

Emissive Properties and Intramolecular Charge Transfer of Pyrazoloquinoline Derivatives

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The fluorescence properties of several pyrazoloquinoline derivatives were performed by stationary as well as by time-resolved spectroscopy. Non-donor-substituted compounds show a high quantum yield; transition dipole moments of absorption and fluorescence as well as experimental and calculated lifetimes are in excellent agreement. The donor-substituted compound DMA-DPPQ exhibits a charge transfer fluorescence in polar solvents. Additionally, dual fluorescence appears in polar protic solvents. The nature of the charge transfer state is discussed with respect to the TICT model.

KEY WORDS: Pyrazoloquinoline derivatives; charge transfer; emissive properties.

INTRODUCTION

Bulky π -electron donor and acceptor systems, connected by a single bond, have recently been the subject of numerous publications.⁽¹⁻⁷⁾ Special attention is paid to the structure of those large molecules in their CT excited state. For 9-[4-(*N,N*-dimethylamino)-phenyl]-anthracene and its derivatives as well as for 9,9'-bianthryl and different carbazole derivatives containing different cyano-phenyl moieties as electron acceptors, the D-A conformation in their excited states was postulated to become more coplanar than in the ground state. Recently, some of us have reported the CT interactions in excited 4-[(4'-*N,N*-dimethylamino)-phenyl]-3,5-dimethyl-1,7-diphenyl-bispyrazolo-[3,4-*b*;4',3'-*e*]-pyridine (DMA-DMPP).⁽⁶⁾ In this case the problem of mutual orientation

of the donor and acceptor subunits remains an open question.

The experimental results of photophysical investigations on DMA-DMPP and theoretical calculations performed by Parusel *et al.*⁽⁸⁾ suggest the perpendicular geometry of donor and acceptor subunits in the CT state, as postulated for the so-called TICT state model.^(9,10)

Recently several new derivatives of pyrazolo[3,4-*b*]quinoline have been synthesized. In the present paper we report the results of (i) the photophysical properties of the non-donor-substituted derivatives, (ii) the influence of substituents of pyrazoloquinoline derivatives on their emissive properties, and (iii) the photoinduced charge transfer in the donor-acceptor derivative, i.e., DMA-DPPQ (see formulae), especially the influence of the solvent properties on the process.

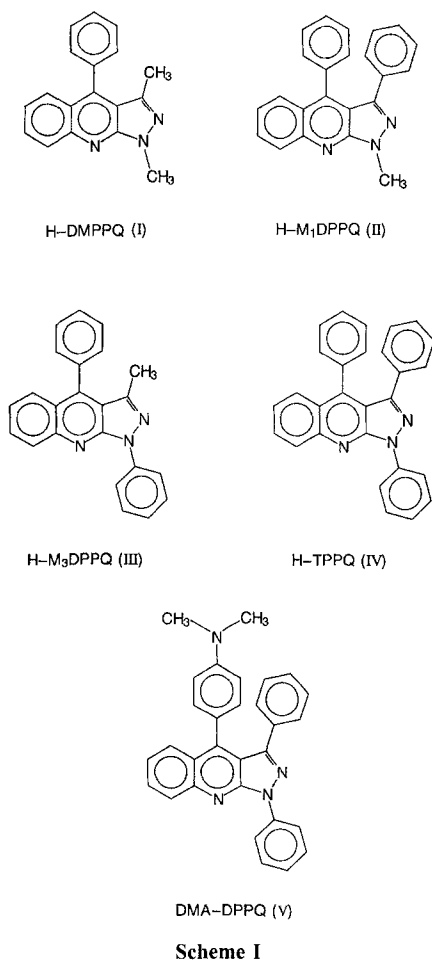
EXPERIMENTAL

The pyrazoloquinoline derivatives H-DMPPQ (**I**) (1,3-dimethyl-4-phenyl-pyrazolo[3,4-*b*]-quinoline), H-M₁DPPQ (**II**) (1-methyl-3,4-diphenyl-pyrazolo[3,4-*b*]-

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quinoline), H-M₃DPPQ (**III**) (3-methyl-1,4-diphenyl-pyrazolo[3,4-b]-quinoline), H-TPPQ (**IV**) (1,3,4-triphenyl-pyrazolo[3,4-b]-quinoline), and DMA-DPPQ (**V**) [4-(4'-*N,N*-dimethylamino)-phenyl-1,3-diphenyl-pyrazolo[3,4-b]-quinoline] (see Scheme I) were synthesized by some of us (A.D., P.T., K.Ch.). The synthesis will be described elsewhere.

