increase in the excitation pulse energy led to the appearance of a weak absorption band in the region 550—630 nm (Fig. 4). Coincidence of the transient absorption spectrum at high intensity of excitation light (see 4, curve *2*) with the spectrum of carbazolyl radical[27—29] suggests that two-photon excitation of CBZ at 266 nm produces the radical $CBZ^{\cdot}$ with a maximum concentration estimated at 10^{-5} mol L^{-1}. No absorption bands of the radical cation $CBZ^{\cdot}$ and solvated electron were observed.

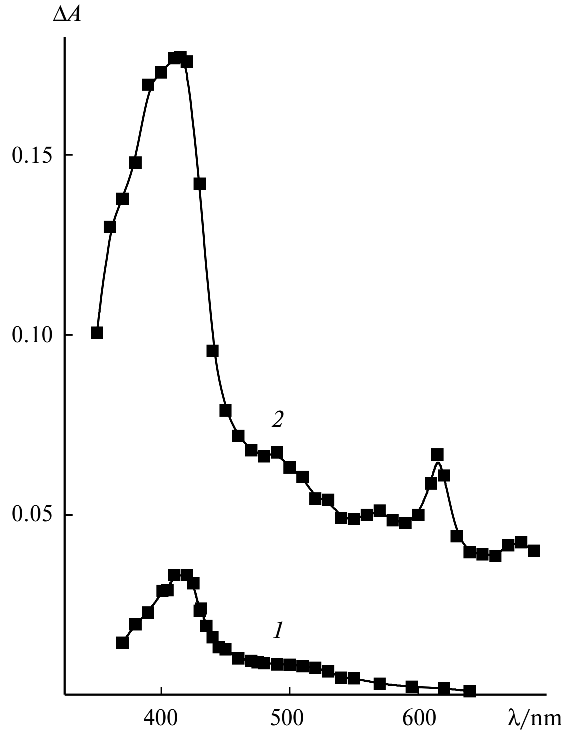


Fig. 4. Production of carbazolyl radical under two-photon excitation of carbazole: laser flash photolysis (266 nm) of carbazole ($1.26 \cdot 10^{-4}$ mol L^{-1}) in MeCN (1-cm cell, solution was bubbled with argon for 15 min). The transient absorption spectra were recorded immediately after laser pulse; spectra *1* and *2* correspond to a pulse energy ratio of 1 : 5.7.

Further experiments with ^{3*}CBZ were carried out at low intensity of excitation radiation, which ensured the absence of the radicals $CBZ^{\cdot}$ and other products of two-photon photochemistry in the system (see Fig. 4, curve *1*).

To establish the ^{3*}CBZ loss regularities, we measured the dependence of the initial apparent first-order rate constant k_{app} on the initial optical density at the maximum of the T—T-absorption band (*i.e.*, in fact on the concentration of triplets). The k_{app} value was determined from the portions of the kinetic curves corresponding to the degree of conversion of about 20%. The initial concentration of triplets was varied by varying the excitation pulse energy. Experimental results are shown in Fig. 5. Linear dependence, which does not pass through the origin, indicates that both first- and second-order reactions contribute to the loss of ^{3*}CBZ:

$$^{3*}\mathrm{CBZ} + {}^{3}\mathrm{X} \xrightarrow{k_{\mathrm{mono}}} \mathrm{CBZ} + {}^{1*}\mathrm{X}, \qquad (4)$$

$$^{3*}\mathrm{CBZ} + {}^{3*}\mathrm{CBZ} \xrightarrow{k_{\mathrm{bim}}} {}^{1*}\mathrm{CBZ} + \mathrm{CBZ}. \qquad (5)$$

The apparent rate constant for the loss of ^{3*}CBZ determined from the initial portion of the kinetic curves is

$$k_{\mathrm{app}} = k_{\mathrm{mono}} + 2\,k_{\mathrm{bim}}[^{3*}\mathrm{CBZ}]. \qquad (6)$$

