Fluorescent symmetric phenazines from naphthoquinones 3. Steady-state spectroscopy and solvent effect of seven phenazine derivatives: structure–photophysics correlations [☆],[1]

Carlos Eduardo M. Carvalho [a], Ira M. Brinn [a],[*],
Antonio Ventura Pinto [b], Maria do Carmo F.R. Pinto [b]

[a] *Laboratório de Espectroscopia Resolvida no Tempo, Instituto de Química, Universidade Federal do Rio de Janeiro,
Ilha do Fundão, C.P. 68 563, Rio de Janeiro, R.J. 21 945-970, Brazil*
[b] *Núcleo de Pesquisas de Produtos Naturais, Universidade Federal do Rio de Janeiro Ilha do Fundão,
C.P. 68 035, Rio de Janeiro, R.J. 21 945-970, Brazil*

Abstract

The fluorescence spectra of seven phenazines (two belonging to the C_{2h} point group, two to the C_{2v} point group, two to the C_s point group and one to the C_1 point group) in organic solvents of varying polarity show a bathochromic shift in all cases. Fluorescence quantum yields increase as the polarity of the solvent increases for the C_{2h} and the C_s compounds, however, no appreciable changes are noted in the C_{2v} compounds. The unexpectedly strong solvent interactions with the two centrosymmetric phenazines are explained on the basis of a localized excited state. This explanation was supported by excited state dipole moment measurements, which indicated similar moments for the C_{2h} and C_{2v} compounds. Two of the compounds undergo lasing when placed in a laser cavity and pumped with the third harmonic of an Nd-YAG laser. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Solvent effect; Phenazine derivatives; Fluorescence quantum yields; Excited state dipole moments

1. Introduction

Using fluorescence spectroscopy as a probe in solution has become a common technique in the last half century, or so. Its utility is based on its high sensitivity to changes in polarity, as well as high inherent detectability. The latter allows one to use very small quantities of the fluorescent probe, therefore guaranteeing that its presence does not appreciably alter the medium that is being measured. To the extent that the fluorescence quantum yield (ϕ_{fl}) of the probe increases, this advantage over other methods becomes even more pronounced. In addition, compounds that demonstrate high ϕ_{fl} are obvious candidates for lasing media.

Based on the known [3–9] photochemical properties of phenazine, its derivatives might seem to be dubious candidates as high ϕ_{fl} compounds. Singlet phenazine decays pre-dominantly via intersystem crossing ($\phi_{isc} \cong 0.98$) whereas $\phi_{fl} \cong 10^{-5}$. In spite of this there have been reports [10,11] of naturally occurring substituted phenazines, isolated from *Pseudomonas* spp, as well as synthetic phenazines, such as neutral red [12], which have appreciable fluorescence.

What follows is a description of the steady state fluorescence properties of seven different high ϕ_{fl} phenazine derivatives. The fluorescence maxima and quantum yields, as a function of solvent polarity, are reported. The experimental evidence for a surprisingly strong solvent effect on the spectroscopy and photochemistry of the two centrosymmetric, as well as three less symmetric, phenazines studied here is discussed.

2. Methods

Three of the phenazines reported here, 3,3,12,12-tetramethyl-3H,12H-di-1,4-pyran[3,2-c,j]dibenzo[e,l]phenazine (DPZ6t, Fig. 1), 2,2,14,14-tetramethyl-1H,15H-difuran[2,3-e,j]dibenzo[c,l]phenazine (DPZ5c, Fig. 2) and 2,2,8,8-tetramethyl- 3H, 7H-di- 1,4-pyran[3,2-c, l]dibenzo[e,j]phenazine
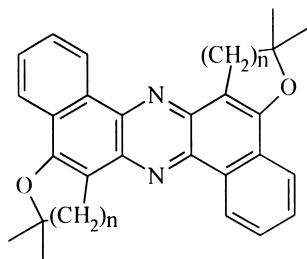
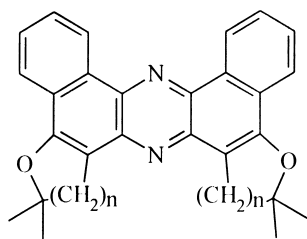Fig. 1. Molecular structures: DPZ5t ($n=1$) and DPZ6t ($n=2$).

Fig. 2. Molecular structures: DPZ5c ($n=1$) and DPZ6c ($n=2$).

(DPZ6c, Fig. 2) were prepared as previously [13] described. The synthesis of 2,2,10,10-tetramethyl-1H,9H-difuran[3,2-c,j]dibenzo[e,l]phenazine (DPZ5t, Fig. 1) has also been reported [1,2]. The compounds 2,2-dimethyl-3H-furan[3,2-c]benzo[e]phenazine (PZ5, Fig. 3), 2,2-dimethyl-3H-1,4-pyran[3,2-c]benzo[e]phenazine (PZ6, Fig. 3) and 2,2-di-methyl-3-Br-1,4-pyran[3,2-c]benzo[e]phenazine (PZ6Br, Fig. 3) were prepared [14] in the usual fashion. The purity of each compound was checked by thin layer chromatography and the structure verified by NMR spectroscopy. The specific data and description of the synthesis of the previously unreported PZ6Br will be published separately.

The following spectroquality grade solvents were used for spectroscopy: methylcyclohexane (MCH, Aldrich), ace-tonitrile, benzene, chloroform, diethyl ether, 1,4-dioxane, n-hexane, methanol and 2-propanol (Grupo Química/Brazil), dimethylformamide (DMF) and tetrahydrofuran (THF, Merck/Brazil) and cyclohexane (Vetec/Brazil). Fluorescence quantum yield measurements were done using a
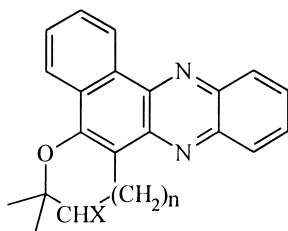

Fig. 3. Molecular structures: PZ5 ($n=0$, X=H); PZ6 ($n=1$, X=H) and PZ6Br ($n=1$, X=Br).

deaerated solution of 9,10-biphenylanthracene in MCH [15] as the standard, with a $\phi_{fl}\equiv0.90$. (The method of calculation was taken from the same reference.)

