

Synthesis and characterization of some new Nitrones derived from phthalocyanine compounds

Nesreen N.Majeed , Abbas.F.Abbas , Adil A.Al-Fregi

Chemistry Department , Collage of Science , University of Basrah , Basrah , Iraq

(Received: 28 / 12 / 2011 ---- Accepted: 13 / 3 / 2012)

Abstract

Five novel nitrones driven from 4,4',4'',4'''-tetrakis nitro copper phthalocyanine have been prepared by the treatment of 4,4',4'',4'''-tetrakis n-hydroxylamine copper phthalocyanine with benzaldehyde derivatives, These compounds have been characterized by FT-IR, UV-Visible, elemental analysis (C.H.N.) and ¹H NMR spectroscopy.

1. Introduction

One of the most thermally stable systems of coordination complexes known is the metallo phthalocyanines family⁽¹⁾. Various attempts have been made to prepare metallo phthalocyanines and its analogues complexes with several metals such as copper and iron^(2,3), there is another method which might be easier by the reaction of phthalic anhydride or its analogues with excess of urea in presence of ammonium chloride and ammonium molybdate hydrate⁽⁴⁻⁵⁾. The metals reported in these complexes are cobalt, copper, chromium and iron, but up to date platinum phthalocyanine complexes have not been reported⁽⁶⁻⁸⁾.

Metallo phthalocyanine and their analogues have been investigated in detail for many years, especially with regard to their properties as dyestuffs, pigments and paints. In the last decade phthalocyanine and metallo phthalocyanine exhibit singular and unconventional physical properties interesting for applications in materials science⁽⁹⁻¹¹⁾. Thus, in addition to basic research, the interest in phthalocyanines and metallo phthalocyanines have been recently expanding among others into applied fields such as photovoltaics, optical data storage, laser dyes, liquid crystals, chemical sensors and photosensitizers for photodynamic therapy⁽¹¹⁻¹³⁾.

From their early discovery until the present time, nitrones were quite versatile intermediates in organic synthesis and have proved to be very useful tools in the construction of structurally complex molecules, usually allowing a high degree of diastereocontrol^(14,15); for instance, they are employed in stereoselective formation of synthetically useful isoxazolidines by their 1,3-dipolar cycloaddition with alkene⁽¹⁶⁾. In addition, the alkylation of nitrones by organometallic reagents has been extensively developed and has become a reliable synthetic procedure^(17,18).

They are also used in the synthesis of many-nitrogen-containing biologically active compounds⁽¹⁹⁾. Also, some nitrones have been used for the trapping and identification of free radicals, particularly in biological studies⁽²⁰⁻²²⁾.

2. Experimental methods

2.1 General:

Melting points were uncorrected. NMR spectra were acquired with a Bruker Ultra Shield (¹H : 300 MHz) (University of AL-al-Bayt, Jordan). The chemical

shifts were referenced to tetra methyl silane (TMS) as an internal standard. The elemental analysis (C.H.N.) were performed by using Euro Vector EA3000A (University of AL-al-Bayt, Jordan). The FT-IR spectra were performed by using FT-IR-SHIMADZU for the region between (400-4000) cm⁻¹. A double beam scan 80D was used to record the UV-Visible spectra, a concentration of 1 x 10⁻⁴ mole / l of the prepared compounds in DMSO as solvent, was used with quartz cell of 1 cm path length in the range (200-800) nm.

2.2 Synthesis of nitrones:

General procedure:

In a 100 ml round flask, (0.01 mole) (7.021 gm) of 4,4',4'',4'''-tetrakis n-hydroxylamine copper phthalocyanine (which was prepared as mention in the literature)^(5,23,24) and 15 ml of ethyl alcohol were stirred and warmed to 50°C. An additional 5 ml of solvent was added slowly to complete dissolving the N-phthalocyanenyl hydroxylamine. Then (0.04mole) of benzaldehyde derivatives were added to the mixture. Then the mixture was refluxed for (4) hours, and cooled to 0°C and kept in this temperature overnight, the crude nitron products were filtered off and dried in vacuum. Then, recrystallisation of the products was performed by using dry toluene, the resulted pure products were in different colored crystals. Table (1) show the melting points, colored and yield of prepared compounds.