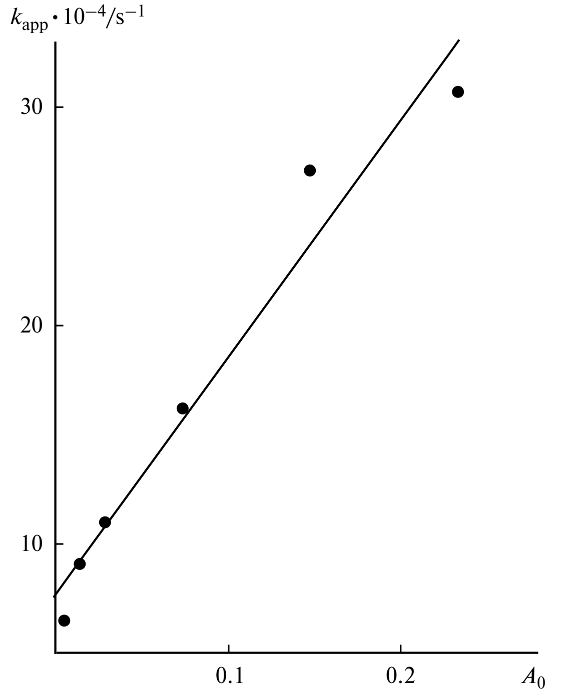


Fig. 5. Determination of the rate constant for T—T-annihilation of carbazole in acetonitrile: apparent rate constant for loss of ^{3*}CBZ (k_{app}) plotted *vs.* initial change in the optical density (ΔA_0) of the sample under laser flash photolysis (266 nm) of carbazole ($1.26 \cdot 10^{-4}$ mol L^{-1}); $\lambda = 420$ nm.

The rate constant for T—T-annihilation k_{bim} calculated taking into account the slope of the straight line (see Fig. 5) is $(7.5\pm0.2) \cdot 10^9$ L mol^{-1} s^{-1} (the value ε = = 14000 L mol^{-1} cm^{-1} was taken from Ref. 26). Using a known expression[36]

$$k_d = 8\,RT/(3000\eta)\ (\text{L mol}^{-1}\ \text{s}^{-1}) \qquad (7)$$

and the MeCN viscosity ($\eta = 3.45 \cdot 10^{-3}$ P),[37] the diffusion rate constant was estimated: $k_d = 1.9 \cdot 10^{10}$ L mol^{-1} s^{-1}. Thus, one gets $k_d = 2.5k_{bim}$. Similar results were obtained[38] for T—T-annihilation of carbazole triplets in cyclohexane, *viz.*, $k_{bim} = 4.1 \cdot 10^9$ L mol^{-1} s^{-1} at a solvent viscosity of $9.0 \cdot 10^{-3}$ P (see Ref. 37) and a diffusion rate constant of $7.3 \cdot 10^9$ L mol^{-1} s^{-1}.

The intercept in Fig. 5 is $k_{mono} = (7.7\pm1.3) \cdot 10^4$ s^{-1}; this corresponds to a ^{3*}CBZ lifetime of 13 μs, which is most likely determined by quenching of ^{3*}CBZ by the residual oxygen present in the solvent. Indeed, assuming that quenching of triplet carbazole is diffusion-controlled, the oxygen concentration is estimated at $[O_2]$ = $= 4 \cdot 10^{-6}$ mol L^{-1}, *i.e.*, bubbling argon through the samples reduces the O_2 concentration by three orders of magnitude.

The rate constant $k_q{}^T$ for quenching of ^{3*}CBZ by radical **3** was determined from the reaction

$$^{3*}\text{CBZ} + \mathbf{3} \xrightarrow{k_q{}^T} \text{CBZ} + \mathbf{3}. \qquad (8)$$

The apparent rate constant for the loss of ^{3*}CBZ in the presence of radical **3** is given by

$$k_{app} = k_{eff} + 2\,k_{bim}[^{3*}\text{CBZ}], \qquad (9)$$

where

$$k_{eff} = k_{mono} + k_q{}^T[\text{R}]. \qquad (10)$$

For a series of samples with a constant CBZ concentration and a variable concentration of radical **3**, we measured the rate constants k_{eff} and k_{bim} using a procedure similar to that described above for the determination of k_{mono} and k_{bim} in the absence of radical **3**. The dependence of k_{eff} on the concentration of radicals is linear (Fig. 6). Then, k_{mono} and $k_q{}^T$ were calculated using the dependence of k_{eff} on [R] (see Fig. 6). The measured rate constant $k_q{}^T$ for bimolecular quenching of ^{3*}CBZ by radicals **3** was found to be $(1.5\pm0.2) \cdot 10^9$ L mol^{-1} s^{-1}, which is an order of magnitude lower than the diffusion limit for MeCN. This can be to some extent due to spin statistics, which introduces a factor of 1/3 for the probability of the process "triplet + doublet = singlet + doublet".

