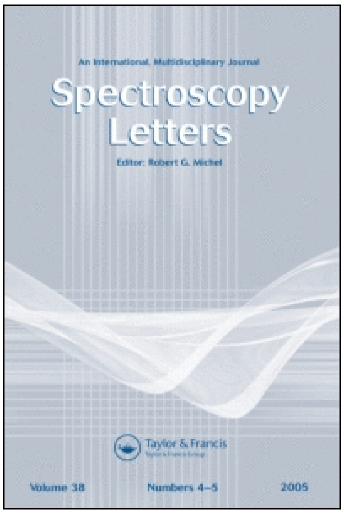

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Lowest Triplet State in 1,4-Dinitronaphalene

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LOWEST TRIPLET STATE IN 1,4-DINITRONAPHALENE

Key words: Solvent effect, phosphorescence decay,
proximity effect

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ABSTRACT

The phosphorescence emission characteristics of 1,4-dinitronaphthatene in some protic and nonprotic solvents at 77°K have been investigated and the lowest triplet state is assigned as $^3\pi\pi^*$ in this molecule. The observed low phosphorescence intensity and the lifetime values have been attributed to the 'proximity effect'.

INTRODUCTION

Roy and Becker (1) have assigned the lowest triplet state of 1,4-dinitronaphthalene as $^3n\pi^*$. The ambiguity in their result has been pointed out by Khalil, Back and McGlynn (2). In 1-nitro 4-methyl naphthalene molecule, the lowest triplet state is $^3\pi\pi^*$. Thus, the assignment of the lowest triplet state in 1,4-dinitronaphthalene which seems to be quite doubtful needs a careful reinvestigation. In this paper, we report the results of our investigations on the phosphorescence emission. Here, we assign the lowest triplet state from solvent effect, polarisation study and the decay of phosphorescence.

EXPERIMENTAL

Eastman Organic Chemical 1,4-dinitronaphthalene was recrystallised several times from purified methanol. Solvents used were of spectrograde quality. Phosphorescence spectra were recorded on a Perkin Elmer MPF 44A spectrofluorimeter at 77°K using rotating can phosphoroscope. The spectra in the acidic ethanol (1 : 1 mixture of sulfuric acid with ethanol by volume) obtained immediately upon mixing did not change with time thereafter ensure that no chemical reaction occured there. Phosphorescence life time was measured using ECIL OS769 oscilloscope display.

RESULTS AND DISCUSSIONS

The phosphorescence spectrum of 1,4-dinitronaphthalene as shown in FIG.1 in methylcyclohexane, ethanol and acidic ethanol has 0-0 band at 18050, 17955 and 17950 cm^{-1} respectively, thus, showing a red shift in protic solvents. It consists of three bands and the vibrational spacing between them is about 1355 cm^{-1} .

Absorption spectrum of 1,4-dinitronaphthalene shows a broad band at 337 nm . The $^1n\pi^*$ state may be located at the tail of this band at about 380 nm which is not resolved. To avoid a low probability associated with the excitation into weak $^1n\pi^*$ region, we have used 337 nm excitation corresponding to $^1\pi$-π^* for phosphorescence study in ethanol glass at 77°K. Excitation into the poorly resolved $^1n\pi^*$ region may lead to the ambiguous results (2). The degree of polarisation is negative throughout the spectral range and the phosphorescence origin has a negative value of 0.13 . It has also been shown in FIG.1 . We, thus, assign the lowest triplet state as $^3\pi\pi^*$ contrary to that previously reported (1). Indeed, the phosphorescence of this molecule is naphthalenic in structure.

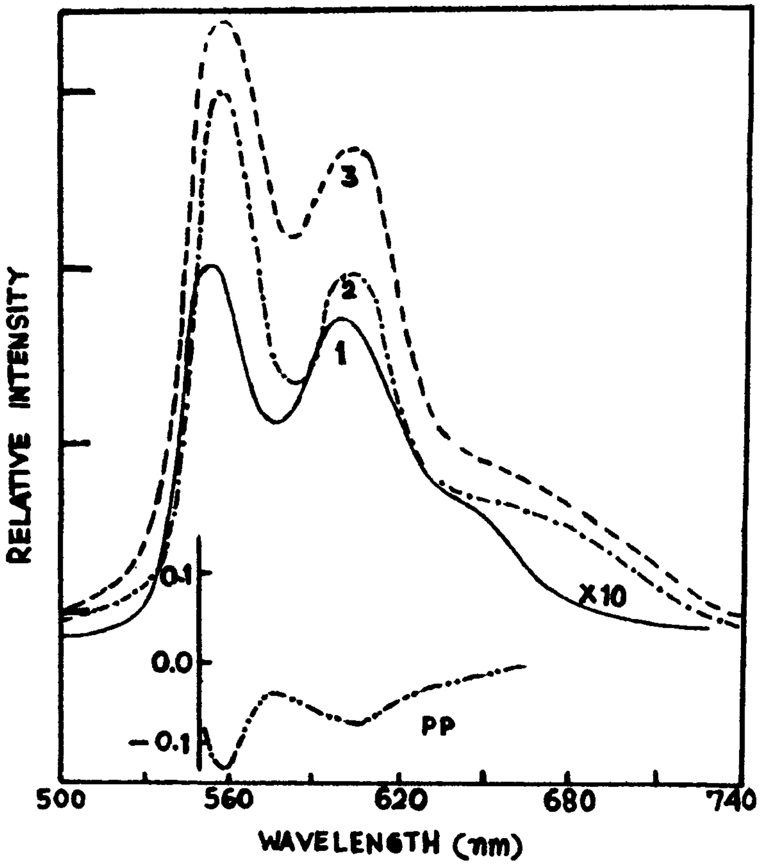

FIG.1 The phosphorescence spectrum of 1,4-dinitronaphthalene in (1) methylcyclohexane (——), (2) ethanol (---) and (3) acidic ethanol (-·-·-) at 77°K. The phosphorescence polarisation in ethanol glass is shown by the curve PP (···-···-) upon π-π excitation.

The phosphorescence life time of this molecule in ethanol has also been measured monitoring the decay of both 557 nm and 602 nm peaks, which is 10 ms only. This is significantly low for the decay of a π-electronic triplet state. The mean lifetime of phosphorescence decay of naphthalene is 2.0 seconds. It has been shown by Lim (3) that a close-lying $^3n\pi^*$ state can shorten the $^3\pi\pi^* \rightarrow S_o$ phosphorescence lifetime significantly due to vibronic interaction between $^3n\pi^*$ and $^3\pi\pi^*$ states i.e. due to the so called 'proximity effect'.

The phosphorescence intensity increases in going from methylcyclohexane to protic solvents. We estimate the phosphorescence quantum yield of about 10^{-2} in methylcyclohexane. The low phosphorescence quantum yield can reasonably be attributed (3) to a very efficient radiationless transition resulting from the proximity effect.

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