tion appears to be an important extension of icr mass spectroscopy. The icr CI products observed and their relative intensities agree well with the results from more conventional high source pressure techniques where comparisons are available. The minor discrepancies noted can be reconciled once the different experimental conditions of the two techniques are considered.

The use of the trapping field ejection makes it possible to investigate the mechanisms of chemical ionization. The utilization of this technique in CI of $C_6$ hydrocarbons with methane reagent distinguishes which of the major reagent ions, $CH_5^+$ and $C_2H_5^+$ in methane, are precursors to the various CI products. As an illustration, the work on the $C_6$ paraffins has shown that $CH_5^+$ leads exclusively to $C_5H_{11}^+$ while all the other fragments have varying but systematic degrees of contribution from both $CH_5^+$ and $C_2H_5^+$.

In the future, the use of isotopically labeled compounds could be used to study in more detail the mechanisms of CI reactions. Further, the use of different reagent gases and the CI study of other functional groups are natural extensions of this icr CI study.

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# Emission Properties of Aromatic Amines in Solution. Phenoxazine System[1]

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**Abstract:** The absorption and emission properties of phenoxazine and 10-phenylphenoxazine in EPA and 3-methylpentane were investigated over a temperature range from 298 to 77°K. A PPP (SCF–MO–CI) calculation was used in conjunction with the absorption spectrum and polarization data to assign four electronic transitions in the region 27,000–40,000 cm$^{-1}$. The transitions of phenoxazine ($C_{2v}$ symmetry) in order of increasing energy are $^1B_1 \leftarrow {}^1A_1$ (28,850 cm$^{-1}$), $^1B_1 \leftarrow {}^1A_1$ (31,970 cm$^{-1}$), $^1A_1 \leftarrow {}^1A_1$ (39,800 cm$^{-1}$), and $^1B_1 \leftarrow {}^1A_1$ ($\sim$42,000 cm$^{-1}$). The spectral appearance of the emission as well as the results of lifetime and quantum yield determinations can be explained on the basis of a change in geometry of the excited singlet and triplet states with respect to the planar ground state. The fact that phenoxazines exhibit in-plane phosphorescence polarization, whereas planar aromatic hydrocarbons are polarized out-of-plane, and the more effective spin–orbit coupling of the former, can also be attributed to such a geometry change.

Aromatic amines often exhibit unusual photochemistry such as photoionization *via* biphotonic absorption and dissociation processes with excited singlet states as the reactive intermediates.[2,3] For a clear understanding of the nature of these phenomena, it is necessary to examine the absorption spectra as well as the emission properties of these compounds. The present study deals with the emission characteristics of two such amines, phenoxazine (*cf.* Figure 1b) and 10-phenylphenoxazine in polar and nonpolar solvents.

In a recently published paper[3] we reported the results of a flash-photolytic study of phenoxazine (PH) which indicated a primary photolytic dissociation of an excited singlet state(s), leading to the neutral radical P·. Moreover, it was found that the observed photoionization process, which generates the monopositive cation, is consistent with a biphotonic mechanism in which the lowest triplet state acts as an intermediate. The emission spectrum of PH has also received some recent attention. In an attempt to elucidate the reactivity of heterocyclic systems, Mantsch and Dehler[4] have measured the polarized fluorescence excitation spectrum of PH using the photoselection method in a rigid ethanol glass. These workers found that all transitions below 45,000 cm$^{-1}$ are polarized parallel with respect to the fluorescence, except for a transition around 40,000 cm$^{-1}$ (barely discernible in absorption) which is negatively polarized. These results are in agreement with recent measurements by Lhoste and Merceille,[5] but only below 40,000 cm$^{-1}$.

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(2) K. S. Bagdasar'yan, *Kinet. Catal.* (*USSR*), **8**, 920 (1967); *Kinet. Katal.*, **8**, 1073 (1967); K. D. Cadogan and A. C. Albrecht, *J. Phys. Chem.*, 72, 929 (1968); H. S. Piloff and A. C. Albrecht, *J. Chem. Phys.*, **49**, 4891 (1968); V. Zanker and D. Benicke, *Z. Phys. Chem.* (*Frankfurt am Main*), **66**, 34 (1969).

(3) D. Gegiou, J. R. Huber, and K. Weiss, *J. Amer. Chem. Soc.*, **92**, 5058 (1970).

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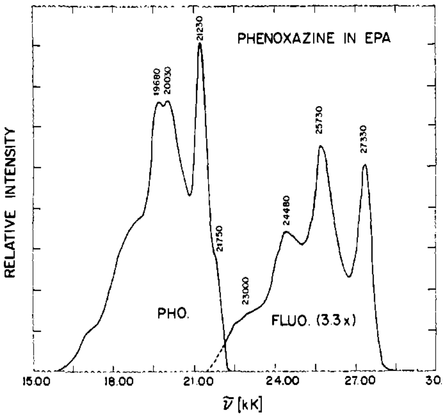

Figure 1a. Fluorescence and phosphorescence spectra of phenoxazine in EPA at 77°K. Solute concentration, $2 \times 10^{-5}$ *M* (the intensity scale of the fluorescence is expanded 3.3 times).

