

INFLUENCE OF RESTRICTED INTRAMOLECULAR MOTIONS ON THE FLUORESCENCE QUANTUM YIELD OF FLUOROPHORES

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Summary

Fluorescence spectra, fluorescence quantum yields and decay times were measured for fluorophores capable of either conformational or rotational mobility in dilute solutions of benzene, methyl methacrylate (MMA) and in the rigid poly(methyl methacrylate) (PMMA) matrix at room temperature. When passing from fluid solutions of MMA to the polymeric matrix of PMMA a dramatic increase in the fluorescence quantum yield from zero to values of about 0.60 is obtained for structurally related molecules of 1,3-diphenyl-2-pyrazoline such as 1-phenyl-3-mesityl-2-pyrazoline, 1,3-diphenyl-1,4,5,6-tetrahydro-1,2-diazine and benzaldehyde phenylhydrazone, all containing the same aryl—C=N—N—aryl chromophore. The rigidity of the PMMA matrix slows down the rate of intramolecular motions such as ring inversion or rotational mobility within the fluorophore and lengthens the time interval between the electronic excitation and achievement of those conformations that give rise to fast non-radiative deactivation processes. In contrast with these compounds the fluorescence quantum yield of the nitrogen hetero aromatic compound 1,3-diphenylindazole decreases when going from MMA to PMMA at the expense of phosphorescence. The practical consequences of the effect of restricted intramolecular motions on the fluorescence quantum yield of fluorescent dyes in polymers are briefly discussed.

1. Introduction

It is now well established that the fluorescence quantum yield of organic molecules increases as the molecular rigidity of the chromophore (or fluorophore) increases [1, 2], as the solvent viscosity increases [3 - 5] and as the ambient temperature of the solvent decreases [6, 7]. Recently, a marked viscosity dependence has been reported of the fluorescence quantum yield of meso-substituted anthracenes when fluid organic solutions were replaced by the rigid matrix of poly(methyl methacrylate) (PMMA) [8, 9]. At room temperature the fluorescence quantum yield of 9-*tert*-butylanthracene in-

creases from 0.01 in *n*-heptane to 0.1 in glycerol and 0.43 in PMMA [8]. In view of the practical application of fluorescent molecules in polymers such as plastic scintillators [10] and fluorescence solar collectors [11] we started an investigation into the influence of variation in molecular structure on the fluorescence quantum yield of a good fluorophore in PMMA. PMMA offers advantages over other polymers. It forms a clear glass with UV transparency until about 300 nm, an extremely rigid matrix with a viscosity of more than 10^{13} P [12] and shows a high glass transition temperature of more than 100 °C. With regard to its solvatochromic behaviour to solute molecules the polarity of PMMA is considered as low [13]. As a model for a good fluorophore we choose structurally related compounds of 1,3-diphenyl-2-pyrazolines, all of them containing the phenyl—C=N—N—phenyl chromophore.

2. Experimental details

2.1. Instrumentation and techniques

The absolute fluorescence spectra, the fluorescence quantum yield and the fluorescence decay time were measured using a recording spectrofluorometer and a fluorometer relying on the pulse-sampling technique. The spectral sensitivity of the spectrofluorometer was determined in the spectral range 320 - 800 nm with a quartz-iodine lamp of known intensity distribution together with a white reflectance standard of MgO which replaced the sample. Details about the instrumentation built at this laboratory and about the measurement techniques have been published previously [14, 15]. For the determination of the fluorescence quantum yield according to the method of Parker and Rees [16], quinine bisulphate in 0.1 N H₂SO₄ was used as a reference standard, on the assumption of a fluorescence quantum yield of 0.55 at room temperature [17]. Refractive indices of 1.414 for methyl methacrylate (MMA) and 1.491 for PMMA at room temperature were taken into account for the calculation of the fluorescence quantum yields. The concentrations of solutions and of the fluorescence standard were adjusted so that their optical densities were equal at the exciting wavelength. To avoid errors due to reabsorption and possible aggregation of the fluorophores in fluid solution as well as in PMMA, low concentrations of about 10^{-5} mol dm⁻³ were used.

Solid solutions of the compounds investigated in PMMA were prepared by bulk polymerization of the purified monomer with a trace of dibenzoyl peroxide under carefully degassed conditions in sealed Pyrex tubes of 2 cm diameter. Degassing was performed in three freeze-pump-thaw cycles at 10^{-5} Torr. Thermal polymerization was carried out in the dark at 40 °C for 2 days. The plastic sample was easily machined and polished to a 1 cm² square of 4 cm length. A blank PMMA sample was prepared in the same manner.

