

PHOSPHORESCENCE EMISSION AND POLARIZATION OF HARMANE

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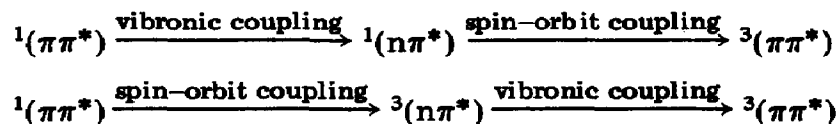
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Summary

Phosphorescence and excitation spectra, phosphorescence and excitation polarization spectra and phosphorescence lifetimes were measured in methylcyclohexane (MC) and EPA glasses at 77 K for harmane (1-methyl-9H-pyrido[3,4-*b*]indole).

It has been found that the 0-0 band of the phosphorescence emission is polarized out of plane, using the excitations corresponding to absorptions into the first and second excited $\pi\pi^*$ singlet states. This fact and the order of the lifetimes measured indicate an emitting triplet that is $^3(\pi\pi^*)$ in both solvents. The origin of this polarization is very likely $^1(n\pi^*) \rightarrow ^3(\pi\pi^*)$ mixing as a result of spin-orbit coupling. However, the vibrational structure and changing polarization outside the 0-0 band indicate that second-order effects involving spin-orbit coupling and vibronic interactions are important and the mixing scheme appears to be



The "proximity effect" can qualitatively explain the low intensity of phosphorescence and the stronger vibronic interaction between the $n\pi^*$ and $\pi\pi^*$ states of harmane in a hydrocarbon solvent (MC).

1. Introduction

The emission properties of nitrogen heterocyclic compounds have been studied extensively [1, 2]. Interactions of electronic and nuclear motions leading to the appearance of electronic transitions which are forbidden in the fixed-nuclei approximation represent one of the most important topics in molecular emission spectroscopy. The theory of electronic transitions due to vibrational-electronic (vibronic) interactions was developed by Herzberg and Teller [3] and it has been extended by Albrecht [4], Liehr [5] and Murrell and Pople [4].

Vibronic interactions between close-lying $n\pi^*$ and $\pi\pi^*$ states have important consequences in molecular electronic transitions of heteroaromatic compounds [7, 8].

The contribution of $n\pi^*$ states to the radiative properties of $\pi\pi^*$ triplet states in aromatic heterocyclic compounds has been discussed by numerous research groups [9 - 13].

Two important mechanisms through which the emitting $^3(\pi\pi^*)$ state acquires dipole-allowed character [11] are (i) first-order spin-orbit perturbation of the $^3(\pi\pi^*)$ state by an out-of-plane polarized $^1(n\pi^*)$ singlet-singlet transition, and (ii) second-order mechanisms consisting of vibronic coupling of the $^3(\pi\pi^*)$ state with a higher-lying $^3(n\pi^*)$ state which is spin-orbit coupled to in-plane polarized $^1(\pi\pi^*)$ states and/or spin-orbit coupling of the $^3(\pi\pi^*)$ state with the $^1(n\pi^*)$ state which is vibronically coupled to in-plane polarized $^1(\pi\pi^*)$ states.

The purpose of this paper is to investigate the phosphorescence polarization and phosphorescence lifetimes of harmane (1-methyl-9H-pyrido[3,4-*b*]indole) in EPA (ethyl ether-isopentane-ethanol (5:5:2 by volume)) and methylcyclohexane (MC) glasses at 77 K with the aim of characterizing the triplet state responsible for phosphorescence as well as to elucidate qualitatively the importance of the first-order and second-order spin-coupling effects in relation to the mechanisms of the phosphorescence process.

2. Experimental details

2.1. Materials

Harmane (Fig. 1) was obtained from Fluka AG. Buchs. S. S. and purified twice by vacuum sublimation.

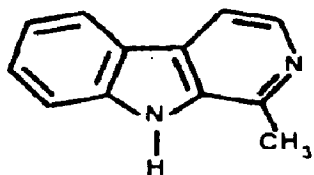


Fig. 1. Molecular structure of harmane.

The solvents used in these studies were EPA and MC. The isopentane, ethyl ether and ethanol (Uvasol grade (Merck)) were used without further purification. Methylcyclohexane (Merck) was distilled twice before use.