Absorption spectra were taken on a Cary E-1 Spectropho-tometer. Fluorescence spectra were taken on a Hitachi F-4500 Spectrofotofluorimeter. All fluorescence spectra re-ported here are corrected using Rhodamine B as an internal standard to correct the lamp output, whose scattering is then used to correct [16] the instrument response function. This standard is considered to be valid for correcting spectra in the region between 16,700 and 50,000 cm^{-1}. The fluo-rescence spectra of some of the compounds studied here displayed a very weak tail outside of this region. The third harmonic of a Continuum, model Surelite II Nd-YAG laser, which puts out 180 mJ at 28,200 cm^{-1}, was used to test for potential laser material.

Spectra were manipulated using ORIGIN 5.0 and ground state dipole moments were calculated with the MMX Force Field using an IBM compatible 486 microcomputer.
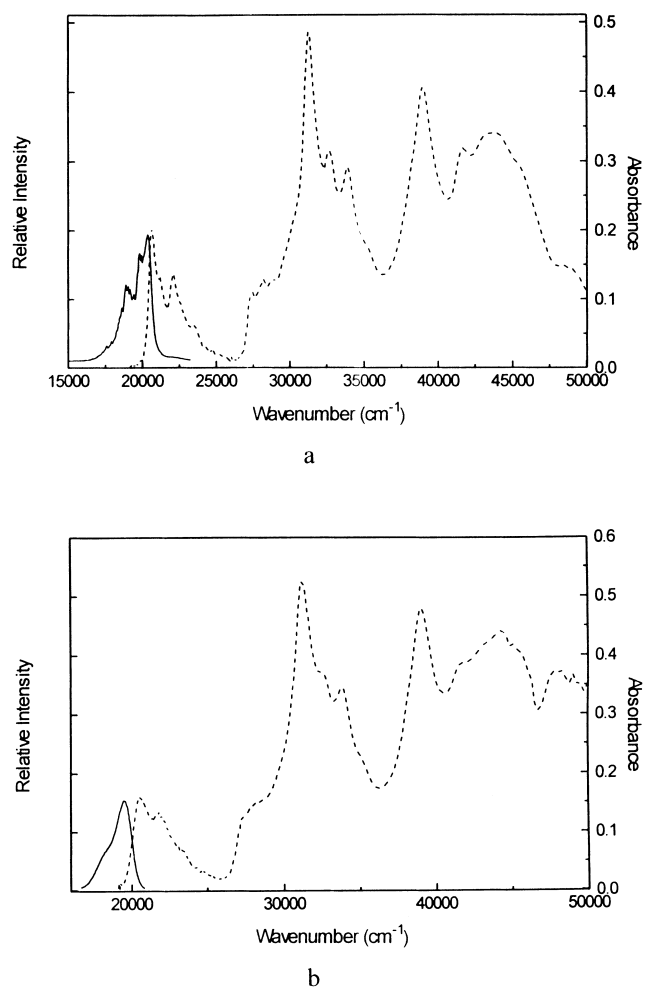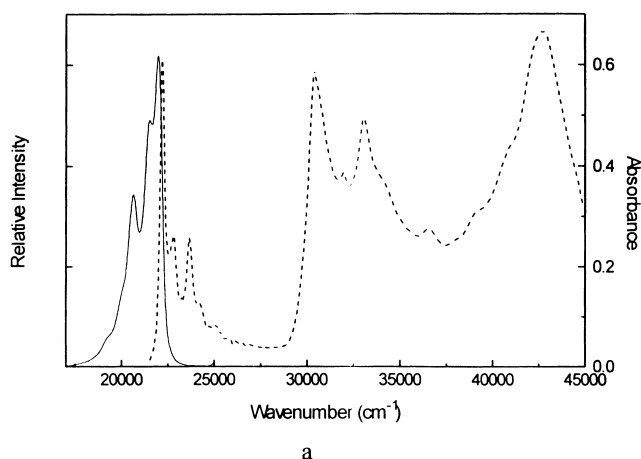

a

b

Fig. 4. Absorption (dashed lines) and fluorescence (solid line) spectra of DPZ5t: (a) [DPZ5t]=1.03×10^{-5} M in cyclohexane; (b) [DPZ5t]=2.78×10^{-5} M in acetonitrile. For the fluorescence spectra (a) $\bar{v}_{Exc}$=28,600 cm^{-1} and (b) $\bar{v}_{Exc}$=28,200 cm^{-1}.

3. Results and discussion

3.1. Solvent effect

Sample absorption and fluorescence spectra for DPZ5t, DPZ5c, PZ5, PZ6 and PZ6Br in cyclohexane (a) and acetonitrile (b) are shown in Figs. 4–8, respectively. Excitation spectra were done for all of the phenazines studied here and coincide with the absorption spectra in all cases. The mirror image relationship between the fluorescence spectrum and the first absorption band is obvious in all cases, indicating that fluorescence originates from the same electronic state which is excited via absorption into the lowest energy band.