To cross check the whole procedure the fluorescence quantum yield of anthracene (about 10^{-5} mol dm⁻³) in PMMA was compared with a value previously measured by Melhuish [18] since this compound tends to aggregate at

higher concentrations in PMMA [19]. We obtained a value of 0.23 in excellent agreement with the value of 0.24 measured by Melhuish. On the basis of the reproducibility the values of the fluorescence quantum yields given below are thus believed to be accurate to within at least 5%.

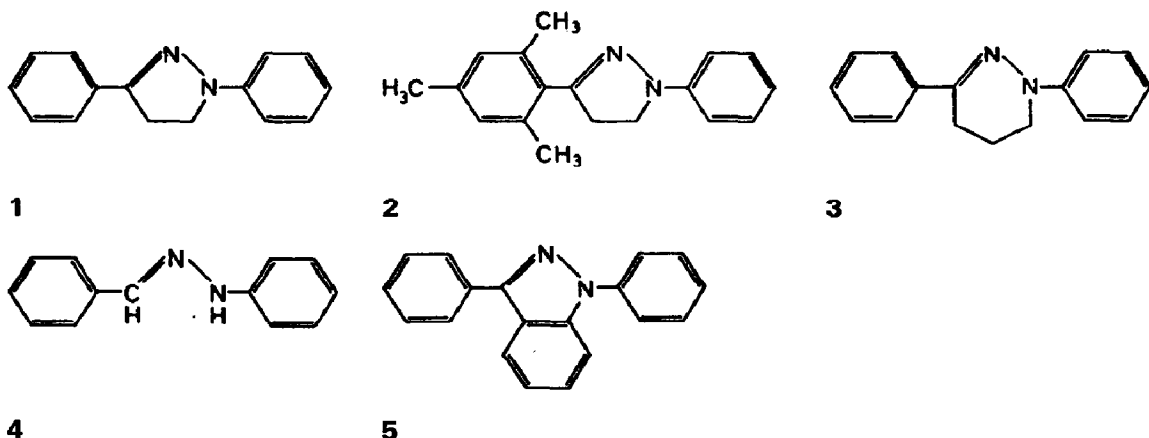
2.2. Substances

MMA was purified by column chromatography on neutral aluminium oxide and final distillation. The purified monomer was stored in a refrigerator until use.

1,3-diphenyl-2-pyrazoline (melting point, 151 °C) was prepared by the condensation of the Mannich base of acetophenone with phenylhydrazine according to a standard procedure [20]. 1-phenyl-3-mesityl-2-pyrazoline (melting point, 96 °C) was synthesized by condensation of mesityl vinyl ketone with phenylhydrazine. 1,3-diphenyl-1,4,5,6-tetrahydro-1,2-diazine (melting point, 141 °C [21]), benzaldehyde phenylhydrazone (melting point, 157 °C) and 1,3-diphenylindazole (melting point, 100 - 101 °C [22]) were prepared according to procedure given in the literature.

3. Results and discussion

1,3-diphenyl-2-pyrazolines show fluorescence with high quantum yields in non-polar solvents [23]. The fluorescence has been attributed to planarity of the molecule in the excited singlet state due to an intramolecular charge transfer within the main aryl-C=N-N-aryl chromophore [23]. Distortion from planarity was achieved by the following molecules which all contain the aryl-C=N-N-aryl chromophore: 1-phenyl-3-mesityl-2-pyrazoline 2, 1,3-diphenyl-1,4,5,6-tetrahydro-1,2-diazine 3 and benzaldehyde phenylhydrazone 4. For comparison we investigated also the nitrogen hetero aromatic compound 1,3-diphenylindazole 5 in which the intramolecular charge transfer along the aryl-C=N-N-aryl chromophore no longer exists:



In **2** the bulky methyl groups in the *ortho ortho'* positions of one phenyl ring cause distortion in the planar 1,3-diphenyl-2-pyrazoline **1** as is indicated by its UV spectrum [23]. Enlargement of the central five-membered ring to a six-membered ring in **3** allows ring inversion. This fast intramolecular ring as well as nitrogen atom inversion at room temperature in solution (as can be observed in the nuclear magnetic resonance spectrum of **3**) obviously quenches the fluorescence completely [20]. In solution the slow process of fluorescence emission of **4** cannot compete with the faster non-radiative process of the photochemical *syn-anti* isomerization, a general feature of electronically excited phenylhydrazones [24].

