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Electronic Absortion Spectra of Copper Phthalocyanine Dye

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The electronic absorption of Cu phthalocyanine dye has been measured at room temperature in four solvents of different polarity and from which oscillator strength has been calculated. The measured band shift and intensities provide evidence for the assigment of the possible electronic transitions. The longest wavelength band which appears at 727 nm with higher intensity has been assigned as the charge transfer band resulting in charge transfer from the phthalocyanine ligand to the copper central atom of the dye molecule.

INTRODUCTION

The UV spectrum of copper phthalocyanine has been known for some time, but the interpretation of the observed bands in solvents of different polarity has not been clear so far. Rather qualitative theoretical considerations by Mulliken[1] and by Walsh[2] have shown that likely low lying transition would involve promotion of electrons from an orbital or from various non-bonding orbitals to an antibonding π-orbital. The absorption spectra of phthalocyanine complex in organic solvents and in H_2SO_4 differ to such extent that one can speak of a strong chemical interaction[3]. A strong bathochromic shift of almost all bands occurs except one at a wavelength of about 225–230 nm[4–8].

Because of this situation we have measured the effects of four different solvents on the ultraviolet spectrum of copper phthalocyanine. Such studies on the ultraviolet spectrum of this dye molecule have often been useful in assigning transitions and ultimately to evaluate the oscillator strength, *i.e.*, the probability of electronic transition, and we believe that it provides good evidence of the nature of the orbital involved in the transitions.

EXPERIMENTAL

As copper phthalocyanine is hardly soluble in common solvents, only four suitable solvents like *p*-xylene, orthophosphoric acid, chloroform and conc. H_2SO_4 have been selected. The solutions of known concentrations were prepared by weighing required amounts of copper phthalocyanine and dissolving in the appropriate amount of above selected solvents.

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The spectra were obtained in the shape of broad bands as plots of transmittance against wavelength from which the positions of maximum absorption (λ_{max}) were estimated from the centre by symmetry of the graph. In case the graphs went beyond the scale the solutions were diluted such that the peak position fell within the desired range.

Extinction coefficients (ε), were calculated at each wavelength using the Beers law equation. After coverng the λ's into wavenumbers (ν cm^{-1}) values of ε were plotted against ν. The area under the curves (ε *vs.* ν) calculated from the product $\varepsilon \times 1/2$ band width gave the value of the integrated absorption intensity I_a for the transition under consideration. From the ratio of I_{obs}/I_{theo} the values of oscillator strengths of the transitions were calculated.

RESULTS AND DISCUSSION

The spectra obtained are shown in Fig. A. The list of bands of copper phthalocyanine in four suitable solvents in given in Tables 1–6.

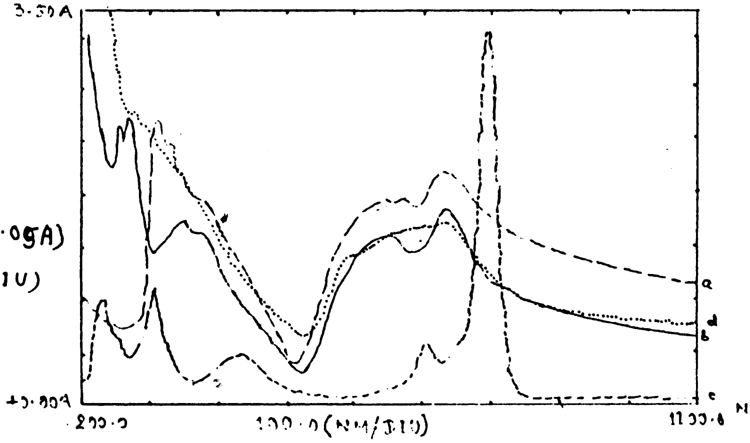
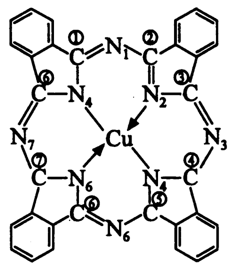


