

Studies on polymorphic modifications of copper phthalocyanine

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Abstract

Four α -, β -, γ - and ϵ -polymorphic forms of copper phthalocyanine are synthesized. They are characterized and their properties are compared based on the IR spectral measurements in the finger print region, magnetic susceptibility measurements, ESR study, powder X-ray diffraction and electrical conductivity studies. The data support the existence of all the four polymorphic forms. All the forms are having the monoclinic structure with different crystal lattice constants. The electrical conductivity study in air from 25°C to 200°C for all the four polymorphic modifications are done and their differences may be accounted for difference in interplanar spacing, molecular orientations, intermolecular interactions and mobilities of the charge carriers.

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1. Introduction

Metal phthalocyanines are of great interest for various applications including photovoltaic effect, photoconduction, catalysis, etc. [1–7]. Many of these applications are based on the electrical properties of these materials, and detailed understanding of the same requires an accurate knowledge of molecular as well as crystal structures. Dependence of crystal structure becomes more significant if the compound exists in more than one crystalline modification. Although copper phthalocyanine has been reported to exist in many polymorphic forms, only β -form's crystal structure has been thoroughly studied because it is the most thermodynamically stable compound [1–2,8]. Detailed X-ray analyses of other polymorphs are not studied as it is difficult to get a single crystal in other phases. As a result, the data reported based on powder X-ray diffraction studies are not agreeable [9–13]. Existence of ϵ -form though reported in the literature, the work done on this polymorph is meagre [14]. Magnetic susceptibility measurement on α -, β -, γ - and ϵ -forms of copper phthalocyanine with different magnetic field strengths have not been studied so far. Earlier X-ray diffraction patterns, IR absorption spectra and ESR

studies showed only the existence of α - and β -polymorphs of copper phthalocyanine [15]. Present study involves the synthesis of α -, β -, γ - and ϵ -copper phthalocyanine polymorphs following the reported procedures and characterization of the same using IR spectral, magnetic susceptibility measurements, ESR spectroscopy, powder X-ray diffraction and electrical conductivity measurement [2,14,16].

2. Experimental

2.1. Synthesis of α -, β -, γ - and ϵ -polymorphs of copper phthalocyanine

Copper phthalocyanine was synthesized by adapting the procedures described earlier [1,17]. Copper sulfate pentahydrate (1.05 mol), phthalic anhydride (4.0 mol) and excess of urea with a catalytic quantity of ammonium chloride and ammonium molybdate were finely ground and the mixture was heated at $180 \pm 5^\circ\text{C}$ for 4 h. The resulting product was purified using methanol, hydrochloric acid and sodium hydroxide.

Anal. Calcd. for copper phthalocyanine, $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$: C, 66.72; H, 2.79; N, 19.45; Cu, 11.03. Found: C, 67.20; H, 2.91; N, 19.63; Cu, 11.05.

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2.2. α -Copper phthalocyanine

Pure 1.0 g copper phthalocyanine was dissolved in 50 mL concentrated sulfuric acid and stirred well. It was then poured into 250 mL water slowly drop by drop. The precipitate was filtered and washed with water till the filtrate was acid free. Finally washed with acetone and dried over phosphorus pentoxide [1].

2.3. β -Copper phthalocyanine

A 1.0 g of α -copper phthalocyanine was added to 130 mL *o*-xylene. It was heated on a water bath for 1 h at a temperature of 60°C. It was filtered, washed with acetone and dried over phosphorus pentoxide [1].

2.4. γ -Copper phthalocyanine

A 1.0 g of α -copper phthalocyanine was heated at 60°C for 2 h in 98% sulfuric acid diluted with 22.7 g tetrahydrofuran. The reaction mixture was poured into water. The precipitate was filtered, washed with water until the filtrate was neutral and then dried over phosphorus pentoxide [16].

2.5. ε -Copper phthalocyanine

A mixture of 1.75 g urea, 0.015 g sulfuric acid (92%), 2.0 g pure copper phthalocyanine, 7.5 g sodium chloride, and 0.5 g water was heated at 50–60°C for 18 h. Then 85 mL of water was added, boiled for 1 h, filtered, washed several times with water and dried at 60°C [14].

