Synthesis of Some New Copper Phthalocyanine-3-Acid Amides

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Abstract:

A number of copper phthalocyanine 3-acid amides were synthesized by treating aminoacid chlorides with copper 3,3`,3``,3```-tetra aminophthalocyanine. The synthesized compounds were confirmed by physical and spectroscopic analysis.

Introduction:

Various approaches to the synthesis of copper phthalocyanine were reported in the literature, some of which were the fusion of phthalonitrile with copper or its salts[1] in the presence of ammonium molybdate as catalyst, fusion of phthalic anhydride or phthalic acid with urea and copper or copper salts[2]. Development[3,4] in the previous two methods to synthesize substituted copper phthalocyanine were reported too.

Copper phthalocyanine or its derivatives is the most stable compounds in the series of metal phthalocyanine and plays an important role in the field of dyes and pigments[5], and it undergoes two type of reactions, the first is the direct nuceophilic substitution reaction[6], such as halogenation, sulphonation at position three. The second is the indirect method which can furnish copper phthalocyanine derivatives with different groups such as (halo, alkyl and nitro derivatives). This method is carried out by the fusion of the corresponding phthalic anhydride derivatives with urea and copper or its salts.

According to the above facts an approach to the synthesis of new copper phthalocyanine acid amides was adopted depending on preparing the copper 3,3`,3``,3```-tetra aminophthalocyanine using the second method by fusion 3-nitrophthalic anhydride with urea and copper chloride in the presence of ammonium molybdate as catalyst.

In present paper copper 3,3`,3``,3```-tetra nitro phthalocyanine was prepared by the fusion of 3-nitro phthalic anhydride with urea and copper chloride in the presence of ammonium molybdate as catalyst. The obtained product was then reduced with sodium polysulphide in aqueous solution to give 3,3`,3``,3```-tetra aminophthalocyanine which was treated with different amino acid chlorides[7,8] in a basic medium. Six new different copper phthalocyanine acid amides were synthesized and characterized.

Experimental:

Uncorrected melting points were determined using Galknkamp melting point apparatus. I.R. spectra were recorded by using Py-Unicam SP 1100 spectrophotometer as KBr disc. U.V. visible spectra were performed on double beam Shimadzu UV-160 (U.V. visible) spectrophotometer. Theoretical physical calculation and three dimensional (3D) configuration were pointed out using “Chem Office” program-version 7 and MOPAC method.

Synthesis of 3-nitro phthalic acid (I):

Phthalic anhydride (3.7 gm, 0.025 mole) and nitric acid (3.5 ml, 0.025 mole) were placed in flask. Sulfuric acid (3.5 gm, 0.025 mole) was added slowly to the reaction mixture with vigorous stirring. After the addition, the reaction mixture was heated on steam bath for (3 h) then cooled and poured into water (100 ml), filtered and washed with water to obtain solid material. The crude solid was mixed with benzene (60 ml) and distilled until the distillate was no longer turbid. After filtering the crude yellow residue was dissolved in acetic acid. On cooling the precipitate was filtered off and recrystallized from acetic acid to give 3-nitrophthalic acid (3.1 gm, 58%). m.p. = 207-209 (Lit.[9] = 213 ^{o}C).

I.R (KBr disk) ν cm^{-1} 3220 broad, 1740, 1612, 1590, 1355, 800 cm^{-1}.

Synthesis of 3-nitrophthalic anhydride (II):

3-Nitrophthalic acid (21 gm, 0.1 mole) and acetic anhydride (20 ml) were heated until the solid was dissolved. The clear solution was refluxed for (1 hr.) and poured into porcelain dish to cool. The solid was grounded, filtered and ether was added, this process was then repeated. The product was filtered, dried to give pale yellow crystals (17 gm, 88%). m.p. = 160-162 (Lit.[10] = 163-164 °C).

I.R (KBr disk) ν cm^{-1} 3015, 1750, 1250, 1160, 920 cm^{-1}

Synthesis of copper 3,3`,3``,3```-tetra nitrophthalocyanine[2] (III):

(13 gm, 0.067 mole) of 3-nitrophthalic anhydride was mixed with (3.8 gm, 0.067 mole) urea, (2.24 gm) copper chloride and (6.5 gm) of ammonium molybdate, then (30 ml) of nitrobenzene was added. the reaction mixture was heated with stirring at (170-180 °C) until it became solid mass with blue green colour, when the temperature arised to 200-210 °C, the colour became blue. After cooling the mixture mass was treated with (100 ml) 0.2 N hydrochloric acid was stirred for ½ hr. The product separated and washed with ethanol several times to give (III) (9.6 gm, 83%). m.p. > 300 °C (Lit.[2] m.p. > 300 °C).