Solvents used were of the highest available purity and were checked for impurities by absorption and fluorescence. The following numbering of solvents is used throughout the text: cyclohexane (1), benzene (2), toluene (3), butyl ether (4), *t*-butyl methyl ether (5), 1-chlorobutane (6), tetrahydrofuran (7), dichloromethane (8), 1,2-dichloroethane (9), pentanol-1 (10), butanol-1 (11), cyclohexanone (12), propanol-1 (13), ethanol (14), methanol (15), *N,N*-dimethylformamide (16), acetonitrile (17), and dimethyl sulfoxide (18). Absorption and fluorescence spectra as well as fluorescence decay times were measured as described previously.⁽⁶⁾

RESULTS AND DISCUSSION

Photophysical Properties of Non-Donor-Substituted Pyrazoloquinolines

All four compounds (**I–IV**) are characterized by a high fluorescence quantum yield, i.e., unity or almost-unity, independent of solvent polarity. The absorption shows a very slight blue shift and slight red shift of fluorescence with increasing solvent polarity. It can be caused by a change of the direction and the value of the dipole moment in the excited state. The photophysical features characterizing compounds (**I–IV**) are collected in Table I–IV.

Absorption and normalized fluorescence spectra of all four compounds in isooctane are presented in Figs. 1 and 2, respectively. The oscillator strength f , the values of transition dipole moments ($\mu_{m \leftarrow n}$ in absorption, $\mu_{m \rightarrow n}$ in fluorescence), and the natural lifetime τ_f^0 are obtained using Eqs. (1)–(4).

$$f = \frac{4 \ln 10 \cdot m_e c^2 \epsilon_0}{e^2 N_L n_{\text{abs}}} \cdot \int \epsilon d\tilde{\nu} \quad (1)$$

$$|\vec{\mu}_{m \leftarrow n}|^2 = \frac{3 \ln 10 \cdot h c \epsilon_0}{2 \pi^2 N_L n_{\text{abs}} \tilde{\nu}_{\text{abs}}} \cdot \int \epsilon d\tilde{\nu} \quad (2)$$

$$|\vec{\mu}_{m \rightarrow n}|^2 = \frac{3 h \epsilon_0}{16 \pi^3} \cdot \frac{Q_f}{n_f^3 \tilde{\nu}_f^3 \tau_f} \quad (3)$$

$$\frac{1}{\tau_f^0} = \frac{8 \pi c \cdot \ln 10}{N_L} \cdot \frac{n_f^3}{n_{\text{abs}}} \cdot \frac{1}{\langle \tilde{\nu}_f^{-3} \rangle_{\text{av}}} \cdot \int \epsilon d \ln \tilde{\nu} \quad (4)$$

In these equations n_{abs} and n_f denote the refractive indices of solvent at the absorption and fluorescence maximum, respectively, Q_f the quantum yield of fluorescence, ϵ the absorption coefficient, and $\tilde{\nu}_{\text{abs}}$ and $\tilde{\nu}_f$ the wavelength maxima of absorption and fluorescence, respectively. All other constants have their usual meaning.

The experimental fluorescence lifetimes τ_f are given in the tables for comparison with the calculated lifetimes.⁽¹¹⁾ The very good agreement between them (τ_f is practically equal to the natural lifetime due to the fluorescence quantum yield of unity) has to be stressed. Also, both transition dipole moments are in excellent agreement.

All these results as well as the small Stokes shift prove the stability of the pyrazoloquinoline structure, as there is practically no change in geometry after excitation. That offers the possibility of application of these compounds as fluorescence standards in the blue–green

Table I. Photophysical Properties of H-DMPPQ (I) in Several Solvents

| | Isooctane | Benzene | Butyl ether | Tetrahydrofuran | 1-Chlorobutane | Acetonitrile | Ethanol |
|--|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\tilde{\nu}_{\text{abs}}$ (cm ⁻¹) | 25,140 26,400 | 25,020 26,160 | 25,160 26,340 | 25,190 26,310 | 25,160 26,320 | 25,290 26,300 | 25,210 26,290 |
| ϵ (m ² mol ⁻¹) | 729;757 | 727;787 | 661;706 | 663;717 | 647;702 | 667;727 | 684;748 |
| f | 0.076 | 0.075 | 0.072 | 0.075 | 0.072 | 0.080 | 0.081 |
| $ \mu_{\text{m} \rightarrow \text{n}} $ (10 ⁻³⁰ Cm) | 8.2 | 8.2 | 8.1 | 8.2 | 8.0 | 8.5 | 8.5 |
| $\tilde{\nu}_{\text{r}}$ (cm ⁻¹) | 23,300 | 23,000 | 23,300 | 22,800 | 23,100 | 22,900 | 22,900 |
| Q_{r} | 0.95 | 1.00 | 0.82 | 0.94 | 0.99 | 0.98 | 0.95 |
| τ_{r} (ns) | 14.18 | 13.75 | 12.77 | 14.86 | 14.93 | 17.03 | 16.34 |
| Γ_{r} (cm ⁻¹) | 3,000 | 3,100 | 3,100 | 3,200 | 3,100 | 3,200 | 3,200 |
| $ \mu_{\text{m} \rightarrow \text{n}} $ (10 ⁻³⁰ Cm) | 8.3 | 7.7 | 8.0 | 8.2 | 8.2 | 8.3 | 8.2 |
| $\tau_{\text{r,calc}}^0$ (ns) | 16.2 | 13.4 | 17.2 | 17.0 | 17.3 | 18.3 | 17.2 |