The concentrations of the samples were 10^{-4} M before freezing.

2.2. Apparatus

Corrected excitation and phosphorescence spectra were recorded using a Perkin-Elmer MPF-44A spectrofluorometer equipped with a phosphores-

cence accessory and a corrector accessory (Differential Corrected Spectra Unit-2 (DCSU-2)). The degrees of polarization of phosphorescence and excitation were obtained by the method of photoselection [14] at liquid nitrogen temperature (77 K) using the polarizer accessory of the Perkin-Elmer MPF-44A spectrofluorometer.

The degree of polarization P is defined as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

where I_{\parallel} and I_{\perp} are the intensities of the emitted light polarized respectively parallel and perpendicular to the exciting light which is polarized with the electrical vector perpendicular to the plane formed by the excitation beam and the emission beam. The P values were corrected for instrumental factors in the usual manner [15].

The mean lifetimes of the phosphorescence were determined from the emission decay curves by means of a Tektronix 5223 oscilloscope.

3. Results and discussion

3.1. Phosphorescence excitation and polarization spectra

The phosphorescence excitation and polarization spectra of harmane in the hydroxyl (EPA) glass at 77 K are shown in Fig. 2. The excitation polarization spectrum is negative with respect to emission at the phosphorescence 0-0 band ($\lambda_{em} = 425$ nm) and it shows variations in the P values. In the first band of excitation P is at a minimum over the 0-0 band. This behaviour, combined with the fact that the two excitation bands are unquestionably of $\pi\pi^*$ type and thus necessarily polarized in the molecular plane, indicates that the phosphorescence 0-0 band is polarized perpendicular to the molecular plane. When the wavelength of phosphorescence is fixed at 436 nm, the polarization of phosphorescence excitation is positive in the second band of excitation and the P values decrease towards higher frequencies. In the first band of excitation the polarization is negative, and P is at a minimum nearly in the 0-0 band. This behaviour indicates that these transitions are very nearly perpendicular to each other, each lying in the molecular plane, *i.e.* in the plane of the ring.

The phosphorescence excitation and polarization spectra of harmane in the non-hydroxyl (MC) glass at 77 K are shown in Fig. 3. In this solvent the variations in the P values are very small for the two fixed phosphorescence wavelengths.

3.2. Phosphorescence and polarization spectra

Figures 4 and 5 present the phosphorescence and polarization spectra of harmane in EPA glass and in MC glass respectively at 77 K. The phosphorescence polarization is found to be wavelength dependent in all cases. The changing polarization of phosphorescence, which is similar to that in