## Experimental Section

**Materials.** Phenoxazine (Aldrich Chemical Co.) was purified by recrystallization from aqueous ethanol and subsequent sublimation just prior to use. 10-Phenylphenoxazine was synthesized according to the procedure of Gilman and Moore,[6] and the purification procedure employed for this compound was the same as above.

3-Methylpentane (3-MP) (Aldrich; puriss) contained traces of emitting impurities which were removed by frontal analysis chromatography (adsorptive filtration), employing a basic alumina column. EPA (isopentane, diethyl ether, ethanol, 5:5:2; American Instrument Co.) was used as received. The remaining solvents were of spectral quality and required no further purification. The purification and polymerization of methyl methacrylate (Eastman Organic Chemicals) followed a published procedure.[7]

**Apparatus and Procedure.** The spectrophotofluorimeter employed in this study consists of a 450-W Xenon arc excitation source, a Bausch and Lomb 500-mm, f/4.4 monochromator, and a Spex 750-mm, f/6.8 analyzing spectrophotometer. A more detailed description of this apparatus is presented elsewhere.[8] The emission spectra are corrected for the response characteristics of the instrument and are plotted by computer. Provision is made for temperature control of the samples from room temperature to 77°K, using a quartz dewar vessel equipped with a copper block sample compartment.[9] The samples (solute concentration $\leqslant 10^{-5}$ *M*) were prepared either in quartz cells or as bare "popsicles."[10] The solutions in the quartz cells were deoxygenated either by repeated freeze-pump-thaw cycles or by passing nitrogen gas through the solution.

The fluorescence lifetimes were measured by the single photon technique.[11] The apparatus employed utilized a nanosecond flash lamp filled with ~37 cm of deuterium gas.[12]

The quantum yields at room temperature were determined relative to the quantum yield of quinine bisulfate in aqueous 0.1 *N* sulfuric acid ($\phi_{\text{fluo}} = 0.55$[13]). Compensation was made for differences between the index of refraction of the standard solution and the various sample solutions, but corrections for reabsorption were neglected since all measurements were performed on highly diluted solutions (the optical density of the samples at the wavelength of excitation was in all instances <0.025/cm). The quantum yields at temperatures less than 298°K were established relative to the room temperature quantum yield of the same sample with correction for changes of density and index of refraction with temperature.

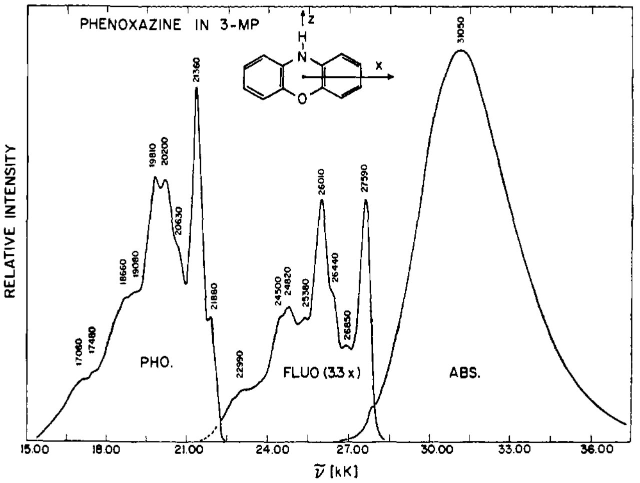

Figure 1b. Fluorescence and phosphorescence spectra of phenoxazine in 3-MP at 77°K. Solute concentration, $1 \times 10^{-5}$ *M* (the intensity scale of the fluorescence is expanded 3 times).

## Results

**Absorption Spectra.** The main features of the absorption spectra of phenoxazine (PH) and 10-phenylphenoxazine (PhP) in 3-MP at room temperature are summarized in Table I. The spectrum of PH is in agreement with recently published data.[4,5] The PhP spectrum is very similar to the PH spectrum, except for a red shift of 400–900 cm$^{-1}$ of the individual bands. The first electronic transition (28,850 cm$^{-1}$) of PH has a low oscillator strength (*cf.* Table I) and becomes clearly resolved only at low temperature or in nonpolar solvents at room temperature. At 77°K identical emission spectra are obtained with excitation into this small band and into the intense band at 31,000 cm$^{-1}$. This finding demonstrates that the weak band is indeed the lowest electronic transition of PH. At room temperature the lowest frequency band of PhP appears as a shoulder and a reliable estimation of its oscillator strength is therefore not possible.