Table II. Photophysical Properties of H-M₁DPPQ (II) in Several Solvents

| | Isooctane | Benzene | Butyl ether | Tetrahydrofuran | 1-Chlorobutane | Acetonitrile | Ethanol |
|--|-----------|---------|-------------|-----------------|----------------|--------------|---------|
| $\tilde{\nu}_{\text{abs}}$ (cm ⁻¹) | 25,940 | 25,770 | 25,930 | 25,850 | 25,900 | 25,950 | 25,910 |
| ϵ (m ² mol ⁻¹) | 910 | 893 | 899 | 916 | 897 | 879 | 919 |
| f | 0.098 | 0.088 | 0.096 | 0.099 | 0.097 | 0.100 | 0.103 |
| $ \mu_{\text{m} \rightarrow \text{n}} $ (10 ⁻³⁰ Cm) | 9.4 | 9.0 | 9.4 | 9.5 | 9.4 | 9.5 | 9.7 |
| $\tilde{\nu}_{\text{r}}$ (cm ⁻¹) | 22,600 | 22,000 | 22,400 | 21,900 | 22,000 | 21,700 | 21,600 |
| Q_{r} | 0.90 | 0.98 | 0.79 | 0.97 | 0.98 | 0.98 | 1.00 |
| τ_{r} (ns) | 14.41 | 13.82 | 12.79 | 15.95 | 16.12 | 19.86 | 20.09 |
| Γ_{r} (cm ⁻¹) | 3,100 | 3,200 | 3,200 | 3,300 | 3,300 | 3,400 | 3,500 |
| $ \mu_{\text{m} \rightarrow \text{n}} $ (10 ⁻³⁰ Cm) | 8.4 | 8.2 | 8.4 | 8.5 | 8.5 | 8.4 | 8.3 |
| $\tau_{\text{r,calc}}^0$ (ns) | 13.8 | 12.8 | 14.5 | 14.5 | 14.6 | 17.2 | 16.2 |

Table III. Photophysical Properties of H-M₂DPPQ (III) in Several Solvents

| | Isooctane | Benzene | Butyl ether | Tetrahydrofuran | 1-Chlorobutane | Acetonitrile | Ethanol |
|--|-----------|---------|-------------|-----------------|----------------|--------------|---------|
| $\tilde{\nu}_{\text{abs}}$ (cm ⁻¹) | 25,350 | 25,380 | 25,460 | 25,460 | 25,480 | 25,620 | 25,600 |
| ϵ (m ² mol ⁻¹) | 600 | 602 | 586 | 624 | 596 | 606 | 630 |
| f | 0.065 | 0.061 | 0.064 | 0.069 | 0.066 | 0.070 | 0.071 |
| $ \mu_{\text{m} \rightarrow \text{n}} $ (10 ⁻³⁰ Cm) | 7.8 | 7.5 | 7.7 | 8.0 | 7.8 | 8.0 | 8.1 |
| $\tilde{\nu}_{\text{r}}$ (cm ⁻¹) | 22,000 | 21,400 | 21,700 | 21,300 | 21,400 | 20,800 | 21,300 |
| Q_{r} | 1.00 | 0.98 | 0.92 | 0.88 | 0.97 | 0.78 | 0.90 |
| τ_{r} (ns) | 23.36 | 23.52 | 24.61 | 26.17 | 26.12 | 28.24 | 28.90 |
| Γ_{r} (cm ⁻¹) | 3,400 | 3,400 | 3,500 | 3,600 | 3,400 | 3,800 | 3,700 |
| $ \mu_{\text{m} \rightarrow \text{n}} $ (10 ⁻³⁰ Cm) | 7.2 | 6.6 | 6.8 | 6.6 | 6.9 | 6.7 | 6.7 |
| $\tau_{\text{r,calc}}^0$ (ns) | 21.9 | 20.2 | 23.0 | 22.8 | 23.3 | 27.9 | 24.5 |

region and the issue of fluorescing probes in biological systems.