I.R (KBr disk) ν cm^{-1} 1532 (NO_2 asym, stre.)[11], 1355 (NO_2 symm, stre.)

Synthesis of copper 3,3`,3``,3```-tetra aminophthalocyanine[2] (IV):

(100 ml) water was added to (6.5 gm, 0.38 mole) copper 3,3`,3``,3```-tetra nitrophthalocyanine (III) in round bottom flask with mechanical stirrer, condenser and separating funnel containing fresh solution of sodium poly sulphide. The reaction mixture was heated until boiling, with stirring. Sodium polysulphide solution was added dropwise for (45 min.), the stirring was continue for (5 hr.). After cooling, the precipitate was washed with cold water, and boiled with (10 ml) 2 N hydrochloric acid for (15 min.). The solution was cooled and excess conc. ammonium hydroxide was added. The product was filtered, washed with ammonia solution and dried gave (IV). (10.5 gm, 94%), m.p. > 300 °C (Li.[2] m.p. > 300 °C).

I.R (KBr disk) ν cm^{-1} 3380 (NH_2, str), 1618 (NH_2 def, 1330 cm^{-1} C-N str.)

Synthesis of phthaloyl amino acids$^{(7)}$ (Va-f):

A mixture of (0.06 mole) of appropriate amino acid and (0.06 mole) of finely grounded phthalic anhydride was heated for (30 min.), with stirring in an oil bath at 145-150 °C. After cooling, the solid material was dissolve in (40 ml) of hot methanol, the filtrate solution was diluted with (40 ml) of water, and the product allowed to crystallize slowly. For physical and spectra data see Table (1).

Table (1): Physical and spectroscopic data of phthaloyl amino acid (Va-f)

Comp. V	m.p. °C	Yield %	Formula	I.R. KBr ν cm^{-1}			U.V. (EtOH) λ_{max} (nm)
				C=O amide	C=O acid	OH	
a	182-184	65	$C_{10}H_7NO_4$	1680	1715	3340	296, 242, 215
b	176-178	61	$C_{11}H_9NO_4$	1685	1710	3400	298, 250, 232
c	84-86	73	$C_{13}H_{12}NO_4$	1675	1715	3350	292, 253, 225
d	96-98	64	$C_{14}H_{15}NO_4$	1670	1720	3400	292, 249, 220
e	200-202	70	$C_{14}H_{15}NO_4$	1680	1715	3380	294, 243, 215
f	160-164	75	$C_{18}H_{15}NO_4$	1670	1720	3375	298, 232, 225

Synthesis of phthaloly amino acid chloride (VIa-f):

A mixture of phthaloyl amino acid (Va-f) (0.05 mole) and thionyl chloride (25 ml) was placed in a round bottomed flask equipped with a condenser. After heating under reflux on a hot plate for (4 hr.), the excess of thionyl chloride was removed by distillation. The residue which was concentrated to give the pthaloyl amino acid chloride. For physical and spectral data see Table (2).

Table (2): Physical and spectroscopic data of phthaloyl amino acids chloride (VIa-f)

Comp. VI	m.p. °C	Yield %	Formula	I.R. KBr ν cm^{-1}		U.V. (EtOH) λ_{max} (nm)
				C=O amide	C=O acid	
a	154-156	75	$C_{10}H_6ClNO_3$	1675	1720	294, 278, 242
b	162-165	62	$C_{11}H_8ClNO_3$	1680	1725	293, 274, 253
c	212-218	70	$C_{13}H_{11}ClNO_3$	1670	1730	298, 250, 214
d	191-193	64	$C_{14}H_{14}ClNO_3$	1675 1670	1715 1722	292, 258, 235 293, 240, 225
e	168-171	71	$C_{14}H_{14}ClNO_3$	1680	1725	298, 274, 253
f	91-93	73	$C_{18}H_{14}ClNO_3$	1674	1715	292, 270, 210

Synthesis of copper 3,3`,3``,3```-tetra aminophthalocyanine amino acid (VIIa-f):