Fig. A UV Spectra of copper phthalocyanine in
(s) *p*-xylene (b) Chloroform (c) Conc. sulphouric acid (d) *o*-phosphoric acid

The spectra of copper phthalocyanine complex have been recorded in *p*-xylene, chloroform, conc. H_2SO_4 and ortho-phosphoric acid, where *p*-xylene is the least polar, almost nonpolar, of these solvents. The spectrum of pure *p*-xylene does not contain any band beyond 900 nm, but in cyclohexane solvent, a dilute solution of *p*-xylene gives band at 275 and 245 nm. Considering the structure of the molecule the longest wavelength band can be attributed to the solute molecule; in all probability, this band may be assigned as the charge transfer band resulting in transfer from the ligand to the central metal ion. The other wavelength transition of 643 nm and which is completely less intense is assigned to the d-d transition of the copper ion.



Cu-Phthalocyanine

TABLE-1
CHARACTERISTIC BANDS OF COPPER PHTHALOCYANINE IN FOUR SOLVENTS

S. No.	Solvent Used	Concentration	λ_{max} (in nm)	Absorbance
1.	*p*-xylene	0.06 g/L	727	0.92
			643	0.81
			308	1.11
2.	Chloroform	0.06 g/L	725	1.24
			642	1.08
			345	1.19
			263	1.19
			249	1.77
3.	Conc. H_2SO_4	0.07 g/L	790	1.89
			305	0.58
			230	0.53
4.	Orthophosphoric acid	0.06 g/L	734	0.34

TABLE-2
MOLAR EXTINCTION COEFFICIENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR BANDS OF COPPER PHTHALOCYANINE IN *p*-XYLENE SOLVENT

Concentration of the Sample = 0.06 g/c; $\frac{0.06}{572.0}$ gm mole/litre = C;

Path length = 1 cm and $\frac{1}{C \cdot l} = \frac{572}{0.06}\ g = 9533.33\ g\ mol^{-1}\ cm^{2}$

	ν (cm^{-1})	$A = \log I_0/I$	$\varepsilon = \frac{1}{C \cdot l} \times \log \frac{I_0}{I}$
For band (a):	11000	0.500	4861.99
	11500	0.650	6196.66
	12000	0.700	6673.33
	12500	0.750	7149.99
	13000	0.850	8103.33
	13500	0.880	8389.39
	14000	0.970	8742.06
	14500	0.720	6863.99
For band (b):	14500	0.720	6863.99
	15000	0.608	7750.59
	15500	0.813	7750.53
	16000	0.734	7060.19
	16500	0.630	7005.99
	17000	0.490	6005.99
	17500	0.290	4671.33
	18000	0.210	2001.99

	ν (cm^{-1})	$A = \log I_0/I$	$\varepsilon = \frac{1}{C \cdot l} \times \log \frac{I_0}{I}$
For band (c):	28500	0.821	7826.86
	29000	0.840	8007.00
	29500	0.901	8589.53
	30000	0.940	9171.06
	30500	0.962	9214.65
	31000	0.975	9294.99
	31500	0.990	9437.99
	32000	1.000	9533.33
	32500	1.113	10610.59
	33000	0.400	3813.33
	33500	0.312	2974.39
For band (d):	33500	0.900	8579.99
	34000	1.000	9533.33
	34500	1.251	11926.19
	35000	1.310	12488.66
	35500	1.325	12488.66
	36000	1.412	12631.66
	36500	1.550	13461.06
	37000	1.610	14776.66
	37500	1.710	15873.99
	38000	1.890	17341.12
	38500	1.800	17519.99
	39000	1.789	17055.12
	39500	1.718	16383.52
	40000	1.613	15473.99
	40500	1.620	14343.99
	41000	1.500	14209.99

