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Nature of the lowest triplet states of 4′-substituted *N*-phenylphenothiazine derivatives†

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The nature of the lowest triplet state of the donor–acceptor *N*-phenylphenothiazine derivatives has been studied by means of phosphorescence and EPR spectroscopy in various low temperature glasses. The triplet excitation of *N*-phenylphenothiazine and *N*-(*p*-anisyl)-phenothiazine is localised within the phenothiazine subunit. On the contrary, the 77 K phosphorescence of the molecules containing an electron acceptor group (*i.e.* –CN, $-COCH_3$ or $-COC_6H_5$ at the 4′ position) is similar to that for benzonitrile, acetophenone or benzophenone, respectively, although the energy levels of their T_1 states are higher than that of phenothiazine. With increasing temperature, however, their phosphorescence becomes similar to that characteristic for phenothiazine. This finding has been explained in terms of the excited-state intramolecular energy transfer accompanied by the planarisation of the phenothiazine kernel. The results of crystallographic investigations support this hypothesis.

1 Introduction

The concept of excited-state intramolecular electron transfer in acceptor (A)–donor (D) compounds linked by a single bond plays a central role in the discussion of their photophysical properties.[1–12] It has been shown previously that in the case of the A–D molecules containing large aromatic and/or heteroaromatic subunits the primary excited singlet state ^{1}(A–D)* undergoes a solvent assisted femto/picosecond relaxation to a polar charge-transfer (CT) fluorescent state ^{1}(A$^-$–D$^+$). Alternatively, the excitation can lead directly to a ^{1}CT state. The solvatochromic effects on the spectral position and profile of the stationary fluorescence spectra proved the CT character of the emitting singlet states. The nonradiative depopulation of the excited ^{1}(A$^-$–D$^+$) state is usually controlled by two competitive mechanisms. The first (with the rate constant k_{nr}) which corresponds to a direct radiationless charge recombination in the singlet manifold leads to the ground state S_0 of the particular A–D molecule. In the second the lowest excited triplet ^{3}(A–D)* state, localised typically in the A or D subunit, is populated by the intersystem crossing process (ISC with the rate constant k_{isc}), most probably *via* a CT triplet state ^{3}(A$^-$–D$^+$).

In some A–D systems, with the energies of the ^{1,3}(A$^-$–D$^+$) states lower than those of the ^{3}(A–D)* states, this deactivation channel seems not to be operative (Fig. 1). This case is especially interesting from the theoretical point of view, because it allows examination of the relationship between radiative (k_f) and nonradiative (k_{nr}) rate constants of electron transfer in the inverted Marcus region.[13,14] CT fluorescence band shape analysis leads to the quantities (the free energy of the CT process ΔG_{CT}, inner λ_i and outer λ_o reorganisation energies and the average energy spacing $h\nu_i$ of the vibronic states coupled to electron transfer) relevant for electron transfer in the Marcus inverted region. Correspondingly, the electronic coupling elements V can be estimated from analysis of the solvent polarity effects[15] on the experimental electronic transition dipole moment M in terms of the Mulliken[16,17] and Murrel[18] models. Using these parameters, k_{nr} values can be calculated in terms of a non-adiabatic theory of electron transfer and compared with experimental ones. This allows us to verify the theoretical predictions.

A precondition for such a study is to find a particular A–D system with the appropriate energy levels. An acceptable strategy can involve a lowering of the energy of the CT ^{1,3}(A$^-$–D$^+$) states with respect to those of the locally excited triplet states ^{3}(A–D)* by selection of the acceptor and donor subunits with appropriate redox potentials. Of course, this strategy assumes that the energy levels of the particular donor or acceptor chromophore remain unchanged after forming the A–D molecule. In the approximation of a weakly interacting radical ion pair the states ^{1}(A$^-$–D$^+$) and ^{3}(A$^-$–D$^+$) should be nearly degenerate. The energy splitting between both ^{1,3}CT states, however, is usually not equal to zero, *e.g.*, because of the exchange interactions.

