

FLUORESCENCE PROPERTIES OF AN ELECTRON  
ACCEPTOR SUBSTITUTED  
BIS-PYRAZOLO-PYRIDINE DERIVATIVE:  
NO<sub>2</sub>-DMPP\*

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The fluorescence properties of 3,5-dimethyl-1,7-diphenyl-4-(4'-nitrophenyl)-bis-pyrazolo-[3,4-b;4',3'-e]-pyridine (NO<sub>2</sub>-DMPP) and its parent compound 3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b;4',3'-e]-pyridine (BPP, without the nitrophenyl substituent) were investigated. BPP is a highly fluorescent blue emitter and the fluorescence properties, the emission wavelength, and the fluorescence quantum yield, depend only slightly on solvent. On the contrary, acceptor substituted NO<sub>2</sub>-DMPP shows dual fluorescence: A long-wavelength component experiences a red-shift with increasing solvent polarity but is efficiently quenched when the polarity exceeds that of solvents like 1,2-dichloroethane or 1-bromopropane. A weak short-wavelength component changes only slightly its position and intensity upon variation of the solvent but its yield increases strongly at low temperatures. The experimental results are discussed in the context of the results of semiempirical calculations which show that fluorescence originates from two closely lying fluorescent states which change their sequence and properties when the polarity of the solvent is varied. A twisted intramolecular charge transfer (TICT) state does most likely not contribute to the emission properties, because of its high energy.

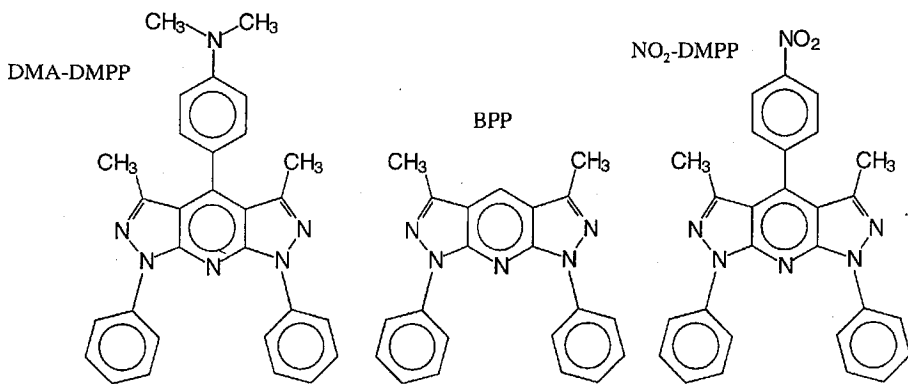
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## 1. Introduction

During the last few years bis-pyrazolo-pyridine derivatives became very interesting fluorescent compounds with highly efficient emission in the blue-green spectral region. Their photophysical properties can widely be varied by substitution and electron-donor substituted bis-pyrazolo-pyridines became good examples for compounds with bulky electron donor and acceptor groups. The most important example is DMA-DMPP, 4-(4'-*N,N*-dimethylamino-phenyl)-3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-*b*;4',3'-*e*]-pyridine, which has been investigated experimentally and theoretically [1-4]. DMA-DMPP fluoresces with large quantum yield in nonpolar solvents. The quantum yield decreases in polar solvents, and the emitting state changes its character from a weakly polar to a highly polar charge transfer (CT) state [1]. Semiempirical calculations including solute-solvent interactions assign the CT fluorescence to an excited state in which a weakly bound electron located on the *N,N*-dimethylanilino moiety is promoted into an excited orbital located on the bis-pyrazolo-pyridine acceptor subunit. This state is found at high energies in the gas phase but is strongly stabilized in a polar environment [3, 4]. In protic solvents dual fluorescence is observed and the long-wavelength band can be ascribed to the CT emission [1].

In this context it became interesting to examine the photophysical properties of parent BPP and of the derivative NO<sub>2</sub>-DMPP, where the electron donating group is replaced by an electron withdrawing group (see the formulae below).



## 2. Materials and methods

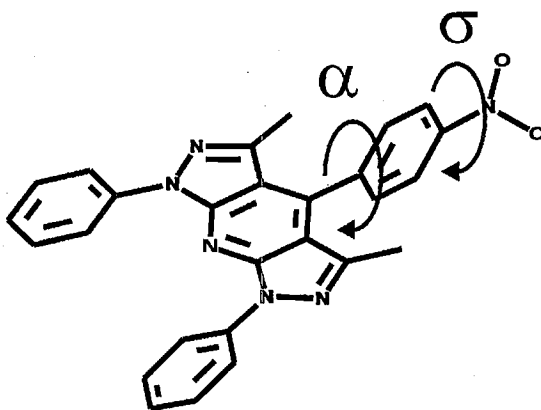
### 2.1. Experimental section

The investigated compounds NO<sub>2</sub>-DMPP and BPP were synthesized in the Department of Organic Chemistry of the Institute of Chemistry of the Pedagogical University in Kielce, Poland [1, 2]. The solvents were of the highest available quality, purified by standard methods if necessary and checked for impurities by means of absorption and fluorescence spectroscopy. Absorption and fluorescence spectra as well as fluorescence decay times were measured as described previously [1]. Low temperature measurements were performed with the Jasny spec-