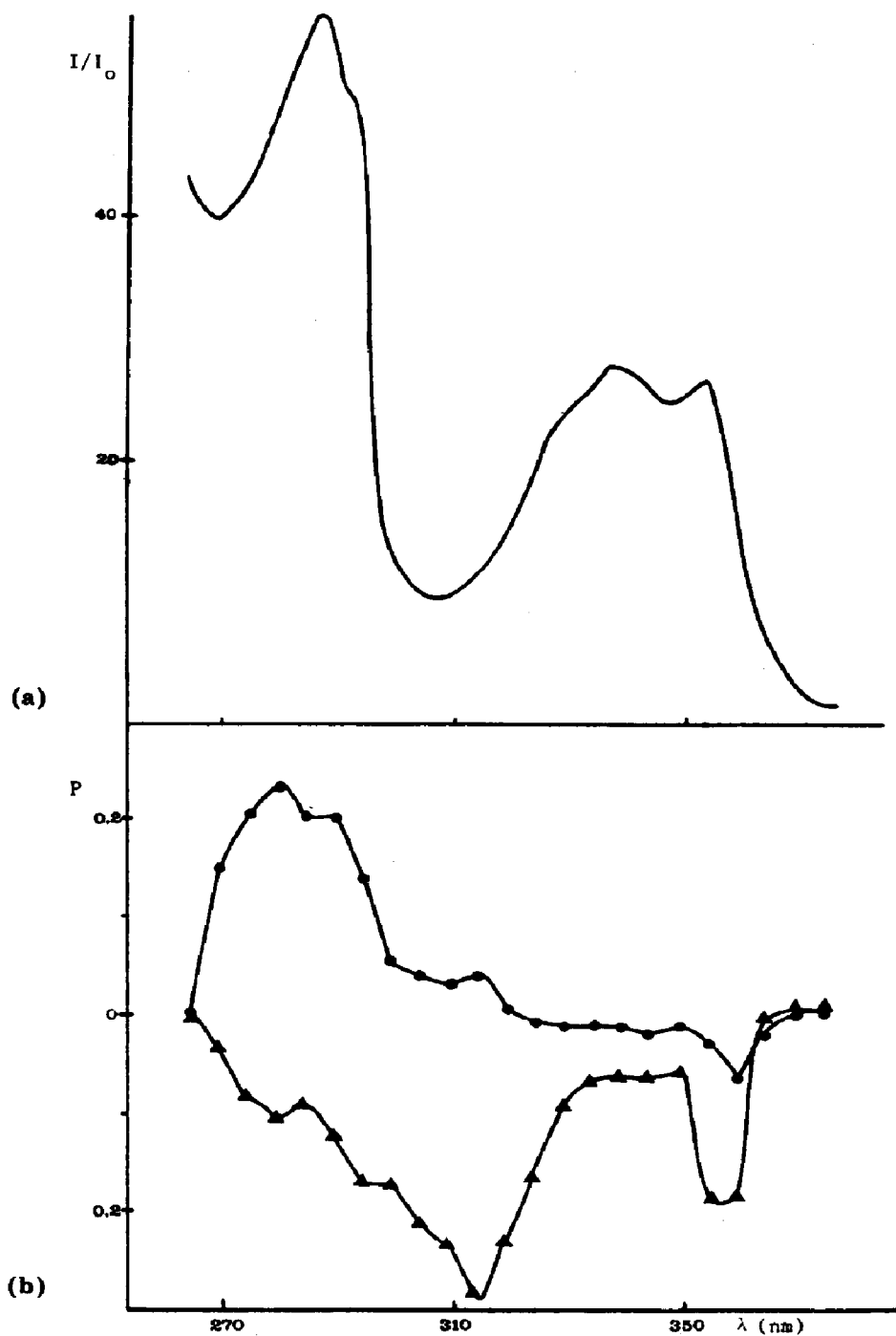


Fig. 2. Phosphorescence excitation and polarization spectra of harmane in EPA at 77 K. (a) Excitation spectrum; (b) excitation polarization spectra determined by monitoring the phosphorescence at 425 (phosphorescence 0-0 band) and 436 nm: \bullet , $\lambda_{em} = 436$ nm; \blacktriangle , $\lambda_{em} = 425$ nm.