The large fluorescence solvent shifts can also be noted easily in the spectra shown. Tables 1–3 show the solvatochromic fluorescence results for the phenazines studied here as a function of solvent polarity. The latter was measured by the parameter Δf [17]:
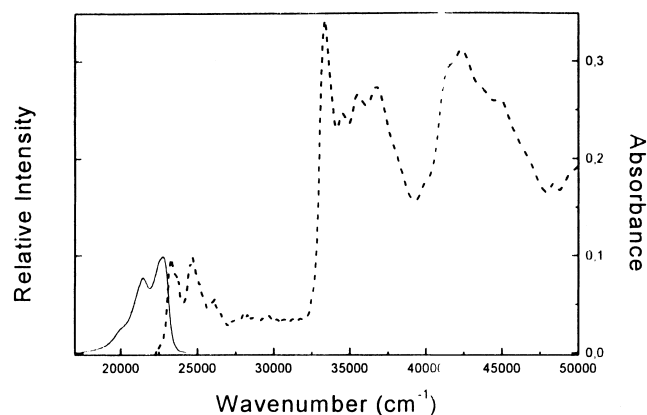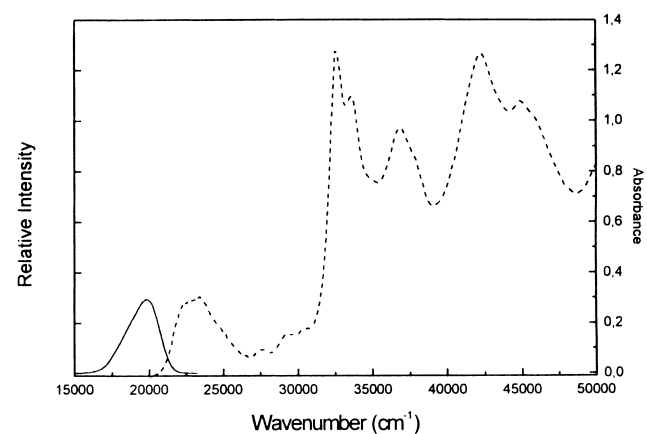

a
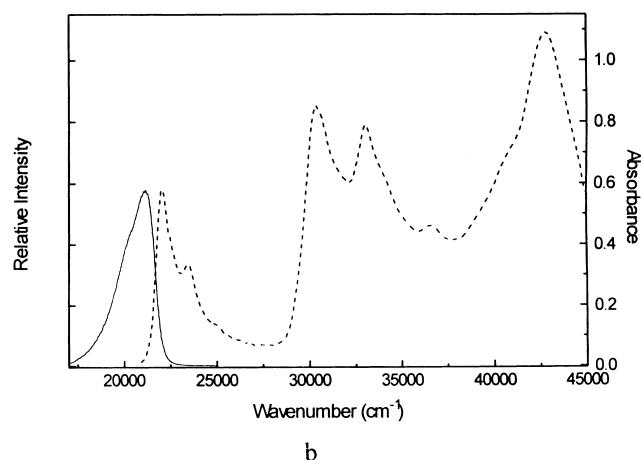
b

Fig. 5. Absorption (dashed lines) and fluorescence (solid line) spectra of DPZ5c: (a) [DPZ5c]=9.84×10^{-6} M in cyclohexane; (b) [DPZ5c]=2.31×10^{-5} M in acetonitrile. For both fluorescence spectra, $\bar{v}_{Exc}$=25,300 cm^{-1}.
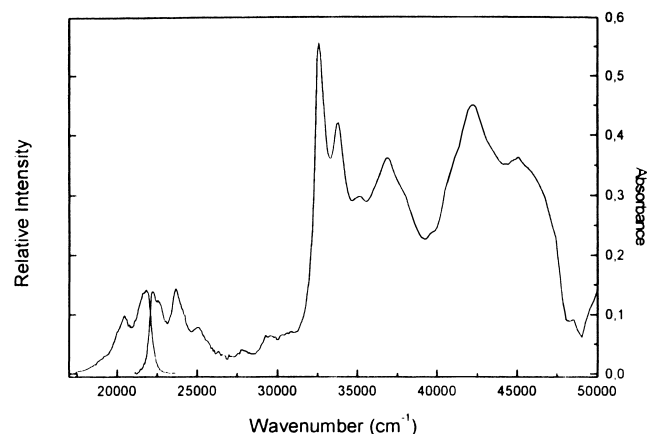

a

b

Fig. 6. Absorption (dashed lines) and fluorescence (solid line) spectra of PZ5: (a) [PZ5]=9.84×10^{-6} M in cyclohexane; (b) [PZ5] =2.31×10^{-5} M in acetonitrile. For both fluorescence spectra, $\bar{v}_{Exc}$=25,300 cm^{-1}.

$$\Delta f \equiv \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{1}$$

where ε is the dielectric constant and n the index of refraction of the pure solvent, and the parameter E_T^N [18,19], being the normalized empirical polarity parameter $E_T(30)$ [20]. The values of these parameters, for each solvent used, are collected in Table 4.

Possibly the simplest way to understand the results in these tables is to consider separately the effect of: (A) the five-membered versus the six-membered aliphatic ring; (B) the structural arrangement of the rings, i.e. *cis*, *trans* or non-symmetrical and (C) solvent polarity, on the physical variables: (i) absorption ($\bar{v}_{Ab}$) and fluorescence ($\bar{v}_{fl}$) frequency maxima and (ii) ϕ_{fl}.

(A-i) Comparing the effect of the size of the aliphatic ring (i.e. Table 1 versus Tables 2 and 3) one notices that in a given solvent and for each of the three geometrical arrangements the six-membered aliphatic ring compound fluoresces to the

a
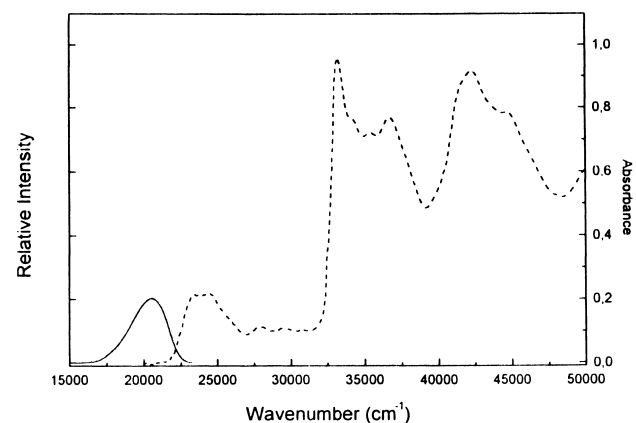
b

Fig. 7. Absorption (dashed lines) and fluorescence (solid line) spectra of PZ6: (a) [PZ6]=9.84×10^{-6} M in cyclohexane; (b) [PZ6] =2.31×10^{-5} M in acetonitrile. For both fluorescence spectra, $\bar{v}_{Exc}$=25,300 cm^{-1}.