**Table I.** Absorption Spectra of Phenoxazine (PH) and 10-Phenylphenoxazine (PhP) in 3-MP at Room Temperature

| Compd | Band, assignment | Absorption maxima, cm$^{-1}$ | Oscillator strength | ε, l. mol$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|
| PH | I, $^1B_1 \longleftarrow {}^1A_1$ | 28,850<br>(27,700)[a] | $2.6 \times 10^{-3}$ | ~750 |
| | II, $^1B_1 \longleftarrow {}^1A_1$ | 31,970<br>(30,900)[a] | $1.7 \times 10^{-1}$ | ~8,600 |
| | III, $^1A_1 \longleftarrow {}^1A_1$ | 39,800 | Shoulder | |
| | IV, $^1B_1 \longleftarrow {}^1A_1$ | 41,980<br>42,790 | (0.73) | 58,000 |
| | V | 46,840 | | |
| PhP | I | ~28,000 | ($<2 \times 10^{-3}$) | |
| | II | 30,900 | $2.1 \times 10^{-1}$ | ~9,500 |
| | IV | 41,630<br>42,370 | (0.85) | 78,000 |
| | V | 46,500 | | |

[a] At 77°K.

The relative polarization of absorption bands I and II was determined by means of the polarized phosphorescence excitation spectra. Monitored at ~21,300 cm$^{-1}$ (*cf.* Figures 1 and 2), the polarization of these two bands

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Table II. Fluorescence Quantum Yields $\phi_{\mathrm{fluo}}$ and Fluorescence Lifetimes $\tau_{\mathrm{fluo}}$ of Phenoxazine (PH) and 10-Phenylphenoxazine (10-PhP)

| Compd | Solvent | $\phi_{\mathrm{fluo}}$(298 °K)[a] | $\tau_{\mathrm{fluo}}$(298 °K),[a] nsec | $k_{\mathrm{fluo}}$(rad)[b] (298 °K), sec$^{-1}$ | $\phi_{\mathrm{fluo}}$(77 °K)[a] |
|---|---|---|---|---|---|
| PH | Ethanol | 0.023 ± 0.004 | 1.1 ± 0.1 | $2.0 \times 10^7$ | 0.108 ± 0.010 (EPA) |
| | Cyclohexane | 0.027 ± 0.004 | 1.5 ± 0.1 | $1.8 \times 10^7$ | 0.064 ± 0.07 (3-MP) |
| 10-PhP | Ethanol | 0.040 ± 0.004 | 2.9 ± 0.2 | $1.40 \times 10^7$ | 0.12 ± 0.02 (EPA) |
| | Cyclohexane | 0.047 ± 0.005 | 3.2 ± 0.2 | $1.47 \times 10^7$ | 0.082 ± 0.09 (3-MP) |

[a] Excitation wavelength 320 and 310 nm. [b] $k_{\mathrm{fluo}}(\mathrm{rad}) = \phi_{\mathrm{fluo}}/\tau_{\mathrm{fluo}}$.

Table III. Phosphorescence Quantum Yields $\phi_{\mathrm{phos}}$ and Phosphorescence Lifetimes $\tau_{\mathrm{phos}}$ of Phenoxazine (PH) and 10-Phenylphenoxazine (10-PhP)

| Compd | Solvent | $\tau_{\mathrm{TT}}$(298 °K), μsec | $\tau_{\mathrm{phos}}$(77 °K), sec | $\phi_{\mathrm{phos}}$(77 °K) | $\phi_{\mathrm{phos}}/\phi_{\mathrm{fluo}}$(77 °K) | $\phi_{\mathrm{fluo}}$(77 °K) + $\phi_{\mathrm{phos}}$ (77 °K) |
|---|---|---|---|---|---|---|
| PH | EPA | 44[a] | 2.76 ± 0.08 | 0.41 | 3.8 | 0.52 |
| | 3-MP | 32[b] | 2.60 ± 0.06 | 0.29 | 4.5 | 0.35 |
| 10-PhP | EPA | 49[a] | 2.65 ± 0.08 | 0.72 | 6.0 | 0.84 |
| | 3-MP | | 2.31 ± 0.10 | 0.94 | 11.5 | 1.02 |

[a] Ethanol solution. [b] Cyclohexane solution.

for both compounds was found to be positive with a value of *ca.* 0.4.[4]

**Emission Spectra.** The fluorescence and phosphorescence spectra of PH and PhP in 3-MP at 77 °K are shown in Figures 1 and 2. A strong 0–0 transition of the fluorescence of PH is evident, while the same transition in the more intense phosphorescence spectrum is relatively weak (*cf.* Figure 1). The 0–0 band pattern for PhP is different (*cf.* Figure 2). In this case the phosphorescence 0–0 band is relatively strong, whereas the corresponding fluorescence band is weaker than the other emission bands. This effect is especially pronounced in 3-MP. The 1640- and 1580-cm$^{-1}$ vibrations of PH and PhP, respectively, in 3-MP dominate the vibrational activity of the fluorescence. The most intense vibrations of the phosphorescence in 3-MP are 690 and 1610 cm$^{-1}$ for PhP, and 520 and 1680 cm$^{-1}$ for PH.