In fact, we have successfully applied the above mentioned strategy in such cases as the carbazol-9-yl derivatives of aromatic nitriles[19,20] and ketones,[21] as well as phenoxazine and phenothiazine derivatives containing benzonitrile as an electron acceptor.[22] The experimental and computed k_{nr} values were in satisfactory agreement for ΔG_{CT} values lower than the energies of the lowest locally excited triplet states (as taken for the isolated chromophores). This indicates that a particular A–D molecule can be treated as a superposition of the donor and acceptor subunits, only slightly perturbed by their interactions. UV–VIS absorption spectra (corresponding to the sum of the donor and acceptor bands with additional CT

† Electronic Supplementary Information available. See http://www.rsc.org/suppdata/cp/b0/b005058j/

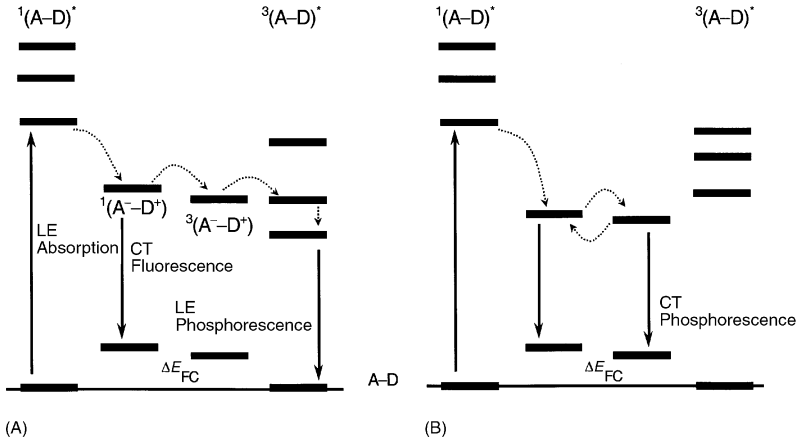

Fig. 1 Energy level diagrams for A–D systems with the energies of the lowest locally excited triplet(s) ^{3}(A–D)* below (A) and above (B) the excited intramolecular charge transfer states ^{1,3}(A$^-$–D$^+$).

excitation) as well as the results from the phosphorescence studies (with spectral features characteristic of the T_1 states of A or D) have supported the above conclusions. Unexpected results were obtained for the A–D derivatives of phenothiazine which are N-substituted by acetophenone, benzophenone or benzonitrile as an electron acceptor (Fig. 2). The spectral positions and shapes of their phosphorescence spectra in various glasses at 77 K are similar to those of the acceptor chromophores in spite of the fact that their energy levels are *ca.* 0.30–0.40 eV higher than that of phenothiazine. Contrary to that, the phosphorescence of the analogous derivatives of phenoxazine is similar to the emission from the donor subunit. Explanation of the above finding is the aim of the present work.

2 Experimental

2.1 Materials

4-Phenothiazin-10-yl-anisole (APS), *N*-phenylphenothiazine (PPS), (4-phenothiazin-10-yl-phenyl)-phenylmethanone (PBS), 1-(4-phenothiazin-10-yl-phenyl)-ethanone (PAS), and 4-phenothiazin-10-yl-benzonitrile (PCS) were prepared by Ullmann arylation[23] of phenothiazine with an appropriate aryl bromide. The reagents in 1 : 1 molar ratio were refluxed for 24 h in pyridine in the presence of potassium carbonate and copper bronze. The crude products, obtained after distillation of the pyridine solvent, were purified on a column of alumina or silicagel with hexane–methylene chloride (1 : 1) or methylene chloride as eluent and recrystallised from ethanol. Satisfactory results of NMR and elementary analyses were obtained for all the studied compounds (with the melting points in agreement with the literature data[24]).

The solvents used for our studies: methylcyclohexane (MCH), 3-methylpentane (3MP), and n-propanol (PrOH) were of spectroscopic or fluorescence grade (Aldrich or Merck). All solvents showed no traces of luminescence. The solutions for phosphorescence and EPR studies were deoxygenated by saturation with argon.

2.2 Experimental techniques

Absorption spectra were recorded using a Shimadzu UV 2401 PC spectrophotometer. Fluorescence and excitation spectra (corrected for the spectral sensitivity of the instrument) were measured by means of an Edinburgh Instruments FS900 steady-state fluorimeter. Phosphorescence spectra and lifetimes were measured with a "Jasny multifunctional spectrofluorimeter".[25] The phosphorescence decays were recorded by means of a Tektronix-TDS420A digitising oscilloscope. The χ^2 test and the distribution of residuals were the main criteria in the evaluation of the quality of the monoexponential fit of the experimental decay curves.