Absorption and Fluorescence Spectra of DMA-DPPQ in Neat Solvents

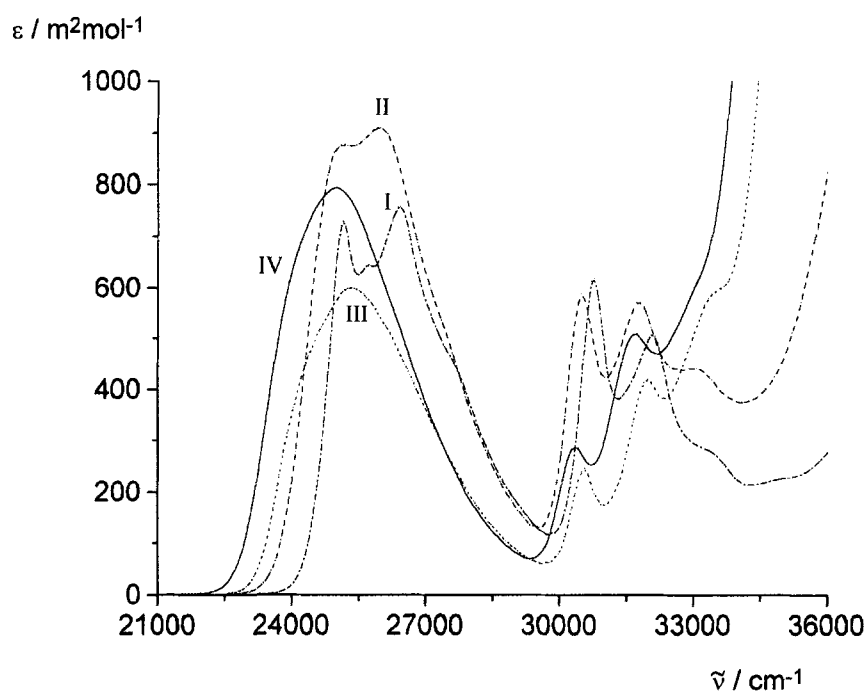
Introduction of the *N,N*-dimethylamino group in position 4ⁱ produces a molecule composed of an electron donor and a bulky π -electron acceptor. This changes the

photophysical properties remarkably. The spectra are presented in Fig. 3; photophysical data, in Table V.

The longest-wavelength absorption band, peaking at 24,300 cm⁻¹, is broad and practically independent on the solvent polarity (deviation in all solvents, ± 1 nm at most, i.e., within the error limit due to the broadness of the band). Its absorption coefficient is approximately 1200 m²mol⁻¹. The spectrum seems to show a superposition of at least two bands.

Table IV. Photophysical Properties of H-TPPQ (IV) in Several Solvents

| | Isooctane | Benzene | Butyl ether | Tetrahydrofuran | 1-Chlorobutane | Acetonitrile | Ethanol |
|--|-----------|---------|-------------|-----------------|----------------|--------------|---------|
| $\tilde{\nu}_{\text{abs}}$ (cm ⁻¹) | 24,960 | 24,950 | 25,000 | 25,090 | 25,030 | 25,240 | 25,140 |
| ϵ (m ² mol ⁻¹) | 794 | 807 | 819 | 860 | 831 | 799 | 848 |
| f | 0.088 | 0.081 | 0.091 | 0.094 | 0.093 | 0.092 | 0.096 |
| $ \mu_{m \leftarrow n} $ (10 ⁻³⁰ Cm) | 9.1 | 8.8 | 9.3 | 9.4 | 9.4 | 9.3 | 9.5 |
| $\tilde{\nu}_f$ (cm ⁻¹) | 21,600 | 21,200 | 21,500 | 21,100 | 21,200 | 20,600 | 21,100 |
| Q_f | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| τ_f (ns) | 17.36 | 16.75 | 17.98 | 20.03 | 19.82 | 24.19 | 21.26 |
| Γ_f (cm ⁻¹) | 3,100 | 3,100 | 3,200 | 3,300 | 3,200 | 3,400 | 3,300 |
| $ \mu_{m \rightarrow n} $ (10 ⁻³⁰ Cm) | 8.6 | 8.0 | 8.4 | 8.2 | 8.2 | 8.3 | 8.3 |
| $\tau_{f,\text{calc}}^0$ (ns) | 16.9 | 15.3 | 16.8 | 17.0 | 17.0 | 21.4 | 18.4 |

Fig. 1. Absorption spectra of H-DMPP (I), H-M₁DMPP (II), H-M₃DMPP (III), and H-TPPQ (IV) in isooctane.

The transition energy, intensity, and shape of the fluorescence spectra depend strongly on the solvent polarity. From the behavior of some photophysical quantities (see Fig. 4), it can be derived that the main emission in solvents more polar than 1-chlorobutane can be ascribed to a CT state. Also, the value of $\mu_{m \rightarrow n}$ changes from (13 ... 16) · 10⁻³⁰ Cm in nonpolar and weakly polar solvents to 6 · 10⁻³⁰ Cm in the most polar one used, DMSO. In protic solvents and in some dipolar aprotic ones dual fluorescence can be seen distinctly. The dependences of the fluorescence lifetime and half-maximum band width (Γ_f) of the main band on the sol-

vent polarity, expressed as $\Delta f = (D - 1)/(2D + 1) - (n^2 - 1)/(2n^2 + 1)$, show similar character in aprotic solvents.