The band in the short wavelength region (308 nm) which is also fairly intense owes its origin to the organic ligand part of the complex. This band is the result of the longest wavelength electronic transition in the highly conjugated system. The conjugation extends from the benzene ring to the C_1—N_1, C_2—N_2, C_3—N_3, upto C_8—N_8, atoms vide Fig. B given above. Considered in this way the conjugation involves as many as 16 atoms of carbon and nitrogen taken together besides 4 benezene rings and yet the wavelength of absorption is not very large as observed in the case of long chain polyenes and cyanine dyes[10]. This may perhaps be due to the involvement of nitrogen atoms in the chains. From the point of view of chromophoric properties, the distribution pattern of π electrons over the contours of phthalocyanine ligand gives an insight into the extent of participation of heteroatomic n electrons in the formation of the π electron cloud of the molecule.

Further we have seen that there are two more intense bands at 269 and 249 nm in chloroform and such-bands are absent in nonpolar solvents. We understand that these bands are forbidden in nonpolar solvents due to symmetry considerations and the solute-solvent interaction perhaps leading to some sort of chemical

TABLE-3

MOLAR EXTINCTION COEFFICIENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR BANDS OF COPPER PHTHALOCYANINE IN CHLOROFORM SOLVENT

Concentration of the sample = 0.06 g/c; $\frac{0.06}{572.0}$ g mole/litre = C

Path length = 1 cm and $\frac{1}{C\cdot 1} = \frac{1.572}{0.06}$ g = 9533.33 g mol^{-1} cm^2

	ν (cm^{-1})	$A = \log I_0/I$	$\varepsilon = \frac{1}{C\cdot 1} \times \log \frac{I_0}{I}$
For band (a):	11800	0.600	5719.99
	12300	0.740	7056.66
	12800	1.180	8039.33
	13300	1.120	8533.33
	13800	1.240	11821.33
	14300	1.000	9533.33
	14800	1.000	9533.33
	15300	1.000	9533.33
For band (b):	15300	1.000	9533.33
	15500	1.083	10324.59
	15800	1.050	10009.99
	16300	1.000	9533.33
	16800	0.750	7149.99
	17300	0.500	4766.66
	17800	0.450	4289.99
For band (c):	25000	0.750	7149.99
	25500	0.840	8007.99
	26000	1.000	9533.33
	26500	1.000	9533.33
	27000	1.000	9533.33
	27500	1.050	10009.9
	28000	1.100	10486.66
	28500	1.120	10677.72
	29000	1.189	11335.13
	29500	1.100	10486.66
For band (d):	33500	0.900	8579.99
	34000	1.800	9533.33
	34500	1.251	11926.19
	35000	1.310	12488.66
	35500	1.325	13461.06
	36000	1.412	14776.66
	36500	1.550	15348.66
	37000	1.610	16873.99
	37500	1.710	17341.12
	38000	1.819	17159.99
	38500	1.800	17055.12
	39000	1.789	16383.52
	39500	1.718	15473.99
	40000	1.623	14343.99
	40500	1.620	14209.99
	41000	1.580	14100.12

TABLE-4

MOLAR EXTINCTION COEFFICIENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR BANDS OF COPPER PHTHALOCYANINE IN CONC. H_2SO_4

Concentration of the sample = 0.06 g/c; $\frac{0.07}{572.0}$ g mole/litre = C.

Path length = 1 cm and $\frac{1}{C \cdot 1} = \frac{532}{0.07}$ g = 8171.42 g mol^{-1} cm^2