a

b

Fig. 8. Absorption (dashed lines) and fluorescence (solid line) spectra of PZ6Br: (a) [PZ6Br]=9.84×10^{-6} M in cyclohexane; (b) [PZ6Br]=2.31×10^{-5} M in acetonitrile. For both fluorescence spectra, $\bar{v}_{Exc}$=25,300 cm^{-1}.
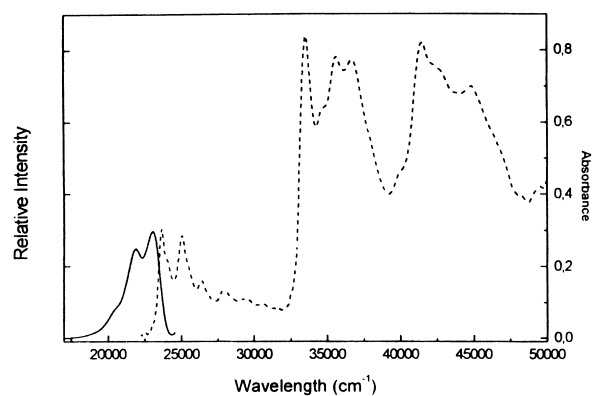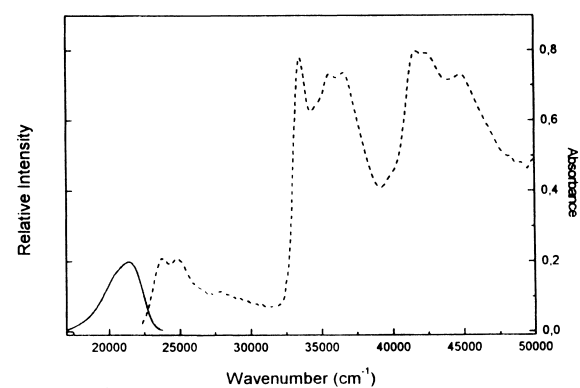
blue of the corresponding five-membered aliphatic ring compound, without exception, the difference being in the order of 1000 cm^{-1}. (The absorption spectra show similar results.) This can be rationalized considering that the five-membered ring has greater strain and this, in turn, causes a strain in the neighboring aromatic system, therefore raising its energy. This effect is more important in the ground state (S$_0$) than in the first excited singlet state (S$_1$) because in the latter case the bonds are, on average, a bit longer and therefore more malleable.

(B-i) Comparing the effect of geometry (Tables 1 and 2 versus Table 3) on $\bar{v}_{fl}$ in any given solvent and with a given aliphatic ring present, one notices that the spread is not particularly large considering the diversity of the structures (approximately 1600 cm^{-1}, at the greatest) and that the *cis* structure exhibits the most blue shifted spectra, without exception. The nonsymmetrical structure and *trans* structure emit at about the same frequency. (The absorption spectra

show similar results, however, the frequencies of the non-symmetrical structures clearly approach those of the *cis* structures.) The nonsymmetrical structures emit further to the blue when a five-membered aliphatic ring is present, the

Table 1
Solvatochromic fluorescence results for DPZ5t and DPZ5c

Solvent	DPZ5t			DPZ5c		
	$\bar{v}_{Ab}$ (cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]	$\bar{v}_{Ab}$ (cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]
Cyclohexane	20620	20440	0.42	22170	22010	0.43
n-Hexane	20700	20430	0.27	22220	22020	0.40
Benzene	20490	20160	0.52	21980	21590	0.39
1,4-Dioxane	20450	20080	0.47	22030	21640	0.53
Chloroform	20370	19530	0.53	21880	21260	0.43
2-Propanol	20580	19640	1.0	22120	21310	0.57
Acetonitrile	20450	19650	1.0	21980	21190	0.39
Methanol	–	19650	1.0	–	–	–

[a] Band maxima (all wavenumbers±20 cm^{-1}).
[b] Fluorescence quantum yields (±10%). Errors given as most probable error.

Table 2
Solvatochromic fluorescence results for DPZ6t and DPZ6c

Solvent	DPZ6t			DPZ6c		
	$\bar{v}_{Ab}$ (cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]	$\bar{v}_{Ab}$ (cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]
Cyclohexane	–	21790	0.38±0.04	23200	22990	0.33±0.03
n-Hexane	22120	21880	0.31±0.03	23260	23030	0.37±0.04
Benzene	21740	21290	0.42±0.04	22990	22640	0.29±0.03
1,4-Dioxane	21740	21260	0.26±0.03	22990	22560	0.47±0.05
Chloroform	21690	20960	0.43±0.04	22880	22400	0.42±0.04
THF	21830	21400	0.34±0.03	–	–	–
DMF	21790	20960	0.57±0.06	–	–	–
2-Propanol	21980	21050	0.53±0.05	23150	22320	0.40±0.04
Acetonitrile	21740	20960	0.61±0.06	22990	22270	0.28±0.03
Methanol	21880	20880	0.62±0.06	–	–	–

[a] Band maxima (all wavenumbers±20 cm^{-1}).
[b] Fluorescence quantum yields (±10%). Errors given as most probable error.

phenomenon inverting when a six-member ring is present, with only one exception.

It is well known that, among otherwise identical polycyclic compounds, smaller aromatic systems absorb and emit further to the blue than larger systems. Thus, one would expect the smaller systems, PZ5 and PZ6, to emit furthest to the blue. If, in addition, one considers solvation relaxation to differentiate between the *cis* and *trans* structures (which are about the same size), one expects the *cis* structure to emit to the red of the *trans* structure. The fact that neither is the case can be interpreted as indicating that excitation in S_1 is localized on only part of the conjugated section of the molecule, presumably about half of the molecule, instead of being delocalized over the entire structure. Although a reasonable explanation for this would be that these phenazines are bent in S_1, another possible interpretation is that these compounds are too large to allow complete delocalization of the excitation. Distinguishing between these two possible explanations will be treated below.

