Characteristics of the excited states of 3-substituted coumarin derivatives and transfer of electronic energy to N-oxyl radicals

Marián Kaholek, Pavol Hrdlovič *

Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Dúbravská cesta 9, Slovak Republic

Abstract

Photophysical properties and characteristics of electronic energy transfer of coumarin derivatives substituted by bulky group in position 3 and 7-diethylamino-4-methyl coumarin (Coumarin 1) were investigated in solution and polymer matrices. The bulky electron donating groups were: phenyl-, phenylthio-, 2-methylphenylthio-, 2,6-dimethylphenylthio-, dimethylamino- and benzoylamino- in position 3. Fluorescence of coumarin derivatives was quenched by polar methanol with bimolecular rate constant (k_q) larger than the diffusion controlled limit indicating static quenching. The increased polarity of mixed solvent prefers processes leading to intramolecular charge transfer (ICT) or twisted intramolecular charge transfer (TICT) which effectively compete with fluorescence. The experimental and theoretical values for the rate constants of the electronic energy transfer (k_{ET}) and critical radius (R_0) were determined for derivatives of coumarin as donors and N-oxyl radical as acceptor. For selected pairs, the experimental and theoretical values of the electronic energy transfer for k_{ET} and R_0 were compared in various solvents like cyclohexane, heptadecane and methanol in order to determine the type of the electronic energy transfer, influence of the solvent and number of paramagnetic centers on this process. The resonance transfer seems to be the prevailing mechanism of energy transfer. In non-polar glassy polystyrene matrix at temperature lower than T_g, the energy transfer from coumarin donor to N-oxyl acceptor follows the Perrin's model for static quenching in solid phase. There is strong indication that resonance energy transfer is operative as well. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: 3-substituted coumarin derivatives; N-oxyls; Resonance energy transfer; Polymer matrices
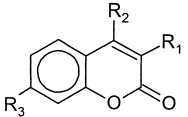
1. Introduction

The concept of twisted intramolecular charge transfer (TICT) was introduced by Grabowski et al [1] in order to explain the presence of the dual fluorescence of N,N-dimethylaminobenzonitrile (DMABN) in polar solvents. In ground state this molecule is planar so that the conjugation between dimethylamino group and aromatic ring is maximal. This geometry is preserved after direct excitation. The TICT state can be reached from originally excited planar S_1 state by rotation of dimethylamino group to the right angle so the conjugation is disrupted. In this state, complete charge separation occurs between dimethylamino group and cyanobenzene part of the molecule. The polar solvent stabilizes this dipolar TICT-state, which lies lower than S_1.
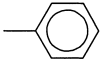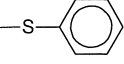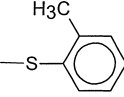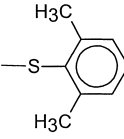
Recently, we have shown [2] that several coumarin derivatives substituted in position 3 by bulky electron donating substituents exhibit the large Stoke's shift in going from non-polar cyclohexane to polar ethanol. At the same time the decrease in quantum yield of fluorescence is observed as well. Several authors [3–5] observed the decrease of quantum yield of fluorescence for coumarin derivatives in position 3,4,6,7 and 8 in polar solvents as compared with non-polar. This stabilization of the excited state in polar solvents indicates that large extent of intramolecular charge transfer (ICT) or twisted intramolecular charge transfer (TICT) is involved which results in the rapid radiationless decay of the excited state.

In order to elucidate the processes more thoroughly, we investigated the quenching of coumarin derivatives substituted in positions 3 and 7-diethylamino-4-methylcoumarin (Scheme 1) by polar methanol in non-polar cyclohexane and for some derivatives in more viscose heptadecane.

The resonance energy transfer was extensively investigated on several donor acceptor pairs [6–8]. Recently, it has

* Corresponding author. Tel.: +42-7-373448; fax: +42-7-375923
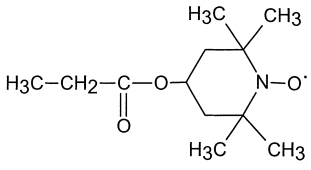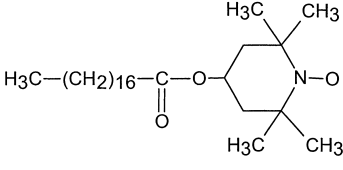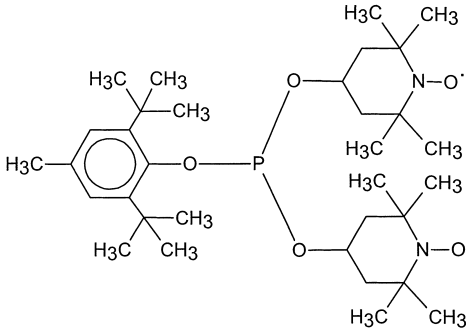*E-mail address:* upolhrdl@savba.sk (P. Hrdlovič)

	m.t.	R_1	R_2	R_3
I	135-138°C		H	H
II	117-119°C		H	H
III	143-147°C		H	H
IV	167-168°C		H	H
V	84.5-85.5°C	—N(CH₃)₂	H	H
VI	172-174°C	—NH-CO-	H	H
VII	72-75°C	H	CH₃	—N(C₂H₅)₂

Scheme 1. Structure of coumarin derivatives.

	m.t.	Structure
Q1	55.5-58°C	
Q2	37-39°C	
Q3	120-122°C	

Scheme 2. Structure of N-oxyl radicals.

been observed that resonance energy transfer occurs between laser dyes based on coumarin in solution [9,10]. Long range dipole–dipole interaction at resonance energy transfer is in fact the interaction between the transition moments of deactivation on donor part (D*) and excitation on acceptor part (Q). If electron of excited donor (D*) falls on lower orbital of donor (D), there is a change in dipole moment which forms electric field. This field is directly proportional to transition moment ($\vec{M}$) and reciprocal value of third power of the distance (r^{-3}). The force proportional to $\vec{M}/r^3$ acts on electron in the molecule of acceptor (Q). If it is transferred to higher orbital, then it creates its own electric field which is applied on electron in molecule D*. As result of downward motion of electron in D* and upward motion of electron in Q their electric fields are in resonance interaction.

In this paper we focus besides quenching of excited states of coumarin derivatives substituted in position 3 (Scheme 1) by polar methanol as well as on quenching by several N-oxyls derived from sterically hindered amines (Scheme 2) in solution and in glassy polystyrene matrix. The experimental and theoretical parameters for all pairs under investigation were determined in cyclohexane. For selected pairs these studies were performed in more viscose (heptadecane) and more polar (methanol) media.

2. Experimental details

2.1. Materials

The coumarin derivatives (Scheme 1) substituted at position 3, were obtained from Department of Organic Chemistry, Faculty of Science, Comenius University, Bratislava, and several of them were used previously [2,11]. Their structure, given on Scheme 1, is: 3-phenylcoumarin (**I**), 3-phenylthiocoumarin (**II**), 3-(2-methylphenylthio) coumarin (**III**), 3-(2,6-dimethylphenylthio)coumarin (**IV**), 3-dimethylaminocoumarin (**V**) and 3-benzoylaminocoumarin (**VI**). Laser dye Coumarin 1 (7-diethylamino-4-methylcoumarin, **VII**) was a commercial product (Aldrich, Steinheim, F.R.G). The concentration of coumarin derivatives in solution was 10^{-5} or 10^{-4} mol l^{-1}.