Table (1) Physical properties of prepared compounds

Number of compound	Melting point (°C)	Color	Yield
1	232-234	Yellow	75 %
2	80-82	Brown	72 %
3	108-110	Brown	72 %
4	218-220	Yellow	88 %
5	110-112	Yellow	86 %

4,4',4'',4'''-tetrakis (benzylidene) copper phthalocyaninamine oxide (1)

This complex was prepared from the reaction of N-phthalocyanenyl hydroxylamine (7.021 gm) with benzaldehyde (4.245 gm); Yield: 7.909 gm, 75 % ; m.p. (232-234)°c; CHN analysis for C₆₀H₃₈N₁₂O₄Cu; C 68.34; H 3.63; N 15.94 Found; C 68.24; H 3.58; N

15.84, FT-IR spectra (KBr pellet) $\nu(\text{cm}^{-1})$ 3090 cm^{-1} (C-H) aromatic, 2800 cm^{-1} (C-H) aliphatic, 1604 cm^{-1} (C=N); 1166 cm^{-1} (N-O), 530 cm^{-1} (Cu-N). UV-Visible λ_{nm} 660 nm (ϵ 39000 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (Q-band), λ_{nm} 363 nm (ϵ 27000 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (B-band); $\delta_{\text{H}}(\text{CDCl}_3)$ 9.115 ppm (4H,s,imino group); (7.418-7.481) ppm (32H,m,aromatic); 4.781 ppm (1H,s,NH(a)); 2.175 ppm (1H,s,NH(b)).

4,4',4'',4'''-tetrakis (4,4-dimethyl amino benzylidene) copper phthalocyaninamine oxide (2)

This complex was prepared by reaction of N-phthalocyanenyl hydroxylamine (7.021 gm) with 4,4-dimethylamino benzaldehyde (5.968 gm); Yield: 8.833 gm, 72 %; m.p. (80-82) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{68}\text{H}_{58}\text{N}_{16}\text{O}_4\text{Cu}$; C 66.57; H 4.77; N 18.27 Found; C 66.48; H 4.70; N 18.17, FT-IR spectra (KBr pellet) $\nu(\text{cm}^{-1})$ 3094 cm^{-1} (C-H) aromatic, 2805 cm^{-1} (C-H) aliphatic, 1638 cm^{-1} (C=N); 1234 cm^{-1} (N-O), 534 cm^{-1} (Cu-N). UV-Visible λ_{nm} 640 nm (ϵ 45000 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (Q-band), λ_{nm} 341 nm (ϵ 29500 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (B-band); $\delta_{\text{H}}(\text{CDCl}_3)$ 9.115 ppm (4H,s,imino group); (7.418-7.481) ppm (28H,m,aromatic); 4.781 ppm (1H,s,NH(a)); 3.072 ppm (24H,s,CH₃); 2.175 ppm (1H,s,NH(b)).

4,4',4'',4'''-tetrakis (4-methoxy benzylidene) copper phthalocyaninamine oxide (3)

This complex was prepared through reaction of N-phthalocyanenyl hydroxylamine (7.021 gm) with 4-methoxy benzaldehyde (5.446 gm); Yield: 8.458 gm, 72 %; m.p. (108-110) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{64}\text{H}_{46}\text{N}_{12}\text{O}_8\text{Cu}$; C 65.44; H 3.95; N 14.31 Found; C 65.40; H 3.88; N 14.21, FT-IR spectra (KBr pellet) $\nu(\text{cm}^{-1})$ 3098 cm^{-1} (C-H) aromatic, 2810 cm^{-1} (C-H) aliphatic, 1638 cm^{-1} (C=N); 1259 cm^{-1} (N-O), 540 cm^{-1} (Cu-N). UV-Visible λ_{nm} 648 nm (ϵ 42250 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (Q-band), λ_{nm} 348 nm (ϵ 28960 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (B-band); $\delta_{\text{H}}(\text{CDCl}_3)$ 9.115 ppm (4H,s,imino group); (7.418-7.481) ppm (28H,m,aromatic); 4.781 ppm (1H,s,NH(a)); 3.072 ppm (12H,s,OCH₃); 2.175 ppm (1H,s,NH(b)).