trofluorimeter in Warsaw [5]. Solutions for room temperature measurements were purged for several minutes with argon to remove oxygen. The fluorescence quantum yields were determined as described in Refs. [6] and [7]. BBOT (2,5-bis-(5-*tert*-butyl-2-benzoxazolyl)-thiophene) in isoctane ( $Q_f = 0.74$ ) was chosen as fluorescence standard for BPP, coumarin 152 (7-*N,N*-dimethyl-amino-4-trifluoromethyl-coumarin) in propanol-1 ( $Q_f = 0.30$ ) for NO<sub>2</sub>-DMPP. The absorption of solutions was  $< 0.14$ , the excitation wavelength — 360 nm for BPP, 390 nm for NO<sub>2</sub>-DMPP at room temperature, unless otherwise indicated.

## 2.2. Computational methods

The ground state equilibrium geometry of NO<sub>2</sub>-DMPP was derived by a full optimization with the semiempirical AM1 [8] Hamiltonian. Based on this geometry, several structural parameters were varied to ascertain conformational changes in the excited state with solvent polarity. The influences of a polar solvent on the excited state properties are explicitly calculated for these molecules. A self consistent reaction field (SCRF) model [9] with an extension for electronically excited states in a semiempirical AM1 based method is used for the description of these solvent effects. The excited state properties of solvated NO<sub>2</sub>-DMPP are presented in order to describe the spectroscopic behaviour in various solvents. State energies are calculated for the gas phase and for solutions in ethyl ether, dichloromethane, and acetonitrile. The resulting transition energies are compared to experimental data.



Scheme 1. Definition of the rotation angle  $\alpha$  of the nitrophenyl subunit and of the rotation angle  $\sigma$  of the nitro group for NO<sub>2</sub>-DMPP.

The properties of the important excited states are characterized by their excitation energies, dipole moments, and orbital analyses for a variation of the nitrophenyl rotation angle. This torsion angle  $\alpha$  (see Scheme 1) of the nitrophenyl moiety is discussed as the main relaxation mode resulting in a red-shifted fluorescence band. Also the influence of the rotation of the nitro group separately, as defined by the rotation angle  $\sigma$ , is investigated in order to determine whether

the nitro or the nitrophenyl group can be considered as the acceptor. The solvated excited states are described by configuration interaction (CI) with the CISD method using an active space of 10 orbitals and including all single and double excitations. This CI scheme corresponds to 876 configurations. The pairwise excited configuration interaction (PECI) [10] method with 10 active orbitals is used for the calculation of oscillator strengths. For all computations, the semiempirical AM1 Hamiltonian as included in the VAMP program package, version 6.1 [11], is used. Standard AM1 parameters were used throughout this work [8].

The molecular orbitals and excited states are assigned within pseudo  $C_{2v}$  symmetry which is approximately obtained for a perpendicular orientation of the nitrophenyl group ( $\alpha = 90^\circ$  and  $\sigma = 0^\circ$ ). The axis describing the symmetry is the long axis pointing from the pyridine nitrogen atom to the nitrogen atom of the nitro group. The decisive plane is taken orthogonal to the plane of the DMPP subunit, thereby coinciding with the plane of the nitrophenyl group. All given molecular orbitals and excited state symmetries correspond to this conformation. These calculations were performed on Indy workstations (MIPS R4400, Silicon Graphics Inc.).

### 3. Results and discussion

#### 3.1. BPP

The longest wavelength absorption of BPP is merely represented by a shoulder near to  $28000 \text{ cm}^{-1}$ . The fluorescence spectra are generally structureless with a Stokes shift of about  $4000 \text{ cm}^{-1}$  (see Fig. 1). The fluorescence spectra and lifetimes are only slightly dependent on the solvent and the quantum yield is almost unity (Table I). The transition dipole moment of the fluorescence transition,  $\mu_f$ , is calculated [12] according to Eq. (1)

$$|\mu_f| = \sqrt{\frac{3h\varepsilon_0 Q_f}{16\pi^3 n^3 \tilde{\nu}_f^3 \tau_f}} \quad (1)$$

and is constant for all solvents within error limits. In this formula  $Q_f$  denotes

TABLE I

Fluorescence properties of BPP in different solvents ( $\nu_f$  denotes the wavenumber of the fluorescence maximum,  $Q_f$  — the fluorescence quantum yield,  $\tau_f$  — the experimental fluorescence lifetime, and  $\mu_f$  — the transition dipole moment of fluorescence).