Two N-oxyl radicals were prepared at the Polymer Institute. Their structures, given on Scheme 2, are: 4-propionyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (**Q1**), 4- stearyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl (**Q2**). 2,6- di-tert.butyl-4-methylphenylbis(2,2,6,6-tetramethyl-4-piperidyl-N-oxyl)phosphite (**Q3**) was a gift of Dr. Habicher of TU Dresden, FRG.

The purity of the coumarin derivatives and N-oxyl radicals was controlled by spectroscopy and thin layer chromatography (TLC).

Anthracene was zonally refined (Lachema, Brno, CR). Quinine sulphate was an analytical reagent (Lachema, Brno, CR). Cyclohexane and methanol were of UV spectroscopy grade (Merck, Darmstadt, FRG), chloroform (Mikrochem, Bratislava, SR) and heptadecane (Fluka AG) were analytical reagents.

Polymer films were prepared by casting from solution. Polystyrene (PS, Vestyron, Huls AG, FRG.) films were prepared by casting of polymer solution (chloroform, $5\,g\,100\,ml^{-1}$) on the glass plate ($26\,mm \times 38\,mm$). The solvent was allowed to evaporate slowly. All films were self-supporting. The thickness of the films was $50\,\mu m$ and the dopant concentration was $0.002\,mol\,kg^{-1}$.

2.2. Instrumentation

The absorption spectra were measured on an M-40 spectrometer (C. Zeiss, Jena, FGR). The emission spectra were taken on an MPF-4 spectrofluorometer (Perkin–Elmer, Norwalk, USA) which was connected through an A/D converter and interfaced to a microcomputer [12]. The emission spectra of the solutions were measured in a right angle arrangement in the cell with controlled temperature. The emission spectra of the polymer films were recorded in a front face arrangement in a solid sample holder at room temperature. The quantum yield was determined relative to anthracene in solution and in a polymer matrix. The quantum yield of anthracene in solution was checked with quinine sulphate. The absolute quantum yields of coumarin derivatives were determined assuming that anthracene flourescence is independent of the medium. The quantum yield (Φ_F) was determined according to the relationship [13]:

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(\tilde{\nu})\,d\tilde{\nu}}{\int_0^\infty I_F^S(\tilde{\nu})\,d\tilde{\nu}} \left(\frac{1-10^{-A^S}}{1-10^{-A}}\right)\left(\frac{n}{n^S}\right)^2 \quad (1)$$

where Φ_F^S is the quantum yield of anthracene as standard, which was assumed to be 0.25 for all environments. The integrals $\int_0^\infty I_F(\tilde{\nu})\,d\tilde{\nu}$ and $\int_0^\infty I_F^S(\tilde{\nu})\,d\tilde{\nu}$ are the areas under the emission curves of the investigated compound and standard, A and A^S are the absorbances at the wavelength of excitation, n and n^S are the refractive indices for the investigated compounds and standard, respectively.

The decay of emission was measured on set up LIF 200 (LTB GmbH, Berlin) which operates as a stroboscope. The analogous output was digitized in an A/D converter and transferred to a microcomputer [14]. The decay curves were evaluated by the phase plane method [15]. The standard deviation $G^{1/2} = \sum((I_{cal} - I_{exp})^2/n)^{1/2}$ characterized the quality of fitting. The standard deviation ($G^{1/2}$) higher than 5% indicates that a mono-exponential function does not fit the decay satisfactorily. The decay of fluorescence of coumarin derivatives **I** and **VII** in polystyrene matrix and **VII** in cyclohexane and heptadecane solution obeys mono-exponential ($\mathbf{G}^{1/2} < 5\%$). The decay of other derivatives **I–VI** in solution does not obey mono-exponential. The lifetime in solution is

shorter than 0.15 ns which is the limit of the time resolution of LIF 200 set up since the half-width of pulse of nitrogen laser is 0.5 ns.

Therefore, the lifetime of the excited state (τ_F) of coumarin derivatives **I–VI** in solution was determined according to the relationship:

$$\tau_F = \Phi_F/k_r \quad (2)$$

where (k_r) is the rate constant of the radiation process (fluorescence). The theoretical absorption rate coefficient (k_A) expressed by the absorption and emission integral was determined according to relationship [16]:

$$k_A = \frac{8000\pi \ln 10 c n_F^3}{N n_A} \left\langle \tilde{\nu}_F^{-3} \right\rangle^{-1} \frac{g_e}{g_g} \int_0^\infty \frac{\varepsilon(\tilde{\nu})\,d\tilde{\nu}}{\tilde{\nu}} \quad (3)$$

where

$$\left\langle \tilde{\nu}_F^{-3} \right\rangle^{-1} = \frac{\int_0^\infty I_F(\tilde{\nu})\,d\tilde{\nu}}{\int_0^\infty (I_F(\tilde{\nu})/(\tilde{\nu}^3))\,d\tilde{\nu}} \quad (4)$$

n_F, n_A are the solvent refraction indices for the wavelengths corresponding to the fluorescence and the absorption band, N is Avogadro's number, c denotes the velocity of light in vacuo, $\varepsilon(\tilde{\nu})$ is the molar absorption coefficient, $I_F(\tilde{\nu})$ describes the normalized energy distribution of the fluorescence spectrum, and g_e, g_g are degeneracy coefficients for the excited and the ground state, respectively. If the molecules are in dilute solution in a transparent solvent of negligible optical dispersion, then $n_F = n_A = n$. Eq. (3) allows calculation of the value of the radiative transition rate coefficient k_A (or the natural lifetime of the excited S_1 state) based on absorption data. Generally, the values of k_A obtained should be equal to k_r, provided that the mirror-symmetry condition is fulfilled. This is valid when the values of the transition moments for absorption and emission are equal ($\vec{M}_{ge} = \vec{M}_{eg}$) and the populations of the vibrational states of S_o and S_1 are described by the same distribution function. According to Strickler and Berg [17] and Birks and Dyson [16], greater discrepancies between the k_A and k_r values can be explained only by configurational changes of the molecule in the excited state.

