

Electronic spectra of dimethyl-2, 6-pyridine dicarboxylate in various Solvents

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ABSTRACT

Electronic spectra of dimethyl-2, 6-pyridine dicarboxylate in different solvents are reported. Different bands and their shift are explained on the basis of molecular complex approach. Solvent effect is also reported.

Key words: Electronic spectrum, ultraviolet spectrum, dimethyl-2, 6 - pyridine dicarboxylate, solvent effect.

INTRODUCTION

Electronic spectra of molecules usually lie in near ultraviolet and visible region. Chief excitations are due to the loosely held n and π electrons which give rise to $n-\pi^*$ and $\pi-\pi^*$ bands. In the present work, electronic spectra of dimethyl-2, 6 - pyridine dicarboxylate has been investigated. Steric hinderance plays important role in deciding the shift of the bands. Similarity with other 2, 6 disubstituted aromatic compounds^{1,2} is discussed.

EXPERIMENTAL

The spec-pure compound dimethyl -2,6-pyridine dicarboxylate was purchased from M/s Sigma Aldrich Chemicals, U.S.A. and was used as such. UV spectra were recorded in the region of 350-200 nm in liquid state, using various polar solvents. The solvents used for preparing the solutions of the said compound were of spectroscopic grade.

RESULTS AND DISCUSSION

The molecular structure of dimethyl - 2, 6 -

pyridine dicarboxylate is shown in Fig. - 1. Its electronic spectra in (1) ethanol (2) methanol and (3) water are shown in figure 2, 3 and 4 respectively. Various bands obtained are listed in Table -1 along with the bands of other relevant compounds.

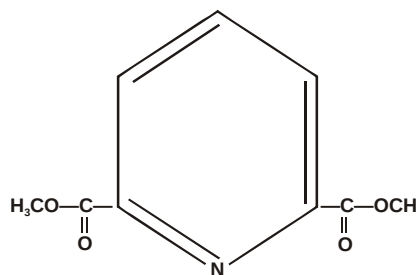


Fig. - 1. Molecular structure of dimethyl - 2, 6 - pyridine dicarboxylate.

Local excitation bands

UV spectrum of pyridine closely resembles to that to benzene³. Benzene displays three characteristic bands at 260 nm, 200 nm and 180 nm due to $\pi-\pi^*$ transitions. Out of these, 180 nm bands is most intense and is due to ${}^1A_{1g} \rightarrow {}^1E_{1u}$ transition. It is a symmetry allowed transition and is

called the b band⁴. 200 nm band is a symmetry forbidden band and appears due to $^1A_{1g} \rightarrow ^1B_{1u}$ transition. It is a moderately intense band and is designated as π band. 260 nm band is a weak band. This band is called the α band and appears due to $^1A_{1g} \rightarrow ^1B_{2u}$ transition. It is also a symmetry forbidden transition. Replacement of one methine group, =CH-, in benzene by =N- affords pyridine. The most important difference of the spectra of the

azaaromatic compounds from the spectra of the corresponding aromatic hydrocarbons lies in greater intensity and partial loss of vibrational structure of the α band⁵. In the present compound, carbon atom of the carboxyl group is linked to the pyridine ring while single bonded oxygen atom is linked to the methyl group. A molecular complex can be regarded as a loose reversible association of two or more distinct chemical components⁵.