Solvent	$\nu_f/\text{cm}^{-1}$	$Q_f$	$\tau_f/\text{ns}$	$ \mu_f /10^{-30} \text{ C m}$
Isooctane	23800	0.84	28.1	5.4
Benzene	23400	0.91	27.1	5.2
Tetrahydrofuran	23400	0.99	31.7	5.6
1-Chlorobutane	23500	0.95	30.1	5.6
Acetonitrile	22700	0.84	35.3	5.5
Methanol	22500	0.8	37.2	5.3

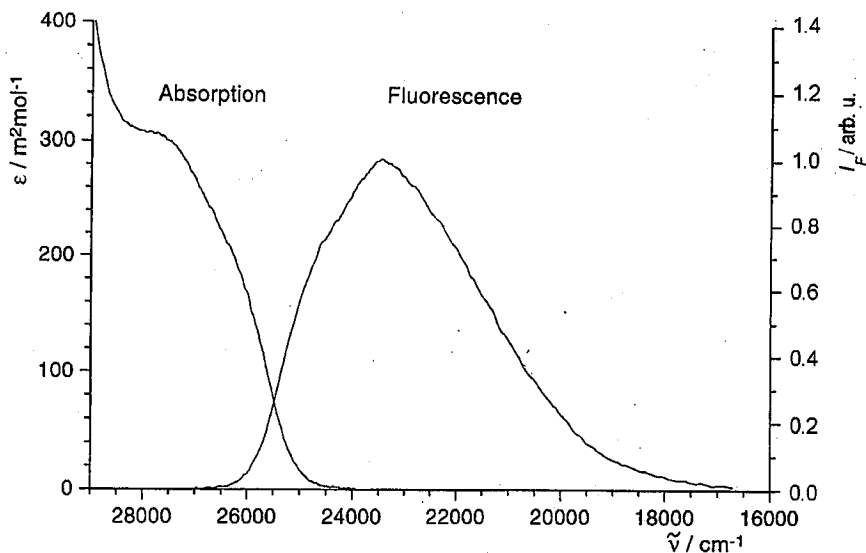


Fig. 1. Absorption and corrected fluorescence spectrum of BPP in 1-chlorobutane.

the fluorescence quantum yield,  $n$  — the refractive index of the solvent,  $\tilde{\nu}_f$  — the wavenumber of the fluorescence maximum, and  $\tau_f$  — the experimental fluorescence lifetime. All other constants have their usual meaning.

### 3.2. $NO_2$ -DMPP

#### 3.2.1. Absorption spectra

The longest-wavelength absorption band consists of two maxima peaking at about  $26000\text{ cm}^{-1}$  and  $30000\text{ cm}^{-1}$  (see Fig. 2); the second, much more intensive, band consists also of two peaks which are found at  $36000\text{ cm}^{-1}$  ( $\epsilon = 6300\text{ m}^2\text{ mol}^{-1}$ ) and  $38000\text{ cm}^{-1}$  ( $\epsilon = 6800\text{ m}^2\text{ mol}^{-1}$ ).

#### 3.2.2. Fluorescence spectra, transition dipole moments of fluorescence, and fluorescence lifetimes

**3.2.2.1. Room temperature measurements.** In solvents of low polarity (dielectric permittivity  $D < 8.2$ ) an intensive long-wavelength band is found, which is red-shifted with increasing solvent polarity. This emission originates, therefore, from a polar excited state. The Stokes shift in hexane amounts to  $5700\text{ cm}^{-1}$ . This is not an anomalously large value but it indicates a certain change of excited state geometry. A weak band at the short-wavelength side is observed in all solvents and remains essentially at a constant position independent of the solvent. The broad maximum is found near to  $(21800 \pm 1000)\text{ cm}^{-1}$  in all solvents and the transition moment associated with this weak emission is  $(1.6 \pm 0.4) \times 10^{-30}\text{ C m}$ . The fluorescence lifetimes and quantum yields of fluorescence found at low polarities vary strongly for various solvents but the respective transition moment remains constant  $(8.4 \pm 0.6) \times 10^{-30}\text{ C m}$ , as both quantities vary in parallel. As, however, the dielectric permittivity exceeds 8.2, the long-wavelength band is suddenly almost

