

Fluorescence Quenching in Bichromophoric Systems with Nonconjugated Chromophores: 5-Substituted Derivatives of 1,3,5-Triaryl-2-Pyrazoline

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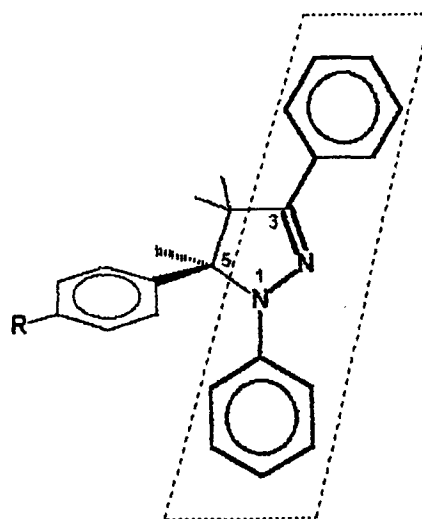
The spectral and fluorescent properties of 1,3,5-triphenyl-2-pyrazoline derivatives with acceptor substituents in benzene ring in the 5 position of the pyrazoline cycle were investigated. The corresponding pyrazoline derivative, in which phenyl radical in the 5 position is replaced by a fragment with an extended conjugated system—2,5-diphenyloxazolyl—was studied as well. The noticeable decrease in fluorescence quantum yield in comparison with the nonsubstituted molecule is characteristic of the compounds studied, which belong to the broader class of bichromophoric molecules with nonconjugated chromophores. The existence of excited states of “mixed” or “cross” (charge transfer) type, formed with participation of occupied molecular orbitals of one chromophoric fragment and vacant molecular orbitals of another, is typical of such a bichromophoric system. On the basis of our experimental and theoretical data, the assumption was made that the fluorescence quenching in the investigated bichromophoric molecules could be connected with the thermal population of the excited states of “mixed” type.

KEY WORDS: Bichromophoric systems with nonconjugated chromophores; 1,3,5-triaryl-2-pyrazoline.

INTRODUCTION

According to widespread insights, the spectral and luminescent properties of luminophores belonging to the 1,3,5-triaryl-2-pyrazoline series (I) are defined, mainly, by their extended π -electron-conjugated system, including aryl radicals in positions 1 and 3 and the hydrazonic group $\text{N}=\text{C}$ of the heterocyclic ring.⁽¹⁻⁶⁾

It is commonly understood that the introduction of substituents on the phenyl radical in position 5 of the pyrazoline ring, which is not conjugated with the basic chromophoric system of the molecule and is almost orthogonal to it,⁽⁷⁾ does not have much effect on the luminescent characteristics. The absorption spectra of such substances, it is thought, would be similar to a definite superposition of spectra of 1,3-diaryl-2-pyrazoline and



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an appropriate model molecule. However, evidence to the contrary^(8,9) has been published. Data reported⁽⁸⁾ show

that derivatives of I, having in position 5 of the pyrazoline ring any chromophoric fragment with an extended conjugated system, are characterized by a significant lowering of their quantum yield. In fact, an absence of fluorescence was reported⁽⁹⁾ for derivatives of I having in the benzene ring in position 5 of the pyrazoline cycle acceptor substituents such as SO₂X, where X is a completely or partially fluorinated methyl group. It was also reported that the introduction of these substituents onto the other benzene rings of the molecule does not result in an appreciable reduction in fluorescence efficiency. So a possible reason for the above-mentioned disappearance of fluorescence for the derivatives of I that have such an acceptor group *cannot* be the negative influence of $n\pi^*$ levels² brought into the system of excited terms of the molecule by substituents like SO₂X. As a probable explanation for the described quenching of fluorescence, the authors⁽⁹⁾ suggested an inductive influence of a strong acceptor substituent to the donor properties of nitrogen atom in position 1 of the pyrazoline cycle (the N₁ atom plays an important role in the chromophoric system of I). But this does not seem convincing to us in view of the large distance between the introduced acceptor substituent and the N₁ atom—donor center of the molecule. Further, these conclusions⁽⁹⁾ cannot explain the near-absence of fluorescence, for example, in bichromophoric derivatives of I, in which fragments of 2,5-diphenyloxazole or stilbene are attached to the 5 position of the pyrazoline cycle, as reported in Ref. 8.

