Preparation of some soluble Shiff- bases derived from zinc phthalocynine compounds

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Abstract

A shiff- base of aminophthalocynine with benzaldehyde and p-methyl benzaldehyde were prepared and characterized spectroscopecally. Their electrical properties were also studied. The study shows that the conductivities of the shiff- bases are less then that of aminophthalocynines.

Key words: peripheral substituted zinc phthalocynine, Shiff- bases, electrical conductivity.

Introduction

Peripherally unsubstituted phthalocynine are practically insoluble in common organic solvents. The introduction of bulky substitutents in the peripheral position of the macrocycle drastically increases their solubility in organic solvents ⁽¹⁾ which extend actual and potential field of their technology.

Tetra and octa substituted phthalocynines⁽²⁾ have been intensively studied which show that tetra substituted macrocycle exhibit a higher solubility than octasubstituted derivative⁽³⁾.

The spectral and electrochemical properties of phthalocynines are strongly influenced by peripheral substitutents on the macrocycles. Recent studies show interesting optical and electrochemical properties $^{(4, 5)}$.

We report here for the first time the synthesis of tetra substituted shiff-bases of tetra aminophthalocynines with benzaldehyde and p-methyl benzaldehyde which show some interesting properties with high solubility compared to phthalocynines with unsubstituted.

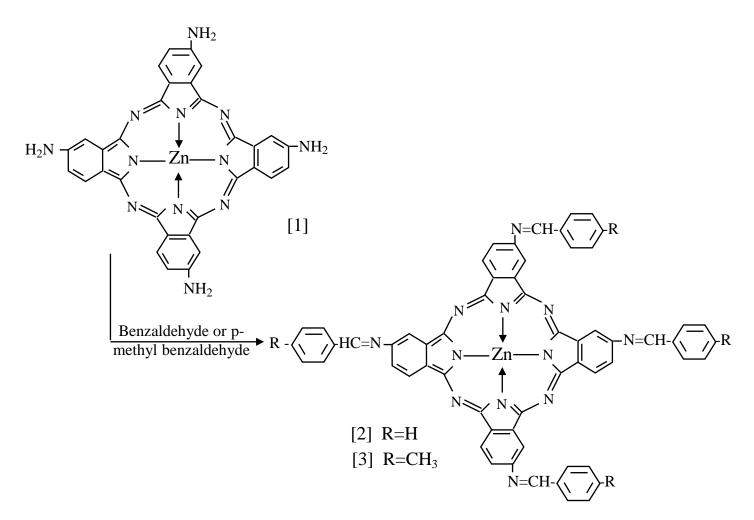
The soluble phthalocynines have an important practical electrical applications, since they are easily purified and processed ⁽⁶⁾.

Experimental

The shiff bases (4-Ph CH=N)₄ Pc Zn [2] and (4-P-CH₃Ph CH=N)₄ Pc Zn [3] were prepared according the reaction of $(4-NH_2)_4$ Pc Zn $.2H_2O$ [1] with benzaldehyde and p-methyl benzaldehyde respectivly. Compound [1] was prepared according to the references (5,7) C.H.N. analysis (calcld; C: 57.05, N: 24.96, H: 3.56; found C: 56.71, N: 25.72, H: 3.01). Compounds [2] & [3] were prepared as follows: 1gm (0.0015 mole) of compound [1] was refluxed with 15 ml(excess) of benzaldehyde or p-methyl benzaldehyde respectively for 3 hours, then the product was cooled and poured in to cold water, filtered and recrystallised from ethanol, the products were 0.91 g (65%) from compound [2] or 0.94g (62%) from compound [3], they are both polycrystalline greenish-yellow compounds.

The compounds were then characterized by I.R. spectroscopy using FT.IR.8400 S from Shimadzu Company and by U.V./visible spectroscopy using Cintra 5 U.V./visible spectrometer.

The electrical properties were studied using the D.C.electric circuit as in references (5,7) under vacuum of 1×10^{-3} Tore and at temperature range of (283 – 373 Kelvin).



Result & Discussion

The I.R. spectrum of the compound [1] shows the characteristic appearance as in reference (5, 7). The spectrum shows also the N-H streching vibration at 3305 cm⁻¹ and 3320 cm⁻¹ (W) (sym and assym) ,C=C and C= N streching at 1490 cm⁻¹ and 1600 cm⁻¹ respectively,C-N stretching at 1228 cm⁻¹ ,C-H aromatic bending at 1145 cm⁻¹ and 775 cm⁻¹.

The U.V. – visible spectum of compound [1] in DMSO shows the characteristic bands as in the previous references with Q- band at 736nm and B-band at 360nm $^{(6)}$.

The IR spectra of the new compounds shows the new aliphatic C-H streching at 2900- 2800 cm^{-1} (fig. 1).

The U.V. – visible spectra in DMSO show the disappearance of the Q- bands from their positions in the measured rang with an appearance of a band at 404 nm and 400 nm for

compounds [2] and [3] respectively (fig. 2). This strange behaviors has also been found in Mn(II) and UO₂ phthalocynines compounds where the Q-bands appear near I.R. at around 830- 880 nm $^{(8)}$.

The Shiff bases have higher decomposition temperatures (>350 C) than the amino compound, where the amino compound started to decompose before the Shiff base compounds.

In addition they show a good solubility in many solvents such as ethanol, methanol which is an important property for purification and application purposes as semiconductors.

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The electrical properties of the prepared compounds (fig.3) show the D.C. conductivity (σ) sequence as follows:

$$\sigma$$
 [1] > σ [3] > σ [2].

The low conductivity of the Shiff bases [2] & [3] is compared to the amino compound may be due to the presence of the big side substituted groups which reduce the packing efficiency of the phthalocynine ring which then reduce the crystallization of the compounds $^{(6)}$.

The higher conductivity of the compound [3] in compared to the compound [2] is due to the presence of the donor CH_3 group, which increase the electron density on the phthalocynine ring ^(6,9).

Fig: (1) I.R. spectrum of compound [3]

Fig: (2) UV – visible spectrum of compounds [1] and [2]

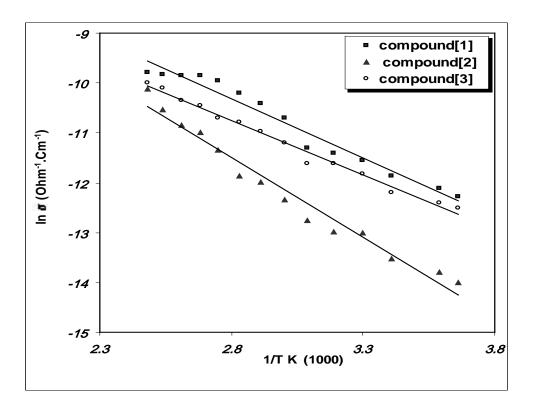


Fig: (3) D.C.conductivity of compounds [1],[2] and[3]

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تحضير بعض قواعد شف الذائبة والمشتقة من مركبات فثالوسيانين الزنك

نزار عبد الأمير حسين ، داوود سالم عبد ، رافد حميدان الاسدي *فزلطه قي ليد؟ أقي بطهة ظي بـ جة لع بطها* شنب - *طها* شنب - *طه حق*

<u>ىلى خېر شدې:</u>

حضرت قواعد شف من مركبات الفثالوسيانين الأمينية مع البنزلديهايد والبارا-مثيل بنزلديهايد وشخصت طيفياً درست الصفات الكهربائية لقواعد شف ووجد إن توصيليتها اقل من مركبات الفثالوسياتين الأمينية. Preparation of some soluble Shiff- bases derived...

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