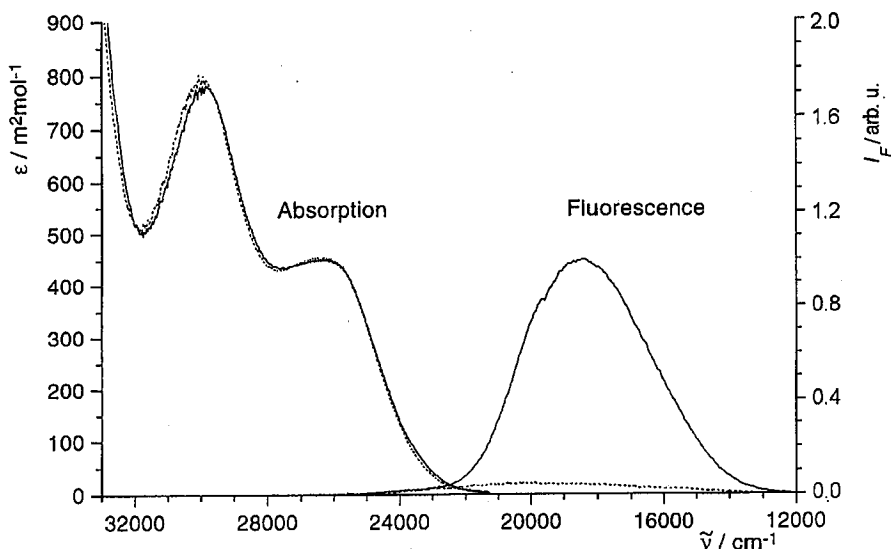


Fig. 2. Absorption and corrected fluorescence spectra of  $\text{NO}_2\text{-DMPP}$  in 1-chlorobutane (solid line) and in butanol-1 (dashed line).

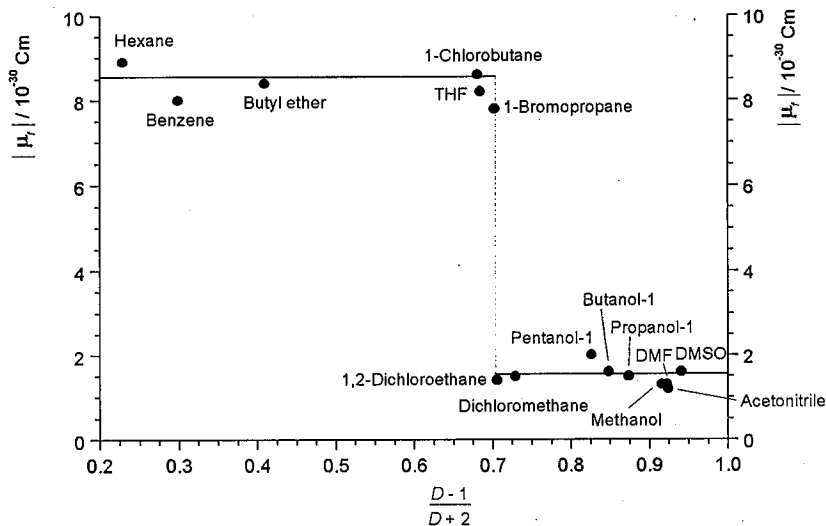


Fig. 3. Plot of transition dipole moments of fluorescence of  $\text{NO}_2\text{-DMPP}$  versus the solvent polarity function  $(D-1)/(D+2)$ .

completely quenched. This is most clearly seen from a plot of the transition dipole moment of fluorescence versus solvent polarity, as the transition moment changes suddenly between the two values (see Fig. 3). Only the weak short-wavelength component remains at higher polarities.

TABLE II

Fluorescence properties of NO<sub>2</sub>-DMPP in different solvents ( $\nu_f$  denotes the wavenumber of the fluorescence maximum,  $Q_f$  — the fluorescence quantum yield,  $\tau_f$  — the experimental fluorescence lifetime, and  $\mu_f$  — the transition dipole moment of fluorescence).

Solvent	$\nu_f / \text{cm}^{-1}$	$Q_f$	$\tau_f / \text{ns}$	$ \mu_f  / 10^{-30} \text{ C m}$
Hexane	20700	0.031	0.6	8.9
Benzene	19000	0.26	6.23	8.0
Butyl ether	20200	0.08	1.76	8.4
1-Chlorobutane	18500	0.26	7.14	8.6
Tetrahydrofuran	18200	0.18	5.72	8.2
1-Bromopropane	18000	0.19	6.47	7.8
1,1,2,2-Tetrachloroethane	20900	0.006	3.4	1.4
Dichloromethane	22700	0.005	2.35	1.5
Pentanol-1	21000	0.007	2.21	2.0
Butanol-1	21300	0.004	2.06	1.6
Propanol-1	21800	0.003	1.97	1.5
Acetonitrile	21600	0.002	1.87	1.2
Methanol	22600	0.002	1.49	1.3
Dimethylsulfoxide	21700	0.004	1.79	1.6
<i>N,N</i> -Dimethylformamide	22200	0.003	1.95	1.3

The fluorescence lifetimes are generally single exponential. The photophysical properties are collected in Table II.

From measurements in binary solvent mixtures of 1-chlorobutane and acetonitrile it is obvious that the strong fluorescence is red-shifted from 18500 cm<sup>-1</sup> in neat 1-chlorobutane to 17200 cm<sup>-1</sup> after addition of acetonitrile (molar fraction 0.182), and it is already strongly quenched at those rather low concentrations of polar cosolvent (Fig. 4).