3. Results and discussion

3.1. Quenching of fluorescence by formation of excited states with charge transfer (ICT or TICT)

Several authors [3–5] have explained the decreased quantum yield of fluorescence in polar environments through the formation of ICT or TICT states, which open new radiationless route [18]. Population of this state depends on the donor-acceptor ability of the respective groups and on the polarity of the solvent stabilising the highly polar final state [19].
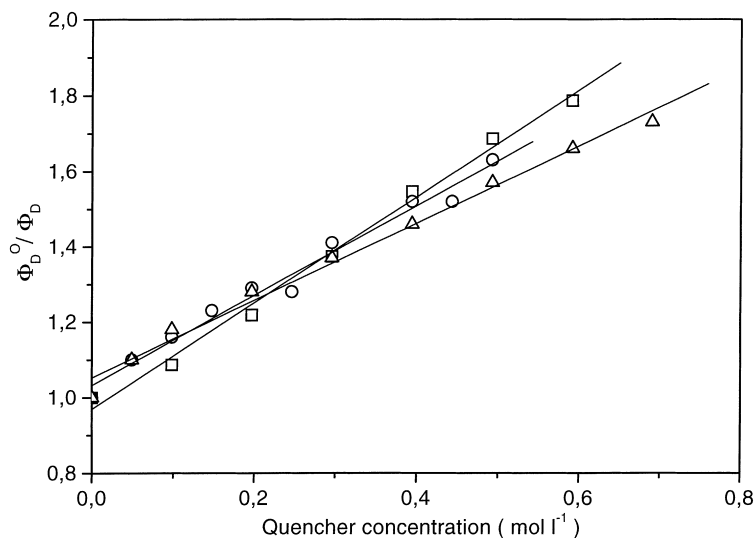
Fig. 1. Stern–Volmer dependence of quenching fluorescence of coumarin derivatives: **II** (□), **III** (○) and **IV** (△) with methanol in cyclohexane.

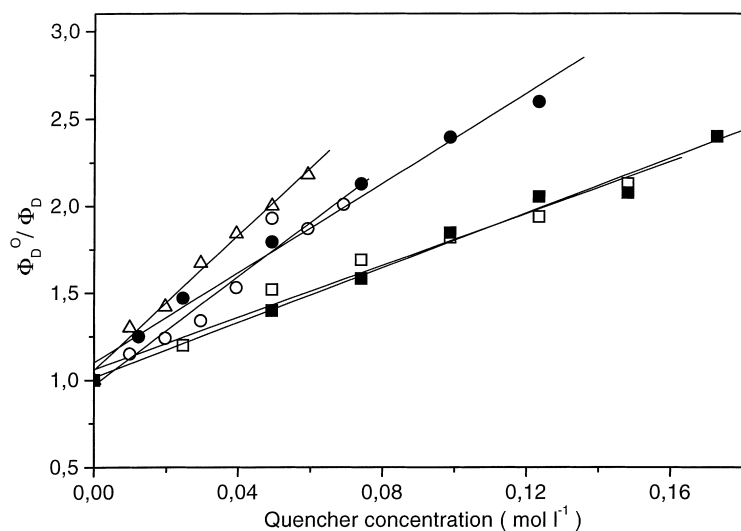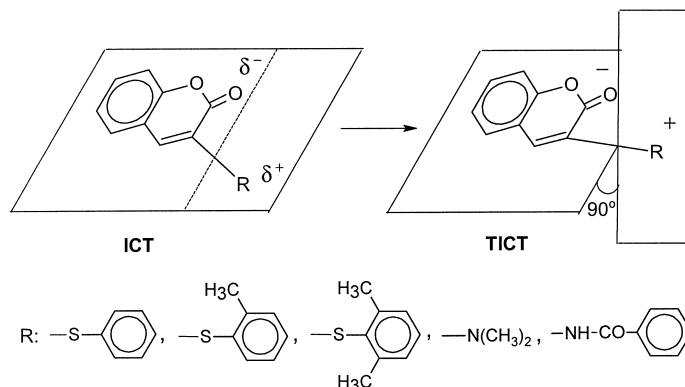Fig. 2. Stern–Volmer dependence of quenching fluorescence of coumarin derivatives: **V** (○), **VI** (△), **VII** (□) with methanol in cyclohexane and **V** (●), **VII** (■) with methanol in heptadecane.

Polar solvents quench the emission of coumarin derivatives **II–VII**. Since the quencher (polar solvent) is used in high concentration dynamic and static quenching might operate at the same time. If both static and dynamic quenching occur, the modified Stern–Volmer equation is to be applied [20]:

$$\frac{\Phi_D^0}{\Phi_D} = (1 + k_q \tau_D^0 [Q])(1 + K[Q]) \qquad (5)$$

where Φ_D^0 and Φ_D are fluorescence quantum yields of donor without and with quencher, k_q is the bimolecular rate constant, τ_D^0 is the fluorescence lifetime without quencher, K is the equilibrium constant for formation of the dark ground state complex 'AQ' and [Q] is the quencher concentration. In the absence of static quenching ($K = 0$), the standard Stern–Volmer applies. Addition of methanol to cyclo-

hexane solutions of coumarin derivatives (**II–VII**) except of **I** decreases their fluorescence and the ratio of Φ_D^0/Φ_D on quencher concentration is linear (Figs. 1 and 2). The calculated quenching bimolecular rate constants (Table 1), k_q, using estimated values of lifetime, τ_D^0, are higher than the diffusion controlled bimolecular rate constant in cyclohexane ($k_{diff}^{20} = 0.66 \times 10^{10}\,1\,mol^{-1}\,s^{-1}$). Lifetime of the fluorescence (τ_D^0) was determined according to relationship (2), where the rate constant of radiation process (k_r) was calculated by relationship (3). Since the estimated lifetimes are very short (Table 1), it is less probable that during the lifetime of excited state collision occurs. Therefore, static quenching is operating. Molecules of coumarin derivatives are preferentially solvated by methanol forming 'dark complex' AQ which is transformed to ICT state after excitation. This polar ICT attracts even more polar methanol molecules.

Scheme 3. Charge distribution in excited states of 3-substituted coumarin derivatives.

Table 1
Quenching of coumarin probes by methanol

Comp[a]	M[b]	$\Phi_D^{0\,c}$	$\tau_D^{0\,d}$(ns)	K^e (l mol^{-1})	$k_q \times 10^{-10}$ (l mol^{-1} s^{-1})[f]
II	Cy	0.002	0.015	1.4	9.3
III	Cy	0.0008	0.0053	1.2	22.6
IV	Cy	0.0011	0.0066	1.0	15.2
V	Cy	0.0065	0.019	15.6	82.1
	C$_{17}$	0.0080	0.076	12.9	17.0
VI	Cy	0.005	0.012	19.4	162
VII	Cy	0.703	2.53^g	7.5^h	0.30
	C$_{17}$	0.75	2.74^g	7.9^h	0.29

[a] Designed according to Scheme 1.

[b] Medium: Cy-cyclohexane, C$_{17}$-heptadecane.

[c] Quantum yield of the pure donor (Eq. (1)).

[d] Fluorescence lifetime of the pure donor determined according to relationship (2), where the rate constant of radiation process (k_r) was calculated by relationship (3).

[e] Equilibrium constants for formation of dark complex.

[f] Rate constant for bimolecular quenching.

[g] Lifetime of the fluorescence determined by phase plane method.

[h] Stern–Volmer constant.