The conclusion that the excitation is restricted to the aromatic system, the aliphatic system merely exercising a secondary effect, was supported by the solvatochromic results of PZ6Br, shown in Table 3. Comparing emission frequencies, in any given solvent, with those of Table 3, one notes that the effect of the addition of an atom of bromine to the aliphatic ring is to shift the emission to higher frequencies. This result suggests that the effect of this substitution is not to alter directly the system where the electronic excitation is localized, because if it were the effect of the bromine would be to decrease the emission frequencies. The fact that the addition of the bromine atom increases the emission frequencies indicates that the effect is skeletal, the presence of the Br stabilizing S_0 more than S_1, probably by restricting the torsional motion of the aliphatic ring and increasing planarity in the aromatic ring.

(C-i) One notices from Tables 1 and 2 that a bathochromic shift of approximately 950 cm^{-1} is observed for the nonpolar DPZ5t and DPZ6t compounds. This solvatochromic shift is slightly greater than that shown by the two *cis* structures, DPZ5c and DPZ6c, of 750 cm^{-1}. The corresponding red shifts for the three nonsymmetric structures (Table 3) are considerably larger, in the order of 2100 cm^{-1}. In general, the effect of increasing solvent polarity is to increase solvent–solute interactions, predominantly through

Table 3
Solvatochromic fluorescence results for PZ5, PZ6 and PZ6Br

Solvent	PZ5			PZ6			PZ6Br		
	$\bar{v}_{Ab}$(cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]	$\bar{v}_{Ab}$ (cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]	$\bar{v}_{Ab}$ (cm^{-1})[a]	$\bar{v}_{fl}$ (cm^{-1})[a]	ϕ_{fl}[b]
Cyclohexane	21930	21010	0.082	23260	21740	0.050	23640	23200	0.28
n-Hexane	–	–	–	–	–	–	23690	23220	0.25
Benzene	21830	20700	0.20	23200	21230	0.12	23640	22510	0.28
1,4-Dioxane	–	–	–	–	–	–	23530	22250	0.44
Chloroform	21740	19800	0.26	22880	20370	0.17	23420	–	–
THF	21740	19800	0.13	23040	20700	0.10	23420	22280	0.39
DMF	21880	19160	0.44	22780	19960	0.13	23640	21820	0.34
2-Propanol	–	–	–	–	–	–	23640	21540	0.39
Acetonitrile	–	–	–	–	–	–	23640	21880	0.49
Methanol	21830	18900	0.37	22990	19570	0.23	23530	21010	0.57

[a] Band maxima (all wavenumbers±20 cm^{-1}).
[b] Fluorescence quantum yields (±10%). Errors given as most probable error.

a dipole–dipole mechanism. It is normally observed that this increased solvent–solute interaction causes fluorescence band shifting and to a lesser extent, absorption band shifting. Centrosymmetric solutes, in function of their zero dipole moment, apparently are incapable of dipole–dipole interactions; therefore, they are expected to be relatively free of these shifts. Although the shifts for PZ5 and PZ6 are quite reasonable, the sizes of the shifts in the cases of DPZ5t and DPZ6t are quite surprising. There have been a few cases of solvent effects in the absorption and emission spectra of compounds, whose ground state dipole moment is zero because of symmetry, reported [19–25] recently, creating controversy in the literature regarding their origin. Because the usual argument of dipole–dipole interaction is assumed to be inapplicable in these cases, it has been suggested that these dislocations are the result of either solvent dipole–solute quadrapole interactions [21,22] in the case of substituted anthracenes or, alternatively, changes [23,24] in the quadrapole moment of the solute during the electronic transition, in the case of the fullerene C_{60}. In both cases the arguments presented rely on the basic idea of electron redistribution in the presence of solvents of different polarity producing differences in electronic energy levels. We prefer to interpret our results as supporting the assumption that the excitation in S_1 is localized on only part of the molecule, as given in B-i above. Whether the same explanation is applicable to substituted naphthalenes [21,22] and fullerenes [23,24] is not clear.

3.2. Excited state dipole moments

Excited state dipole moments (μ_{Ex}) are useful as a simplified measure of electron distribution in the excited state, the latter being responsible for all chemical properties. The most common method for determining μ_{Ex} is the solvatochromic method in which μ_{Ex} is calculated by comparing the shift of the spectrum ($\Delta\bar{v}$) of the compound of interest to a parameter related to solvent polarity. The same polar-

Table 4
Solvent polarity parameters

Solvent	Δf	E_T^N
Cyclohexane	0.0005	0.006
n-Hexane	0.001	0.009
Benzene	0.0039	0.111
1,4-Dioxane	0.0202	0.164
Chloroform	0.1408	0.256
THF	0.2107	0.207
2-Propanol	0.2744	0.546
DMF	0.2755	0.386
Acetonitrile	0.3062	0.460
Methanol	0.3134	0.762

ity parameters shown in Table 4 have been used to calculate μ_{Ex}, i.e. Δf and E_T^N. In the case of the former parameter, $\Delta\mu$ is given [26] by

$$\Delta\mu = \mu_{Ex} - \mu_{Gd} = \left\{\left(\frac{cha^3}{2}\right)\left(\frac{\Delta\bar{v}}{\Delta f}\right)\right\}^{1/2} \quad (2)$$