In the present work an attempt was made to discover the possible reasons for the essential lowering of fluorescent quantum yield of substituted 1,3,5-triaryl-2-pyrazoline with the acceptor substituents in the benzene ring in the 5 position of the pyrazoline cycle or with chromophoric fragments with extended conjugated system attached there. For this purpose, we have investigated in detail the photophysical characteristics of derivatives of I with appropriate substituents ($R = \text{CN}, \text{SO}_2\text{NH}_2, \text{SO}_2\text{CHF}_2, 5\text{'-phenyl-oxazolyl-2}$). Quantum-chemical calculations by the π -electronic PPP MO LCAO CI method were also carried out.

EXPERIMENTAL

Synthesis of the compounds under study was described in Refs. 9 and 12. All investigated substances

² The efficiency of intersystem conversion between $S_{n\pi^*}$ and $T_{n\pi^*}$ levels could exceed the fluorescence efficiency by 2–3 orders of magnitude; for example, see Refs. 10 and 11.

were purified by hot column chromatography on Al₂O₃ with *n*-heptane as eluent, then recrystallized from the appropriate solvent.

The electronic absorption spectra were measured with Specord M40 and HITACHI U3210 spectrophotometers, and the fluorescence spectra by means of an Hitachi F4010 spectrofluorimeter. In order to assign the low-intensity luminescence, recorded at the sensitivity limit of the latter instrument, to the emission of molecules of the investigated substances, we also made use of their fluorescence excitation spectra. The fluorescence quantum yields were determined relative to quinine bisulfate in 1 *N* sulfuric acid ($\mu_r = 0.546$,⁽¹³⁾) with an excitation wavelength of 360 nm. The obtained quantum yield values were corrected by the ratio of squares of the refraction indices of reference and sample solutions. The optical density of the solutions, upon determination of the quantum yields, did not exceed 0.2 at a thickness of the absorbing layer of 1 cm. The fluorescence kinetics were studied with a pulse fluorometer, working in the single-photon mode in the nanosecond range.^(14,15) Mathematical processing of the measured fluorescence decay curves was made by the nonlinear least-squares method.⁽¹⁶⁾ PPP MO LCAO CI calculations, with up to 100 singly excited configurations, were carried out with the set of parameters from Ref. 17.

RESULTS AND DISCUSSION

The basic spectral and fluorescent characteristics of the investigated compounds are presented in Table I. Unfortunately, for some poorly fluorescent samples, it was not possible to measure the fluorescence decay kinetics. And for the efficiently fluorescent compound IX, it was possible to determine only the position of emission maximum in octane, because of the very low solubility.

The introduction into fluorescent molecules of an acceptor substituent such as the CN group does not usually result in a noticeable quenching of fluorescence, compared, for example, to the NO₂ group, the other acceptor substituent, commonly used by organic chemists, which is a well-known quencher of fluorescence.⁽¹⁸⁾ In our case (Table I), the CN group in the benzene ring in position 5 of the pyrazoline cycle causes a reduction in the emission quantum yield by almost two orders of magnitude. As the reason for such behavior, one could consider, among other explanations, electron transfer quenching, intramolecular exciplex formation, intramolecular singlet–triplet energy transfer, etc. We have at-

Table I. Spectral Characteristics of Some 1,3,5-Triaryl-2-pyrazoline Derivatives in Solvents of Different Polarities (20°C)^a

Compound	Substituent	Solvent	ν_a (cm ⁻¹)	ν_f (cm ⁻¹)	$\Delta\nu_{ST}$ (cm ⁻¹)	φ_f	τ_f (ns)
I	H	O	27,960	23,180	4,780	0.86	3.28
		T	27,760	22,620	5,140	0.72	3.49
		A	28,020	21,480	6,540	0.64	4.33
II	5-CN	O	28,900	22,960	5,940	0.0075	—
		T	28,040	22,600	5,440	0.0062	—
		A	28,500	20,440	8,060	0.0022	—
III	5-SO ₂ NH ₂	O	28,180	23,080	5,100	0.030	—
		T	27,700	22,700	4,900	0.046	0.34
		A	28,060	21,000	7,060	0.010	—
IV	5-SO ₂ CHF ₂	O	28,820	23,360	5,460	0.0007	—
		T	28,500	22,700	5,800	0.0012	—
		A	28,940	22,880	6,060	0.0006	—
V	1-SO ₂ CHF ₂	O	28,140	24,540	3,600	0.86	1.77
		T	27,740	24,080	3,660	0.83	1.85
VI	1,5-(SO ₂ CHF ₂) ₂	O	28,320	24,600	3,720	0.011	—
		T	27,980	24,300	3,620	0.007	0.06
		A	28,100	24,040	4,060	0.001	—
VII	5-(5'-Phenyloxazolil-2)	O	27,960	23,280	4,680	0.052	0.51
		T	27,600	22,880	4,720	0.039	0.38
		A	28,000	24,560	3,440	0.017	—
VIII	3-SO ₂ CHF ₂	O	24,540	20,640	3,900	0.77	3.85
		T	24,280	19,940	4,340	0.54	3.94
		A	24,560	18,360	6,200	0.44	4.06
IX	3-SO ₂ CHF ₂ , 5-SO ₂ NH ₂	O	—	20,820	—	—	—
		T	24,660	20,000	4,660	0.58	3.98
		A	24,840	18,400	6,440	0.41	4.05