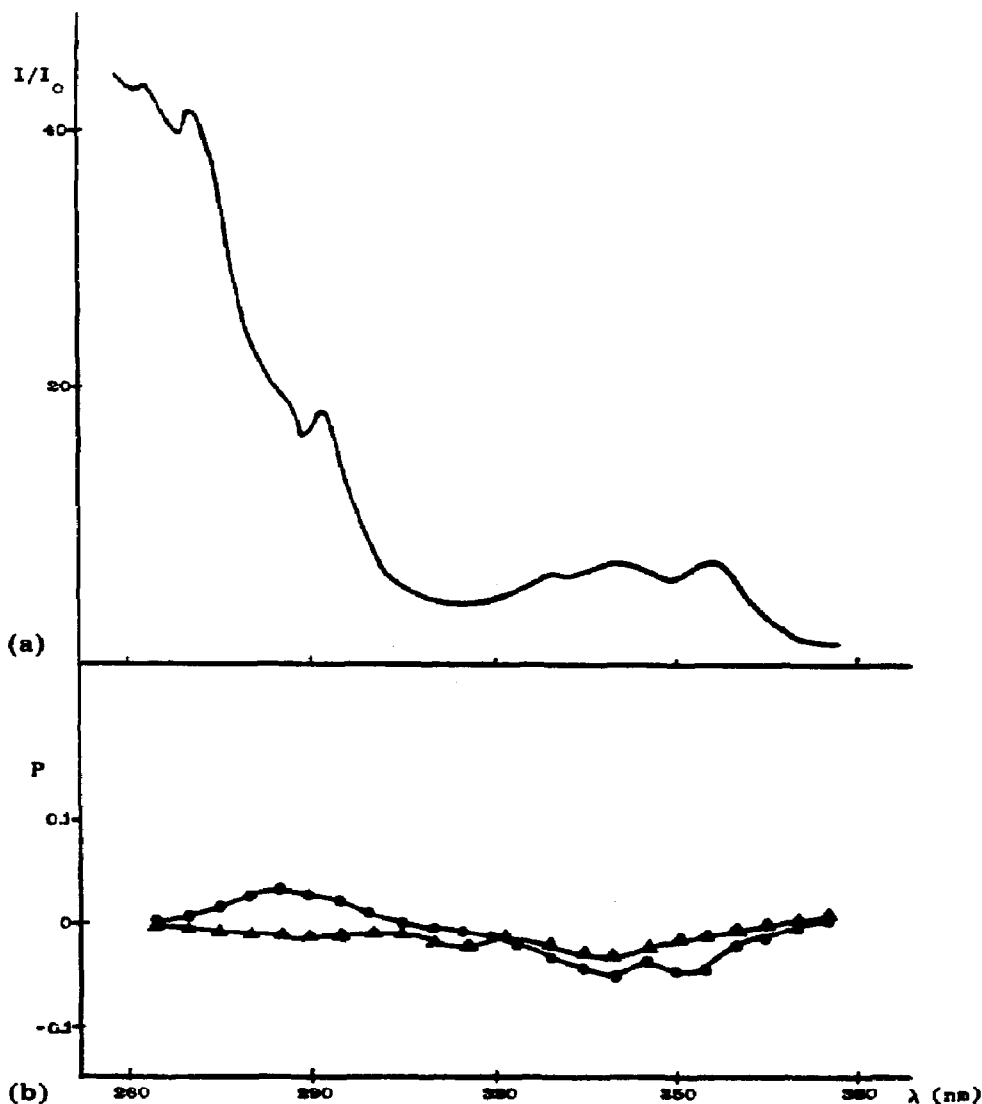


Fig. 3. Phosphorescence excitation and polarization spectra of harmane in MC at 77 K. (a) Excitation spectrum; (b) excitation polarization spectra determined by monitoring the phosphorescence at 426 (phosphorescence 0-0 band) and 438 nm: \bullet , $\lambda_{em} = 438$ nm; \blacktriangle , $\lambda_{em} = 426$ nm.

excitation, indicates the presence of vibronic activity [4]. The phosphorescence 0-0 band is polarized out of plane (negative) using the excitations corresponding to absorptions into the first and second excited $\pi\pi^*$ singlet states. This fact and the values of the lifetimes measured (4.9 s in EPA and 4.6 s in MC) indicate an emitting triplet that is $^3\pi\pi^*$ in both solvents. The origin of this polarization is due to the first-order spin-orbit coupling $^1(n\pi^*) \rightarrow ^3(\pi\pi^*)$. However, the vibrational structure and changing polarization outside the 0-0 band indicate that second-order effects involving