μ_{Gd} being the ground state dipole moment, c the velocity of light, h Planck's constant and a being the Onsager 'effective' spherical radius of the solute. In the case of the latter solvent polarity parameter, $\Delta\mu$ is given by [27]

$$\Delta\mu = 5.4823 \times 10^{-3} a^{3/2}\left(\frac{\Delta\bar{v}}{\Delta E_T^N}\right)^{1/2} \quad (3)$$

where a has the same definition as in Eq. (2). Although $\Delta\bar{v}$ can be taken from either the absorption or fluorescence spectrum, it is most usually set equal to the difference between the absorption and fluorescence maxima, as has been done here. Sample plots of ($\Delta\bar{v}/\Delta f$) and ($\Delta\bar{v}/\Delta E_T^N$) for DPZ5c are shown in Fig. 9 and the results for all seven compounds, using Eqs. (2) and (3) are tabulated in Table 5. To calculate $\Delta\mu$ one needs to know a of the solute. This part is probably the Achilles heel of the model, because most molecules studied are far from spherical. Even so, an approximation of
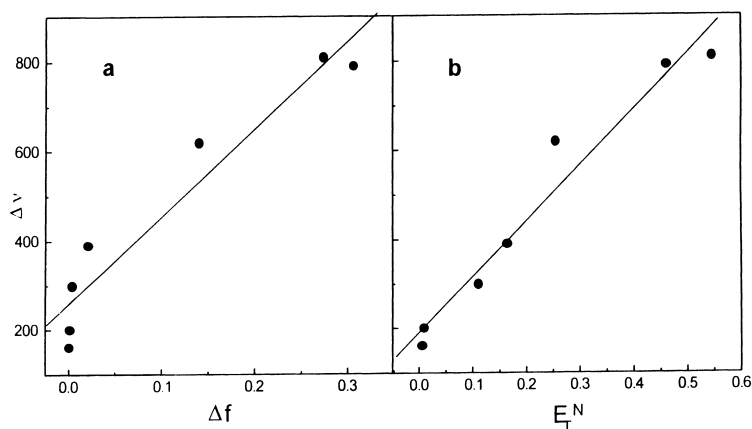

Fig. 9. Plots of $\Delta\bar{v}$ vs. solvent polarity parameter for DPZ5c: (a) Eq. (2) and (b) Eq. (3).

Table 5
Dipole moments

Phenazine	Radius (Å)[a]	μ_{Gd} (D)[b]	Plotted against Δf (Eq. (2))			Plotted against E_T^N (Eq. (3))		
			$\Delta\mu$ (D)	Multiple r	μ_{Ex} (D)	$\Delta\mu$ (D)	Multiple r	μ_{Ex} (D)
DPZ5t	5.50	0.25	5.9±0.8	0.92	6.1±0.8	2.6±0.3	0.93	2.9±0.3
DPZ5c	5.50	1.06	5.6±0.6	0.96	6.7±0.6	2.5±0.3	0.98	3.6±0.3
DPZ6t	5.62	0.63	5.5±0.8	0.87	6.1±0.8	2.4±0.3	0.95	3.0±0.3
DPZ6c	5.62	1.05	5.4±0.7	0.94	6.4±0.7	2.4±0.2	1.00	3.5±0.2
PZ5	4.92	0.96	8±1	0.92	9 ± 1	3.2±0.5	0.92	4.2±0.5
PZ6	4.99	0.80	7±1	0.92	8±1	3.0±0.3	0.97	3.8±0.3
PZ6Br	5.38	2.09	8±1	0.85	10±1	3.5±0.4	0.97	5.6±0.4

[a] Calculated assuming density of 1.00.
[b] Calculated theoretically using an MMX Force Field. Errors given as most probable error.

a, in Å, can be obtained from

$$a = 10^8 \left(\frac{3M}{4\pi N\rho} \right)^{1/3} \qquad (4)$$

where M is the molecular weight of the compound of interest, N Avogadro's number and ρ the density in g/cc. One should note that the method also requires a knowledge of μ_{Gd} in order to calculate μ_{Ex}. To the best of our knowledge, none of these values has been determined experimentally. The values given in Table 5 for μ_{Gd} are calculated theoretically, using the molecular mechanics MMX Force Field. The μ_{Ex} values have been assumed to be the sum of μ_{Gd} and $\Delta\mu$. This assumption is consistent with the idea that the nitrogen atoms are electron withdrawing in S_0 and even more so in S_1. However, even if the dipole vectors are not perfectly aligned, the difference in the calculation of μ_{Ex} will be trivial, because $\Delta\mu \gg \mu_{Gd}$.

Table 5 shows the calculated μ_{Ex} for the seven compounds considered here, using Eqs. (2) and (3). The multiple r values and most probable errors (calculated from the deviation of the slopes in Eqs. (2) and (3) and assuming an uncertainty of 20% in ρ) are consistently better using the E_T^N polarity scale, as has been found previously [27] for other compounds. The goodness of fit (as evidenced by the multiple r values) especially using the E_T^N polarity scale, is taken as evidence for the absence of specific solvent–solute interactions in the systems studied here. For both polarity parameters used, all seven compounds presented reasonably linear ($\Delta\bar{v}/\Delta f$) and ($\Delta\bar{v}/\Delta E_T^N$) plots, indicating that S_1 can be attributed to the same excited state, independent of solvent. In general, Eq. (2) generates values of μ_{Ex} which are approximately twice those generated by Eq. (3). Eq. (3) normally yields results which are closer [27] to those calculated by quantum mechanics. If the compounds being studied have excited state properties which are significantly different from those of the reference compound (betaine) used to derive Eq. (3), the empirical assumptions may not hold.

It is generally expected that small solvent shifts would be observed in the case of a centrosymmetric compound, where both μ_{Ex} and μ_{Gd} should be close to zero. However, in the case of centrosymmetric compounds whose excited state wavefunction does not reflect molecular symmetry, i.e. $\mu_{Gd} \cong 0$ and $\mu_{Ex} \neq 0$, one might expect surprisingly large solvatochromic shifts, because increasing the polarity of the solvents stabilizes the excited state considerably more than it stabilizes the ground state. The fact that, within experimental error, the μ_{Ex}, values for the *trans* isomers are approximately equal to the values for the corresponding *cis* isomers, in the case of both methods used, supports the model of localized excitation in S_1, proposed here for these compounds.