^a ν_a and ν_f , positions of the long-wavelength absorption and fluorescence band maxima; $\Delta\nu_{ST}$, Stokes shift; φ_f , fluorescence quantum yield; τ_f , fluorescence lifetime. Solvents used: O, *n*-octane; T, toluene; A, acetonitrile.

tempted to model these prospective intramolecular processes in molecules of compound II by observing solutions of unsubstituted 1,3,5-triphenyl-2-pyrazoline in solvents containing CN groups. We expected interactions of excited molecules of I with those solvents similar to those in excited molecules of compound II. No appreciable fluorescence quenching was observed for I in acetonitrile and benzonitrile solutions (in the latter case, $\varphi = 0.59$, $\tau = 4.10$ ns). This fact allows us to exclude from the list of possible reasons for quenching processes such as electron transfer or S-T energy transfer. In the latter case, there is some possibility of quenching of the Franck-Condon excited state of I, $E_{SI}(FC) \sim 26,000$ – $28,000$ cm⁻¹, which may co-incide with the energy of the lowest triplet state of PhCN, $E_T \sim 27,000$ cm⁻¹. However, the probability of such a process in the structurally and solvent-relaxed excited state of I ($E \sim 21,000$ – $23,000$ cm⁻¹) is very low. The absence of appreciable broadening of the fluorescence bands of

I in CH₃CN and PhCN in comparison with the reference solutions in octane or toluene also allows us to exclude among the possible reasons for quenching processes such as exciplex formation.³

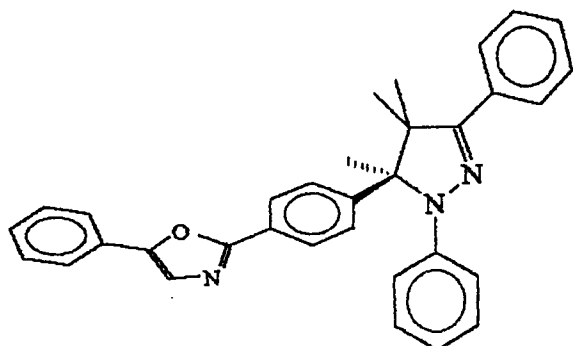
There is some evidence that allows us to propose a connection between the studied quenching of fluorescence and the nonconjugated nature of the molecules under study. No decrease in fluorescence efficiency was observed when an acceptor substituent was introduced onto the benzene rings at positions 1 or 3 of the pyrazoline cycle of I (For example, see compounds V and VIII. For molecule IX, the possible quenching influence of the SO₂NH₂ group on phenyl-5 is affected by the SO₂CHF₂ substituent on phenyl-3, which results in a lowering of the energy of the S₁ state by more than 3000 cm⁻¹.)

³ In most cases, the so-called intramolecular exciplexes, for example, Ref. 19, have their intermolecular analogues.

Table II. Fluorescent Properties of Some 1,3,5-Triaryl-2-pyrazole Derivatives (Octane; 20°C), Obtained via Oxidation of the Corresponding Derivatives of Pyrazoline^a

Substituent	ν_a (cm^{-1})	ν_f (cm^{-1})	$\Delta\nu_{ST}$ (cm^{-1})	φ_f	τ_f (ns)	k_f (s^{-1})	k_d (s^{-1})
H	33940	26520	7420	0.09	0.95	$1.0 \cdot 10^8$	$9.5 \cdot 10^8$
5-SO ₂ NH ₂	32350	24700	7650	0.16	1.72	$1.0 \cdot 10^8$	$4.9 \cdot 10^8$
1,5-(SO ₂ CHF ₂) ₂	31390	25000	6390	0.18	1.59	$1.2 \cdot 10^8$	$5.2 \cdot 10^8$