EPR spectra were recorded with a modified JEOL-3BX spectrometer operating at the X-band with 100 kHz magnetic field modulation. Magnetic field intensity measurements were performed with a NMR gaussmeter Drusch NMR-2. A 500 W high-pressure mercury arc lamp was used for irradiation of the sample within the cavity of the spectrometer.

The X-ray measurements of single crystals of PCS were carried out on a KM-4 KUMA diffractometer with graphite monochromated CuKα radiation. The data were collected for Lorentz and polarisation effects and absorption correction was used.[26] The structure was solved by a direct method[27] and refined using SHELXL.[28] The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were

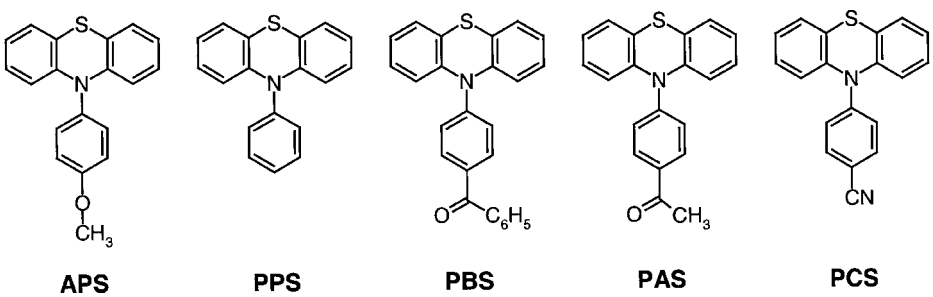

Fig. 2 Formulae of the phenothiazine derivatives studied and their abbreviations used in the text.

placed in the calculated positions, and their thermal parameters were refined isotropically. The atomic scattering factors were taken from International Tables.[29] Details of the X-ray measurements and crystal data for the studied 4-phenothiazin-10-yl-benzonitrile (PCS) are given in Table 1. Crystallographic data are available in .cif format as Electronic Supplementary Information (CCDC ref. no. 1326/11).†

3 Results and discussion

3.1 UV–VIS absorption and fluorescence spectra

Room temperature absorption spectra of the studied compounds in MCH are presented in Fig. 3. The near-UV spectra show two absorption regions centred around 29 750—31 550 cm^{-1} and 39 000—40 000 cm^{-1}. Both bands are related to the electronic transitions localised mainly in the phenothiazine subunit. The molar absorption coefficients of the first band are similar for PCS, PBS and PAS (being 1.4×10^4, 1.3×10^4 and 1.7×10^4 M^{-1} cm^{-1}, respectively) but markedly higher than that of phenothiazine[30] (4.0×10^3 M^{-1} cm^{-1}) and PPS[31] (3.6×10^3 M^{-1} cm^{-1}) or APS. The opposite trend is observed for the second band. This finding is most probably related to the changes in the conformation of phenothiazine (*vide infra*) induced by the strong electron acceptor substituent at the N10 nitrogen atom. The effect of the lowest transitions in the acceptor moieties[32,33] (with relatively low intensities) is manifested only by an increase in the width and intensity of the first and second absorption bands of the A–D molecules with respect to those of PPS. Moreover, the A–D phenothiazine derivatives (PAS, PBS and PCS) showed a long-wave shoulder of relatively low intensity which has been attributed to a CT transition.[22]

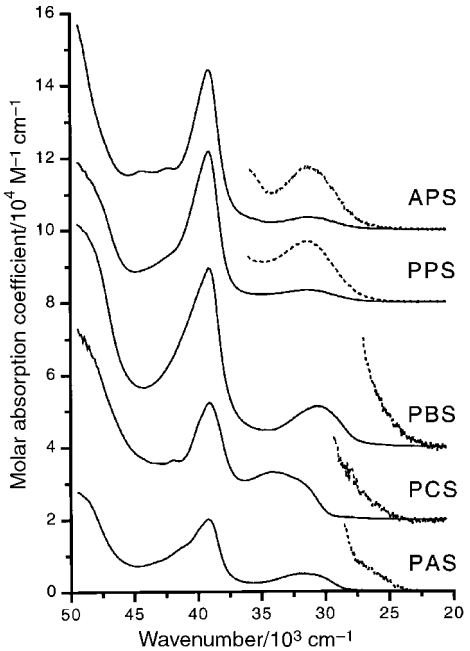

Fig. 3 Room-temperature absorption spectra of APS, PPS, PBS, PCS and PAS in MCH. Low-energy parts of the absorption spectra are expanded by a factor of 5 (for APS and PPS) or 25 (for PBS, PCS and PAS). The spectra are respectively shifted along the *y*-axis (by 2×10^4 M^{-1} cm^{-1} or 4×10^4 M^{-1} cm^{-1}).