Carbon, hydrogen and nitrogen analysis were done by the Regional Sophisticated Center, Lucknow. IR spectra were recorded using Shimadzu 8201 PC FT-IR spectrophotometer by Nujol-mull technique. Magnetic susceptibility measurements were done using a Gouy magnetic balance consisting of the type NP-53 electrometer with DC power supply type MP-1053 and a Keroy semimicro balance supplied by Universal Scientific, Bombay, India. Pure $\text{HgCo}(\text{SCN})_4$ was synthesized and used as a calibration standard [18]. The ESR spectra were recorded using a Varian E-109, X-band spectrometer. DPPH was used as a reference standard for *g*-factor measurements. The spectra were recorded in solid state at ambient temperature. A JEOL-JDX-8P X-ray diffractometer was used to study powder X-ray diffraction of the samples. Powdered copper phthalocyanine complexes were compressed into pellets of 1.3 cm and thickness ranging from 0.15 to 0.25 cm under pressure of 500 kg/cm². The Carver laboratory Press Model—diaton capacity was been used for the purpose. Conducting silver paint (ELTECKS preparation No. 1228-C) was coated on both flat surfaces of the pellet and electrical contacts to the samples were made using the same silver paint to the electrodes. The electrical

contacts were checked to verify the ohmic connection and resistance measurements were done from 25°C to 200°C using Milli Ohm Meter digital, Dot 402 and Insulation Resistance Tester Dot 425.

3. Results and discussions

3.1. IR spectral study

IR spectra recorded in the fingerprint region using the Nujol-mull technique are presented in Fig. 1. Absorption peaks observed around 1456, 1377 and 730 cm⁻¹ are due to Nujol. The relevant absorption data along with the possible vibrational transitions are presented in Table 1. The peaks around 1121–1123, 1090–1092, 1067–1070, 947–949, 872–885 and 754 cm⁻¹ are due to phthalocyanine skeletal vibrations [21]. All the polymorphic forms of copper phthalocyanine showed common absorption peaks at 1420–23, 1335, 1286–88, 1202–10, 1165–67, 1001–05, 901, 799–802 and 770–773 cm⁻¹. α , γ and ε polymorphic forms of copper phthalocyanine showed absorption peaks around 1190 cm⁻¹ which is absent in β -form. Similarly, all the forms showed absorption peaks around 957 and 781 cm⁻¹ except the α -form. But this form showed a peak at 941 cm⁻¹. β - and γ -forms showed absorption peaks around 1178 cm⁻¹ which is not shown by the other two forms. Two peaks around 1100 and 980 cm⁻¹ are observed only in the case of β - and ε -forms. Absorption peak at 864 cm⁻¹ is observed by α - and γ -forms only. Additional peaks at 743 and 710 cm⁻¹ are observed by the γ -form of copper phthalocyanine. Thus, the experimental data in IR absorption peaks show sufficient evidence for the existence of the four α -, β -, γ - and ε -polymorphs of copper phthalocyanine. The presently observed data does not agree with the earlier conclusion of having the same structure for the α and γ phases [15].

3.2. Magnetic susceptibility measurements

Magnetic susceptibility properties of α -, β -, γ - and ε -copper phthalocyanine polymorphs have been studied in solid state at ambient temperature and varying magnetic field strengths ranging from 1.02 to 3.58 kG. Magnetic moment values are calculated using the corrected susceptibility data. The experimental data are in agreement with the paramagnetic nature of the complexes. The nature of variation of the magnetic moment values with field strength for all the four polymorphs are presented in Fig. 2 and the data are summarized in Table 2. The variations of magnetic susceptibility values with respect to the magnetic field strengths for α , β and ε are found to be qualitatively similar except for γ -form. Higher or lower values of μ_{eff} indicate the contribution