^a ν_a and ν_f , positions of the long-wavelength absorption and fluorescence band maxima; $\Delta\nu_{ST}$, Stokes shift; φ_f , fluorescence quantum yield; τ_f , fluorescence lifetime. The rate constants of primary photophysical processes, presented in this table (and also in the subsequent tables), were estimated according to the following equations: fluorescence emission rate constants, $k_f = \varphi_f / \tau_f$, total rate constants of the radiationless deactivation, $k_d = (1 - \varphi_f) / \tau_f$.



The conjugation between the benzene ring in position 5 of the heterocycle and the rest of the molecule could be restored by chemical oxidation of the pyrazoline cycle. The introduction of a double bond at position 4 of the heterocycle results in the formation of a conjugated pyrazole system (as much as a steric hindrance allows). We have synthesized three corresponding pyrazole derivatives via oxidation by CrO₃ in acetic acid of the unsubstituted I molecule and two of its least fluorescent 5-acceptor-substituted derivatives. The spectral data concerning compounds, obtained in this way, are presented in Table II. No fluorescence quenching, in comparison with unsubstituted 1,3,5-triphenyltriazole, is observed in these cases. In fact, nearly double the fluorescence efficiency was found for these triphenylpyrazole derivatives with acceptor substituents in phenyl 5 as opposed to the corresponding derivatives of pyrazoline.

The example of compound VII was rather indicative to us. This molecule is a combination of chromophoric fragments of two widely known effective organic luminophores—1,3-diphenyl-2-pyrazoline and 2,5-diphenyloxazole, each with fluorescence quantum yields

in the range 0.7–0.9. The quantum yield of compound VII, however, does not exceed 0.05 in nonpolar solvents and is less than 0.02 in polar media. This, and the preceding evidence, convinced us that the investigated process of fluorescence quenching might be connected with the bichromophoric nature of the compounds under study.

According to the theory developed,^(20–22) in the absorption spectra of bichromophoric substances with nonconjugated chromophores, one should observe electronic transitions specific to each chromophoric subsystem present in a molecule. These transitions are practically indistinguishable in energy and intensity from similar transitions in the spectra of isolated molecule fragments. But, in addition, “mixed” or “cross” transitions (and, accordingly, “mixed” or “cross” excited states), which are formed with the participation of the occupied molecular orbitals (MO) of one and the vacant MO of another chromophoric fragment, are also present. On the basis of quantum-chemical calculations,^(20,21) the assumption was made that, in bichromophoric systems with nonconjugated chromophoric fragments, the process of intramolecular energy transfer originates by the mechanism of internal conversion. Therefore, after excitation of the donor fragment, the internal conversion, via “mixed” states, brings a molecule to the lowest excited state located on the acceptor fragment. Owing to the absence of conjugation between chromophoric fragments and, consequently, the pronounced difference in localization of the above-mentioned occupied and vacant orbitals, the “mixed” transitions are forbidden and have a charge-transfer (CT) character. Moreover, direct experimental observation of electronic transitions of the “mixed” CT type in the absorption spectra would be practically impossible due to the overlap by bands of neighboring intense electronic transitions.

Table III. Rate Constants of Primary Photophysical Processes in Molecules of Some 1,3,5-Triaryl-2-pyrazoline Derivatives^a

Compound	Substituent	Solvent	k_f (s ⁻¹)	k_d (s ⁻¹)
I	H	Octane	2.6·10 ⁸	4.3·10 ⁷
		Toluene	2.2·10 ⁸	7.6·10 ⁷
		CH ₃ CN	1.5·10 ⁸	8.4·10 ⁷
		C ₆ H ₅ CN	1.4·10 ⁸	1.0·10 ⁸
III	5-SO ₂ NH ₂	Toluene	1.4·10 ⁸	2.8·10 ⁹
V	1-SO ₂ CHF ₂	Toluene	4.5·10 ⁸	9.2·10 ⁷
VI	1,5-(SO ₂ CHF ₂) ₂	Toluene	1.1·10 ⁸	1.7·10 ¹⁰
VII	5-(5'-Phenylloxazolyl-2)	Toluene	1.3·10 ⁸	3.1·10 ⁹
VIII	3-SO ₂ CHF ₂	Toluene	1.4·10 ⁸	1.2·10 ⁸
		CH ₃ CN	1.1·10 ⁸	1.4·10 ⁸
IX	3-SO ₂ CHF ₂ , 5-SO ₂ NH ₂	Toluene	1.5·10 ⁸	1.1·10 ⁸
		CH ₃ CN	1.0·10 ⁸	1.5·10 ⁸

^a See comments to Tables I and II, footnotes *a*. The value of fluorescence emission constant for 1,3,5-triphenyl-2-pyrazoline, obtained from its absorption spectra in toluene, is 2.1·10⁸ s⁻¹.