All the studied compounds emit a single fluorescence band at room temperature.[22] The spectral position of the emission maximum of PPS and APS does not depend on solvent polarity. Contrary to that, the energies corresponding to the spectral position of the fluorescence maxima of PAS, PBS and PCS are correlated (in the given solvent) with the difference in the standard redox potentials $E^{o}_{ox}(D) - E^{o}_{red}(A)$ (corresponding to the oxidation of the donor and the reduction of the acceptor subunits, respectively). This finding, as well as a considerable red shift of the emission with a parallel increase of the Stokes shift and of the emission bandwidth with increasing solvent polarity, points to the distinct CT character of the fluorescent states.

An analysis of the CT fluorescence (performed in our previous work[22] for PAS, PBS and PCS) leads to the quantities (*i.e.* ΔG_{CT}, λ_o, λ_i and $h\nu_i$) relevant to radiative electron transfer in the Marcus inverted region. The derived data allowed us to discuss quantitatively the relationship between ΔG_{CT} and the solvent polarity. The increase in the solvent polarity (and, correspondingly, the decrease in the CT $^{1,3}(A^{-}–D^{+})$ states energy) should lead to changes in the electronic structure of the lowest triplet states in a particular A–D molecule. It arises from the interactions between the $^3(A^{-}–D^{+})$ state and the locally excited ^{3}(A–D)* triplet states resulting from the electronic transitions localised either in the acceptor or donor subunits. In the polar solvent the fluorescent $^1(A^{-}–D^{+})$ states are lying close to (or below) the lowest excited triplet states of phenothiazine[34] (2.62 eV). Consequently, in a highly polar environment, the $^3(A^{-}–D^{+})$ states seem to be localised below the ^{3}(A–D)* state for the studied A–D systems. On the other hand, the opposite sequence was observed in the non-polar media, the electronic interactions destabilise the $^3(A–D^{+})$ states because these states are located above the locally excited triplet states.

3.2 Phosphorescence spectra

The results of the phosphorescence studies, which indicate the dominant ^{3}(A–D)* character of the phosphorescent state,

Table 1 Crystal data and structure refinement for 4-phenothiazin-10-yl-benzonitrile (PCS)

Parameter	Value
Chemical formula	$C_{19}H_{12}N_2S$
Formula weight	300.37
Crystal system	Triclinic
Unit-cell dimensions	$a = 10.437(2)$ Å; $\alpha = 91.22(3)°$ $b = 12.707(3)$ Å; $\beta = 108.34(3)°$ $c = 12.841(3)$ Å $\gamma = 111.03(3)°$
Unit-cell volume	1491.4(6) Å^3
Temperature of data collection	293(2) K
Space group symbol	*P*-1
Number of formula units in unit-cell	4
Linear absorption coefficient	0.214 mm^{-1}
Measured reflections	5723
Independent reflections	5409, $R_{int} = 0.0265$
R indices (all data)	0.1759, $wR(F^2) = 0.1828$
Final *R* indices [$I > 2\sigma(I)$]	0.0471, $wR(F^2) = 0.1225$

agree well with the above hypothesis. The spectral position and shape of the PPS and APS phosphorescence spectra are very similar to that obtained for phenothiazine. Somewhat surprisingly, however, the phosphorescence spectra of PAS, PBS and PCS recorded at 77 K can be hardly attributed to the triplet states localised in the phenothiazine subunit. The energies of the lowest (most probably 0,0) bands are distinctly higher than that of PPS or APS (*cf.* Fig. 4). The observed shapes and spectral positions of phosphorescence suggest that the excitation is mainly localised in the acceptor subunits of the studied A–D compounds. The observed shifts of the phosphorescence maxima to lower energies (*ca.* 2000–3000 cm^{-1}) as compared to the unsubstituted acceptors chromophores are similar to those reported[35] for the corresponding 4′-amino derivatives. These findings indicate that the sequence of the locally excited ^{3}(A–D)* states in PAS, PBS and PCS in rigid media is different to that in PPS and APS. Similarly, to the effects observed in UV–VIS absorption spectra, this may probably be related to the changes in the conformation of the phenothiazine moiety (described below), induced by the strong electron acceptor subunit connected to the N10 nitrogen atom.