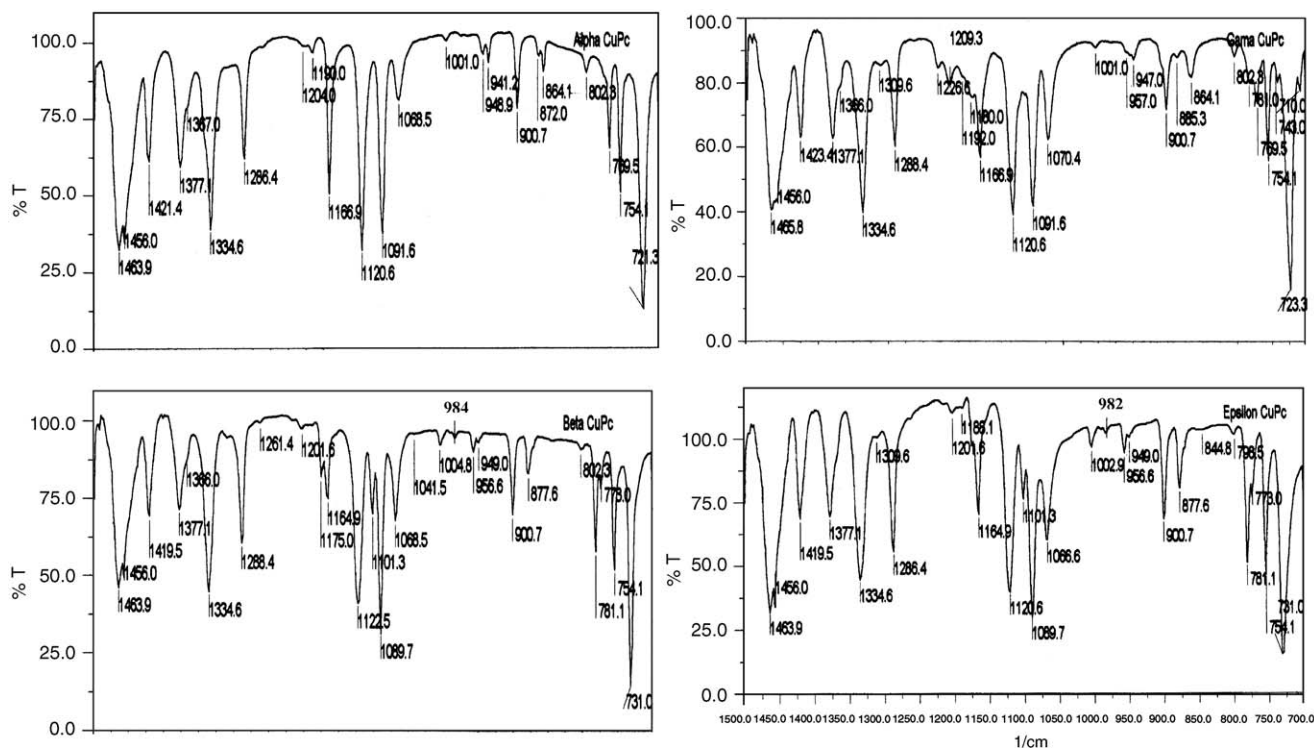


Fig. 1. IR spectra of α -, β -, γ - and ϵ -copper phthalocyanine polymorphic forms in the 'finger print' region.

Table 1

IR spectral data for the four polymorphic forms (α , β , γ and ϵ) of copper phthalocyanine (CuPc)

α -CuPc	β -CuPc	γ -CuPc	ϵ -CuPc	Assignments	
1121	1123	1121	1121	Phthalocyanine skeletal vibrations	
1092	1090	1092	1090		
1069	1069	1070	1067		
949	949	947	949		
872	878	885	878		
754	754	754	754		
1421	1420	1423	1420		Aromatic phenyl ring
1335	1335	1335	1335		C–N = stretch
1286	1288	1288	1286		
—	1226	1227	1227		
1204	1202	1210	1202		
1190	—	1192	1188	C–H in-plane bending	
—	1175	1180	—		
1167	1165	1167	1165		
—	1101	—	1101		
1001	1005	1001	1003	C–N = bending	
—	984	—	982		
—	957	957	957		
941	—	—	—		
901	901	901	901	C–H out-of-plane bending	
864	—	864	—		
802	802	802	799		
—	781	781	781		
770	773	770	773	C–H out-of-plane bending	
—	—	743	—		
—	—	710	—		