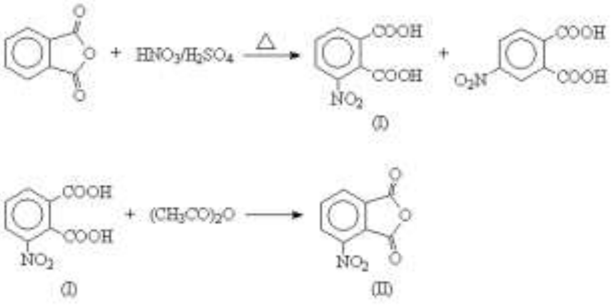
(0.03 mole) phthaloyl amino acid chloride was added to a solution of (2 gm, 0.03 mole) copper 3,3`,3``,3```-tetra aminophthalo-cyanine (V) in (15 ml) pyridine, the mixture was refluxed for (2 hr.) at 40-50 °C with stirring. After cooling the precipitate was filtered, dried. (0.01 mole) of the crude product was dissolved in (50 ml) ethanol and (0.1 mole) of hydrazine hydrate was added and the reaction mixture was refluxed for (3 hr.). After cooling the precipitate was washed with ethanol and water, recrystallized from ethyl acetate to give (VIIa-f). For physical and spectral data see Table (3).

Table (3): Physical properties and spectral data of compounds (VIIa-f)

Comp. VII	Colour	m.p. °C	Yield %	I.R. ν cm^{-1} KBr		U.V (EtOH) λ_{max} nm
				N-H	C=O	
a	Blue	> 300	89	3330	1675	620, 581, 214
b	Green-blue	> 300	85	3479	1671	635, 275, 215
c	Green	> 300	91	3420	1676	630, 410, 214
d	Blue	> 300	82	3510	1680	660, 280, 220
e	Green	> 300	29	3480	1680	640, 230, 215
f	Green	> 300	90	3500	1679	680, 228, 225

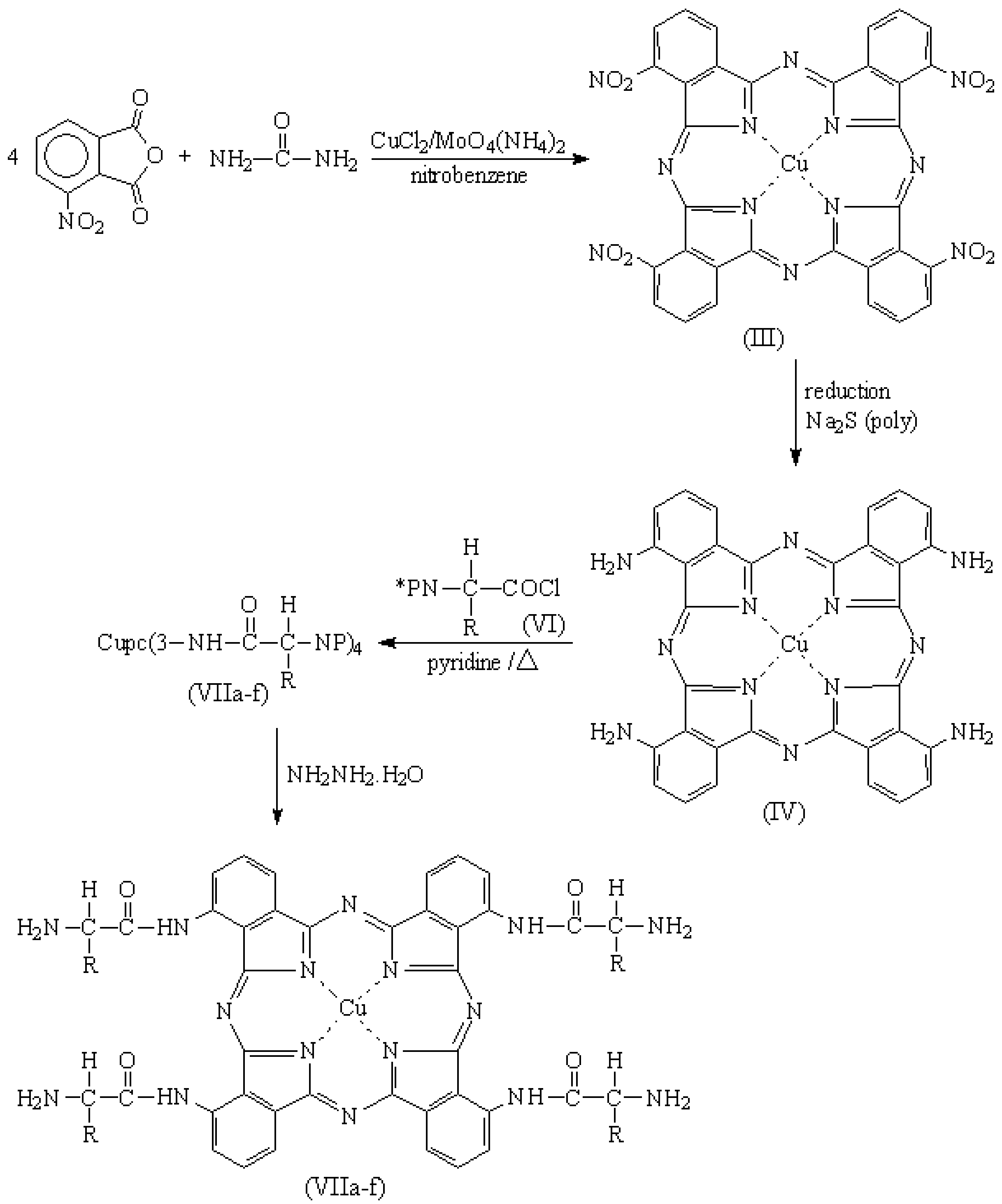
Results And Discussion:

Following the reaction sequence shown in Scheme (I). 3-Nitro phthalic anhydride (II) was prepared by the reaction of the isomer 3-nitro phthalic acid (I) with acetic anhydride[10]. Isomer (I) was prepared and isolated according to published method[11].



Scheme (I)

Compound (III) was prepared by the fusion of four moles of 3-nitro phthalic anhydride (II) with urea and one mole of copper chloride in a solvent have high boiling point such as nitrobenzene[12] in the presence of catalyst. Reduction of (III) with sodium poly sulphide gave (IV) in very high yield (Scheme II).



R

a = $-H$

b = $-CH_3$

c = $-CH(CH_3)_2$

d = $-CH_2CH_2CH(CH_3)_2$

e = $-CH(CH_3)(CH_3CH_2)$

f = $PhCH_2CH-$

*P = protecting group (phthalic anhydride)

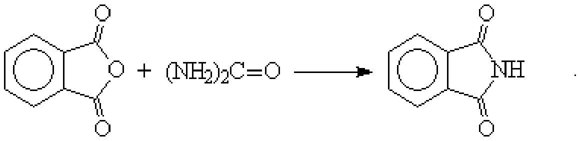
Cupc = copper phthalocyanine

Scheme (II)

The formation of compound (III) was expected to proceed through many stages.

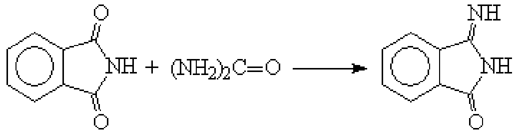
The urea used give 3 molecules of ammonia, this react with one molecule of phthalic anhydride as follows[2]:

Stage one: is the formation of phthalimide



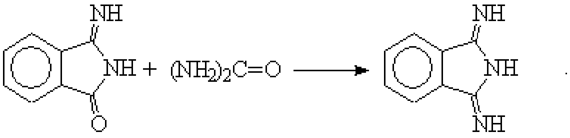
. (1)

Stage two: is the formation of 1-keto-3-imino-isoindole



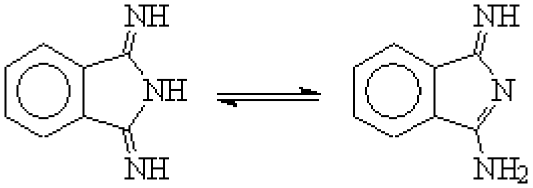
. (2)

Stage three: is the formation of diiminosioindoline by reacting 1-keto-3-iminoisoindole with another molecule of
urea.