(A-(ii)) Independent of the arrangement of the aromatic rings, the five-membered aliphatic ring systems show consistently slightly greater ϕ_{fl} values than the corresponding structures with six-membered aliphatic rings. This result is interpreted as indicating that the aliphatic ring does not participate in the electronic redistribution upon excitation, however, acts as a sink for the degradation of electronic energy via internal conversion and/or intersystem crossing. Supporting the first explanation is the fact that it is well known [28] that S_1–S_0 internal conversion can be associated, to a reasonable approximation, with the high frequency stretches present in the electronically excited molecule. If one restricts consideration to only the methylene groups, one notes twice the number of C–H stretching modes in the compounds with six-membered aliphatic rings, as compared to the compounds with five-membered aliphatic rings. Supporting the second explanation is the fact that the six-membered ring compounds have a greater S_1–S_0 energy separation, which could lead one to expect that they might demonstrate decreased internal conversion and greater intersystem crossing, relative to the five-membered ring compounds. At this point we are not able to distinguish between these two potential explanations.

(B-(ii)) One observes that independent of the size of the aliphatic ring, the *trans* structures show the highest ϕ_{fl} values and the nonsymmetric compounds show the lowest ϕ_{fl} values. These results do not correlate with the S_1–S_0 energy separations, suggesting that differences in intersystem crossing may not be important. The above results do correlate with symmetry allowed vibrational transitions (the nonsymmetrical structures, being of lower molecular
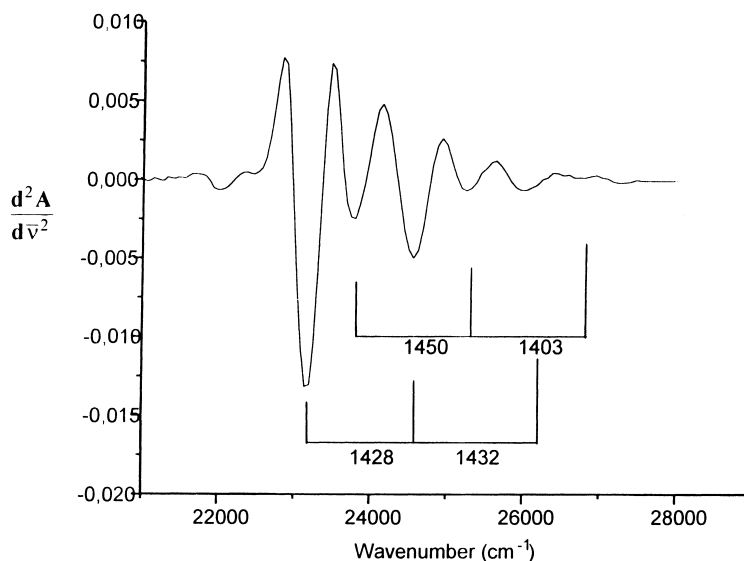
Fig. 10. Second derivative of the absorption spectrum of DPZ6c in cyclohexane. Two vibrational progressions are shown.

symmetry, have more allowed nonradiative transitions), apparently supporting the notion that the differences are due to differences in internal conversion rates.

With the idea of investigating to what extent the differences in vibronic coupling, as a function of the point group of the solute, is responsible for differences in ϕ_{fl}, the second derivative [29] of the absorption and fluorescence spectra of each compound in acetonitrile and cyclohexane was taken. In all cases one or two vibrational series, with splittings of $1450 \pm 50 \, cm^{-1}$ were observed. As an illustration, the second derivative of the absorption spectrum of DPZ6c in cyclohexane is shown in Fig. 10, with the splittings indicated. In general, the vibronic coupling becomes less clear in the fluorescence spectra, as compared to the absorption spectra, and also as the polarity of the solvent increases. Vibronic splittings of this order have been observed [30] previously for similar compounds and the frequency attributed to stretching of a heterocyclic ring with three, or more, condensed rings. The fact that approximately the same frequency was observed in all the compounds studied here leads one to suggest that the first excited singlet state is delocalized over the heterocyclic ring in all cases. Unfortunately, ring stretches, in principle, can contribute to a vibrational mode of any representation and no correlation with molecular symmetry can be made at this time.

(C-(ii)) The effect of solvent polarity on ϕ_{fl} varies as a function of the arrangement of the aromatic system, being almost nil for the *cis* structures, whereas an increase in solvent polarity increases ϕ_{fl} by a factor of 2, or more, for the *trans* and nonsymmetrical structures. It should be noted that this latter behavior is somewhat surprising because, in general, increasing solvent polarity is expected to decrease ϕ_{fl}. This expected effect upon increase of the solvent polarity can be rationalized by three factors, all of which may be present simultaneously:

1. an increase in solvent–solute dipole–dipole interactions, allowing greater energy transfer from electronically excited solute molecules to solvent molecules (that the more polar solvents have stronger interactions with the compounds treated here is confirmed by the bathochromic solvent shifts of the fluorescence spectra);

2. an increase in specific solvent–solute interactions, which should have the same effect as the above factor; and

3. a decrease in S_1–S_0 energy separation, which should increase internal conversion. We are presently endeavoring to determine why this effect is not observed.

The increase of ϕ_{fl} with increasing solvent polarity in rigid aromatic solutes (which cannot undergo twisting and be explained by the TICT model) has been observed previously. One explanation which has been given [31–33] is based on the idea that S_1 is a mixture of two close-lying electronic states, one predominantly covalent and the other considerably more polar (CT). According to this model, the CT state makes a greater contribution to S_1 in polar solvents than in nonpolar solvents and has a considerably smaller overlap with the predominantly covalent S_0, thus leading to higher ϕ_{fl} in polar solvents. However, were two states of different polarities present, a determination of the excited state dipole moment using the solvatochromic method should produce different slopes, in different polarity regions. This was not encountered experimentally (Fig. 9), which argues against invoking this explanation in the case of the phenazines studied here.

Other explanations which have also been offered for the observation of increased ϕ_{fl} with increasing solvent polarity are increased stability of the S_1 state due to greater solvent–solute interactions [34] and increased planarity [35] in S_1 compared to S_0. It should be noted that care must be taken in differentiating between the polarity effect of a solvent and its proton donating ability, which could be a

potent channel for quenching S_1 [33,36,37]. Thus, in the case of the phenazines studied here dissolved in alcohols, one would expect that the proton donating ability of the solvent (which parallels solvent polarity) together with the expected increased basicity of the phenazine nitrogens upon excitation, would be effective in decreasing ϕ_{fl}. The fact that this is not observed with increasing proton donating ability of the alcohols used indicates that this effect is secondary in the case of these phenazines. Another possible interpretation might have been that the expected increased basicity of the phenazine nitrogens upon excitation does not come about due to excitation localization, which partially excludes these groups. However, this last explanation would appear to be excluded by the results of second derivative spectroscopy.