At present, we cannot quantify an increase in local concentration of methanol. Since the longest wavelength absorption band of 3-substituted coumarin derivatives at around 340 nm is not sensitive on polarity or other specific interactions [2], it does not yield any support for formation of the dark ground state complex. On the other hand, in protic solvents as methanol, it can be assumed that there is the strong specific interaction between coumarin derivatives in ground or in excited states and the protic solvent [21]. More polar local environment enriched on methanol induces the transformation of ICT to TICT state [5,18] and its conversion to ground state which is an effective radiationless route competing with fluorescence. As have already been shown by us [2] that coumarin derivatives under study except for **I** exhibit the large Stoke's shift in going from non-polar cyclohexane to polar ethanol. Such stabilization in the excited state in polar ethanol might also indicate the large ICT or TICT (Scheme 3).

According to Grabowski et al. [1] the molecules forming TICT state are coplanar bichromophoric system composed from electron donor and electron acceptor parts connected by simple bond. After excitation, the local excited (LE) state S$_1$ is rapidly relaxed to perpendicular arrangement of donor and acceptor group with full charge transfer from which red shifted emission originates. Coumarin derivatives **II**–**VI** and Coumarin 1 (**VII**) do not exhibit this red shifted emission. Probably, TICT-like state, which is formed in these compounds after excitation, is non-emissive and acts as effective intramolecular quencher [22]. Similar short-lived TICT-like states are formed in diphenylmethane or triphenylmethane dyes [23]. The TICT-like state in coumarin derivatives substituted at position 3 has got two characteristic features namely (Scheme 3):

The TICT state is dipolar with positive charge localised on bulky electron donating group in position 3.

The perpendicular arrangement is achieved by rotation of electron-donating group in position 3.

Several authors have shown that the model compounds with electron donating group bound to ring exhibit intense fluorescence while it diminishes with free rotating groups [23]. Quantum chemical calculations on typical diphenylmethane dye Michler's Hydrol Blue clearly show that formation of TICT-like state can follow after optical excitation [24].

The TICT state of coumarin derivatives **II**–**VII** is formed by slow twisting of two parts of molecule of the planar state. The solvent plays the decisive role in stabilising highly dipolar TICT state. Therefore, it is formed in polar solvents only.

The calculated k_q in this way might be related to reorganization of solvation sphere of coumarin derivative from ground state to excited ICT or TICT states. Since the actual local concentration of methanol around coumarin derivative is not known, the actual rate of reorganization cannot be determined either. Comparison of K or k_q, respectively, shows that amino derivatives **V** and **VI** are quenched by methanol more effectively than **II**, **III**, and **IV**. This points out that the amino derivatives (**V**, **VI**) have probably more polar ICT (TICT) state as **II**, **III**, and **IV**. For Coumarin 1 (**VII**)
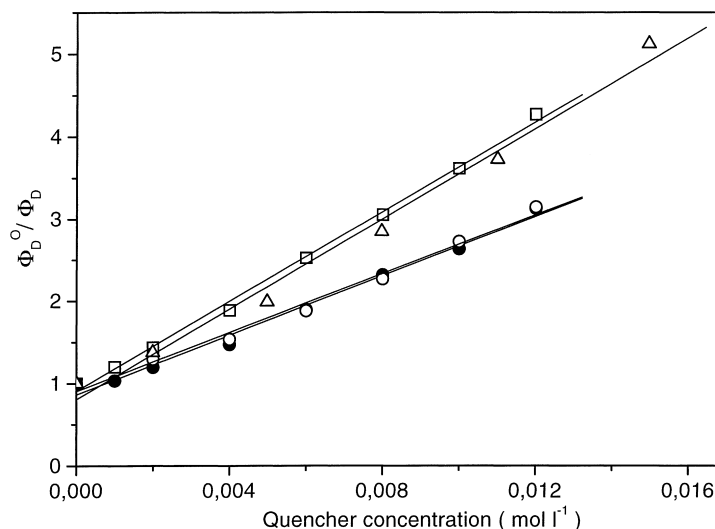
Fig. 3. Stern–Volmer dependence of quenching fluorescence of 7-diethylamino-4-methylcoumarin (**VII**) with quenchers **Q1** (●), **Q2** (□) and **Q3** (△) in cyclohexane and with quencher **Q1** (○) in heptadecane.

the quenching bimolecular rate constant is slightly lower than diffusion controlled one. The fluorescence lifetime of **VII** is substantially longer as compared with other coumarin derivatives. The quenching of **VII** is clearly dynamic although not each collision is effective. Since the estimated lifetimes τ_F are loaded with considerable error, the calculated values of rate constants (k_q) are approximate as well.

Since the relaxation of LE S_1 state to TICT-like state depends on polarity and viscosity of solvent, the effect of viscosity on formation of TICT state was investigated for 3-dimethylaminocoumarin (**V**). Quenching of **V** with polar methanol was followed in less viscose solvent (cyclohexane, $k_{diff}^{20} = 0.66 \times 10^{10}\,1\,mol^{-1}\,s^{-1}$) and more viscose one (heptadecane, $k_{diff}^{25} = 0.188 \times 10^{10}\,1\,mol^{-1}\,s^{-1}$). With growing viscosity the equilibrium constant of formation of the 'dark complex' slightly decreases as a result of slightly limited formation of perpendicular arrangement of two parts of molecule (Table 1, Fig. 2). This decrease might be due to by slight increase in lifetime of **V** in more viscose heptadecane than in cyclohexane as apparent bimolecular rate constant indicates as well (Table 1). No distinct effect of viscosity was observed on bimolecular quenching rate constant (k_q) of Coumarin 1 (**VII**) by methanol (Table 1, Fig. 2). Comparison of k_{diff} and k_q for **VII** by methanol in cyclohexane indicates that no each collision results in quenching. Contrary to it each collision in heptadecane results in quenching.

3-Phenylcoumarin (**I**) is not quenched by polar methanol because it does not form of ICT or TICT states and their complexes with polar solvent.

During last decade the compounds forming TICT states are centre of interest [25] as molecular models for photo-initiated charge separation for important biological and technological processes. Up till recently the existence of TICT states was considered as rare. At present it is accepted that the ICT or TICT states can occur at relaxation of many bichromophoric molecules.

3.2. Resonance energy transfer in solution

The fluorescence of coumarin derivatives (donor) **I**, **V**–**VII** was effectively quenched by N-oxyls with alkyl chain of different length according to Scheme 2 (**Q1, Q2**). Quencher **Q3** with two radical centres was used for quenching of Coumarin 1 (**VII**) besides **Q1** and **Q2**. The plots of steady state quenching of fluorescence are linear (Figs. 3–4) and fulfill the Stern–Volmer relationship [26]:

$$\frac{\Phi_D^0}{\Phi_D} = 1 + K_{SV}[Q] \tag{6}$$

where Φ_D^0 and Φ_D are quantum yields of donor without and with quencher, K_{SV} is the Stern–Volmer constant and [Q] is quencher concentration. The rate constant of energy transfer (k_{ET}) might be calculated using the relationship [27]:

$$k_{ET} = \frac{K_{SV}}{\tau_D^0} \tag{7}$$

where τ_D^0 is fluorescence lifetime of coumarin derivatives in absence of quencher. Values of τ_D were calculated according to Eq. (2), applying k_r based on Eq. (3).