Let us consider some results of our quantum-chemical calculations within the framework of the PPP π -electronic method.⁴ The molecule of 1,3,5-triphenyl-2-pyrazoline with a CN group introduced in the benzene ring at the 5 position of the pyrazoline cycle has a highest occupied molecular orbital [HOMO; $E(\varphi_1) = -8.09$ eV], located on the basic chromophoric fragment, similar in localization to the corresponding MO of the nonsubstituted molecule. At the same time, the lowest unoccupied molecular orbital [LUMO; $E(\varphi_1) = -2.09$ eV] of compound **II** is located on the benzonitrile fragment. The next vacant orbital, above the LUMO, is localized on the diphenylpyrazoline fragment [$E(\varphi_2) = -1.91$ eV] and only slightly exceeds the energy of the "benzonitrile" LUMO.

So if the S₁ state of these molecules is a forbidden state of a "cross" (or "mixed") CT type, it would be logical to assume that the reason for the low luminescence efficiency of the investigated derivatives of 1,3,5-triphenyl-2-pyrazoline with acceptor substituents in the 5 position may be the low fluorescence emission rate constant. In such a case, even the tiny value of the total radiationless rate constant ($k_d \sim 4 \cdot 10^7$ s⁻¹), char-

acteristic of the unsubstituted **I** molecule, would greatly exceed the emission rate constant from the CT "mixed" S₁ state. This would lead to a considerable reduction in the fluorescence quantum yield: $\varphi_f = k_f/(k_f + k_d)$. However, our calculations show that the lowest excited state of a 5-CN derivative is generated mainly by the configuration 1-2' (95%), which is formed with participation of the "pyrazoline" MOs only and, hence, has the same nature as the corresponding S₁ state of the unsubstituted molecule (**I**). The next excited state, S₂, is formed by the configuration 1-1' (93%), with participation of the pyrazoline HOMO and benzonitrile LUMO, and is a state of "mixed" CT type. The experimental estimation of rate constants of primary photophysical processes in the molecules of the investigated substances, presented in Table III, shows that the introduction of acceptor substituents into the 5 position does not result in a change in the nature of fluorescent states of compounds **I-IX**; the energies of long-wavelength transitions S₀-S₁ (Table I) and the fluorescence emission rate constants (Table III; estimated on the basis of experimental values φ_f and τ_f) remain practically unchanged from the corresponding value of the nonsubstituted compound (**I**) in this series of molecules. At the same time, the total efficiency of processes of radiationless dissipation of the excitation energy for all compounds with the acceptor substituents in the benzene ring in position 5 of the pyrazoline cycle (Table III) is increased by several orders of magnitude. Hence, the possible reason for the practical absence of fluorescence for studied derivatives of 1,3,5-triphenyl-2-pyrazoline could not be a low k_f value. There must be a completely new effective channel for the radiationless dissipation of electronic excitation energy.

On the basis of all the theoretical and experimental data, we propose the direct participation of "mixed" excited states, lying slightly higher in energy than the fluorescent level S₁, in the process of fluorescence quenching of bichromophoric molecules with nonconjugated chromophoric fragments. The proposed mechanism of fluorescence quenching in the investigated compounds could include either a very effective intersystem crossing process from the thermally populated S₂ "mixed" (CT) state to an appropriate triplet level or a thermally activated intersystem crossing from the S₁ state to a triplet state of a "mixed" nature (the corresponding singlet and triplet states of a "mixed" CT type, from our calculations, are nearly equal in energy). Unfortunately, the data at our disposal could not specify the multiplicity of the CT state, responsible for fluorescence quenching; therefore, here and later we speak about "mixed" states of nondefined multiplicity.