of direct or super exchange intermolecular interaction to spin only value μ_s [19,20]. In addition, magnetic anisotropy which is about 15 times greater than benzene may also play an important role [21]. The room temperature observed magnetic moment values are above the spin only value of $1.73 \mu_B$ for the three polymorphs except in the case of γ -copper phthalocyanine. The magnetic moment values in all cases found to decrease with increasing field strength, which may be due to the intermolecular effect [17]. Differences in magnetic moment values and their variations may be due to the difference in intermolecular interactions which in turn may be due to the differences in spacing and inclination of the molecules in the crystal lattices.

3.3. ESR spectral study

ESR spectra of the four polymorphs are presented in Fig. 3. The data are in agreement with the magnetic susceptibility measurements regarding the paramagnetic nature of the compounds. The ESR signal observed is due to $-1/2g\beta H$ to $+1/2g\beta H$ transition, where g is the Lande, or spectroscopic splitting factor, β is the electron Bohr magneton and H is the applied magnetic field [21]. This single energy transition signal is modified with the axially symmetric copper phthalocyanine which has D_{4h} symmetry. The spectra observed for the polycrystalline

Table 2
Magnetic susceptibility, ESR, X-ray and electrical conductivity data.

Compound	Magnetic susceptibility		ESR		Electrical conductivity for freshly prepared pellet (Ω/cm)		X-ray lattice constants a , b , c (\AA), β (deg) and volume (\AA^3) ³
	Field strength (kG)	μ_{eff} (BM)	g_{\parallel}	g_{\perp}	25°C	200°C	
α -CuPc	1.02	1.8047	2.1008	2.0067	9.43×10^{-9}	7.83×10^{-8}	$a = 21.7201$ $b = 3.2841$ $c = 15.4382$ $\beta = 107.445$ $V = 1050.57$
	1.92	1.6903					
	2.81	1.6289					
	3.58	1.6202					
β -CuPc	1.02	1.8497	2.0783	2.0074	4.80×10^{-9}	9.35×10^{-7}	$a = 21.8222$ $b = 4.6942$ $c = 13.4934$ $\beta = 123.477$ $V = 1152.92$
	1.92	1.7088					
	2.81	1.6175					
	3.58	1.5599					
γ -CuPc	1.02	1.7083	2.0563	2.0049	3.34×10^{-7}	2.29×10^{-7}	$a = 17.3878$ $b = 8.6483$ $c = 11.074$ $\beta = 113.56$ $V = 1526.44$
	1.92	1.5896					
	2.81	1.4593					
	3.58	1.3308					
ε -CuPc	1.02	1.8095	2.0953	2.0049	4.91×10^{-12}	3.78×10^{-9}	$a = 26.5912$ $b = 2.5903$ $c = 20.2249$ $\beta = 124.352$ $V = 1150.13$
	1.92	1.7019					
	2.81	1.6140					
	3.58	1.5810					

Note: CuPc = copper phthalocyanine.

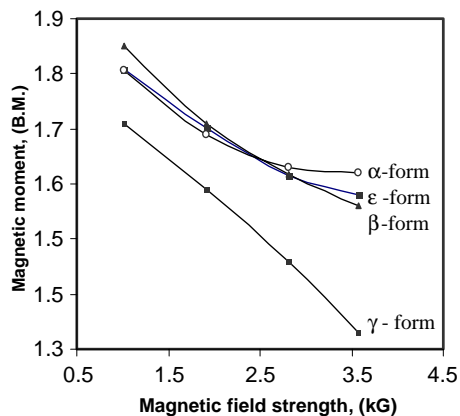


Fig. 2. Variations of magnetic moments of the four polymorphs of copper phthalocyanine with magnetic field strength (kG).

powder copper phthalocyanine are expected due to the sum of the contributions from all orientations of the molecule, electron–electron dipole interactions and exchange effects. The g_{\parallel} and g_{\perp} values are reported in Table 2. ESR analytical data showed $G[(g_{\parallel} - 2)/(g_{\perp} - 2)]$ greater than 4, indicating the presence of unpaired electron in $d_{x^2-y^2}$ ground state [19,20]. In an ideal case for copper phthalocyanine, the unpaired copper $d_{x^2-y^2}$ electron which resides in a D_{4h} symmetry interacts with its own nucleus of spin 3/2 and each of its 4 liganding nitrogen nuclei of spin 1. So, 36 discrete transition signals with the intensity ratio 1:4:10:16:19:16:10:4:1 for each of 4 subsets are expected.