Critical radius of energy transfer R_0 (in Å) is the average distance between coumarin derivative (donor) and N-oxyl radical (acceptor) at which probability of energy transfer equals the probability of other relaxation processes. It was calculated from relationship [28]:

$$R_0 = \frac{7.35}{([Q]_{1/2})^{1/3}} \tag{8}$$

where $[Q]_{1/2}$ is the quencher concentration at which the fluorescence intensity is reduced to half. The pertinent data of concerning the energy transfer are summarised in Table 2. The values of k_{ET} are around 10^{10}–$10^{12}\,1\,mol^{-1}\,s^{-1}$
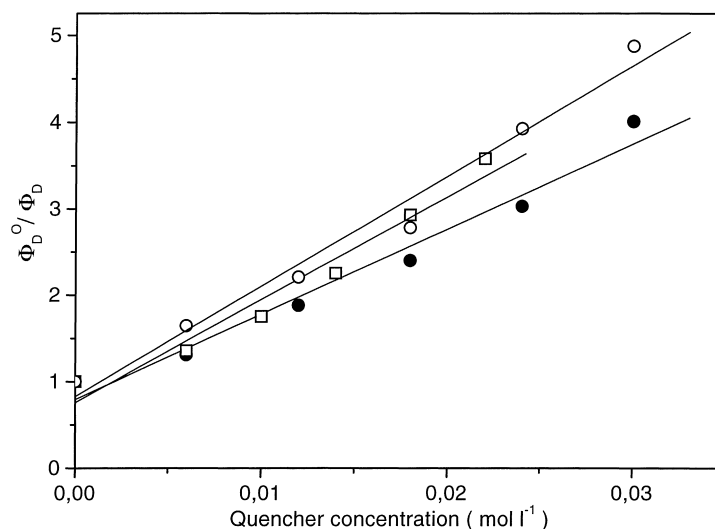
Fig. 4. Stern–Volmer dependence of quenching fluorescence of 3-phenylcoumarin (**I**) with quenchers **Q1** (●) and **Q2** (□) in cyclohexane and with **Q1** (○) in methanol.

Table 2
Theoretically and experimentally determined critical transfer distance (R_0) and rate constants for energy transfer (k_{ET}) of various coumarin derivatives

D^a	A^b	M^c	$\Phi_D^{0\,d}$	$\tau_D^{0\,e}$ (ns)	$J(\tilde{v}) \times 10^{14}$ ($l\,cm^3\,mol^{-1}$)^f	$k_{ET} \times 10^{-11}$ ($l\,mol^{-1}\,s^{-1}$)^g	R_0 (Å)^g	K_{SV} ($l\,mol^{-1}$)^h	$k_{ET} \times 10^{-11}$ ($l\,mol^{-1}\,s^{-1}$)^h	R_0 (Å)^h	R_s (Å)^i
I	**Q1**	Cy	0.014	0.041	4.05	5.7	21	99	24	32	7.4
	Q1	M	0.037	0.14	5.29	3.5	27	127	9.1	35	7.4
	Q2	Cy	0.014	0.041	5.06	6.5	22	119	29	34	
V	**Q1**	Cy	0.0065	0.019	8.29	12	21	85	45	30	7.2
	Q2	Cy	0.0065	0.019	8.36	12	21	126	67	35	
VI	**Q1**	Cy	0.0050	0.012	4.13	12	18	67	56	27	7.6
VII	**Q1**	Cy	0.703	2.53^j	2.72	0.50	37	181	0.72	40	7.6
	Q1	C_{17}	0.75	2.74^j	2.86	0.50	38	179	0.65	40	7.6
	Q2	Cy	0.703	2.53^j	4.00	0.64	40	273	1.08	46	
	Q3	Cy	0.703	2.53^j	4.66	0.69	41	275	1.09	45	9.0

^{a} Donor: designed according to Scheme 1.

^{b} Acceptor: designed according to Scheme 2.

^{c} Medium: Cy-cyclohexane, M-methanol, C_{17}-heptadecane.

^{d} Quantum yield of the pure donor (Eq. (1)).

^{e} Fluorescence lifetime of the pure donor determined according to relationship (2), where the rate constant of radiation process (k_r) was calculated by relationship (3).

^{f} The spectral overlap integral is given by the relationship $J(\tilde{v}) = \int_0^\infty ((F_D(\tilde{v})\varepsilon_A(\tilde{v})/(\tilde{v}_0^4))\,d\tilde{v}$.

^{g} Theoretically calculated using relationships (12) and (10).

^{h} Experimentally determined from Stern–Volmer plots for bimolecular quenching.

^{i} The radius of donor and acceptor collision complex for collision transfer where R_S is sum of donor (R_D) and acceptor (R_Q) radii.

^{j} Lifetime of the fluorescence determined by phase plane method.

which is substantially higher than the bimolecular rate constant controlled by diffusion calculated according to Debye equation [29] for cyclohexane, $k_{diff}^{20} = 6.6 \times 10^9\,l\,mol^{-1}\,s^{-1}$ which is generally accepted for collision energy transfer. The experimental values of R_0 (Table 2) also indicate that the energy transfer occurs under conditions when R_0 is larger than $R_D + R_Q$. The sum of collision radii of coumarin donor and N-oxyl acceptor is about 7–7.5 Å (Table 2). The experimental values of k_{ET} and R_0 clearly indicate that resonance transfer is operative in non-polar cyclohexane. For Coumarin 1 (**VII**) the critical radius R_0 is larger than R_0 of the other coumarin derivatives (**I, V, VI**) as a result of higher quantum yield of fluorescence (Φ_D^0) and longer lifetime (τ_D^0). In order to achieve energy transfer on longer dis-

tance, the higher rate constants (k_{ET}) are needed for **I, V, VI** than for **VII** because low values of lifetime and quantum yield of fluorescence (Table 2). The values of k_{ET} and R_0 are slightly higher for **Q2** with long aliphatic chain. The minimal donor acceptor distance required for collision transfer was calculated assuming spherical shape for coumarin derivatives and **Q1** and **Q3**. The values of van der Waals volumes of respective increments of donors and acceptors, which are given in [30,31], were summarised to get van der Waals volume (V_W) of the respective molecule. The equivalent radius for donor (R_D) and acceptor (R_Q) was calculated from V_W according to $R_W = (3V_W/4\pi)^{1/3}$. The radius of donor and acceptor collision complex for collision transfer is sum of donor (R_D) and acceptor (R_Q) radii. For
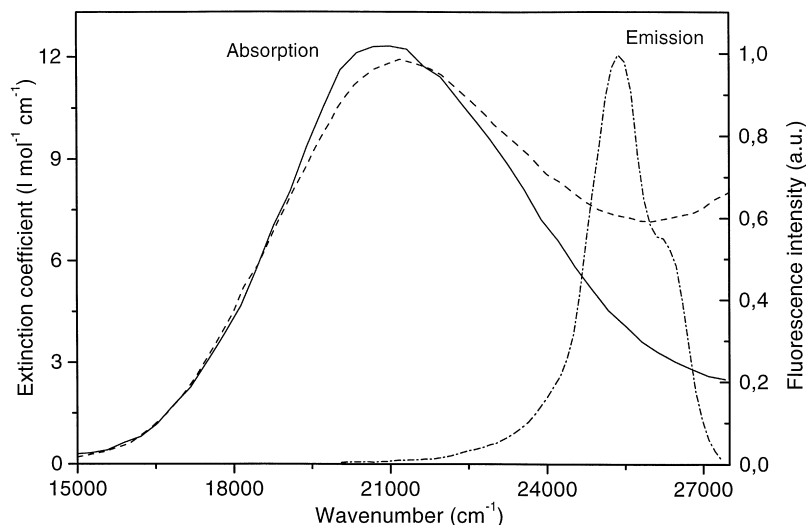
Fig. 5. Absorption spectra of quenchers **Q1** (——) and **Q2** (------) and fluorescence spectrum of derivative **VII** (-·-·-·-) in cyclohexane.