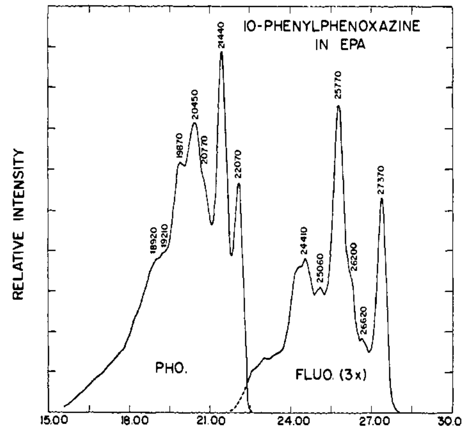

Figure 2a. Fluorescence and phosphorescence spectra of 10-phenylphenoxazine in EPA at 77 °K. Solute concentration, $1 \times 10^{-5}$ *M* (the intensity scale of the fluorescence is expanded 3 times).

The degree of polarization of the emission of phenoxazine and its phenyl derivation was determined with respect to excitation into absorption band II (31,000 cm$^{-1}$). For both compounds the fluorescence and phosphorescence is *parallel* to the excitation, with a polarization degree of 0.40 ± 0.05 throughout the entire emission.

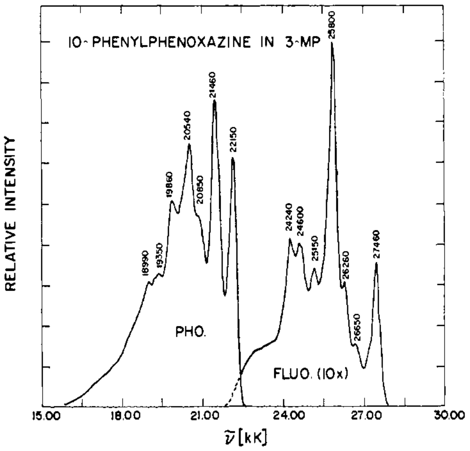

Figure 2b. Fluorescence and phosphorescence spectra of 10-phenylphenoxazine in 3-MP at 77 °K. Solute concentration, $5 \times 10^{-6}$ *M* (the intensity scale of the fluorescence is expanded 10 times).

**Emission Quantum Yields and Lifetimes.** Data pertaining to the fluorescence quantum yields ($\phi_{\mathrm{fluo}}$) and lifetimes ($\tau_{\mathrm{fluo}}$) and the phosphorescence quantum ($\phi_{\mathrm{phos}}$) and lifetimes ($\tau_{\mathrm{phos}}$), measured at room temperature and at 77 °K in 3-MP and EPA, are collected in Tables II and III. For comparison, the lifetimes of triplet–triplet absorption $\tau_{\mathrm{TT}}$ (298 °K) of the lowest lying triplet state, determined with a flash photolysis technique,[3] are included in Table III.

The temperature dependence of the fluorescence quantum yield $\phi_{\mathrm{fluo}}(T)$ is displayed in Figure 3. Values of $\phi_{\mathrm{fluo}}(T)$, corrected for changes in density and index of refraction with temperature, were determined relative to the value of $\phi_{\mathrm{fluo}}$(298 °K). Similarly, $\phi_{\mathrm{phos}}$(77 °K) was obtained with $\phi_{\mathrm{fluo}}$(77 °K) as the reference. In addition, the polymerization stable PhP was embedded in a poly(methyl methacrylate) (PMM) matrix. The temperature dependence $\phi_{\mathrm{fluo}}(T)$ (*cf.* Figure 3b) was found to be significantly less than in liquid solvents.