Laser flash photolysis of compound **2** at low intensity of excitation radiation (*i.e.*, under conditions excluding the occurrence of two-photon processes in the case of free carbazole) does not produce transient absorption. This indicates that the characteristic time of quenching of the local triplet excited state of ^{3*}CBZ in system **2** is with certainty shorter than 50 ns. Note that, owing to the lack

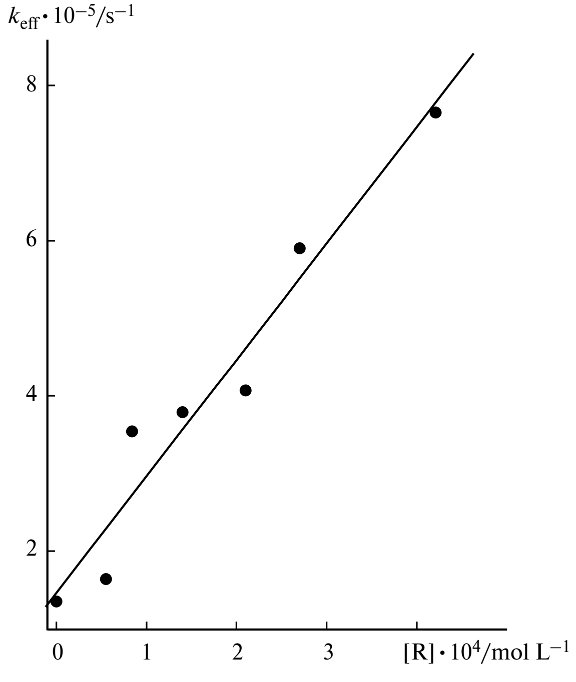


Fig. 6. Rate constant for loss of ^{3*}CBZ (k_{eff}) by the first-order reaction mechanism (see text) plotted *vs.* concentration of radicals **3** in the quenching of the triplet excited state of carbazole by stable 3-imidazolidine radical.

of absorption, which could be ascribed to charge-transfer states, the probability of quenching by the electron transfer mechanism seems to be low.

Thus, quenching of triplet CBZ in system **2** by radical **3** occurs at a rate constant close to the diffusion rate constant. This information is of importance for understanding the fluorescence quenching mechanism of the free and bound carbazole.

Mechanism of ^{1*}CBZ quenching by the nitroxide radical. Consider how different factors affect the quenching of luminescence of compound **2**. The overall rate constant for intramolecular deactivation of a local singlet excited state of carbazole (^{1*}CBZ—R$^{\cdot}$) by radical **3** ($k_q{}^s$) may include contributions from the rate constants for energy transfer by the dipole-dipole (Förster, k_{FT}), exchange (Dexter, k_{DT}), and electron transfer (k_{ET}) mechanisms, as well as acceleration of internal conversion (k_{IC}) and intersystem crossing (k_{ISC}) through electron exchange:

$$k_q{}^s = k_{FT} + k_{DT} + k_{ET} + k_{IC} + k_{ISC}. \qquad (11)$$

In the literature, all five channels of luminescence quenching in the bound system luminophore—nitroxide radical are considered.[7]

The available experimental data allow one to evaluate the contributions of some processes to the quenching of free and bound ^{1*}CBZ.

A. Energy transfer by the dipole-dipole mechanism. In this case, the rate constant for energy transfer (L mol^{-1} s^{-1}) is given by[39]

$$k_{FT} = (4/3000)\pi R^3 N_A k_{dd}(r). \qquad (12)$$

Here R is the sum of the characteristic sizes of the donor and acceptor and $k_{dd}(r)$ is the probability of energy transfer by the dipole-dipole mechanism

$$k_{dd}(r) = (1/\tau_0)(R_0/r)^6, \qquad (13)$$

where τ_0 is the intrinsic lifetime of the fluorophore and R_0 is the critical distance of energy transfer. The R_0 value is determined from the expression

$$R_0{}^6 = 9000(\ln 10)\theta^2\varphi_{fl}J_F/(128\pi^5 n^4 N_A). \qquad (14)$$

Here θ^2 is the orientation factor equal to 2/3 for low-viscosity liquids, n is the refractive index of the solvent, φ_{fl} is the quantum yield of fluorescence, J_F is the Förster overlap integral given by

$$J_F = \int_0^\infty [F(\nu)\varepsilon(\nu)/\nu^4]d\nu/\int_0^\infty F(\nu)d\nu, \qquad (15)$$

where $F(\nu)$ is the fluorophore fluorescence intensity and $\varepsilon(\nu)$ is the extinction coefficient of the acceptor (nitroxide radical) at the frequency ν. The overlap of the absorption spectrum of radical **3** and the luminescence spectrum of CBZ is shown in Fig. 7. It is provided by a weak absorption band of the radical in the visible region.