rod-like molecule **Q2** the spherical approximation is not applicable.

The radiationless energy transfer for dipole–dipole long-range interaction is one step process, which occurs on distance larger than sum of radii of donor and acceptor. Förster derived expressions for the rate of energy transfer (k_{ET}) and for critical radius (R_0) expressed in quantities, accessible by spectroscopic measurements [27,32,33]:

$$k_{ET} = \frac{9000 \ln 10 k^2 \Phi_D^0}{128 \pi^5 n^4 N r^6 \tau_D^0} \int_0^\infty F_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \qquad (9)$$

and

$$R_0^6 = \frac{9000 \ln 10 k^2 \Phi_D^0}{128 \pi^5 n^4 N} \int_0^\infty \frac{F_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu})}{\tilde{\nu}_0^4} d\tilde{\nu} \qquad (10)$$

where $F_D(\tilde{\nu})$ is spectral distribution of emission of donor (expressed in quanta and normalized to unity on a wave-number scale); $\varepsilon_A(\tilde{\nu})$ is spectral distribution of acceptor (expressed as extinction coefficient in wave-number scale); Φ_D^0 is quantum yield of donor emission in absence of acceptor; τ_D^0 is lifetime of donor in absence of acceptor (in s); r is the distance between D and Q (cm); R_0 is critical radius for energy transfer (cm); $\tilde{\nu}_0$ is the average wave-number between maximum of absorption and emission band; n is refractive index of the solvent; k is orientation factor which takes into account angle of transition moments vectors of the molecules which is equal $(2/3)^{1/2}$ for random distribution of molecules involved in energy transfer; N is Avogadro's number. Eq. (9) is valid for solid sate. For solution it must be modified as [34]:

$$k_{ET} = \frac{8}{3} \pi \frac{N R_0^{3/2} D^{3/4}}{1000 (\tau_D^0)^{1/4}} \qquad (11)$$

or the values of k_{ET} can be calculated using the relation [7]:

$$k_{ET} = \frac{R_0^3}{(7.35 \times 10^{-8})^3 \tau_D^0} \qquad (12)$$

where R_0 is the critical radius (cm); τ_D^0 is lifetime of donor in absence of acceptor (s); D is the mutual diffusion coefficient; N is Avogadro's number.

The Eq. (9) was derived assuming that the energy transfer is much slower than vibrational relaxation. Therefore, the energy transfer occurs from the vibrationally relaxed state and molecules of donor and acceptor are sufficiently separated. Consequently, the probability of this process is independent on the excitation wavelength even when higher excited states are considered. Values of k_{ET} and R_0 calculated according to Förster relationships 10 and 12 agree quite with those determined experimentally (Table 2). Both data indicate that the energy transfer occurs on the distance larger than the sum of collision radii. Theoretical and experimental values of R_0 for **VII** are larger than for other coumarin derivatives (**I, V, VI**) due to higher quantum yield of fluorescence (Φ_D^0) and longer lifetime (τ_D^0). Slightly higher values both calculated and experimental of R_0 are observed for **Q2** with long aliphatic chain due to larger overlap of emission spectrum of coumarin donor and absorption spectrum of **Q2** (Table 2, Fig. 5). If transitions in coumarin derivatives (D) and N-oxyls (Q) are Frank–Condon type, then the transferred energy is proportional to the overlap of emission and absorption. The increase of the overlap with the length of aliphatic chain increases the number of the final states and the probability of the transfer. The largest overlap integral $J(\tilde{\nu})$ is for **V** as donor and **Q2** as acceptor (Table 2). Since the quantum yield for **V** is substantially lower than for **VII**, the critical radius R_0 for **V** is smaller than for **VII**. In order to achieve energy transfer on longer distances with **I, V, VI** as donors, higher k_{ET} is required because quantum yields are rather low and lifetimes are rather short as compared with **VII** (Table 2).
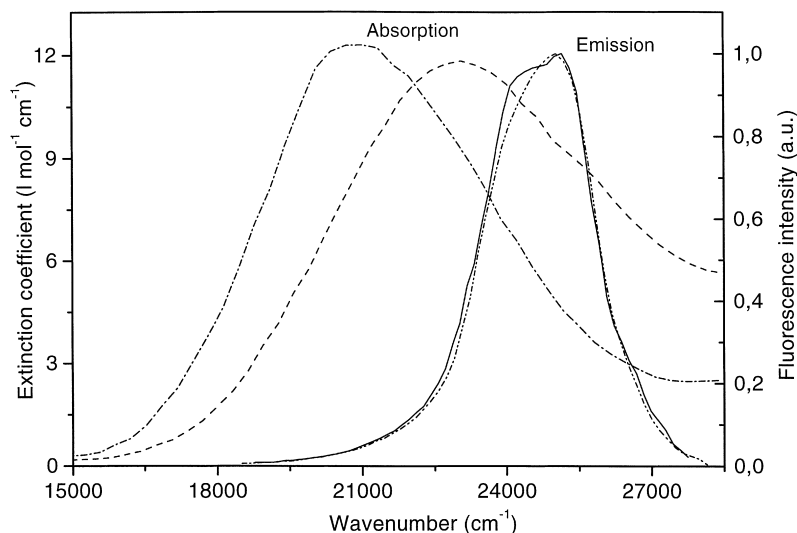
Fig. 6. Absorption spectrum of quencher **Q1** in cyclohexane (·······) and methanol (-----) and fluorescence spectrum of derivative **I** in cyclohexane (——) and methanol (–··–··–).