**Table IV.** PPP (SCF–MO–CI) Calculation[16] of $(\pi,\pi^*)$ State of Phenoxazine[a]

| $(\pi,\pi^*)$ Transition (polarization)[b] | Energy, cm$^{-1}$ (observed maxima)[c] | Oscillator strength (observed)[c] | CI wave functions, $\psi$[d] |
|---|---|---|---|
| $^1B_1 \longleftarrow {}^1A_1$ ($x$) | 27,000 (28,850) | 0.016 (0.003) | $0.94\phi(8 \longrightarrow 9) + 0.13\phi(8 \longrightarrow 10) - 0.16\phi(7 \longrightarrow 10) + 0.19\phi(8 \longrightarrow 13) + \ldots$ |
| $^1B_1 \longleftarrow {}^1A_1$ ($x$) | 32,300 (31,970) | 0.270 (0.17) | $0.86\phi(8 \longrightarrow 10) + 0.33\phi(7 \longrightarrow 9) - 0.28\phi(5 \longrightarrow 11) - 0.21\phi(6 \longrightarrow 12) + \ldots$ |
| $^1A_1 \longleftarrow {}^1A_1$ ($z$) | 35,600 | 0.001 | $0.77\phi(8 \longrightarrow 11) + 0.42\phi(6 \longrightarrow 9) - 0.35\phi(7 \longrightarrow 12) - 0.31\phi(5 \longrightarrow 10) + \ldots$ |
| $^1A_1 \longleftarrow {}^1A_1$ ($z$) | 40,700 (39,800) | 0.038 | $-0.72\phi(8 \longrightarrow 12) - 0.46\phi(7 \longrightarrow 11) - 0.41\phi(6 \longrightarrow 10) - 0.28\phi(5 \longrightarrow 9) + \ldots$ |
| $^1B_1 \longleftarrow {}^1A_1$ ($x$) | 44,900 (42,000) | 1.65 (0.73) | $-0.79\phi(7 \longrightarrow 9) + 0.41\phi(8 \longrightarrow 10) + 0.36\phi(6 \longrightarrow 12) + 0.17\phi(4 \longrightarrow 10) + \ldots$ |
| Lowest $^3(\pi,\pi^*)$ | 22,000 (21,900)[e] |  | $0.92\phi(8 \longrightarrow 9) + 0.27\phi(5 \longrightarrow 12) - 0.18\phi(7 \longrightarrow 10) + 0.14\phi(8 \longrightarrow 13) + \ldots$ |

[a] Parametrization. One-center repulsion integral $\gamma_{\mu\mu}$, eV: $\gamma_{CC} = 10.88$; $\gamma_{NN} = 14.50$; $\gamma_{OO} = 16.10$. Ionization potentials $W$, eV: $W_C = -11.16$; $W_N = -25.50$; $W_O = -29.50$. Resonance integral $\beta_{\mu\nu}^{core}$, eV: $\beta_{CC} = -2.39$; $\beta_{CO} = -2.63$; $\beta_{CN} = -2.37$. The two-center repulsion integral $\gamma_{\mu\nu}$ has been evaluated according to Pariser.[16] A standard geometry was assumed. All bond lengths were taken as 1.39 A and the angles as 120°. In the configuration interaction all singly excited states have been included. [b] For coordinate system *cf.* Figure 1. [c] From Table I. [d] Important contributions to $\psi$. [e] *Cf.* emission spectrum Figure 1.

## Discussion

The absorption spectra of PH and PhP exhibit a striking similarity so that our discussion of them can be limited to PH. The longest wavelength transition (I) is weak. The second transition (II) appears as an intense and broad band with an oscillator strength approximately 60 times that of transition I. Both transitions display the same polarization direction and, for such a nearly planar conjugated $\pi$ system, one would expect the polarization to be in the molecular plane.[14a] The results of a PPP calculation[14b] (*cf.* Table IV) for PH based on a $C_{2v}$ molecular symmetry are summarized in Table IV. This calculation suggests that both transitions I and II lead to a $^1B_1(\pi,\pi^*)$ excited state and are, therefore, polarized along the $x$ axis (long axis) of the molecule (*cf.* Figure 1b). Moreover, the calculation indicates that both transitions involve large charge displacements between the nitrogen atom and the two adjoining benzene rings. A predicted third absorption band at 35,600 cm$^{-1}$ is disregarded as experimentally unobservable. A very weak transition, appearing as a shoulder at about 40,000 cm$^{-1}$,[15] was assigned to the predicted 40,700-cm$^{-1}$ band ($^1A_1 \leftarrow {}^1A_1$). This assignment is strongly supported by the polarization measurements of Mantsch and Dehler.[4] The strongest transition (IV) in the near ultraviolet region, which appears at about 42,000 cm$^{-1}$, exhibits a polarization direction parallel to those of bands I and II. Thus, this transition also leads to a $^1B_1(\pi,\pi^*)$ excited state.

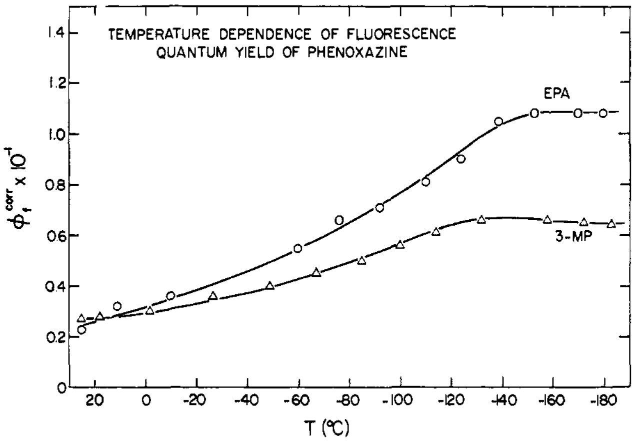

Figure 3a. Temperature dependence of the fluorescence quantum yield of phenoxazine in 3-MP and EPA. Solute concentration, *ca.* $10^{-5}M$; excitation wavelength, 320 nm.