The postulated nature of the T_1 states in rigid media is supported by the results of the phosphorescence lifetime τ_{pho} measurements in PrOH glass at 77 K. The value of τ_{pho} is found to be ~90 ms for both PPS and APS, in agreement with the literature data ($\tau_{pho} \simeq 80$ ms) for phenothiazine.[36] The phosphorescence lifetimes of PAS and PBS (*e.g.*, 0.44 and 0.12 s in PrOH at 77 K, respectively) are distinctly longer than those of the parent carbonyl compounds (acetophenone or benzophenone) corresponding to the lowest ^{3}(n, π*) states,[35] but similar to those found for 4′-amino-acetophenone (0.72 s)[37] or 4′-amino-benzophenone (0.20 s).[38] These results may be explained by the change in the phosphorescent state character from ^{3}(n, π*) to ^{3}(π, π*), induced by the substitution of an electron-donating group at the 4′-position. The long phosphorescence lifetime for PCS (0.96 s) points to a ^{3}(π, π*) character of the T_1 state localised mainly on the benzonitrile subunit.[39]

In order to gain more insight into the nature of the lowest triplet states in A–D molecules we attempted to observe phosphorescence at temperatures higher than 77 K. This was performed in 3MP glass. Fig. 5 presents the most representative results for PCS, but nearly the same behaviour was observed for PBS and PAS. With increase in temperature the emission intensity related to the acceptor part of the particular A–D molecule decreases, and a new phosphorescence band appears, with spectral position and shape characteristic for phenothiazine. Most probably, it is accompanied by the change of molecular conformation which follows photoexcitation. Contrary to the situation at 77 K, the softening of 3MP glass at higher temperatures allows molecular rearrangement. Taking into account the fact that it corresponds to changes in the energetic sequence of the ^{3}(A–D)* states (*i.e.* the lowering of the energy level of the triplet state attributed to the donor subunit) a flattening of phenothiazine may be postulated. The process corresponds to intramolecular energy transfer accompanied by changes in the molecular structure.

3.3 EPR investigation

EPR spectra of the studied compounds were measured in frozen PrOH (Fig. 6). Relatively long lifetimes of the phosphorescent triplet states of PPS and PCS allow us to observe the signals under photostationary conditions. In our investigations we have recorded the transitions in the $\Delta m = 2$ region corresponding to the lowest resonance fields B_{min}. The zero-field splitting (ZFS) parameters D*, characterising the particular, randomly oriented, triplet state, were calculated from the expression:[40]

$$D^* = \sqrt{(D^2 + 3E^2)} = \sqrt{\tfrac{3}{2}(X^2 + Y^2 + Z^2)} = \sqrt{\tfrac{3}{4}(h\nu)^2 + 3(g\mu_B B_{min})^2} \quad (1)$$

where D and E are ZFS parameters related to the principal values X, Y and Z of the spin–spin coupling tensor; $h\nu$ is a resonance microwave energy, and μ_B denotes the Bohr magneton. The isotropic value of $g = 2.0023$ has been assumed in calculations.

The value of the parameter $D^* = 0.125$ cm^{-1} for PPS at 77 K is (within experimental error) the same as that reported for phenothiazine.[41,42] On the contrary, the high-field position of the dominant EPR band for PCS at 77 K results in a markedly smaller value of $D^* = 0.102$ cm^{-1}. This value is distinctly different from that reported for benzonitrile[43] ($D^* = 0.139$ cm^{-1}) but agrees very well with those obtained for the series of *p*-amino derivatives of benzonitrile[39] ($D^* = 0.097$–0.107 cm^{-1}). This indicates that the spin density in the lowest T_1 state is mainly distributed over the π-system of the benzonitrile subunit. However, an additional weak, low-field, EPR signal corresponds to the D* parameter characteristic for phenothiazine. Most probably, two different types of mol-