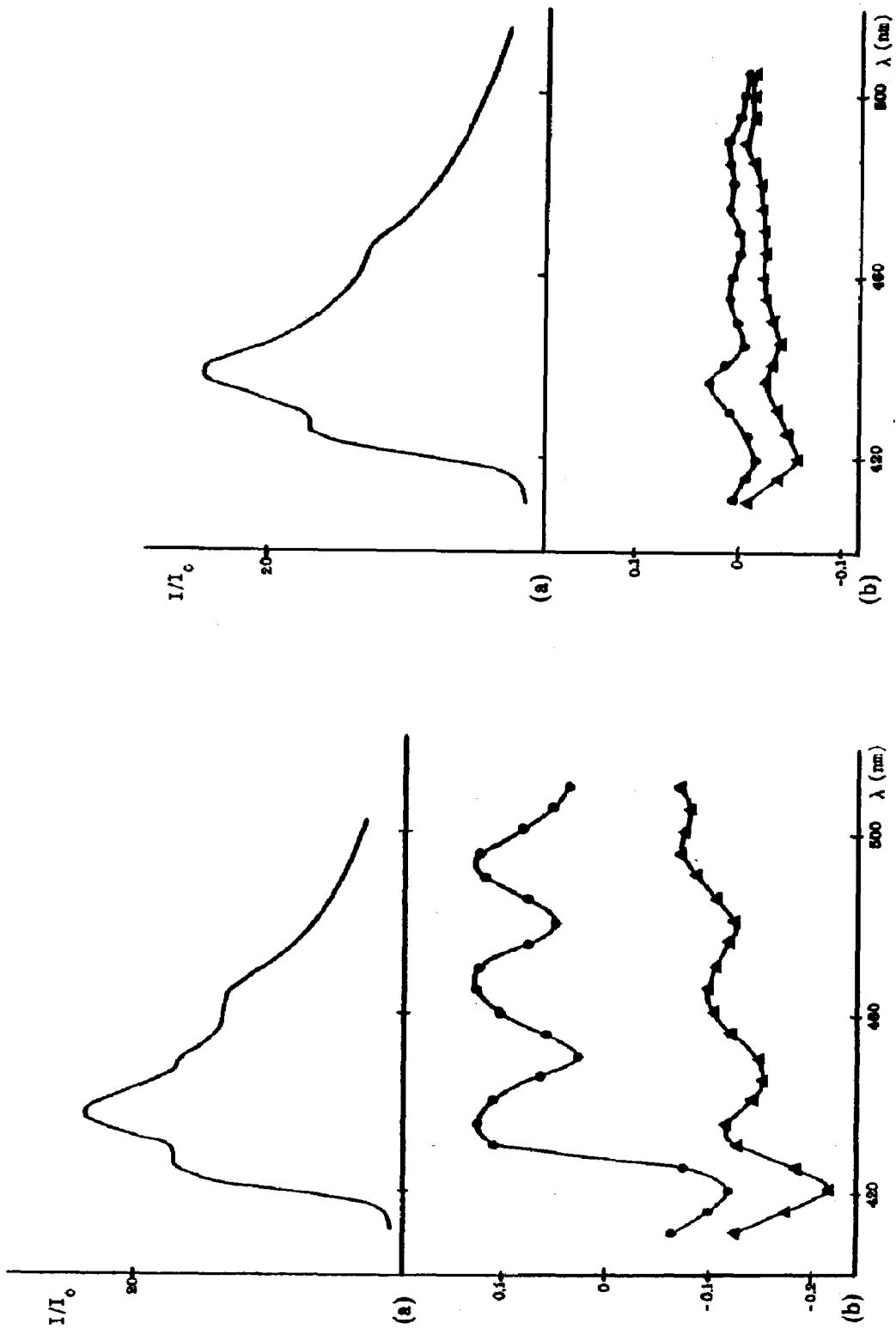


Fig. 4. Phosphorescence and polarization spectra of harmaline in EPA at 77 K. (a) Phosphorescence spectrum; (b) phosphorescence polarization spectra on excitation at 291 and 353 nm: \bullet , $\lambda_{\text{ex}} = 291$ nm; \blacktriangle , $\lambda_{\text{ex}} = 353$ nm.

Fig. 5. Phosphorescence and polarization spectra of harmaline in MC at 77 K. (a) Phosphorescence spectrum; (b) phosphorescence polarization spectra on excitation at 291 and 353 nm: \bullet , $\lambda_{\text{ex}} = 291$ nm; \blacktriangle , $\lambda_{\text{ex}} = 353$ nm.

spin-orbit coupling and vibronic interaction are important. The change in polarization with the wavelength of emission, which is more noticeable for the hydroxyl solvent (EPA) than for the hydrocarbon solvent (MC) is not smooth but goes through peaks and valleys. The phosphorescence 0-0 band and vibronic bands, which appear to involve totally symmetric vibrational modes, coincide with the valleys of the polarization curve when a $^1\pi\pi^*$ band is used for excitation.