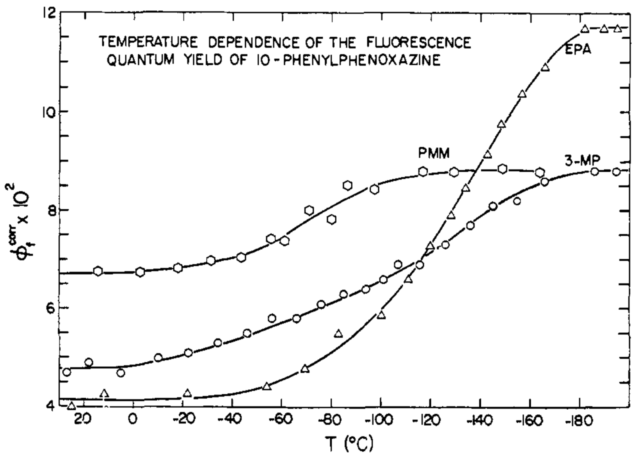

Figure 3b. Temperature dependence of the fluorescence quantum yield of 10-phenylphenoxazine in 3-MP, EPA, and PMM (poly(methyl methacrylate)). Solute concentration, *ca.* $10^{-5}M$; excitation wavelength, 320 nm.

It was determined that the emission is polarized parallel with respect to excitation into absorption band II (31,100 cm$^{-1}$). This fact, in conjunction with the PPP calculation which provided assignments for the absorption bands, establishes the fluorescence as well as the phosphorescence as in-plane ($x$) polarized.[16]

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(14) (a) The geometry of phenothiazine has been determined by J. D. Bell, J. F. Blount, O. V. Briscol, and H. C. Freeman, *Chem. Commun.*, **24**, 1656 (1968). The X-ray study shows that the N atom and S atom are displaced from the plane of the two aromatic rings by *ca.* 0.03 and 0.18 Å, respectively. Since the deviation from planarity is mainly due to the voluminous sulfur atom, it is reasonable to assume that phenoxazine is essentially planar. (b) R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 466, 767 (1953). For a review see, *e.g.*, H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, p 228.

(15) This transition becomes clearly distinguishable in 2-methyltetrahydrofuran solution.

(16) A recent CNDO/2 calculation (K. Weiss and J. R. Huber, unpublished data) yielded essentially the same results as the PPP calculation with respect to energies, polarizations, and intensities.

The dynamic behavior of the first excited singlet ($S_1$) and the lowest lying triplet ($T_1$) is reflected in their lifetimes and quantum yields. For both PH and PhP, the measured fluorescence lifetimes (*cf.* Table II) are short and the $\phi_{\text{fluo}}$ values are low. These facts seem to indicate high probabilities for radiationless processes and/or an unusually photoreactive singlet ($S_1$) state (*vide infra*). The reciprocal values of radiative lifetimes [$k_f$(rad)] obtained from $\phi_{\text{fluo}}$ and $\tau_{\text{fluo}}$ are small, as is to be expected from the weak oscillator strength of transition I.[17]

The effect of temperature on $\phi_{\text{fluo}}$ is striking for both compounds (*cf.* Figures 3a,b). Between room temperature and 77°K the values of $\phi_{\text{fluo}}$ increase by factors of 2–4 with the latter referring to EPA solutions. Such behavior is consistent with the simultaneous occurrence of temperature-dependent and temperature-independent processes which may be expressed as[18]

$$1/\phi_{\text{fluo}} = 1/\phi_{\text{fluo}}(77) + (A/k_{\text{fluo}})e^{-E/RT}$$

where $\phi_{\text{fluo}}(77\,°\text{K})$ is the limiting fluorescence quantum yield (no further change at lower temperature is assumed), $1/k_{\text{fluo}}$ is the temperature-independent radiative fluorescence lifetime, $A$ is the Arrhenius frequency factor, and $E$ is the apparent activation energy. For PH the respective values of $A$ and $E$ were estimated to be $8.4 \times 10^9$ sec$^{-1}$ and 550 cm$^{-1}$ in EPA, and $2.8 \times 10^9$ sec$^{-1}$ and 430 cm$^{-1}$ in 3-MP. For PhP the corresponding values are $11.2 \times 10^9$ sec$^{-1}$ and 450 cm$^{-1}$ in EPA and $0.63 \times 10^9$ sec$^{-1}$ and 250 cm$^{-1}$ in 3-MP.