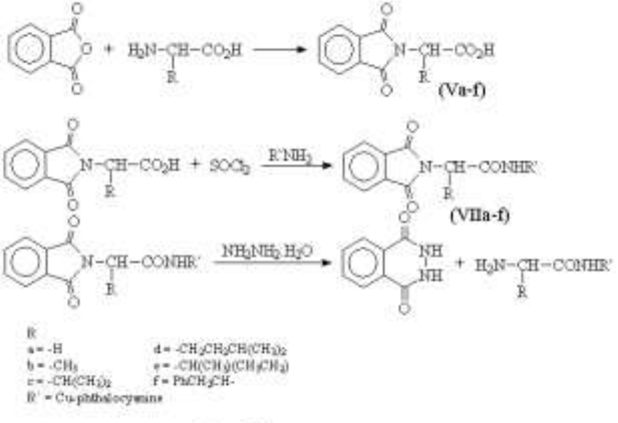
. (3)

The diimino product is in equilibrium with 1-amino-3-iminoisoindoline as shown below:



Reduction of the nitro groups in compound (III) using sodium poly sulfide gave a bright blue crystals with green shade the corresponding amino derivative (IV) (Scheme II).

Fusion of appropriate amino acid with phthalic anhydride afforded the corresponding phthaloyl amino acid (Va-f) Scheme (III).



Scheme (III)

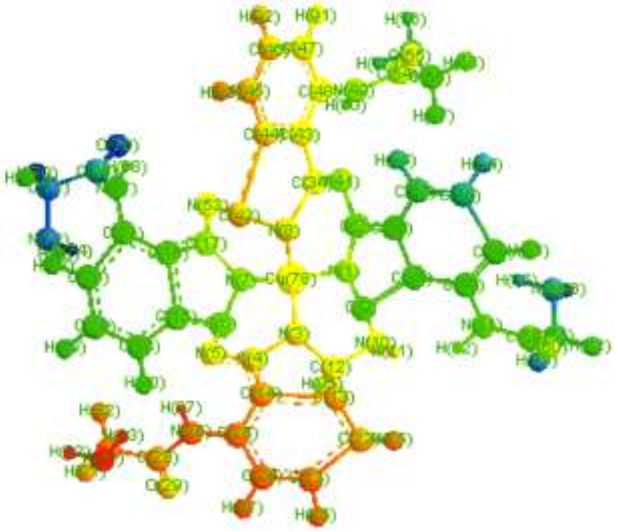
The structure of the prepared compounds (Va-f) have been characterized by their I.R. and U.V. spectra. I.R. spectra (Table 1) showed two bands at (1670-1685 cm^{-1}), (1710-1720 cm^{-1}) and (3340-3400 cm^{-1}) belong to the presence of C=O amide, C=O acid and OH respectively. The U.V. spectra showed λ_{max} (215-298 nm).

Treatment of phthaloyl amino acid (Va-f) with thionyl chloride gave the corresponding phthaloyl amino acid chloride (VIa-f).

The prepared compounds have been characterized by their I.R. and U.V. spectra (Table 2). I.R. spectra showed two absorption bands at (1670-1680 cm^{-1}) and (1715-1730 cm^{-1}) attributed to the presence of C=O amide and C=O acid and the absence of OH band. The U.V. spectra showed λ_{max} (210-298 nm).

Condensation of compound (IV) with compounds (VIa-f) in the presence of pyridine at elevated temperature afforded an crude which treated with hydrazine hydrate in ethanol in order to remove the protecting group from the compounds to afford the final products (VIIa-f) Scheme (II).

The synthesized compounds (VIIa-f) have been characterized by their physical and spectral data I.R. and U.V. (Table 3). I.R. spectra showed absorption band at (3330-3510 cm^{-1}) corresponding to NH_2 stretching and one band at (1675-1680 cm^{-1}) due to C=O amide stretching vibration. The prepared compounds contain some functional groups that increase the polarization of the molecule which lead to increase its absorption at visible region and this was noticed in the U.V spectra between (620-680 nm) due to different R groups which lead to change in colour.Further information about the isolated products (VII) was obtained from theoretical calculation and 3D-configuration which was shown in Figure 1.



Steric energy = 26.33 Kcal/mole
Heat of formation = 260.033 Kcal/mole

Figure (1): 3D-structure of compound (V)

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تحضير عدد من اميدات الحامض لصبغة الفثالوسيانين النحاسية المعوضة في الموقع ٣

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الملخص:

تم تحضير عدد من مركبات اميدات الاحماض لصبغة الفثالوسيانين النحاسية المعوضة في الموقع -٣- وذلك بمعاملة كلوريدات الاحماض الامينية مع 3,3`,3``,3```-رباعي امين فثالوسيانين. وقد تم تشخيص النواتج باستخدام الطرق الفيزيائية والطيفية المتوافرة.