But all the ESR spectral signals for the four polymorphs of copper phthalocyanine showed with partial resolution and overlapping of the hyperfine structure due to copper atom and superfine structures due to the 4 nitrogen atoms (Fig. 3).

3.4. X-ray diffraction study

Powder X-ray diffraction spectra of α -, β -, γ - and ε -polymorphs of copper phthalocyanine are obtained using Cu $K\alpha$ radiation ($\lambda = 1.934 \text{\AA}$). The 2θ values are noted down for all the polymorphic forms and analyzed for the possible crystal structure of the compounds using the procedure DICVOL 91 as outlined elsewhere [22,23]. The lattice constants obtained and the probable crystal structures are given in Table 2. A single crystal structure and the cell parameters are well established for the most stable β -form by the earlier workers which are quite comparable with the analytical data obtained in the present work for the powder sample. This supports the analytical accuracy of the method used. The crystal data reported for α - and γ -forms by the earlier workers are not agreeable to one another [9–13]. This work indicates that all the polymorphic forms are having the monoclinic structure. The data supports the existence of the four polymorphic forms for copper phthalocyanine. However, the difference in room temperature electrical conductivity of the four polymorphic forms cannot be explained based on the crystal lattice constants alone as other factors like

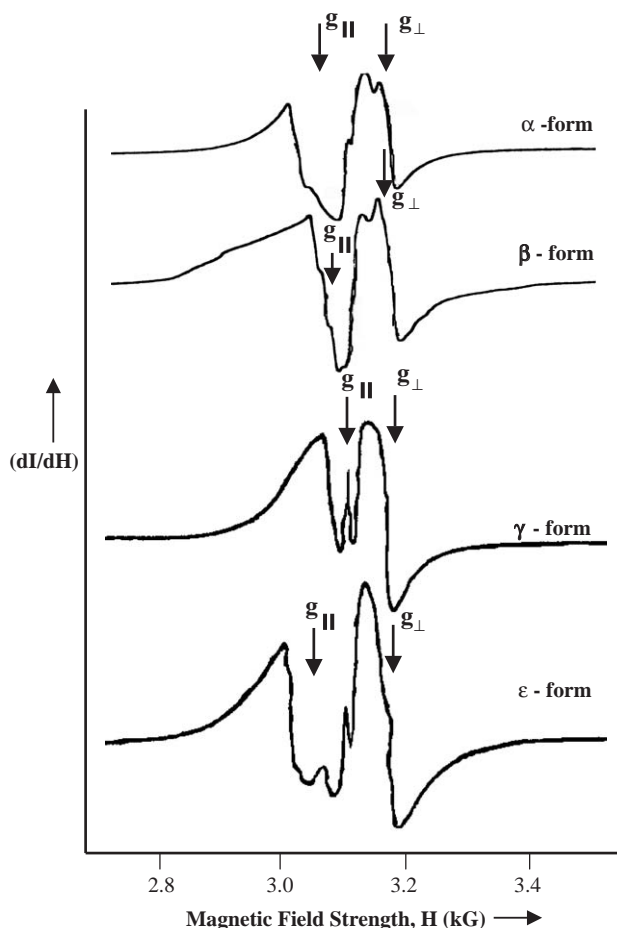


Fig. 3. ESR spectra of four polymorphs of copper phthalocyanine at ambient temperature.

intermolecular distance, molecular orientations and charge mobilities influence the property of electrical conductivity.