The occurrence of a minimum of τ_f versus polarity in weakly polar solvents may suggest an equilibrium between the primary excited molecules and the molecules in a state achieved as the product of an adiabatic reaction, similarly to the case of the TICT-forming compound DMABN [4-(*N,N*-dimethylamino)-benzotrile].^(12,13)

The changes in the slopes of the fluorescence maximum and the natural fluorescence lifetime τ_f^0 ($=\tau_f/Q_f$) versus Δf (Figs. 4A and D; in the case of dual fluores-

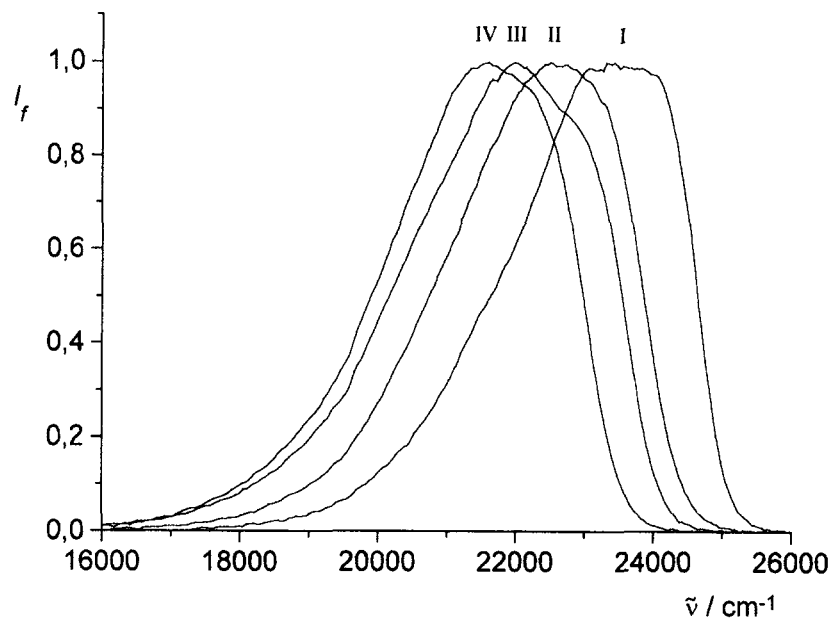


Fig. 2. Normalized fluorescence of H-DMPP (I), H-M₁DMPP (II), H-M₃DMPP (III), and H-TPPQ (IV) in isoctane.