The photophysical data such as the maxima of the electronic absorption ν_a and of the fluorescence ν_f , the fluorescence quantum yield Q_f and the fluorescence decay time τ of 1,3-diphenyl-2-pyrazoline and its structurally related compounds **2**, **3** and **4** in degassed benzene, MMA and PMMA are summarized in Table 1 together with the data of the nitrogen hetero aromatic compound 1,3-diphenylindazole **5**.

While the absorption spectra of the molecules investigated in Table 1 are found to undergo very little change when going from benzene to MMA and PMMA, the emission spectra in PMMA are shifted hypsochromically by 11 - 12 nm compared with MMA. Since the fluorescence of 1,3-diphenyl-2-pyrazolines depends strongly on the solvent polarity [23], the rigid environment of PMMA has to be considered as somewhat less polar than that of the fluid MMA. When going from **1** to **2** the Stokes shift in solution as well as in PMMA doubles because of the large hypsochromic shift of the absorption spectrum of **2** caused by steric repulsion of the bulky methyl groups in the *ortho ortho'* positions of the phenyl ring [23, 25]. It is interesting that the fluorescence spectrum of compound **2** remains nearly unaffected, *i.e.* the fluorescence maximum of **2** is close to that of **1**. The result of the steric hindrance is a great energy difference between the Franck-Condon S_1 state in absorption and the unaffected fluorescence emission of the relaxed excited singlet state of **2** which gives rise to an unusually large Stokes shift [25]. This has been attributed to a planar and polar excited singlet state of **1** and **2** which is the result of an intramolecular charge transfer $\pi\pi^*$ excitation [23]. Nevertheless, the polymer effect on the spectroscopic properties is small and supports the basic assumption that the host plastic is an essentially inert matrix which provides only steric constraints on the embedded compounds investigated. Furthermore, the electronic levels of the compounds of Table 1 are sufficiently low to preclude interaction with those of the PMMA matrix. The UV transparency of PMMA lies well above $30\,000\text{ cm}^{-1}$ and the energy of the triplet state near $25\,000\text{ cm}^{-1}$ [26]. The triplet energy level of 1,3-diphenyl-2-pyrazoline has been estimated to be about 88 kJ mol^{-1} below the singlet level [27]. Thus, intermolecular guest-to-host energy transfer in PMMA can be ruled out at the low concentrations used in our experiments.

The fluorescence quantum yield of 1,3-diphenyl-2-pyrazoline is more or less the same in MMA and PMMA. A drop in the fluorescence quantum yield from benzene to MMA and PMMA is due to an increase in the solvent polarity

TABLE 1

Photophysical properties of 1,3-diphenyl-2-pyrazoline and its structurally related compounds 2, 3, 4 and 5 in degassed solutions of benzene, methyl methacrylate and poly(methyl methacrylate) at room temperature

Compound	$\nu_a(\text{max})(\times 10^3 \text{ cm}^{-1})$			$\nu_f(\text{max})(\times 10^3 \text{ cm}^{-1})$			Q_f			τ (ns)		
	Benzene	MMA	PMMA	Benzene	MMA	PMMA	Benzene	MMA	PMMA	Benzene	MMA	PMMA
1	27.55	27.86	28.09	22.57	22.47	23.04	0.92	0.51	0.57	3.25	3.25	3.3
2	33.90	32.84	34.84	23.53	23.15	23.81	0.88	0.02	0.61	3.0	3.0	2.8
3	29.15	29.15	29.50	—	—	21.74	0	0	0.16	—	—	2.5
4	29.22	29.15	28.74	—	—	23.64	0	0	0.59	—	—	3.0
5	31.15	31.25	31.25	26.99	26.60	27.07	0.26 ^a	0.26	0.19	1.05 ^a	1.05 ^a	—

^aIn the presence of oxygen.