	ν (cm^{-1})	$A = \log I_0/I$	$\varepsilon = \frac{1}{C \cdot 1} \times \log \frac{I_0}{I}$
For band (a):	11200	0.050	405.87
	11700	0.050	405.87
	12200	0.080	649.40
	12700	1.890	15341.92
	13200	0.420	3409.32
	13700	0.250	2029.35
	14200	0.189	1946.96
	14700	0.250	2029.35
	15200	0.100	817.14
For band (b):	20000	0.100	817.14
	20500	0.150	1225.71
	21000	0.150	1225.71
	21500	0.180	1225.71
	22000	0.180	1470.85
	22500	0.200	1470.85
	23000	0.210	1715.99
	23500	0.247	2018.34
	24000	0.150	1470.85
	24500	0.150	1225.71
	25000	0.100	817.14
For band (c):	27800	0.15	1225.710
	28300	0.25	2042.850
	28800	0.25	2042.850
	29300	0.30	2451.420
	29800	0.35	2859.990
	30300	0.40	3268.560
	30800	0.40	3268.560
	31300	0.40	3268.560
	31800	0.40	3268.560
	32300	0.40	3268.560
	32800	0.579	4731.25
	33300	0.500	4085.71
	33800	0.850	2859.99
For band (d):	36500	0.250	2042.85
	37500	0.300	2451.42
	38500	0.300	2451.42
	39500	0.350	2859.99
	40500	0.350	2859.99
	41500	0.350	2859.99
	42500	0.400	3268.56
	43500	0.531	4339.02
	44500	0.350	2859.99
	45500	0.150	1225.71

interaction with the polar solvent chloroform making these bands appear. So far the solvent sulphuric acid is concerned, a strong bathochromic shift of bands occurs. This is indicative of the same type of proton attachment and the same sites of its localization. The absence of electron donor centres in the molecule of copper phthalocyanine at the intracyclic nitrogen atoms and the strong bathochromic shift in H_2SO_4 leave no doubt that H^+ is attached to the extracyclic nitrogen atoms of copper phthalocyanine.

TABLE-5

MOLAR EXTINCTION COEFFICIENT (ε) AT DIFFERENT FREQUENCIES (cm^{-1}) FOR BANDS OF COPPER PHTHALOCYANINE IN ORTHOPHOSPHORIC ACID SOLVENT

Concentration of the sample = 0.06 g/c; $\frac{0.06}{572.0}$ g mole/litre = C;

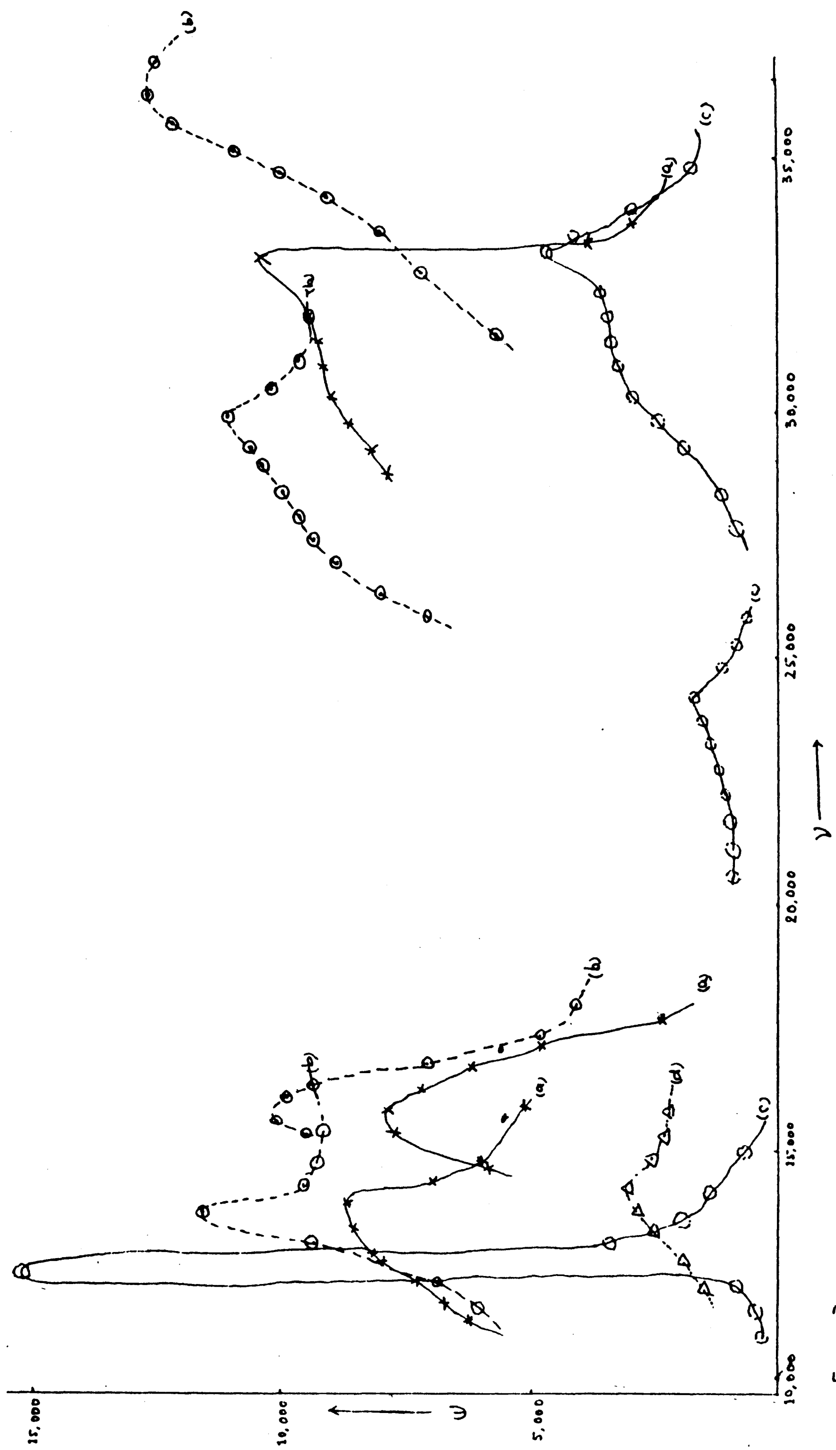
Path length = 1 cm and $\frac{1}{C\cdot l} = \frac{532}{0.06}$ g = 9533.33 g mol^{-1} cm^2