The first peak in the polarization curve corresponds in position to the vibrational peak at about 819 cm^{-1} towards the red from the 0-0 band. This corresponds to the out-of-plane bending vibrations of the hydrogen atoms of the pyridinic ring. This behaviour indicates that in-plane polarized vibronic bands (peaks in the polarization curve) arise from the interaction of nearby $n\pi^*$ and $\pi\pi^*$ states through this non-planar hydrogen mode. The following mechanism accounts for the phosphorescence polarization:



The vibrational analysis of the phosphorescence polarization of harmane in EPA at 77 K obtained on excitation at 291 and 353 nm, corresponding to the 0-0 band in the second and first excitation bands respectively, is summarized in Tables 1 and 2.

TABLE 1

Vibrational analysis of the phosphorescence polarization of harmane in EPA glass at 77 K using $\lambda_{\text{ex}} = 291\text{ nm}$

| $\lambda_{\text{em}}\text{ (nm)}$ | $\bar{\nu}\text{ (cm}^{-1}\text{)}$ | $\Delta\bar{\nu}\text{ (cm}^{-1}\text{)}$ | <i>Interpretation</i> | IR ^a |
|-----------------------------------|-------------------------------------|---|-----------------------|-----------------|
| 420 | 23809 | 0 | 0-0 | |
| 435 | 22988 | 821 | 0-819 | 819 |
| 450 | 22222 | 1587 | 0-1590 | 1590 |
| 465 | 21505 | 2304 | 0-819-1481 | 1481 |
| 480 | 20833 | 2976 | 0-2969 | 2969 |
| 490 | 20408 | 3401 | | |

^aIn KBr pellets; see Fig. 6.

The changes in P outside the phosphorescence 0-0 band show that the P values are positive on excitation at 291 nm and negative on excitation at 353 nm. These values of the phosphorescence polarization are consistent with the perpendicularity of the excitations used.

The polarization of transitions throughout the lowest energy excitation band is seen to be wavelength dependent. This fact is very likely due to the vibronic coupling $^1(n\pi^*) \rightarrow ^1(\pi\pi^*)$ corresponding to the second-order mechanism in the phosphorescence:



TABLE 2

Vibrational analysis of the phosphorescence polarization of harmane in EPA glass at 77 K using $\lambda_{\text{ex}} = 353 \text{ nm}$

| λ_{em} (nm) | $\bar{\nu}$ (cm^{-1}) | $\Delta\bar{\nu}$ (cm^{-1}) | Interpretation | IR ^a |
|----------------------------|----------------------------------|--|----------------|-----------------|
| 420 | 23809 | 0 | 0-0 | |
| 435 | 22988 | 821 | 0-819 | 819 |
| 450 | 22222 | 1587 | 0-1590 | 1590 |
| 465 | 21505 | 2304 | 0-819-1481 | 1481 |
| 480 | 20833 | 2976 | 0-2969 | 2969 |
| 495 | 20202 | 3607 | | |

^aIn KBr pellets; see Fig. 6.

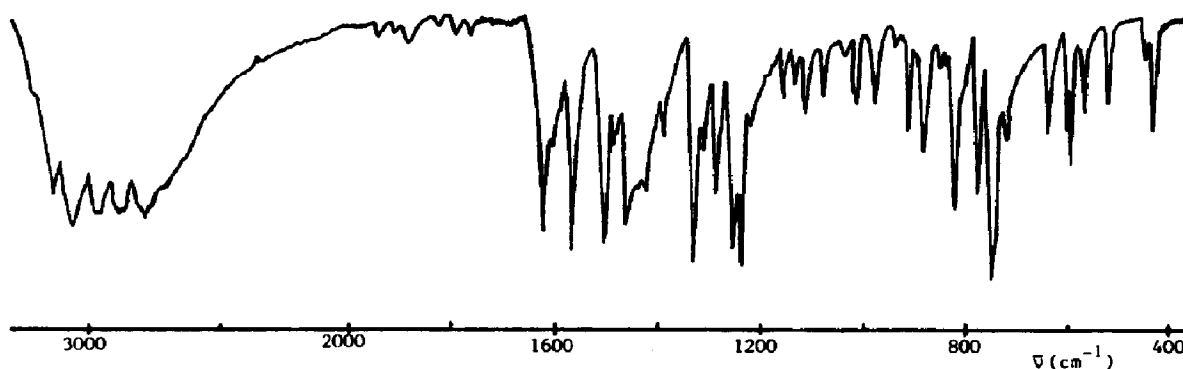


Fig. 6. IR spectrum of harmane in KBr pellets recorded using a Perkin-Elmer 1830 spectrophotometer.