*3.2.2.2. Low temperature measurements.* The fluorescence properties of NO<sub>2</sub>-DMPP were studied in dipolar-aprotic butyronitrile and in protic propanol-1 at low temperatures in the temperature range between room and the glass transition temperature. At room temperature the fluorescence quantum yield is very low in both solvents. In butyronitrile a red-shift of the band is observed with decreasing temperature which is due to the increase in dielectric permittivity; the quantum yield increases slightly. On the other hand, the fluorescence quantum yield increases dramatically in propanol-1 solutions with decreasing temperature (see Fig. 5). The solvatochromism is less distinct as at first a slight red-shift and then, when propanol-1 becomes very viscous, a blue-shift is observed. At 149 K the spectrum is comparable to that found in a solvent of low polarity at room temperature. The fluorescence quantum yield becomes  $Q_f \approx 0.2$ . The emission

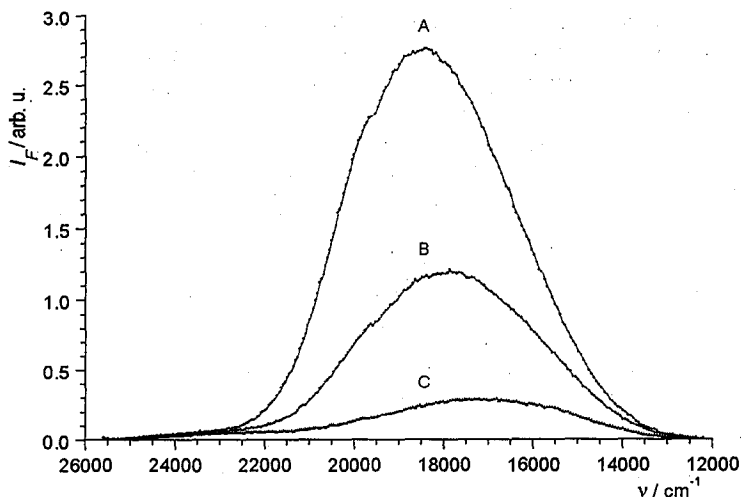


Fig. 4. Corrected fluorescence spectra of  $\text{NO}_2\text{-DMPP}$  ( $c = 4.78 \times 10^{-5} \text{ M}$ ) in binary mixtures of 1-chlorobutane with acetonitrile (the molar fraction of acetonitrile is given in parentheses): A (0.000), B (0.064), C (0.182).

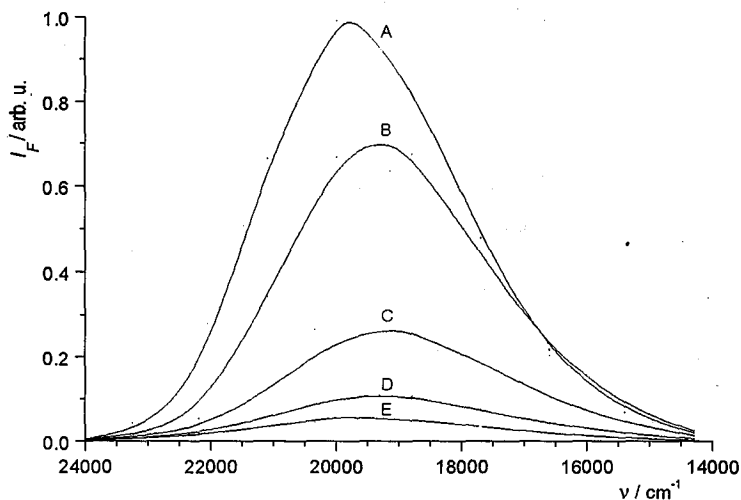


Fig. 5. Corrected fluorescence spectra of  $\text{NO}_2\text{-DMPP}$  in propanol-1 ( $\lambda_{\text{exc}} = 375 \text{ nm}$ ) at different temperatures (the temperature is given in parentheses): A (149 K), B (166 K), C (186 K), D (205 K), E (225 K).

emerges gradually with lowering of the temperature but the half maximum band width passes a maximum at about 230 K (see Fig. 6). This indicates that two different emissions emerge and overlap efficiently in this intermediate temperature range.