The magnitude of $\phi_{\text{phos}}$ (*cf.* Table III) is generally much greater than that of $\phi_{\text{fluo}}$, especially for PhP in 3-MP. This is a particularly interesting system, since the total emission quantum yield ($\phi_{\text{fluo}} + \phi_{\text{phos}}$) is unity. The ineffectiveness of radiationless transitions in PhP in spite of the relatively long $\tau_{\text{phos}}$(rad) may be attributed to small Franck–Condon vibrational overlap factors. The $\tau_{\text{phos}}$ values for PH and PhP in both solvent systems are quite similar (*cf.* Table III) and one may, therefore, assume that not only for PhP but probably also for PH the $\tau_{\text{phos}}$ approximates the corresponding radiative lifetime.[19] The slightly diminished effectiveness of the intersystem crossing process (ISC) for PhP in EPA relative to 3-MP is reflected in a higher value of $\phi_{\text{fluo}}(77\,°\text{K})$ and $\tau_{\text{phos}}(77\,°\text{K})$. This behavior must be ascribed to the different solvent interactions. The main reason for the significantly lower quantum yields of the PH systems with respect to the PhP systems is most probably its greater photoreactivity. By means of flash photolysis it has been shown[3] that for PH, a primary photolytic step involves the production of a neutral radical P·. The corresponding process does not occur with PhP. Moreover, this dissociation appears to occur in the excited singlet state and not in the lowest lying triplet state. A further photochemical path for PH leads to the formation of a cation radical PH·+.[3]

The lowest triplet state ($T_1$) of PH is, according to the PPP calculation, predicted to have $^3B_1$ character. This assignment is in agreement with recent esr studies.[20] The in-plane polarization of the phosphorescence indicates that ($\pi,\pi^*$) states are involved in spin–orbit coupling. This situation is distinctly different from the intersystem crossing process in planar aromatic hydrocarbons, which is evidently dominated by $(\pi,\sigma)^*$ states,[21] since the phosphorescence exhibits out-of-plane polarization.[22] To elucidate the disparity between the behavior of aromatic amines and planar aromatic hydrocarbons two ISC mechanisms for PH may be considered.

1. If the geometry of the excited states $S_1$ and $T_1$ is not appreciably altered from that of the planar ground state ($C_{2v}$), ISC between $S_1$ ($^1B_1$) and $T_1$ ($^3B_1$) is orbitally forbidden.[23] A transition between these states would, therefore, be governed by a relatively ineffective mechanism which is vibronically induced by Herzberg–Teller coupling terms.[24] However, our calculations predict that the second lowest triplet state $T_2$ with a $^3A_1$ character is energetically very close to $S_1$. Since ISC between $^1B_1$ and $^3A_1$ is allowed *via* a spin–orbit coupling operator $H_{\text{so}}(R_z)$, the availability of an intermediate triplet state offers the possibility of the second-order mechanism

$$S_1\ (^1B_1) \xrightarrow{H_{\text{so}}} T_2\ (^3A_1) \xrightarrow{H_{\text{ve}}} T_1\ (^3B_1)$$

By second-order perturbation theory the transition moment $\vec{M}$ between $S_0$ and $T_1$ for this mechanism is[23]

$$\vec{M}(S_0 - T_1) = (E_{T_1} - E_{S_1})^{-1}(E_{T_1} - E_{T_2})^{-1} \times \langle\phi_{S_1}|H_{\text{so}}|\phi_{T_2}\rangle\langle\phi_{T_2}|H_{\text{ve}}|\phi_{T1}\rangle\vec{m}(S_0 - S_1)$$

where $E_K$ corresponds to the energy of the state K, $H_{\text{ve}}$ is the vibronic–electronic coupling operator, and $\vec{m}$ is the transition moment between $S_0$ and the interacting higher singlet state. The active vibration in mixing triplet states $T_1$ and $T_2$ is of symmetry $b_1$, which, in this case, has the same polarization as $\vec{m}$. In spite of the relatively large energy gap between the second excited singlet state $S_2$ and $T_1$, one would expect that $S_2$ also participates in ISC since the transition moment $\vec{m}(S_2 \leftarrow S_0)$ is much larger than $\vec{m}(S_1 \leftarrow S_0)$.

2. If, however, the geometries of $S_1$ and $T_1$ are distinctly nonplanar, direct $\pi,\pi$ spin–orbit coupling becomes possible. Assuming that the $C_{2v}$ symmetry of the ground state is reduced to $C_s$ in the excited state (*e.g.*, folding of PH along the N–O axis), $B_1$ in $C_{2v}$ symmetry becomes $A'$ in $C_s$.[25] ISC between $A'$ states, involving the $H_{\text{so}}(R_z)$ is allowed (N–O axis corresponds to the $x$ direction, plane of symmetry is $\sigma(xy)$). The singlet–triplet transition moment is then

$$\vec{M}(S_0 - T_1) = (E_{T_1} - E_{S_1})^{-1}\langle\phi_{S_1}|H_{\text{so}}|\phi_{T_1}\rangle\vec{m}(S_0 - S_1)$$

Therefore, polarization of the phosphorescence is along the $x$ or $z$ axis. This result is compatible with the

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[17] Evaluation of this parameter by integrating the first absorption band yielded $\tau_{\text{fluo}}$(rad) ~ 120 nsec. It is not surprising that, for transitions of such low oscillator strength, this method fails to give meaningful estimates of the radiative lifetimes.