The mechanisms in eqns. (1) and (2) which lead to the in-plane polarization play an important role. These mechanisms are based on the second-order spin-orbit-vibronic perturbation with low-lying $^1(n\pi^*)$ and/or $^3(n\pi^*)$ states as intermediate states and involve a non-totally symmetric vibration.

Although a vibrational analysis cannot be made from the phosphorescence spectrum itself, the polarization spectrum suggests that there should be at least two vibrational progressions with mutually perpendicular polarizations. The progression associated with the polarization minima (valleys) originates from the 0-0 band and is polarized out of plane, being composed of two fundamental modes of frequencies 1590 and 2969 cm^{-1} . These frequencies correspond very closely to the totally symmetric skeletal and stretching C-H vibrations and are polarized out of plane. The other progression associated with the maxima (peaks) begins at 819 cm^{-1} from the 0-0 band and is polarized in plane.

Nevertheless, the change in polarization which occurs throughout the phosphorescence and excitation bands is more pronounced in EPA glass than in MC glass. This fact together with the shorter phosphorescence

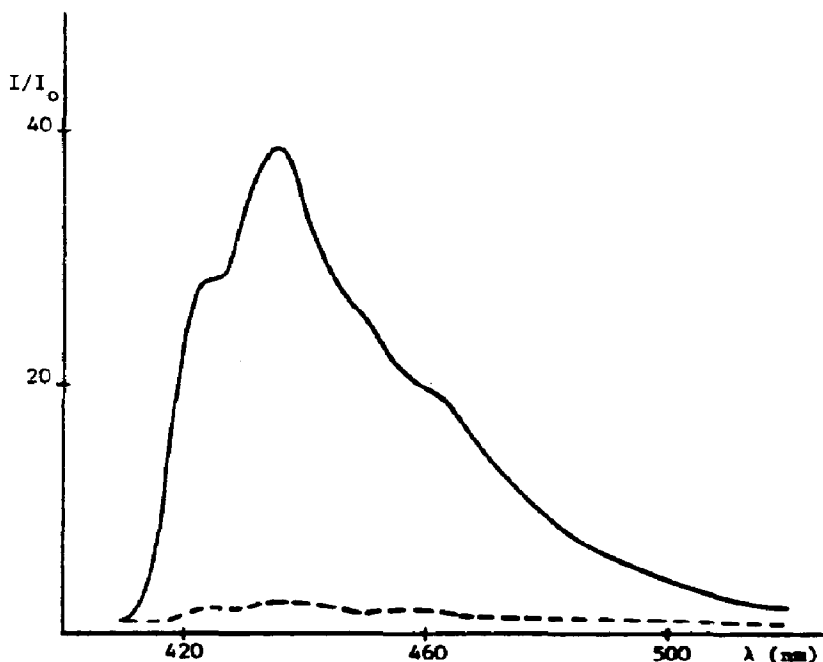


Fig. 7. Phosphorescence spectra of harmane in EPA and MC glasses at 77 K under the same conditions: —, in EPA glass; - - -, in MC glass.

mean lifetime of harmane in MC and the diminished out-of-plane polarization of the phosphorescence 0-0 band indicate the existence of a stronger vibronic interaction between the $n\pi^*$ and $\pi\pi^*$ states in this solvent, since the energy gap between the emitting triplet $\pi\pi^*$ and higher-lying $n\pi^*$ states is expected to be smaller in the hydrocarbon solvent ("proximity effect") and since the $n\pi^*$ triplet-to-ground state transition is expected to be short lived and in-plane polarized owing to spin-orbit coupling with allowed $\pi\pi^*$ transitions [16].

The "proximity effect" [17, 18] can also qualitatively explain the low intensity of phosphorescence in MC (Fig. 7) in terms of the efficient radiationless transitions $T_1 \rightarrow S_0$ which are more important in hydrocarbon solvents because of the greater vibronic interactions between $n\pi^*$ and $\pi\pi^*$ states owing to a small energy gap between these states. This behaviour agrees with that found for many heterocyclic compounds in non-hydroxylic solvents [19].

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