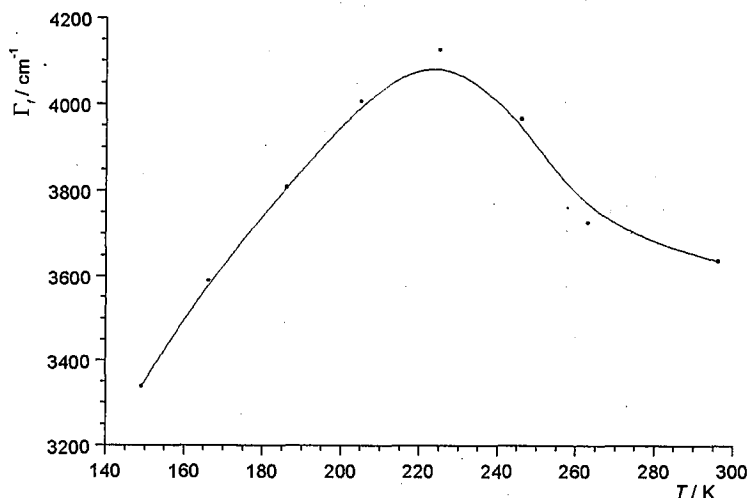


Fig. 6. Plot of the half maximum band width of the fluorescence of  $\text{NO}_2$ -DMPP in propanol-1 as a function of temperature.

### 3.2.3. Semiempirical calculations

In the ground state equilibrium geometry, the nitrophenyl subunit is nearly perpendicular to the DMPP moiety, as  $\alpha = 82^\circ$ . The potential curve for a variation of  $\alpha$  is very flat and the total energy for the ground state of  $\text{NO}_2$ -DMPP depends only slightly on the nitrophenyl torsion angle  $\alpha$  (see Fig. 7). It varies only by  $0.54 \text{ kJ mol}^{-1}$  for  $\alpha$  between  $90^\circ$  and  $70^\circ$ , and a rotation by  $50^\circ$  increases the energy by only  $5.4 \text{ kJ mol}^{-1}$  compared to the minimum geometry.

The rotation of the nitro group itself has an energy minimum for the flat geometry, i.e., for an angle  $\sigma = 0^\circ$ . An analysis of the properties of the important excited states is presented for this fully optimized geometry in Table III. The

TABLE III

Total energies, dipole moments, and an orbital analysis of the important excited state of  $\text{NO}_2$ -DMPP for the ground state equilibrium geometry in gas phase.

State	Energy eV	Dipole moment $10^{-30} \text{ C m}$	Main contribution to the $S_n \leftarrow S_0$ transition	Symmetry
$S_0$	0.00	16.0		$A_1$
$S_1$	3.80	45.0	LUMO + 1 $\leftarrow$ HOMO	$A_1$
$S_2$	3.83	22.0	LUMO + 2 $\leftarrow$ HOMO	$B_2$
$S_3$	4.63	34.4	LUMO + 1 $\leftarrow$ HOMO - 2	$B_2$
$S_4$	4.85	55.4	LUMO + 1 $\leftarrow$ HOMO - 1	$B_2$
$S_5$	4.86	67.4	LUMO $\leftarrow$ HOMO	$A_2$

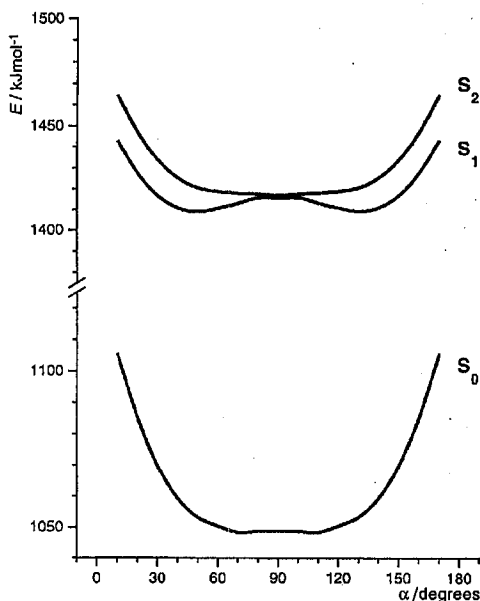
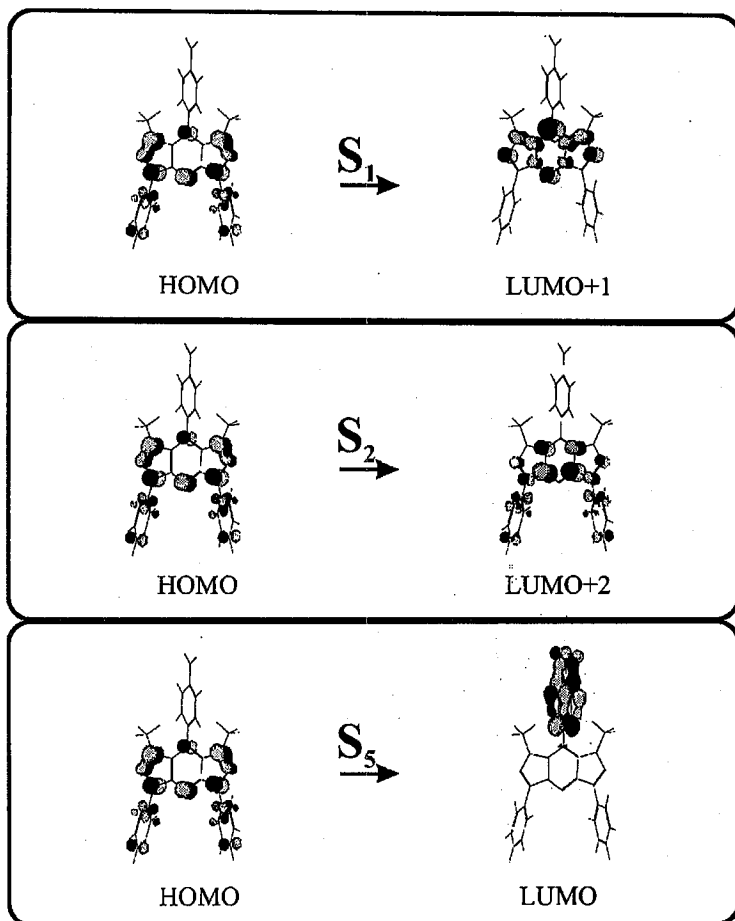