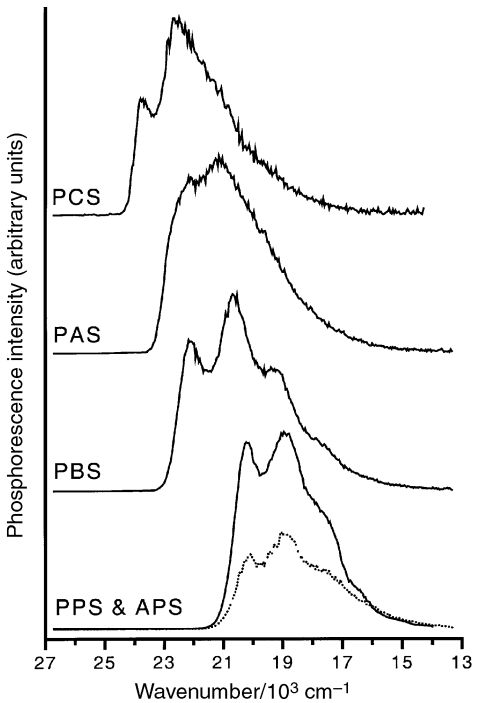

Fig. 4 Phosphorescence spectra (in PrOH glass at 77 K) of the studied phenothiazine derivatives.

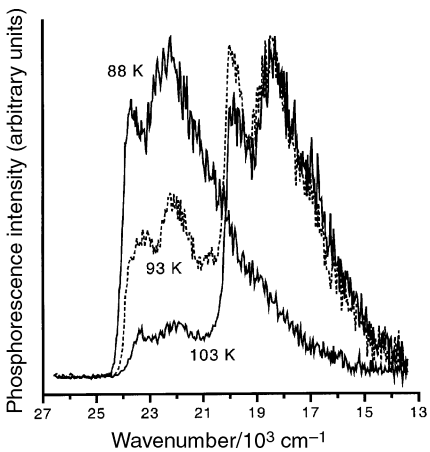

Fig. 5 Temperature effect on the phosphorescence spectra of 4-phenothiazin-10-yl-benzonitrile (PCS) in 3MP glass.

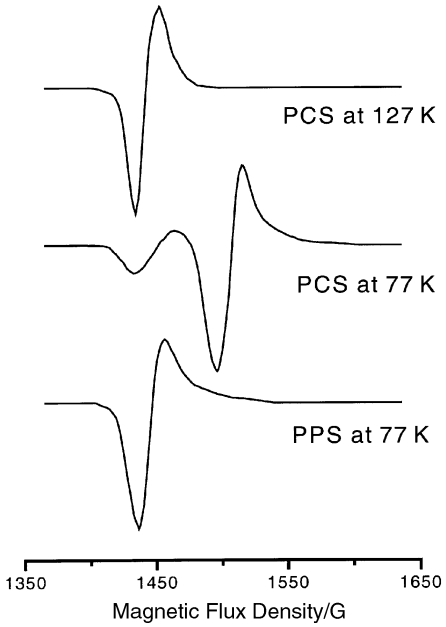

Fig. 6 EPR spectra of the triplet state of *N*-phenylphenothiazine (PPS) and 4-phenothiazin-10-yl-benzonitrile (PCS) recorded in frozen PrOH. The spectrum of PCS recorded at 77 K shows two different signals, corresponding either to the phenothiazine π-system (low-field signal) or to the *p*-amino substituted benzonitrile subunit (high-field signal).

ecules with the triplet excitation localised either within the acceptor or the donor π-system (as postulated above in the discussion of the phosphorescence data) takes place already at 77 K (probably the small number of the latter molecules is insufficient to allow luminescence confirmation). At higher temperatures (*e.g.*, 127 K, just below the melting point of PrOH) only one EPR signal (related to phenothiazine) was found for PCS, in nice agreement with the results of the phosphorescence investigations. It is expected that, at the intermediate temperatures, the relative intensities of both EPR signals (high-field and low-field, respectively) will change similarly to those of the phosphorescence (*cf.* Fig. 4). Unfortunately, our EPR instrumentation does not allow for such kind of measurements.

3.4 Crystallographic structures

The effects observed in the UV–VIS absorption and the low-temperature emission as well as in the EPR spectra of the A–D compounds can be explained by geometrical changes in the phenothiazine subunit. According to the crystallographic data for phenothiazine,[44] the molecule is folded about the S–N axis with a dihedral angle of 158.5°. PPS[45] is a phenothiazine derivative with two unique molecules in the asymmetric unit. Introduction of an additional phenyl ring does not cause, however, any essential changes in the phenothiazine kernel, the corresponding dihedral angles are 162.6° and 150.7°, respectively. The plane of the phenyl ring nearly bisects the benzo planes in each of the two molecules, with the corresponding angles of 78.4° and 84.6°, respectively. Due to the similar geometry of PPS and phenothiazine, the similar behaviour of both molecules seems reasonable.