3.5. Electrical conductivity study

The literature data available with respect to electrical conductivity study for the α -, β -, γ - and ϵ -polymorphs of copper phthalocyanine is meagre. The structure of stable β -form have been thoroughly analyzed by the Robertson and co-workers [1–2,8,11]. The structures of other forms are not studied thoroughly because of the failure in getting single crystals for other polymorphic forms so far. Though the effect of crystal phase change from α to β on electrical properties of copper phthalocyanine studied earlier, the results are not entirely in agreement [24,25]. Yoshiro Sakai et al. [25] studied the frequency and temperature dependence of electrical conductivity as well as capacitance of α - and β -phase copper phthalocyanine thin films. They studied the electrical conductivity in the temperature range from 13°C to 130°C in vacuum, hydrogen atmosphere and oxygen

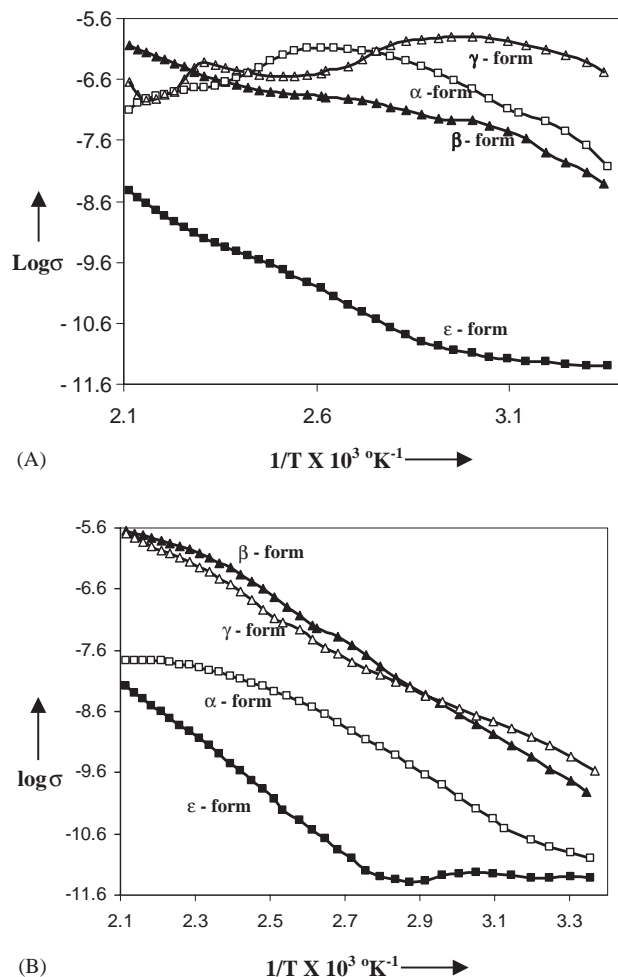


Fig. 4. (A) Variations of electrical conductivity for freshly prepared pellets of the four different polymorphs of copper phthalocyanine. (B) Variations of electrical conductivity for the four different polymorphs after heat treatment.

atmosphere. Harrison and Ludewig [24] studied the temperature dependence of electrical conductivity of α - and β -phase copper phthalocyanine in hydrogen, nitrogen and oxygen atmospheres. Present work deals with the measurements of electrical conductivity for freshly prepared four polymorphic polymorphs in the temperature range 25–200°C in the air atmosphere. The plots of the data $\log \sigma$ versus $1/T \times 10^3 \text{ K}^{-1}$ are presented in Fig. 4. Variation of the electrical conductivity with temperature for the freshly prepared samples are presented in Fig. 4A. In Fig. 4B, the plots represents the variations in electrical conductivities of the four phases obtained after repetition of the electrical conductivity measurements done for the freshly prepared pellets. At 25°C, electrical conductivities of the freshly prepared pellets are in the order $\gamma > \alpha > \beta > \epsilon$. In 200°C, the order of electrical conductivities obtained is $\beta > \gamma > \alpha > \epsilon$, Table 2. The data indicate that electrical conductivity at room temperature as well as their variations with temperature up to 200°C are different