Fig. 7. Energies of some important excited states for varying the rotation angles  $\alpha$  of the nitrophenyl subunit, presented for angles from  $\alpha = 0^\circ$  (planar) to  $\alpha = 90^\circ$  (perpendicular).

dominant contributing orbitals leading to the formation of these excited states are shown in Scheme 2.

In the ground state equilibrium geometry of  $\text{NO}_2\text{-DMPP}$ , the HOMO orbital is a  $\pi$  orbital delocalized over the diphenyl-bis-pyrazolo-pyridine subunit (see Scheme 2). The  $S_1$ , a  $(\pi, \pi^*)$  excited state, is essentially described by the promotion of an electron from the HOMO to the LUMO+1, with a large contributions at the bis-pyrazolo aromatic system and only a minor one from the nitrophenyl  $\pi$  system. The dipole moment of this  $S_1$  state of  $45.0 \times 10^{-30}$  C m is three times higher than that of the electronic ground state ( $16.0 \times 10^{-30}$  C m). The  $S_2$  state with a dipole moment of  $22.0 \times 10^{-30}$  C m, corresponds to the LUMO+2  $\leftarrow$  HOMO transition. Like the HOMO, the LUMO+2 is localized on the diphenyl-bis-pyrazolo-pyridine. The  $S_5$  state is essentially the LUMO  $\leftarrow$  HOMO transition. It has a large dipole moment of  $67.4 \times 10^{-30}$  C m and can be characterized by an electron transfer from the diphenyl-bis-pyrazolo-pyridine moiety (HOMO) to a nitrophenyl  $\pi^*$  orbital (LUMO).

The influence of the rotation of the nitro group on the excited state energies and dipole moments was also investigated. The planar conformation of the nitrophenyl moiety, with a nitro group torsion angle  $\sigma = 0^\circ$ , has the lowest energy for the ground and all relevant excited states ( $S_1$  to  $S_6$  investigated). The state energies increase when the conformation deviates from the planar geometry and no significant changes in the energy gaps between the states are observed. The rotation of the nitro group has, therefore, no influence on the fluorescence behaviour of  $\text{NO}_2\text{-DMPP}$ . All calculations show that the acceptor group is the nitrophenyl moiety and not the nitro group alone.



Scheme 2. Analysis of the orbital composition of the excited states  $S_1$  (polar  $\pi, \pi^*$  state),  $S_2$  (low polar state), and  $S_5$  (CT state) in the gas phase.

The energy of the polar  $S_1$  state changes considerably with the twist angle  $\alpha$  and this results in a symmetric double minimum potential with minima at  $50^\circ$  and  $130^\circ$  (see Fig. 8a), which are separated by an energy barrier of  $2.8 \text{ kJ mol}^{-1}$ . The oscillator strength increases with planarization and shows a minimal value for orthogonal subunits (from  $\alpha = 70^\circ$  to  $\alpha = 90^\circ$ ). For the most stable conformation at  $\alpha = 50^\circ$  the oscillator strength is calculated to be  $f = 0.169$ .

The apolar  $S_2$  state has a minimal potential energy for  $\alpha = 90^\circ$  and an oscillator strength of  $f = 0.056$ , which is smaller than that for the polar  $S_1$  state at  $\alpha = 50^\circ$  from which the fluorescence should preferentially occur in nonpolar solvents. The difference between the both minima of the  $S_1$  and the  $S_2$  state equals  $5.7 \text{ kJ mol}^{-1}$  (see Fig. 8a) and thermal population of the apolar  $S_2$  state from the minimum  $S_1$  is thus possible. However, due to the Maxwell-Boltzmann factor and the larger oscillator strength for transition from the planarized (i.e.,  $\alpha = 50^\circ$ )