[18] E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959); C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 81.

[19] It is not unusual that aromatic amines show phosphorescence decay times close to radiative lifetimes; see, *e.g.*, ref 28.

[20] J. M. Lhoste, M. Ptak, and D. Lexa, *J. Chim. Phys. Physicochim. Biol.*, **65**, 1876 (1968).

[21] B. R. Henry and W. Siebrand, *ibid.*, **51**, 2396 (1969); W. S. Veeman and J. G. van der Waals, *Mol. Phys.*, **18**, 63 (1970).

[22] V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **37**, 912 (1962).

[23] See, *e.g.*, R. Hochstrasser, "Molecular Aspects of Symmetry," W. A. Benjamin, New York, N. Y., 1966.

[24] B. R. Henry and W. Siebrand, *J. Chem. Phys.*, **54**, 1072 (1971).

[25] See, *e.g.*, G. Herzberg, "Infra Red and Raman Spectra," Van Nostrand, Princeton, N. J., 1945, p 237.

experimental findings since absorption to the $S_1$ (or $S_2$) state of the planar molecule can be polarized parallel to the phosphorescence of the folded system.

On the basis of the gross spectral features of the emission, the second proposed ISC mechanism appears to be favored. The absorption spectra consist of broad bands with no vibrational structure, while the emission spectra show considerable structure[4] (Figure 1b). This type of behavior is generally taken to indicate a change of geometry between the ground state and the relaxed excited state. Furthermore, strong support is lent to this argument by the weak 0–0 transition of the phosphorescence which is especially evident for PH (*cf.* Figure 1a,b). The differences between aromatic amines and planar aromatic hydrocarbons with respect to phosphorescence polarization and the effectiveness of ISC ($\tau_{\text{phos}}(\text{rad}) \sim 3$ sec for PH as compared to 30–150 sec for aromatic hydrocarbons[26]) can be understood in terms of this mechanism. Similar arguments have recently been advanced by Kasha and Rawls,[27] and by Lim and Chakrabarti,[28] who proposed that the enhanced spin–orbit coupling in aromatic amines is attributable to the nonbonding character of the lone pair electron on the nitrogen atom. Spin–orbit interactions between $\pi$ orbitals in planar aromatic hydrocarbons involve only small three center integrals,[29] and they are orbitally forbidden in planar aromatic amines. From the point of view of $\pi$-molecular orbital theory, deviation of the amine geometry from planarity would cause the nitrogen "lone pair orbital" to be no longer parallel to the $\pi$ orbitals of the adjacent carbon atoms. Such lack of orbital alignment then generates spin–orbit matrix elements in which two center integrals dominate, and which become larger in magnitude as the twist out of the $\pi$ direction of the "lone pair orbital" increases. This concept seems to be reinforced by the striking increase in the $\phi_{\text{phos}}/\phi_{\text{fluo}}$ ratio and the simultaneous decrease in $\tau_{\text{phos}}$ for triphenylamine ($\tau_{\text{phos}} = 0.7$ sec) relative to aniline ($\tau_{\text{phos}} = 4.2$ sec).[30] By contrast, carbazole, a planar molecule, exhibits an accordingly long lifetime ($\tau_{\text{phos}} = 7.6$ sec).[30] For quantitative purposes, however, this concept must be treated with extreme caution. As Plotnikov, *et al.*,[31] have recently pointed out, the deviation of molecular geometry from planarity introduces a more drastic effect on the total wave function than a mere change in the orientation of the symmetry axis of the lone pair orbital. Thus, in the general case nonplanarity leads to spin–orbit interactions for which matrix elements with a one-center integral may dominate.

Finally, we consider the temperature dependence of $\phi_{\text{fluo}}$ in the light of a geometry change in the excited states. The detailed nature of temperature effects in fluorescence are not fully understood, but one is inclined to assume that solute–solvent collisional deactivation, which is expected to diminish with decreasing temperature, plays a role. PH and PhP, however, exhibit a temperature variation of $\phi_{\text{fluo}}$ which is significantly larger than normal,[18] and for these systems an additional mechanism appears to be operative. At room temperature the solute molecules are surrounded by a nonrigid solvent cage and as the temperature is lowered, the solvent cage gradually imposes restraints upon the ability of the aromatic amine to deform from planarity. This inhibition of structural adaptation would be reflected in less effective ISC and, indirectly, in a measured increase in $\phi_{\text{fluo}}$. This explanation is consistent with the experimental finding that, in a plastic matrix which remains structurally unchanged from room temperature to 77°K, only a slight effect on $\phi_{\text{fluo}}$ was observed (*cf.* Figure 3b).

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