ν (cm^{-1})	$A = \log I_0/I$	$\varepsilon = \frac{1}{C\cdot l} \times \log \frac{I_0}{I}$
11800	0.170	1620.66
12300	0.200	1906.66
12800	0.290	2764.66
13300	0.339	3231.79
13800	0.300	2859.99
14300	0.290	2764.66
14800	0.270	2573.99
15300	0.190	1811.33

TABLE-6

RESULTS OF THE ELECTRONIC ABSORPTION SPECTRA OF COPPER PHTHALOCYANINE FOR DIFFERENT BANDS IN DIFFERENT SOLVENTS

S. No.	Solvent used	ν_{max} (cm^{-1})	½ ε_{max}	I = ½ ε_{max} × Δν × (10^8)		f(0.5) I × 4.316 × 10^{-9}
1.	*p*-Xylene	14000	4350	4000	0.1740	0.07508
		15500	3850	3000	0.1155	0.04983
		32500	5250	1000	0.0525	0.02226
2.	Chloroform	13800	5850	3200	0.1872	0.08077
		15500	5200	2000	0.1042	0.04487
		29000	5650	5000	0.2825	0.12189
		38000	8650	7500	0.6847	0.29545
3.	Conc. H_2SO_4	12700	7650	500	0.03825	0.01165
		24000	1000	4500	0.04500	0.01942
		32800	2350	4000	0.09400	0.04056
		43500	1656	9000	0.14900	0.06429
4.	Orthophosphoric acid	13800	1600	3200	0.05120	0.02209



[ε — ν] Graph for multiple bonds of copper phthalocyanine in (a) *p*-xylene (b) chloroform (c) conc. sulphuric acid and (d) *o*-phosphoric acid·

The short wave length band which appears in chloroform (149 nm) and conc. H_2SO_4 (230 nm) have been explained in terms of loss of symmetry due to solute solvent interaction. The former band is more intense and has the highest oscillator strength 0.296·while the latter band has low oscillator strength 0.064. The two bands in the two solvents therefore do not seem to have the same origin.

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