The rate constant for dipole-dipole energy transfer was calculated using relationships (12)—(15) with $\varphi_{fl} = 0.38$,[22] $\tau_0 = 15$ ns,[23] $n = 1.3441$ (see Ref. 37), and $r = r_d + r_a$. The radii of carbazole (r_d) and the nitroxide radical (r_a) were assumed to be 4 and 2.4 Å, respectively (obtained from simulation using the Chem3D Ultra software). This led to a critical distance of energy transfer R_0 of 10.8 Å and a bimolecular rate constant k_{FT} of $2 \cdot 10^9$ L mol^{-1} s^{-1}. Thus, dipole-dipole energy transfer can make only a minor contribution to the rate constant for quenching of free CBZ by radical **3** equal to $1.4 \cdot 10^{10}$ L mol^{-1} s^{-1}. Apparently, this also holds for the bound system CBZ—R$^{\cdot}$.

B. Energy transfer by exchange mechanism. In this case, direct calculations of the rate constant k_{DT} from the values of spectral parameters are impossible because one should know the numerical value of the matrix element of the overlap H in expression (16).[7]

$$k_{DT} = 4\pi^2H^2J_D/h = 4\pi^2H_0{}^2\exp(-2R/L)J_D/h. \qquad (16)$$

Here H_0 is the pre-exponent, $L \approx 1$ Å is the characteristic distance of exponential decrease in the transition probability, h is the Planck constant, and J_D is the Dexter overlap integral equal to

$$J_D = \int_0^\infty [F(\nu)\varepsilon(\nu)d\nu/(\int_0^\infty F(\nu)d\nu\int_0^\infty \varepsilon(\nu)d\nu). \qquad (17)$$

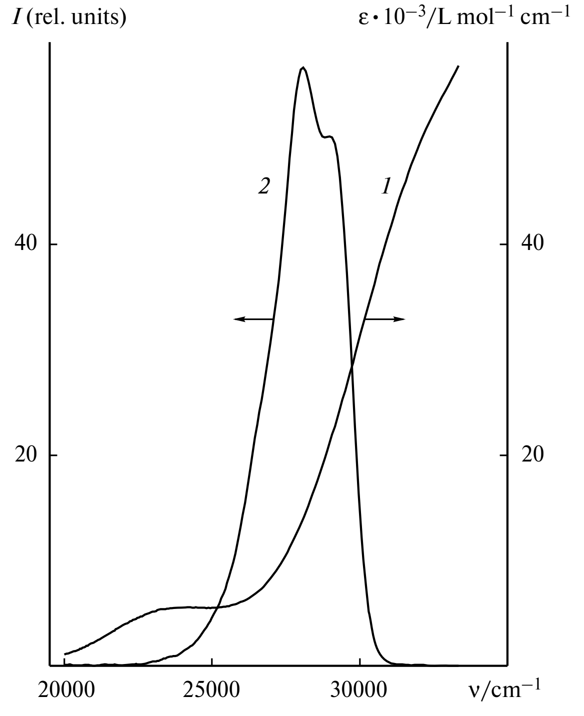


Fig. 7. Absorption spectra of nitroxide radical **3** (*1*) and fluorescence spectra of Carbazole (*2*) in MeCN on a commeansurable scale.

However, following, *e.g.*, Ref. 40, one can estimate the maximum value of the characteristic radius of exchange quenching R_0. The rate constant k_{DT} can be represented in the form[41]

$$k_{DT} = 2\pi L R^2 k_{ex}(R), \qquad (18)$$

where the quenching probability is a function of distance (see Ref. 36):

$$k_{ex}(r) = (1/\tau_0)\exp[-2(r - R_0)/L]. \qquad (19)$$

Assuming that the experimental rate constant for quenching of free carbazole by the nitroxide radical equal to $1.4 \cdot 10^{10}$ L mol^{-1} s^{-1} is due to the Dexter mechanism, for the characteristic distance of energy transfer R_0 in the pair we get a quite realistic value of 14.3 Å, *i.e.*, quenching of ^{1*}CBZ by radical **3** can proceed by the mechanism of exchange energy transfer.