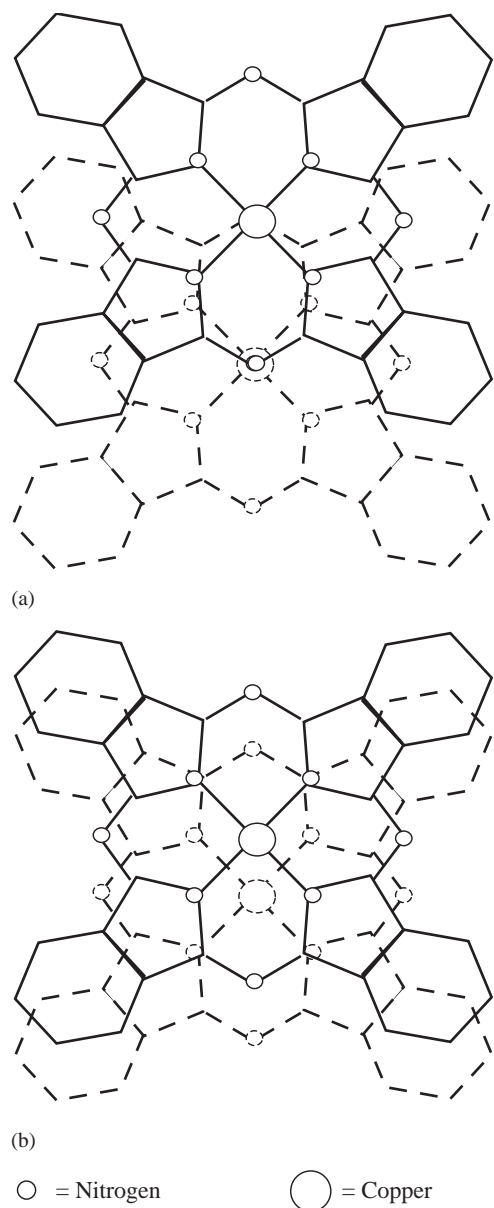


Fig. 5. Molecular stackings of copper phthalocyanine (A) β -copper phthalocyanine and (B) in other polymorphic forms of copper phthalocyanine.

for different polymorphic forms. These variations are found to be more or less same for the β - and γ -forms after the heat treatment, whereas they are different for α - and ε -forms. Further marked differences in the variations of electrical properties with temperature are observed in the case of α and γ phases before and after the heat treatment.

Semiconducting property and the differences in the electrical conductivity of the four polymorphs can be accounted for the differences in the interaction of the highly conjugated π -electrons between the molecules, intermolecular spacing and the nature of the molecular stacking along the ' b '-axis. Among the four polymorphs,

β -form is the most stable which can be crystallized. X-ray crystallographic studies showed that β -copper phthalocyanine crystallizes in the monoclinic lattice and the nearest neighbor molecules along the ' b '-axis contribute a nitrogen atom at the distance of around 3.38 Å, one above and one below the central metal, Fig. 5(A) [1–2,8,11,26]. Other polymorphs which cannot be crystallized appear to have monoclinic lattices as per the data of the present investigation and can be presumed no nitrogen atoms of neighboring molecules situated right over and under the central copper atom, Fig. 5(B). Semiconducting property and the differences in the electrical conductivity may be due to the differences in stacking arrangement of the copper phthalocyanine molecule along the ' b '-axis. This difference in the arrangement may result in altering the interactions of conjugated π -electrons between the different molecules, which may effect the electrical conductivity of the polymorphs [11]. In addition copper phthalocyanine is electron donor in nature and the presence of oxygen in the atmosphere may also alter the electrical conductivity of copper phthalocyanine [27–29]. Also some irregular changes in electrical conducting properties with temperature observed in the case of α and γ polymorphs may be due to the presence of absorbed oxygen molecule and water content.

4. Conclusions

The four α -, β -, γ - and ε -forms of copper phthalocyanine polymorphs are synthesized based on the literature procedures. Literature survey indicated confusions regarding the existence of all the four polymorphs and the data are not agreeable from one worker to another. The above four forms are studied systematically by characterizing them using IR spectra, magnetic susceptibility measurements, ESR, X-ray diffraction and electrical conductivity measurement studies. The differences in the results observed in above physical measurements for each form supported the existence of all the four polymorphs of copper phthalocyanine.

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