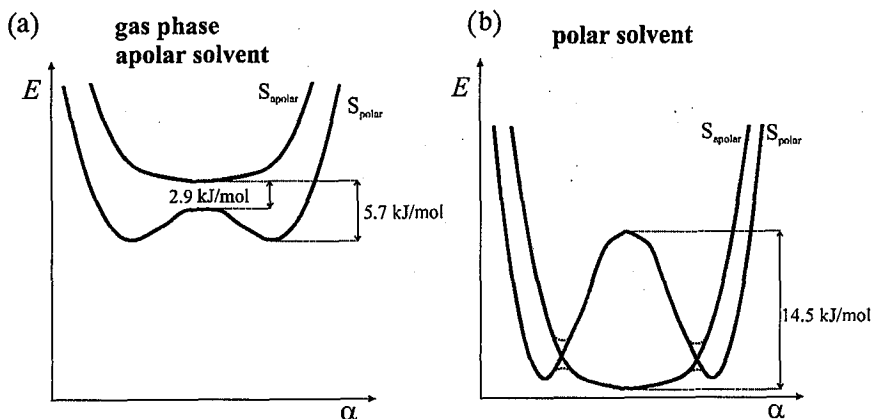


Fig. 8. Schematic plot of the potential energy of the two lowest excited states of  $\text{NO}_2\text{-DMPP}$  in a non-polar (a) and polar solvent (b) versus the rotational angle  $\alpha$ .

polar excited state, emission from this state predominates in gas phase. A similar situation is expected in nonpolar solvents.

Theoretical calculations including the reaction field of the polar solvent acetonitrile indicate most interestingly a larger stabilization of the apolar second excited state by  $\approx 0.2$  eV in comparison to the polar first excited state, for which the stabilization energy becomes only  $\approx 0.1$  eV (see Fig. 8b). The dipole moment of both excited states becomes smaller in a polar solvent: in the gas phase that of the polar state is computed to be  $37.7 \times 10^{-30}$  C m and that of the less polar one becomes  $20.3 \times 10^{-30}$  C m. The values diminish in acetonitrile and reach  $31.7 \times 10^{-30}$  C m and  $12.3 \times 10^{-30}$  C m, respectively. Effects of solvation on the excited state energies, however, cannot be understood by the changes of the dipole moments alone. At an angle  $\alpha = 90^\circ$  the characters of the first and second excited states are reversed, and the apolar state becomes the lowest excited state. It is indicated by the calculations that the influence of the large negative charge on the nitro group which accounts for the intramolecular polarization of the molecule in the gas phase is effectively reduced by solvation. This is mainly an electrostatic effect as orbitals located on the nitrophenyl group are hardly involved in excitation of both the  $S_1$  and the  $S_2$  excited state. The resulting potential energy surfaces in gas phase and in a polar solvent are schematically compared in Fig. 8. The partial inversion of both states leads to a general decrease of the energy difference between the conformational minima of both the polar and the apolar state (see Fig. 8) and the energy barrier between those states becomes also smaller. The apolar state which is now the energetically lowest state, is populated preferentially, and fluorescence from the apolar state becomes thus stronger than in nonpolar solvents. This is in accordance with the experiment and the dramatic change of the transition moment of fluorescence  $\mu_f$  upon increasing solvent polarity is most probably due to this change in the character of the emitting state.

The fifth excited state in the gas phase is characterized as an intramolecular charge transfer (ICT) state but its energy is not lowered sufficiently by geometrical

relaxation and solvent polarity to come close to the  $S_1$  and  $S_2$  states. This ICT state is lowered in acetonitrile in total energy by approximately 1 eV in comparison to the gas phase, but it still remains above the previously discussed locally excited states  $S_1$  and  $S_2$ .

#### 4. Conclusion

The parent compound BPP is an efficient blue emitter with a fluorescence quantum yield of about unity which shows almost no solvatochromism of absorption and fluorescence. Substitution by an electron acceptor as in  $\text{NO}_2$ -DMPP alters the fluorescence properties significantly: Dual fluorescence is observed which is strongly dependent on solvent properties. An efficient long wavelength emission originating from a polar excited state is effectively quenched at medium solvent polarities. At high polarities only a weak fluorescence from a nonpolar excited state remains. Semiempirical calculations indicate that the two lowest excited states, both localized on the BPP moiety, are only separated by a small energy gap. They have different equilibrium geometries, dipole moments, and the  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  transitions have different oscillator strengths. The energy gap is strongly influenced by the electrostatic properties of the nitrophenyl group. Although it is orbitally decoupled from the BPP subunit, solvation effects on the charge distribution on this group changes significantly the ordering of those two states. Because of the small energy gap, this influence is even more significant than direct solvation effects due to electrostatic interactions of the total dipole moments with the reaction field of the solvent. Whereas in nonpolar solvents the polar state with large transition dipole is found as the lowest excited state, in polar solvents the second planar state with lower transition dipole becomes the emitting state. This change in the sequence of the states with solvent polarity manifests in the observed changes of the fluorescence properties of  $\text{NO}_2$ -DMPP.

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