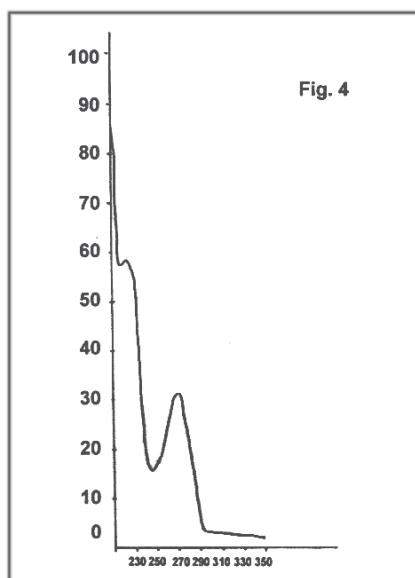
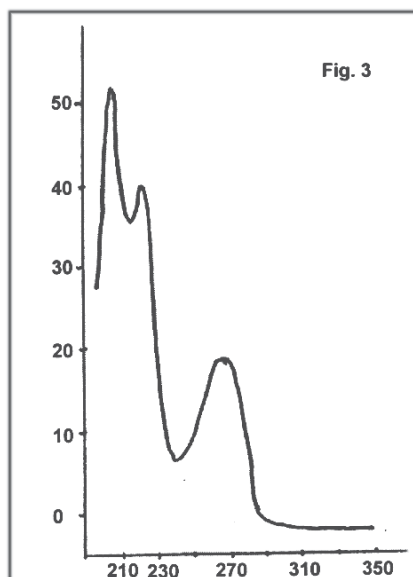
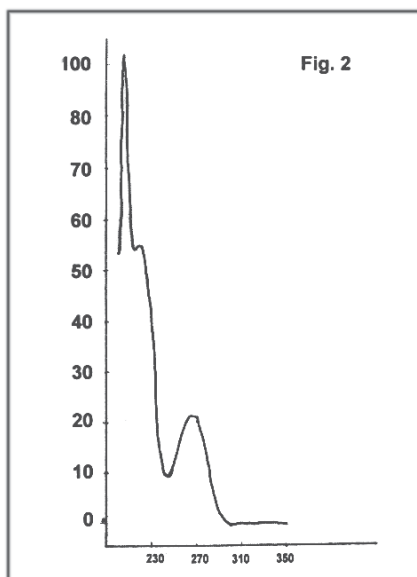


Fig. - 2-4: Electronic spectra of dimethyl-2, 6-pyridine dicarboxylate in various solvents

Table - 1 : Electronic absorption bands of dimethyl - 2, 6-pyridine dicarboxylate and other relevant compounds.

Compound	α band(nm)	π band (nm)	β band (nm)	CT band (nm)	Solvent
Benzene	260	200	180	—	—
Pyridine	250	195	—	—	—
Benzoic acid	280	196	—	229	—
Methyl Benzoate	280	200	—	228	—
2, 6 PDC	270 (21)	208 (93)	—	224 (54)	Ethanol
	262 (19)	206 (52)	—	222 (40)	Methanol
	270 (31)	—	—	220 (58)	Water

2, 6 PDC = dimethyl - 2, 6 - pyridine di carboxylate.

Values in brackets indicate the intensities of the bands.

Therefore, molecular complex formation is usually accompanied with the shift of absorption bands of the components and with the appearance of the new bands. This approach is very useful for correlating the position and intensity of the related absorption bands in a series of related compounds with the structure of the molecules. As a result, Local excitation (LE) bands of benzene appear with a slight red shift in the present case. Since nitrogen is more electronegative than carbon, lowest unoccupied p orbital of benzene is lowered by the aza substitution and hence there is a bathochromic shift of α and π bands⁷. Weak mesomeric effect of -COOR group also contributes to this red shift⁵.

Charge transfer band

Besides two LE bands, a charge transfer band (CT) also appears at about 222 nm. This band shows a small blue shift from the corresponding bands of benzoic acid and methyl benzoate ($\lambda_{\max}$ = 228 nm). This hypsochromic shift is partly due to the steric hinderance and partly due to the twist of the carboxyl group out of the plane of the aromatic ring. Actually, CT band disappears in almost all 2, 6 disubstituted acids as steric hinderance is increased⁴. Broad 270 nm band also confirms the steric hinderance in the present case.

Solvent effect

Position and intensity of the absorption maxima are affected by the environment. The effects of intermolecular interactions upon the energies of the electronic states of the molecule are generally different from one another. But in the present case, most of the bands appear at almost the same wave length and with a nearly constant intensity in all the three solvents. Therefore in analogy to benzoic acid and methyl benzoate, hydrogen bonding is supposed to exist. The lone pair of electrons on the oxygen atom of the carbonyl group forms a hydrogen band with the hydrogen atom of the hydroxyl group of the solvent molecules⁹. Hyperchromic effect is less pronounced with an increase in solvent polarity which is same as that in benzoic acid and methyl benzoate. CT band of benzoic acid in various alcohols and ethers appears at 226-228 nm while that of methyl benzoate at 228 nm with nearly constant intensity. This is due to the negative inductive effect of the carboxyl group. Due to dipole – dipole interaction, negative inductive effect of the carboxyl group increases as the solvent polarity increases¹⁰. Slight blue shift of the bands with increasing solvent polarity shows that intermolecular interaction of solute - solvent molecules stabilizes the excited state less than it does the ground state¹¹.

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