3.3. Lasing

Saturated solutions of DPZ6c and DPZ5t in 1,4-dioxane, in a 10 mm square fluorescence cell, were tested as potential laser dyes, being excited with the third harmonic of a Nd-YAG laser. In both $\phi_{fl}=0.47$. Both were found to undergo lasing, producing a green emission at right angles to the exciting light, when a cylindrical lens was used to concentrate the exciting beam. However, in both cases the lasing ceased within approximately 5 min, i.e. 3000 laser pulses. Thin layer chromatography analysis of the two solutions after irradiation showed a complex mixture of various compounds.

4. Conclusions

Of the seven compounds studied here, by far the best polarity probes were the two nonsymmetrical phenazines, PZ5 and PZ6, which displayed solvatochromic fluorescence shifts of more than $2000\,cm^{-1}$ and variations in fluorescence quantum yield of a factor of 5. All seven compounds have quite high fluorescence quantum yields, especially in polar solvents, and should be considered for use in chemical systems where a low concentration of the fluorescence probe is essential.

Acknowledgements

References

[1] A.V. Pinto, C.N. Pinto, M.C.F.R. Pinto, F.S. Emery, K.C.G. de Moura, C.E.M. Carvalho, I.M. Brinn, J. Chem. Res. (S) (1999) 650 (Part 2).

[2] A.V. Pinto, C.N. Pinto, M.C.F.R. Pinto, F.S. Emery, K.C.G. de Moura, C.E.M. Carvalho, I.M. Brinn, J. Chem. Res. (M) (1999) 2811 (Part 2).

[3] G.M. Badger, I.S. Walker, J. Chem. Soc. (1954) 122.

[4] R. Hochstrasser, J. Chem. Phys. 36 (1962) 1808.

[5] Y. Hirata, I. Tanaka, Chem. Phys. Lett. 43 (1976) 568.

[6] H.-B. Lin, M. Topp, Chem. Phys. 36 (1979) 365.

[7] D.L. Narva, D.S. McClure, Chem. Phys. 56 (1981) 167.

[8] K. Asano, S. Aita, T. Azumi, J. Phys. Chem. 87 (1983) 3829.

[9] B. Nickel, A. Ruth, J. Phys, J. Phys. Chem. 95 (1991) 2027.

[10] A. Gray, F.G. Holliman, Tetrahedron 18 (1962) 1095.

[11] G. Gaertner, A. Gray, F.G. Holliman, Tetrahedron 18 (1962) 1105.

[12] M.K. Singh, H. Pal, A.C. Bhasikuttan, A.V. Sapre, Photochem. Photobiol. 68 (1998) 32.

[13] A.V. Pinto, C.N. Pinto, M.C.F.R. Pinto, F.S. Emery, C.G. de Moura, C.E.M. Carvalho, I.M. Brinn, Heterocycles 45 (1997) 2431.

[14] S.C. Kooker, J. Chem. Soc. 63 (1893) 1376.

[15] D.F. Eaton, Pure Appl. Chem. 60 (1988) 1107.

[16] W.H. Melhuish, J. Opt. Soc. Am. 52 (1962) 1256.

[17] E. Lippert, Z. Electrochem. 61 (1957) 962.

[18] C. Reichardt, Chem. Rev. 94 (1994) 2319.

[19] M. Ravi, A. Samanta, T.P. Radhakrishnan, J. Phys. Chem. 98 (1994) 9133.

[20] C. Reichardt, K. Dimroth, Fortschr. Chem. Forsch. 11 (1968) 1.

[21] N. Ghoneim, P. Suppan, Spectrochim. Acta 51A (1995) 1043.

[22] P. Suppan, J. Phys. Chem. 100 (1996) 5603.

[23] S.H. Gallagher, R.S. Armstrong, P.A. Lay, C.A. Reed, J. Phys. Chem. 99 (1995) 5817.

[24] R.S. Armstrong, S.H. Gallagher, P.A. Lay, J.R. Reimers, C.A. Reed, J. Phys. Chem. 100 (1996) 5604.

[25] J.M. Wessels, M.A.J. Rodgers, J. Phys. Chem. 99 (1995) 17586.

[26] E. Lippert, Z. Naturforsch. 10a (1955) 541.

[27] M. Ravi, T. Soujannya, A. Samanta, T.P. Radhakrishnan, J. Chem. Soc., Faraday Trans. 91 (1995) 2739.

[28] W. Siebrand, D.F. Williams, J. Chem. Phys. 49 (1968) 1860 and references therein.

[29] G. Talsky, L. Mayring, H. Kreuzer, Spectra Angew. Chem., Int. Ed. 17 (1978) 532.

[30] J.P. Byrne, E.F. McCoy, I.G. Ross, Aust. J. Chem. 18 (1965) 1589.

[31] S. Depaemelaere, L. Viaene, M. Van der Auweraer, F.C. De Schryver, R.M. Hermant, J.W. Verhoeven, Chem. Phys. Lett. 215 (1993) 649.

[32] T. Yatsuhashi, Y. Nakajma, T. Shimada, H. Inoue, J. Phys. Chem. 102A (1998) 3018.

[33] C. Cornelissen-Gude, W. Rettig, J. Phys. Chem. 102A (1998) 7754.

[34] T. Häupl, T. Zimmerman, R. Herman, O. Brede, J. Phys. Chem. 103A (1999) 6904.

[35] S.K. Saha, S.K. Dogra, J. Photochem. Photobiol. 110A (1997) 257.

[36] J. Dresner, S.H. Modiano, E.C. Lim, J. Phys. Chem. 96 (1992) 4310.

[37] J. Dey, I.M. Warner, J. Photochem. Photobiol. 116A (1998) 27.