To confirm that the resonance energy transfer operates with coumarin derivatives as donors and N-oxyls as acceptors, the donor **VII** and acceptor **Q1** was investigated in less viscose cyclohexane $k_{\mathrm{diff}}^{20} = 6.6 \times 10^9 \,\mathrm{l\,mol^{-1}\,s^{-1}}$ and more viscose heptadecane $k_{\mathrm{diff}}^{25} = 1.88 \times 10^9 \,\mathrm{l\,mol^{-1}\,s^{-1}}$. Previously, we have determined that quantum yield of all coumarin derivatives **I–VI** except **VII** increases with the viscosity of the medium [2] which should be reflected in values of R_0 and k_{ET}. Therefore, the pair **VII–Q1** was investigated and the independence of R_0 and k_{ET} on viscosity was confirmed. The quenching of fluorescence of **I** by **Q1** was tested in polar methanol as well. Coumarin derivative **I** was chosen because its emission is not quenched by polar methanol as that of **V**, **VI**, **VII**. The values of R_0 and K_{SV} are higher for this pair in methanol because quantum yield of fluorescence, lifetime and overlap integral are larger in methanol than in cyclohexane (Table 2, Fig. 6). On the other hand, the collision is needed for electron transfer from donor to acceptor as quenching mechanism. In this case the following relationships are valid $R_0 = R_D + R_Q$ and $k_{\mathrm{ET}} \sim k_{\mathrm{diff}}$. Since R_0 and k_{ET} are larger, quenching of coumarin derivatives **I**, **V–VII** is not due to electron transfer from free radical centre on coumarin chromophore supported by polar environment. Based on these data, it might be assumed that resonance energy transfer is operative in this case. In fact this is the interaction between transition moments of excitation N-oxyl (Q) → N-oxyl* (Q*) and deactivation of coumarin derivative D* → D. As a result of downward motion of electron in coumarin derivative (D*) and upward motion of electron in N-oxyl radical (Q), their electric fields interact.

Free radicals of N-oxyl type are paramagnetic due to unpaired electron. At paramagnetic quenching, external magnetic field of acceptor molecule can also enhance spin-orbit coupling in donor and consequently the decrease of quantum yield of fluorescence is observed. Therefore, the efficiency of quenching of **VII** by **Q2**, which has one paramagnetic centre, was compared with quenching of **VII** by **Q3**, which has two centres. For both pairs the overlap integral is nearly the same. Although **Q3** is more paramagnetic, the K_{SV} for both pairs is the same (Table 2). It might be assumed that quenching of coumarin derivatives under paramagnetic action of quenchers is not important due to very short lifetime of donor.

Experimental studies and theoretical calculations have shown that the lowest excited state S_1 of unsubstituted coumarin has n,π^* character [35]. The fluorescence originating in this state is low because the n-π^* transition is both symmetry and orbital forbidden. Substitution in positions 3–8 brings about the switch of the lowest state from n, π^* to π,π^* from which more intense fluorescence is observed. Since there is an equilibrium between close laying state S_1 (n,π^*) and S_2 (π,π^*) the easy switch from one state to another brings about higher fluorescence [36]. The resonance energy transfer starts from π,π^* singlet state of coumarin derivatives **I**, **V**, **VI**, **VII**. In order to get efficient transfer, the excited state of N-oxyl radical must be lower than that of coumarin derivative and the process must occur during the lifetime of the coumarin donor. In all cases of radiationless energy transfer the resonance of the original state (D*, Q) and final state (D, Q*) is required. This is fulfilled when transitions D* → D and Q → Q* are nearly equal.

3.3. Transfer of energy in solid matrices

The energy transfer from coumarin donors to N-oxyl quenchers was tested in solid polymer matrix as well. We assume that no ICT or TICT states, which can open new deactivation radiationless route, are formed in non-polar polystyrene matrix similarly as in cyclohexane or hep-
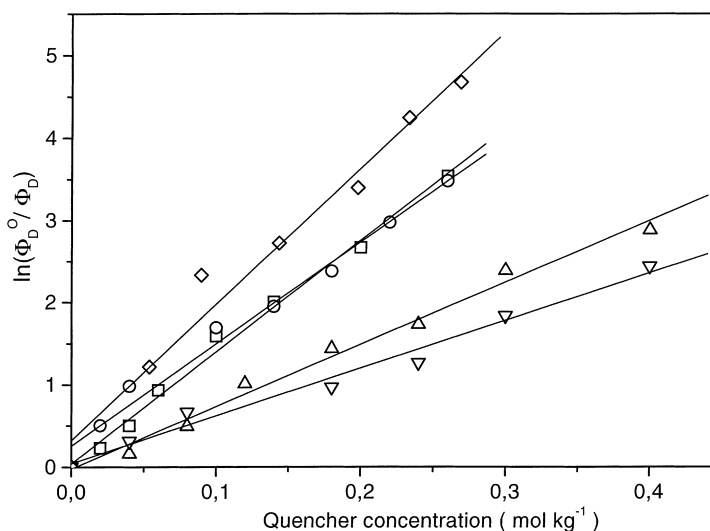
Fig. 7. Dependence of $\ln(\Phi_D^0/\Phi_D)$ on quencher concentration according to Perrin's model for pairs: derivative **I** with quencher **Q1** ($\triangle$) and **Q2** ($\triangledown$) and derivative **VII** with **Q1** ($\square$), **Q2** ($\bigcirc$), and **Q3** ($\diamond$) in polystyrene matrix.

Table 3
Experimentally determined volume (V) and radius (R) of 'active quenching sphere' for energy transfer in polystyrene matrix

D^a	A^b	$\Phi_D^{0\,c}$	$\tau_D^{0\,d}$ (ns)	$G^{1/2\,e}$	ΔQ^f (mol kg^{-1})	V^g (Å^3)	R^g (Å)	R_s (Å)^h
I	**Q1**	0.139	0.56	2.7	0–0.4	12600	14.4	7.4
	Q2				0–0.4	9600	13.2	
VII	**Q1**	0.90	2.8	0.8	0–0.26	22600	17.5	7.6
	Q1				0–1.6	6300	11.5	7.6
	Q2				0–0.26	20600	17.0	
	Q3				0–0.27	27500	18.7	9.0

^{a} Donor: designed according to Scheme 1.
^{b} Acceptor: designed according to Scheme 2.
^{c} Quantum yield of the pure donor (Eq. (1)).
^{d} Fluorescence lifetime of the pure donor determined by phase plane method.
^{e} Standard deviation.
^{f} Concentration range of acceptor.
^{g} Experimentally determined according to Perrin's model for static quenching in solid phase.
^{h} The radius of donor and acceptor collision complex for collision transfer where R_S is sum of donor (R_D) and acceptor (R_Q) radii.

tadecane solutions. Static measurements of fluorescence quenching coumarin derivatives as donor and N-oxyls as acceptors at various concentration fulfill the Perrin's model for static quenching in solid phase [37]:

$$\frac{\Phi_D^0}{\Phi_D} = \exp\left(VN[Q]\right) \qquad (13)$$

where Φ_D^0, and Φ_D are fluorescence quantum yields of donor without and with quencher, V is volume of active sphere of quenching, is quencher concentration and N is Avogadro's number. The radius of active sphere can be calculated assuming its spherical shape in a simple way $R = (3V/4\pi)^{1/3}$.