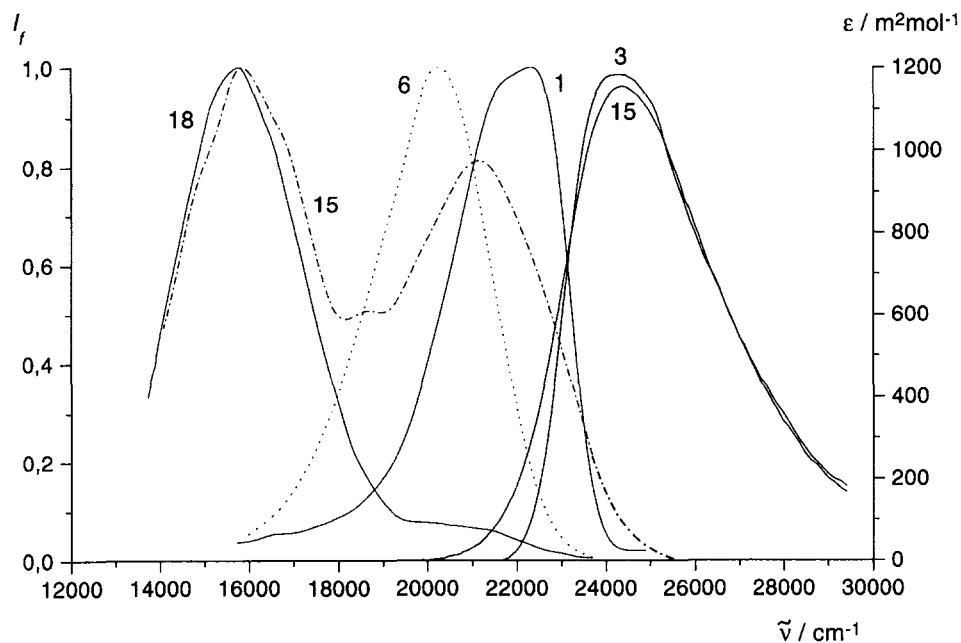


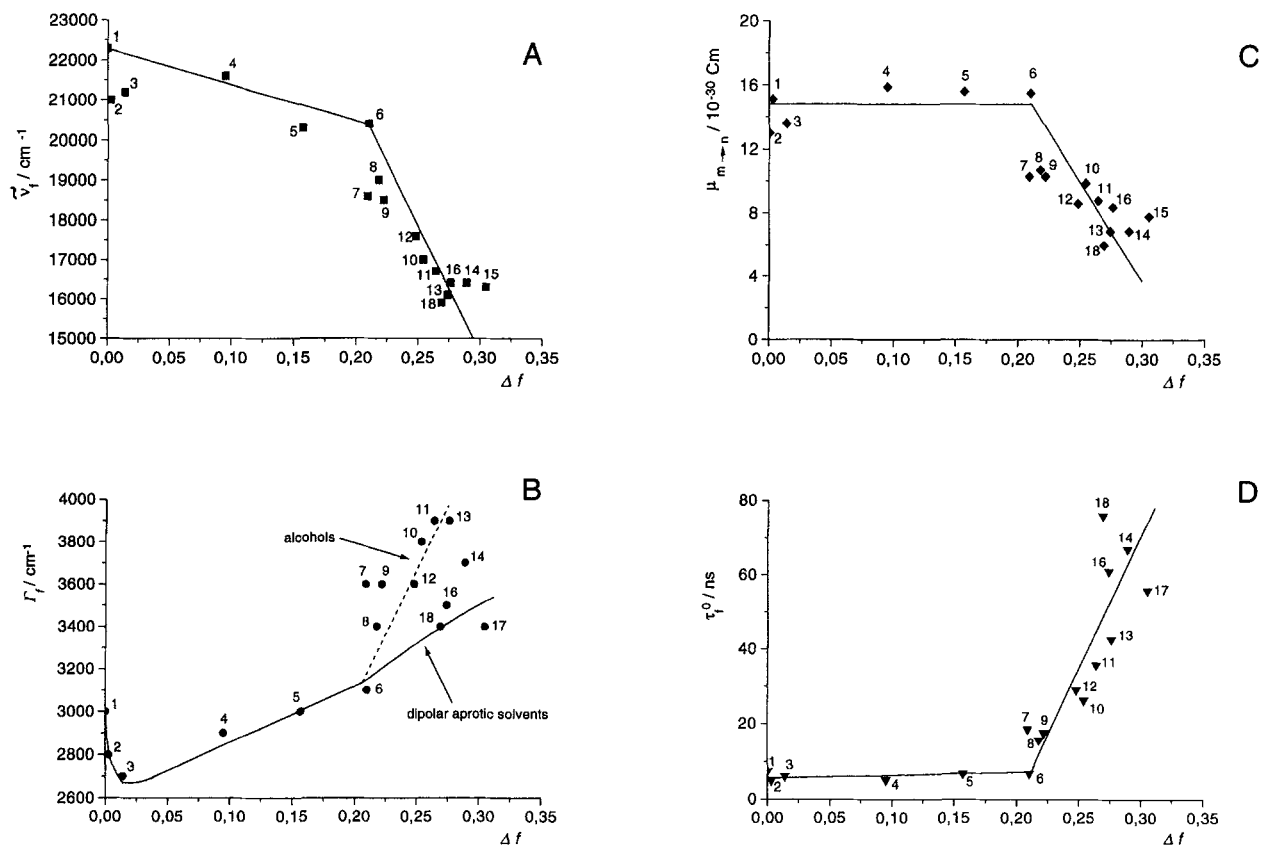
Fig. 3. Normalized fluorescence spectra of DMA-DPPQ (V) in DMSO (18), methanol (15), 1-chlorobutane (6), and cyclohexane (1); absorption spectra of DMA-DPPQ in methanol (15) and toluene (3).

cence the maximum of the long wavelength band) in solvents of higher polarity than 1-chlorobutane lead to the conclusion that the long-wavelength band stems from a CT state, analogously to the case of DMA-

DMPP.⁽⁶⁾ The transition dipole moment of the CT fluorescence is directed along the $S_1 \leftarrow S_0$ transition dipole moment, as the CT fluorescence shows a high positive fluorescence anisotropy grade ($r \approx 0.4$) if the molecule