and has been observed recently for a 1,3,5-triphenyl-2-pyrazoline derivative in organic solvents and a polymeric matrix [28]. In contrast with 1,3-diphenyl-2-pyrazoline a dramatic increase from zero to values of about 0.60 occurs for the fluorescence quantum yield of 2 and 4. It appears that in the rigid environment of PMMA a limiting fluorescence quantum yield of 0.60 is reached for the aryl—C=N—N—aryl chromophore (see Table 1). It is interesting to note that a fairly simple molecule such as benzaldehyde phenylhydrazone, which does not fluoresce in solution, can reach such a high value for the fluorescence quantum yield in the rigid matrix of PMMA. Furthermore, with this technique of embedding organic compounds in PMMA we are able to measure fluorescence spectra of compounds which do not fluoresce in solution. Figure 1 shows the fluorescence spectrum of benzaldehyde phenylhydrazone in PMMA together with the fluorescence spectrum of 1. Accordingly, both spectra are not significantly different. For 3 the fluorescence quantum yield in PMMA is lower than for 1, 2 and 4. To rationalize this difference we assume that the free volume available in the PMMA matrix at room temperature facilitates a fast ring inversion in 3 rather than the more space consuming torsional and rotational motions in 2 and 4. Since the C—aryl and N—aryl rotations in 3 are the same as in 1 and 2, we believe that the ring inversion of the half-chair conformation in the cyclic hydrazone of 3 gives rise to a fast radiationless deactivation of the excited singlet state. Since the energy barrier for the conformation change by ring inversion from the more stable half-chair to a boat conformation might be about 5 kcal mol⁻¹, as in cyclohexene [29], it is likely that in PMMA at room temperature the radiationless deactivation due to ring inversion still competes with the fluorescence emission. In other words, the thermal motions in 3 coupled to the radiationless decay process are not completely frozen out in PMMA at room temperature. At any rate, in 2, 3 and 4 the rigid matrix of PMMA slows down the rate of intramolecular motions and lengthens the time interval between electronic excitation and the achievement of those conformations that give rise to fast non-radiative deactivation processes. In fluid solutions these conformations are reached more rapidly and fluorescence is suppressed by the faster radiationless deactivation process. Rate constants for radiative and non-radiative decay are readily calculated from the relationships $k_r = Q_f/\tau$ and $k_n = 1 - Q_f/\tau$. The k_r and k_n values for 1, 2 and 4 in PMMA range close to 2×10^8 s⁻¹; these are typical values for the radiative lifetime of the lowest energy $\pi\pi^*$ state of fluorescing organic molecules as well as for their radiationless transitions.

The aromatic character of the nitrogen heterocyclic compound 1,3-diphenylindazole 5 is indicated by its short wavelength absorption in comparison with that for 1, 3 and 4 and the ability to phosphoresce in PMMA at room temperature like other aromatic hydrocarbons [26]. The phosphorescence spectrum displays vibronic structure at 20 750, 19 350 and 18 000 cm⁻¹ with a band spacing of about 1400 cm⁻¹. This value, together with a radiative lifetime of 10⁻⁸ s in benzene, indicates that the lowest energy excited singlet state of 5 in PMMA is a $\pi\pi^*$ state. In contrast with com-

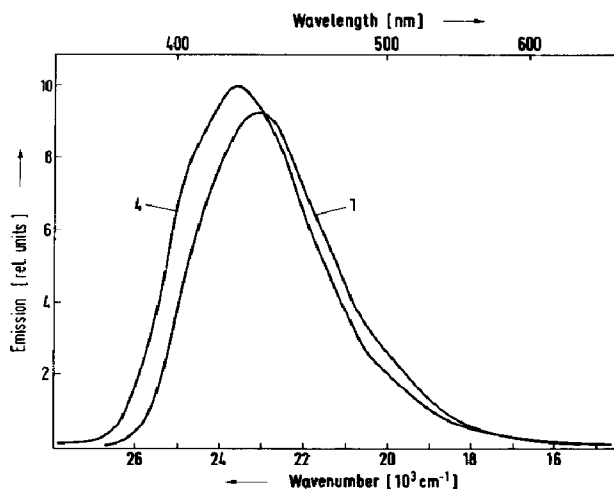


Fig. 1. Absolute fluorescence spectra of 1,3-diphenyl-2-pyrazoline 1 and benzaldehyde phenylhydrazone 4 in PMMA at room temperature.

pounds 2, 3 and 4 the fluorescence quantum yield of 5 decreases when going from benzene and MMA to the rigid matrix of PMMA. The total quantum yield of emission at room temperature, fluorescence plus phosphorescence, remains constant at a value of 0.25, *i.e.* the phosphorescence quantum yield of 5 in PMMA at room temperature is 0.06.

When new fluorescent dyes which are important because of their practical use as plastic scintillators or fluorescent solar collectors are being sought, it is not necessary to focus only on those fluorescent dyes which have already shown high fluorescence quantum yields in solution. A much greater number of organic molecules might now become eligible as fluorophores when these molecules are embedded in a polymeric matrix.

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