No molecular diffusion occurs during lifetime of coumarin donors, which is rather short even in polymer matrix around 2 ns, in glassy polystyrene matrix under $T_g \sim 100°$C. According Perrin's model the coumarin derivative (donor) is quenched by N-oxyls in the active sphere with unit efficiency. Outside this active sphere there is no quench-

ing. The quenching of two derivatives of coumarin **I**, **VII**, which exhibit more intense fluorescence and longer lifetime, was tested in polymer matrix. The plots of $\ln(\Phi_D^0/\Phi_D)$ on quencher concentration were linear with all quenchers (Fig. 7). The data of 'active quenching sphere', R, (Table 3) indicate that the energy transfer occurs on distance slightly larger than $R_D + R_Q = 7.5$ Å. For rod-like molecule **Q2** the spherical approximation is not applicable. High concentrations of quenchers are required to get quencher molecule in active sphere of donor. For **VII** the active quenching sphere is decreasing with increasing concentration of quencher **Q1**. In order to compare the donor-acceptor pairs under similar conditions, the same concentration range of quencher was used. Under these conditions, coumarin donor **VII** exhibit larger 'active sphere' than **I** as a result of higher Φ_D^0 and τ_D^0 for VII. The 'active quenching sphere' of both donors (**I**, **VII**) is slightly smaller with **Q2**. This might be due to the fact that quenching of rod-like molecule **Q2** depends on the orientation to the donor. The rod-like quencher might be

either in or out of the 'active sphere' at given concentration depending on orientation due to its size. This is not the case with **Q1**, which always will quench in the vicinity of donor. Therefore, the 'active sphere' of **Q1** is slightly larger than **Q2** (Table 3). The volume of 'active sphere' **V** and radius **R** is larger for quenching of **VII** with **Q3** as compared with **Q1**. In this case the energy transfer takes place at the distance larger than $R_D + R_Q = 9\,\text{Å}$.

This study of energy transfer from coumarin donors to N-oxyl acceptor in solution and in solid state results in following conclusions:

1. Fluorescence of most coumarin derivatives in cyclohexane solution is quenched by polar methanol. Probably ICT or TICT-like states are formed at these derivatives in polar methanol, which opens new radiationless channel for deactivation of the excited state of these coumarin derivatives.

2. Calculated and experimental values of critical radius R_0 and rate constant k_{ET} for energy transfer from coumarin as donor to free radical of N-oxyl type as acceptor are larger than the corresponding values if the collision mechanism is involved. No new red shifted emission was observed which could indicate formation of an exciplex. The data of R_0 and k_{ET} clearly show that the resonance energy transfer is involved in quenching of coumarin derivatives with N-oxyls in solution.

3. In non-polar glassy polystyrene matrix under T_g, the energy transfer from coumarin donor to N-oxyl acceptor occurs according to Perrin's model. There is strong indication that resonance energy transfer is operative as well.

Acknowledgements

References

[1] Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D.J. Cowley, W. Baumann, Nouv. J. Chim. 3 (1979) 443.
[2] M. Kaholek, P. Hrdlovic, J. Bartoš, Polymer in press.
[3] A. Gáplovský, P. Hrdlovič, J. Donovalová, P. Hrnčiar, J. Photochem. Photobiol. A: Chem. 59 (1991) 221.
[4] T.L. Arbeloa, F.L. Arbeloa, J.L. Arbeloa, J. Luminesc. 68 (1996) 149.
[5] K. Rechthaler, G. Köhler, Chem. Phys. 189 (1994) 99.
[6] S. Speiser, R. Katararo, Opt. Commun. 27 (1978) 287.
[7] W. Ware, J. Am. Chem. Soc. 83 (1961) 4374.
[8] R.G. Bennet, R.E. Kellog, J. Photochem. Photobiol. 7 (1968) 571.
[9] B.B. Raju, T.S. Varadarajan, J. Luminesc. 55 (1993) 49.
[10] B.B. Raju, T.S. Varadarajan, Laser Chem. 16 (1995) 109.
[11] M. Kaholek, P. Hrdlovič, J. Photochem. Photobiol. A. Chem. 108 (1997) 283.
[12] G. Moyze, J. Mlýnek, D. Jurčák, P. Hrdlovič, Chem. Listy 86 (1992) 57.
[13] A. Kawski, A. Kubicki, B. Kubliňsky, J. Photochem. Photobiol. A: Chem. 79 (1993) 161.
[14] D. Jurčák, J. Mlýnek, G. Moyze, P. Hrdlovič, Chem. Listy 83 (1989) 531.
[15] J.N. Demas, A.W. Adamson, J. Phys. Chem. 75 (1971) 2463.
[16] J.B. Birks, J.D. Dyson, Proc. R. Soc. London A 275 (1963) 135.
[17] S.J. Strickler, R.A. Berg, J. Chem. Phys. 37 (1962) 814.
[18] T.L. Arbeloa, F.L. Arbeloa, M.J. Tapia, J.L. Arbeloa, J. Phys. Chem. 97 (1993) 4704.
[19] G. Jones II, C.Y. Choi, W.R. Jackson, W.R. Bergmark, J. Phys. Chem. 89 (1985) 294.
[20] L.K. Fraiji, D.M. Hayes, T.C. Werner, J. Chem. Educ. 69 (1992) 424.
[21] R.S. Moog, W.W. Davis, S.G. Ostrowski, G.L. Wilson, Chem. Phys. Lett. 299 (1999) 265.
[22] F. Momicchioli, I. Baraldi, A. Carnevali, M. Caselli, G. Ponterini, Coord. Chem. Rev. 125 (1993) 301.
[23] M. Vogel, W. Rettig, Ber. Bunsenges. Phys. Chem. 89 (1985) 962.
[24] I. Baraldi, A. Carnevali, F. Momicchioli, G. Ponterini, Chem. Phys. 160 (1992) 85.
[25] W. Rettig, Angew. Chemie. 98 (1986) 969.
[26] O. Stern, M. Volmer, Phys. Z. 20 (1919) 183.
[27] Th. Förster, Disc. Faraday Soc. 27 (1959) 7.
[28] N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, CA, 1978, Chapter 9.
[29] C. Lin, A. Dienes, J. Appl. Phys. 44 (1973) 5050.
[30] A.A. Askadskij, Uspechi Chim. 46 (1977) 1122.
[31] A.A. Askadskij, J.I. Matvejev, Chimičeskoe strojenije i fizičeskije svojstva polimerov, Izdatel'stvo Chimija, Moskva, 1983.
[32] Th. Förster, Ann. Physik. 2 (1948) 55.
[33] J. B. Birks, Photophysics of Aromatic Molecules, Wiley, London 1970, Chapter 11.
[34] A.A. Lamola, N.J. Turro, Energy Transfer and Organic Photochemistry, in: P.A. Leermakers (Ed.), Technique of Organic Chemistry, vol. XIV, New York, 1969, Chapter 2.
[35] J.S. Seixas de Melo, R.S. Becker, A.L. Mačanita, J. Phys. Chem. 98 (1994) 6054.
[36] J.S. Seixas de Melo, R.S. Becker, F. Elisei, A.L. Mačanita, J. Chem. Phys. 107 (1997) 6062.
[37] F. Perrin, C. R. Acad. Sci. Paris 178 (1924) 1978.