Table V. Photophysical Properties of DMA-DPPQ (V) in Several Solvents

| | | $\tilde{\nu}_f$ (cm^{-1}) | Q_f | Γ_f (cm^{-1}) | τ_f (ns) | $\mu_{m \rightarrow n}$ (10^{30} Cm) |
|----|-------------------------------|---|-------|------------------------------------|------------------|---|
| 1 | Cyclohexane | 22,300 | 1.00 | 3,000 | 7.38 | 13.0 |
| 2 | Benzene | 21,000 | 0.98 | 2,800 | 4.86 | 15.1 |
| 3 | Toluene | 21,200 | 0.72 | 2,700 | 4.33 | 13.6 |
| 4 | Butyl ether | 21,600 | 0.92 | 2,900 | 4.68 | 15.9 |
| 5 | t-Butyl methyl ether | 20,300 | 0.91 | 3,000 | 6.18 | 15.6 |
| 6 | 1-Chlorobutane | 20,400 | 1.00 | 3,100 | 6.76 | 15.5 |
| 7 | Dichloromethane | 19,000 | 0.63 | 3,400 | 9.89 | 10.7 |
| 8 | 1,2-Dichloroethane | 18,500 | 0.62 | 3,600 | 10.88 | 10.3 |
| 9 | Tetrahydrofuran | 18,600 | 0.59 | 3,600 | 10.97 | 10.3 |
| 10 | Pentanol-1 | 17,000 | 0.21 | 3,800 | — ^a | 9.9 |
| 11 | Butanol-1 | 16,700 | 0.12 | 3,900 | — ^a | 8.8 |
| 12 | Cyclohexanone | 17,600 | 0.45 | 3,600 | 13.06 | 8.6 |
| 13 | Propanol-1 | 16,400 | 0.058 | 3,900 | — ^a | 8.4 |
| 14 | Ethanol | 16,400 | 0.039 | 3,700 | — ^a | 6.9 |
| 15 | Methanol | 21,400/15,900 | 0.012 | — | — ^a | — |
| 16 | <i>N,N</i> -Dimethylformamide | 16,100 | 0.13 | 3,500 | 7.93 | 6.9 |
| 17 | Acetonitrile | 16,300 | 0.16 | 3,400 | 8.95 | 7.8 |
| 18 | Dimethyl sulfoxide | 15,900 | 0.070 | 3,400 | 5.32 | 6.0 |

^a Not monoexponential because of dual fluorescence.Fig. 4. Plot of ν_f (A), Γ_f (B), $\mu_{m \rightarrow n}$ (C), and τ_f^0 (D) versus Onsager's polarity function Δf .

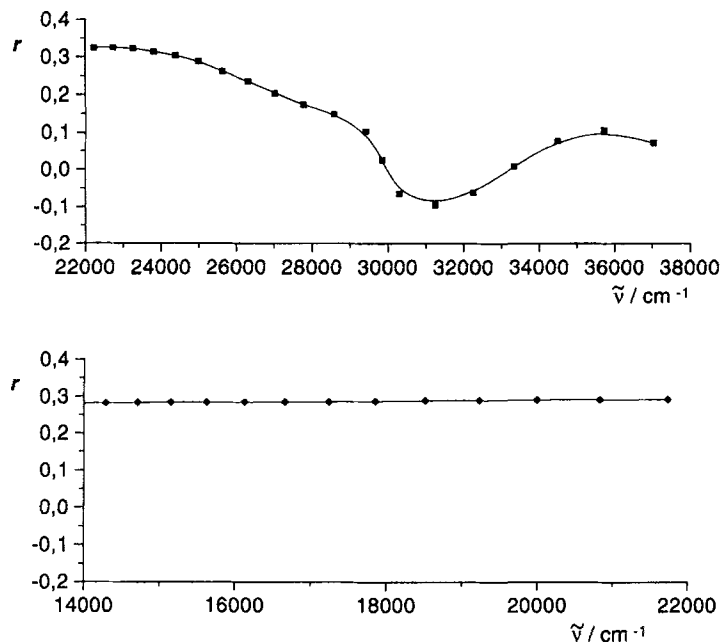


Fig. 5. (a) Excitation spectrum of fluorescence anisotropy degree of DMA-DPPQ in butyronitrile, $\lambda_{em} = 610 \text{ nm}$, $T = 136 \text{ K}$. (b) Emission spectrum of fluorescence anisotropy degree of DMA-DPPQ in butyronitrile, $\lambda_{exc} = 400 \text{ nm}$, $T = 136 \text{ K}$.

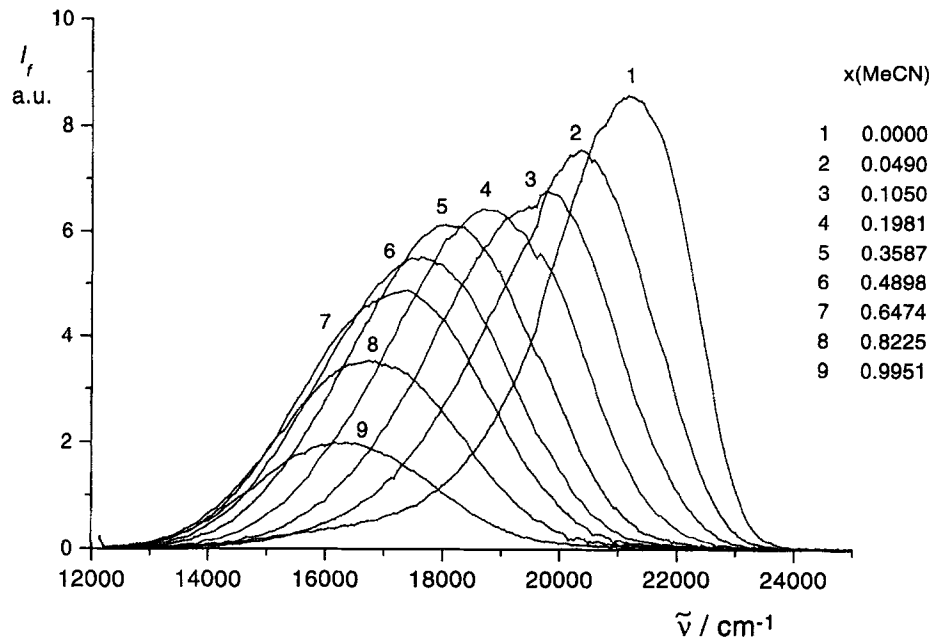


Fig. 6. Fluorescence spectra of DMA-DPPQ in binary mixtures of toluene and acetonitrile.