Introduction of a –CN group at the 4′-position leads to intrinsic changes. Similarly, as was found for PPS,[45] the crystallographic data indicate the presence of two, somewhat different, molecular conformations. The phenothiazine subunit is more folded about the S–N axis with the corresponding dihedral angles of 135.5° and 131.5°. The 4′-cyanophenyl ring is nearly perpendicular to the plane bisecting the folding angle of the phenothiazine ring (*cf.* Fig. 7). Similar changes caused by the presence of the acceptor group were previously reported for 4′-nitro-10-phenylphenothiazine[46] and 10-(2′-pyrazyl)-phenothiazine.[47] It should be noted that 4′-bromophenyl-10-phenothiazine,[48] *i.e.* the *N*-phenylphenothiazine derivative with the weaker acceptor group at the 4′-position is less folded around the S–N axis (corresponding dihedral angles are 150.8° and 144.9°).

The central ring of phenothiazine reveals an approximate boat conformation, depending on the acceptor affinity of the N10 substituent. Further, the butterfly structure of the central ring prevents the overlap of the non-bonding orbital of sulfur with the π–system. This leads to a more or less pronounced aromatic character of the phenothiazine kernel, accompanied by changes of the N10 atom hybridisation from nearly sp^3 to nearly sp^2. Such conformation allows for maximum overlap and, correspondingly, for the electronic interactions between the lone pair of the phenothiazine N10 atom with π-electrons of the acceptor benzene ring. These interactions between the nitrogen N10 lone pair and 4′-substituted phenyl ring seem to be mostly responsible for the observed structural changes.

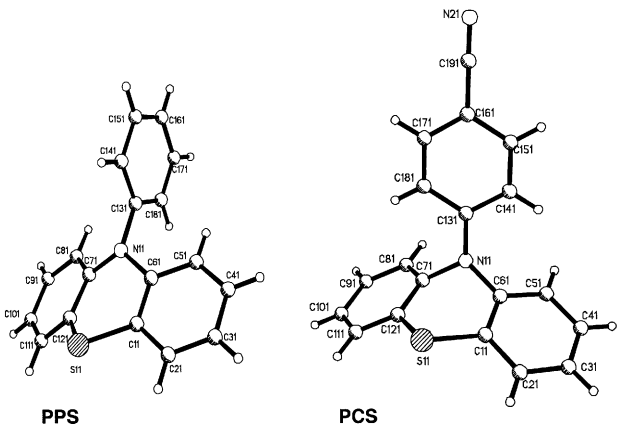

Fig. 7 ORTEP schemes of *N*-phenylphenothiazine (PPS) and 4-phenothiazin-10-yl-benzonitrile (PCS) molecules. ORTEP plot for PPS is drawn using literature crystallographic data.[45]

4 Concluding remarks

The observed phosphorescence behaviour of the A–D molecules under study may be understood assuming the changes in the geometry of the phenothiazine subunit which follow electronic excitation. Flattening of the donor part of the molecule increases its aromatic character, leading, in consequence, to lowering of the energy level of the excited triplet state localised within the donor subunit. This process, which is not possible in the rigid phase, may be observed in a more soft environment or in fluid solvents. Similar changes in molecular conformation have been postulated to explain the effects related to photoinduced intramolecular electron transfer in A–D phenothiazine derivatives.[22] The geometrical rearrangement most probably corresponds to rehybridisation of the N10 atom to more "pure" sp^2 hybridisation, as was found for the oxidation of the phenothiazine derivatives to the corresponding radical cations.[49,50]

The flattening process of folded molecules of the phenothiazine derivatives may be described as a change of the valence angles of the central atoms S and N. The energy needed to change the two angles is only *ca.* 0.10–0.12 eV.[51] This is distinctly smaller than the amount of energy released in the postulated intramolecular energy transfer accompanied by the changes in the molecular structure (0.30–0.40 eV). Consequently, the reaction is strongly favoured thermodynamically and the observed kinetic inhibition at 77 K may be clearly attributed to the rigidity of the reaction medium. In fluid solvents the lowest locally excited triplet states of PAS, PBS and PCS seem to be localised within the phenothiazine

subunit, in agreement with the kinetic data for intramolecular electron transfer in these A–D molecules.

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