⁴ To determine the general applicability of the PPP π -electronic calculation method for the description of bichromophoric systems with nonconjugated chromophoric fragments, we made a set of calculations on molecular systems appearing in Refs. 20-22, in which the full-valent INDO/S method with a specially developed spectroscopic parameterization was used. The fact that our results were in good agreement with the data of Refs. 20 and 21 for the singlet energy levels of the calculated molecules, for both local-chromophoric and for "mixed" type, allowed us to conclude that this calculational method is applicable to the molecules studied here.

Table IV. Temperature Quenching of Fluorescence of Some 1,3,5-Triaryl-2-pyrazoline Derivatives in Toluene^a

Compound	Substituent	<i>t</i> (°C)	φ_f	k_d (s ⁻¹)	ΔE_{act}
II	5-CN	10	0.0071	1.8·10 ¹⁰	2.03 kcal/mol (~700 cm ⁻¹)
		20	0.0062	2.1·10 ¹⁰	
		30	0.0055	2.3·10 ¹⁰	
		40	0.0050	2.6·10 ¹⁰	
		50	0.0045	2.9·10 ¹⁰	
		60	0.0041	3.1·10 ¹⁰	
		70	0.0038	3.4·10 ¹⁰	
III	5-SO ₂ NH ₂	10	0.055	2.4·10 ⁹	3.25 kcal/mol (~1100 cm ⁻¹)
		20	0.046	2.8·10 ⁹	
		30	0.039	3.4·10 ⁹	
		40	0.034	3.9·10 ⁹	
		50	0.029	4.6·10 ⁹	
		60	0.025	5.3·10 ⁹	
		70	0.020	6.7·10 ⁹	
VII	5-(5'-Phenyl-oxazolyl-2)	10	0.045	2.6·10 ⁹	2.42 kcal/mol (~850 cm ⁻¹)
		20	0.039	3.1·10 ⁹	
		30	0.034	3.5·10 ⁹	
		40	0.030	4.0·10 ⁹	
		50	0.027	4.6·10 ⁹	
		60	0.024	5.0·10 ⁹	
		70	0.022	5.7·10 ⁹	

^a Total rate constants of radiationless deactivation (k_d) were estimated from the corresponding quantum yields at different temperatures and fluorescence emission rate constants for 20°C, proposed to be unchanged (Tables I and III).

Because of the charge-transfer character of "cross" transitions, in "mixed" states, mentioned earlier, there would be substantial growth of the dipole moment in comparison to the corresponding ground-state value. In this case, the position of "mixed" states would be essentially dependent on the nature of the solvent; the energy of the specified transitions would decrease with the increase in solvent polarity. The fluorescence efficiency of the investigated pyrazoline derivatives does decrease appreciably in the series of solvents octane-toluene-acetonitrile. This fact, in our opinion, could be connected with the reduction of the energy gap between the fluorescent state and the highly polar "mixed" CT state. This evidence also favors the participation of the latter state in the fluorescence quenching of 5-acceptor-substituted triphenylpyrazolines. If the fluorescence quenching of the investigated pyrazoline derivatives is connected with the population of a CT-type state lying in energy slightly above the fluorescent S_1 state, then it most likely occurs by thermal population. The temperature quenching of fluorescence (Table IV), which was observed for all 5-substituted derivatives of I, and which was completely absent for unsubstituted 1,3,5-triphenyl-2-pyrazoline, supports this idea. The activation energies of

quenching, estimated from the experimental spectral data, fit with the difference in energy between S_1 and such a "mixed" state. The measured values E_{act} , presented in Table IV, lie within the limits 2–3 kcal/mol, or 700–1100 cm⁻¹. There is a correspondence between estimated activation energies of quenching (i.e., difference in energy between S_1 and "mixed" CT states?) and the efficiency of emission; the smaller the activation energy, the smaller the fluorescence quantum yield (Tables I and IV). These facts also confirm the idea of affinity in energy of a fluorescent and "mixed" CT state being responsible for the quenching of fluorescence.