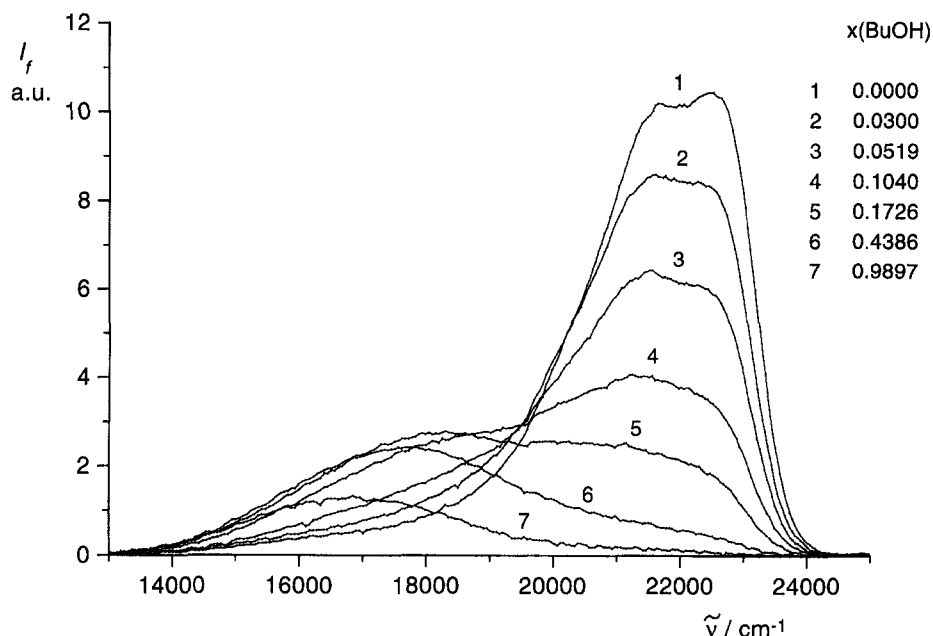


Fig. 7. Fluorescence spectra of DMA-DPPQ in binary mixtures of heptane and butanol-1.

is excited to S_1 (see Fig. 5). The transition $S_2 \leftarrow S_0$ is perpendicularly polarized to the $S_1 \leftarrow S_0$ transition.

Fluorescence Spectra of DMA-DPPQ in Binary Solvent Mixtures

The influence of the solvent has also been tested in binary mixtures: hydrocarbon (nonpolar) and protic or dipolar aprotic solvent (polar). The behavior of the fluorescence is quite different in both kinds of mixtures. In binary mixtures of toluene and acetonitrile, only one fluorescence band appears, constantly red-shifting with increasing molar fractions of acetonitrile (Fig. 6). The half-maximum band width (Γ_f) passes a maximum, showing the superposition of the PE (primary excited) and the CT band. The fluorescence maximum is not a linear function of a molar fraction (it is more strongly red-shifted), thus indicating the formation of a polar inner solvent shell around the excited molecules.^(14,15)

On the contrary, in mixtures of heptane and butanol-1, dual fluorescence is seen (Fig. 7). With increasing amounts of the polar cosolvent, the long-wavelength (CT) fluorescence band increases and the short-wavelength (PE) band decreases. This suggests an energy barrier of the relaxation process to the CT state, probably caused by specific interactions with alcohol, i.e., hydrogen bonding. The total fluorescence quantum yield de-

creases due to widely observed proton quenching of fluorescence. The fluorescence lifetime becomes double-exponential. From a Stern-Volmer-Plot, $k_q = 5.2 \cdot 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is obtained; the relatively small value of the quenching rate constant supports the assumption of specific interactions. Further investigations of the relaxation to the CT state, especially in protic solvents, are in progress.

CONCLUSION

- (1) The non-donor-substituted derivatives of pyrazolo[3,4-b]quinoline show a fluorescence quantum yield equal to unity, independent of the solvent. The geometry is changed only minimally upon excitation. These substances can be proposed as fluorescence standards for determining quantum yields.
- (2) The introduction of the dimethylamino group changes the emissive characteristics of pyrazoloquinoline dramatically. Dual fluorescence appears in polar solvents, especially in protic ones.
- (3) The long-wavelength band can be ascribed to emission from a CT excited state. The hydrogen bonding between alcohol molecules and the dimethylamino group strongly retards the relaxation to the CT state.

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