C. Electron transfer. Now we will consider the possibility of quenching by the electron transfer mechanism. For the Gibbs free energy of a chemical reaction

$$\text{CBZ—R}^{\cdot} + h\nu \longrightarrow \text{CBZ}^{\cdot+} - \text{R}^{-} \qquad (20)$$

one has[42]:

$$\Delta G_{ET} = E_{ox} - E_{red} - E_{00} + \Delta G_{Coul} + \Delta G_{solv}, \qquad (21)$$

where E_{ox} and E_{red} are the oxidation potential of CBZ and the reduction potential of **3**, respectively, E_{00} is the fluorophore excitation energy, ΔG_{Coul} and ΔG_{solv} are the Gibbs free energies of the Coulomb stabilization and solvation, respectively. The oxidation potential of CBZ *vs.* s.c.e. in acetonitrile[43] is E_{ox} = 1.11 eV, the reduction potential of radical **3** *vs.* s.c.e. in water—DMF mixture[43] is E_{red} = = –0.61 eV. The CBZ excitation energy is E_{00} = 3.72 eV (determined from the crossing point of the absorption and luminescence spectra,[42] see Fig. 1, *b*). The Coulomb stabilization energy is

$$\Delta G_{Coul} = -e^2/(\varepsilon R_{D-A}), \qquad (22)$$

where e is the electron charge, ε is the static dielectric permittivity of the solvent (ε = 36.2 for MeCN)[37] and R_{D-A} is the distance between the electron donor and acceptor. The R_{D-A} value was estimated as the distance between the nitrogen atom of the carbazole moiety and the oxygen atom of imidazolidine fragment of the CBZ—R$^{\cdot}$ molecule. Simulation using the Chem3D Ultra software gave R_{D-A} = 4.7 Å. Therefore, one gets $\Delta G_{Coul} \approx$ ≈ –0.08 eV and it is clear that particular procedure for R_{D-A} evaluation is insignificant because of the very small final value.

Would the redox potentials of the donor and acceptor be measured in the same solvent, the solvation energy ΔG_{solv} in expression (21) should be set to zero. Since the redox potential of the nitroxide radical was measured in the water—DMF mixture rather than acetonitrile, an additional term appears[7] in relation (21)

$$\Delta G_{solv} = -(e^2/2)(1/\varepsilon_{H_2O-DMF} - 1/\varepsilon_{MeCN})(1/r_D + 1/r_A), \qquad (23)$$

where r_D and r_A are the radii of the electron donor (CBZ) and acceptor (**3**), respectively. The dielectric permittivity of water—DMF mixture varies from 36.7 (pure DMF) to 78.2 (pure water). The r_D and r_A values are 4 and 2.4 Å, respectively. Because the ε values are high, ΔG_{solv} is at most 0.1 eV and can be ignored. Therefore, one gets $\Delta G_{ET} \approx -2$ eV, *i.e.*, quenching by the electron transfer mechanism is realistic from energy considerations.

However, no radical cations CBZ$^{\cdot+}$ were detected in the experiments on laser flash photolysis of CBZ in the presence of radical **3** in both chemically bound and unbound systems (see above). Thus, the probability of electron transfer seems to be low.

D. Acceleration of ISC. One can assume[16] that introduction of a radical fragment into a molecule leads to acceleration of ISC. This would be a reason for an increase in the quantum yield of triplet excited states compared to the value of 0.36 for free carbazole.[38] However, laser flash photolysis experiments revealed the reverse situation, *viz.*, quenching of ^{3*}CBZ by the nitroxide radical at almost diffusion rate constant.

E. Acceleration of internal conversion. Spin exchange between the singlet excited state of carbazole (^{1*}CBZ) and doublet ground state of radical ^{2}R$^{\cdot}$ may result in acceleration of internal conversion in the fluorophore molecule[7,14,44]

$$^{1*}\text{CBZ} + {}^2\text{R}^{\cdot} \longrightarrow {}^1\text{CBZ} + {}^2\text{R}^{\cdot}. \qquad (24)$$

Experimentally, there are no grounds to reject the mechanism (24).

* * *

Thus, the measured rate constant for intermolecular quenching of singlet excited state of free carbazole by the nitroxide radical R$^{\cdot}$ (**3**) is close to the diffusion limit. In this situation, the choice of the most plausible quenching mechanism is rather complicated.[14] Out of five mechanisms considered, three can be rejected. These are the dipole-dipole energy transfer, electron transfer and accelerated ISC. In any case, none of them can pretend to the role of the main mechanism. Then, using the elimination method, one gets that the most probable mechanisms include the exchange energy transfer and acceleration of internal conversion through electron exchange.

These processes also seem to be responsible for the luminescence quenching in the chemically bound system "luminophore—nitroxide radical". Earlier studies[7,8] of other chemically bound systems showed that the most plausible quenching mechanism is acceleration of internal conversion. Making eventual decision requires pulsed fluorometry experiments with picosecond temporal resolution for both free and bound carbazole.

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