There are some facts, however, which seem to be somewhat inconsistent with the proposed mechanism. In Ref. 8 it was reported that the bichromophoric derivatives of 1,3,5-triphenyl-2-pyrazoline are intensively fluorescent in polymer matrices even though the fluorescence is practically absent in liquid solutions. This circumstance induced us to research the fluorescent properties of several substances from this series in thin polymer films. We made such films by slow evaporation of solvent from a three-component polystyrene-toluene-dye solution on glass plates at room temperature. Because of the difficulty in manufacturing optically

Table V. Fluorescent Properties of Some 1,3,5-Triphenyl-2-pyrazoline Derivatives in Thin Polystyrene Films^a

Compound	Substituent	ν_a (cm^{-1})	ν_r (cm^{-1})	$\Delta\nu_{\text{ST}}$ (cm^{-1})	τ_f (ns)	ϕ_f	k_d (s^{-1})
I	H	27440	22960	4480	3.93	0.81	$4.8 \cdot 10^7$
III	5-SO ₂ NH ₂	27640	23100	4540	2.77	0.38	$2.2 \cdot 10^8$
IV	5-SO ₂ CHF ₂	28380	23040	5340	2.09	0.25	$3.6 \cdot 10^8$
VI	1,5-(SO ₂ CHF ₂) ₂	27800	24320	3480	1.26	0.14	$6.8 \cdot 10^8$

^a The values of ϕ_f and k_d were estimated from the experimental fluorescence lifetimes and emission rate constants for toluene solutions (Tables I and III).

identical films, the emission quantum yields in these cases were not measured directly but were estimated from the measured fluorescence decay kinetics in the films with the fluorescence emission rate constant, determined in this work for toluene solutions (Table V). From those estimates, we found that the fluorescence quenching which is typical for 5-substituted derivatives of 1,3,5-triphenyl-2-pyrazoline in liquid solutions is also present in polymer media, though at a much smaller degree. Apparently, the reduction in fluorescence quenching efficiency in polymer media could be connected with the change in conformation of the studied molecules in polymer media or with the reduction in amplitudes of some high-amplitude vibrations in the solid state. So the opportunity for thermal activation might be reduced also. The other possible reason of the reduction of quenching efficiency might be connected with a possible change in mutual spatial orientation of two chromophoric moieties in the studied molecules in polymer media. If they are interacting by a mechanism like Simmons and Fukunaga' spiroconjugation,⁽²³⁾ the maximal extent of such interaction would occur when the angles between the planes of the chromophoric moieties are close to 90°. For angles less than 90°, the efficiency of interactions related to spiroconjugation would be reduced. The validity of this mutual orientation effect for other interesting bichromophoric systems with nonconjugated chromophoric fragments, the ones which form the so-called intramolecular exciplexes, was reported, for example, by J. W. Verhoeven in Refs. 24 and 25.

It is necessary to note, also, that we observed the temperature quenching, typical of solutions, in polymer matrixes which were prepared by solidifying solutions of the investigated compounds in molten polystyrene.

Rather interesting to us is the fact, that, though quenching of fluorescence of 5-substituted derivatives of I is observed in polymer matrixes, the expected accompanying phosphorescence was not found. Thus, one could conclude that, during the fluorescence quenching

of bichromophoric derivatives of 1,3,5-triphenyl-2-pyrazoline, either triplet energy levels are not populated (as in frozen solutions of the unsubstituted 1,3,5-triphenyl-2-pyrazoline⁽²⁶⁾), or, more probably, subsequent effective quenching of formed triplet states takes place. The mechanism of dissipation of the electronic excitation energy from thermally populated "mixed" CT states remains unclear and demands further special research.

To complete the discussion, let us return to the example of compound VII. The energy of the vacant molecular orbital of the diphenyloxazole fragment lies only slightly below that of the lowest vacant MO of the diphenylpyrazoline fragment. Thus, the proposed mechanism of fluorescence quenching with the participation of CT states, observed for the derivatives of I with acceptor substituents in the 5 position, is also valid for compound VII. It is possible that the described mechanism of fluorescence quenching in bichromophoric systems with nonconjugated chromophores is rather general and could be found in other bichromophoric luminophores, for which the conditions for such an interaction are satisfied: the energy of a corresponding "mixed" CT state is close to the energy of the fluorescent state.

CONCLUSION

The mechanism of fluorescence quenching in 5-substituted derivatives of 1,3,5-triaryl-2-pyrazoline, examples of bichromophoric molecules with nonconjugated chromophoric fragments, is explained with an assumption about the participation of thermally populated "mixed" or "cross" CT states. When these states, formed with the participation of occupied molecular orbitals of one chromophoric fragment and the vacant molecular orbitals of another, are close in energy to the S₁ state, then the fluorescence is noticeably quenched. This proposed mechanism of fluorescence quenching in bichromophoric systems with nonconjugated chromophores

may be rather general and could be found to operate in other bichromophoric systems.

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