4,4',4'',4'''-tetrakis (4-chloro benzylidene) copper phthalocyaninamine oxide (4)

This complex was prepared from the reaction of N-phthalocyanenyl hydroxylamine (7.021 gm) with 4-chloro benzaldehyde (5.623 gm); Yield: 10.493 gm, 88 %; m.p. (218-220) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{60}\text{H}_{34}\text{N}_{12}\text{O}_4\text{Cl}_4\text{Cu}$; C 60.44; H 2.87; N 14.10 Found; C 60.36; H 2.78; N 14.04, FT-IR spectra (KBr pellet) $\nu(\text{cm}^{-1})$ 3100 cm^{-1} (C-H) aromatic, 2820 cm^{-1} (C-H) aliphatic, 1640 cm^{-1} (C=N); 1170 cm^{-1} (N-O), 550 cm^{-1} (Cu-N). UV-Visible λ_{nm} 665 nm (ϵ 38500 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (Q-band), λ_{nm} 370 nm (ϵ 26890 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (B-band); $\delta_{\text{H}}(\text{CDCl}_3)$ 9.115 ppm (4H,s,imino group); (7.418-7.481) ppm (28H,m,aromatic); 4.781 ppm (1H,s,NH(a)); 2.175 ppm (1H,s,NH(b)).

4,4',4'',4'''-tetrakis (4-actemido benzylidene) copper phthalocyaninamine oxide (5)

This complex was prepared by reaction of N-phthalocyanenyl hydroxylamine (7.021 gm) with 4-

actemido benzaldehyde (6.527 gm); Yield: 11.032 gm, 86 %; m.p. (110-112) $^{\circ}\text{C}$; CHN analysis for $\text{C}_{68}\text{H}_{50}\text{N}_{16}\text{O}_8\text{Cu}$; C 63.67; H 3.93; N 17.47 Found; C 63.57; H 3.90; N 17.41, FT-IR spectra (KBr pellet) $\nu(\text{cm}^{-1})$ 3092 cm^{-1} (C-H) aromatic, 2808 cm^{-1} (C-H) aliphatic, 1645 cm^{-1} (C=N); 1267 cm^{-1} (N-O), 545 cm^{-1} (Cu-N). UV-Visible λ_{nm} 652 nm (ϵ 40800 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (Q-band), λ_{nm} 360 nm (ϵ 27500 $\text{l.mole}^{-1}.\text{cm}^{-1}$) (B-band); $\delta_{\text{H}}(\text{CDCl}_3)$ 9.928 ppm (4H,s,NH (actemido)); 9.115 ppm (4H,s,imino group); (7.418-7.481) ppm (28H,m,aromatic); 4.781 ppm (1H,s,NH(a)); 3.072 ppm (12H,s,CH₃); 2.175 ppm (1H,s,NH(b)).

Results and Discussion:

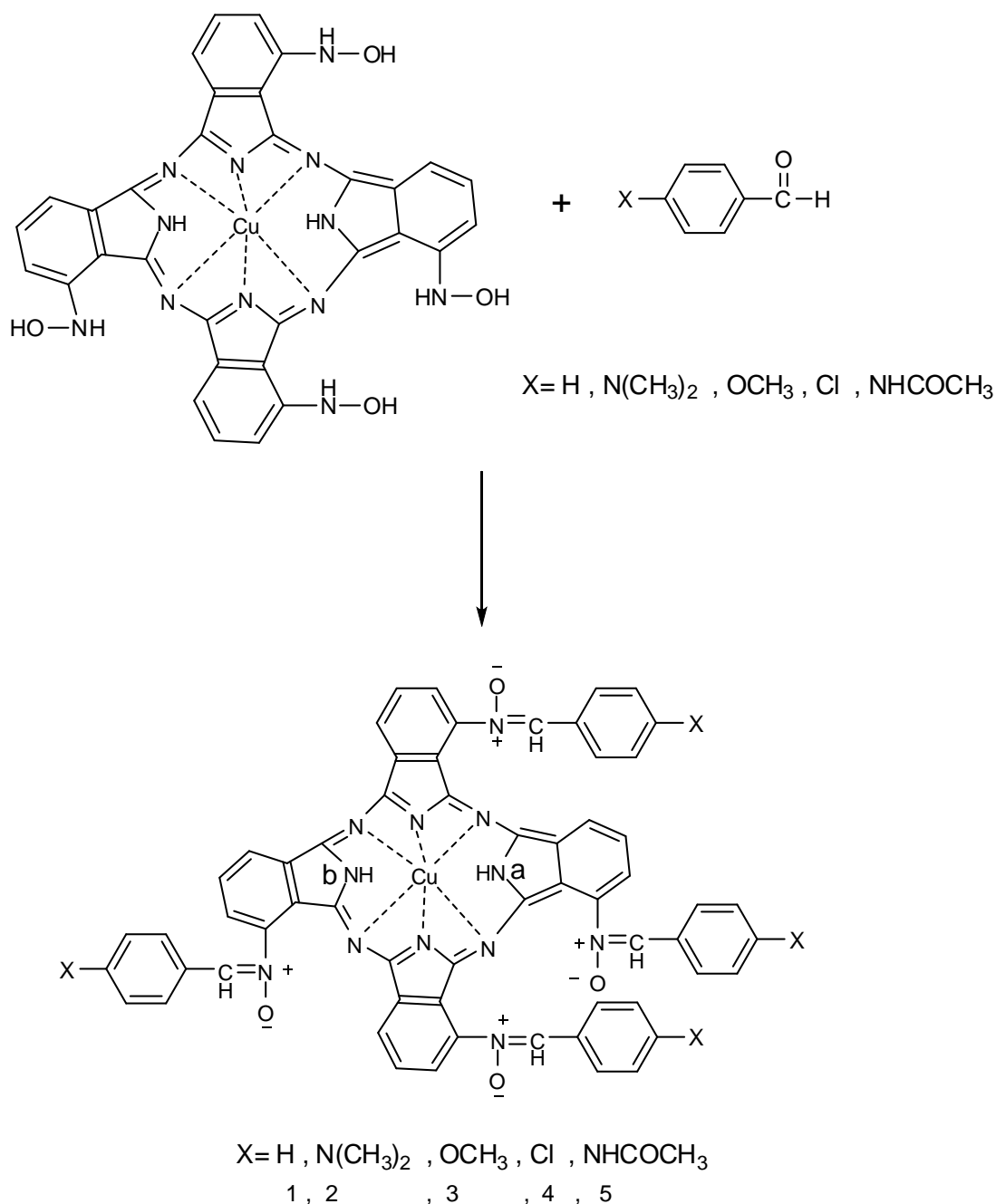
Treatment of N-phthalocyanenyl hydroxylamine (1) with benzaldehyde derivatives (2-6) in boiling ethanol gave nitron compounds, after purification by recrystallization from dry toluene, pure nitron compounds, were obtained as shown in (scheme 1) in good yields (72-88)%. The structures of these products were established from their elemental analysis (C.H.N), FT-IR and ^1H NMR spectra. All the IR spectra of nitrones showed peaks in the region (1604-1645) cm^{-1} due to (C=N) stretching, also peaks at the range (1166-1267) cm^{-1} due to (N-O) stretching, the (C-H) stretching aromatic ring showed peaks at the range (3090-3100) cm^{-1} , while showed peaks in the region (2800-2820) cm^{-1} due to (C-H) stretching aliphatic. The (Cu-N) stretching showed at the range (530-550) cm^{-1} (25). The UV-Visible spectra of all the prepared compounds contain two strong absorption bands which are attributed to $\pi \rightarrow \pi^*$ transitions. The first band was observed in the range (640-665) nm with molar extinction ϵ (38500-45000) $\text{l.mole}^{-1}.\text{cm}^{-1}$ which is can be attributed to a Q-band, which assigned to $a_{1u} \rightarrow e_g$ transition (26,27). The second band were observed in the range (341-370) nm with ϵ (26890-29500) $\text{l.mole}^{-1}.\text{cm}^{-1}$ can be attributed to a B-band, which assigned to $a_{2u} \rightarrow e_g$ transition (26,27). The Q-band in all the prepared compounds were observed to be red shifted when compared un substituted copper (II) phthalocyanine with the prepared compounds (1-5) which contain nitron groups may be due to the decrease in energy levels of $\pi \rightarrow \pi^*$ transitions of the phthalocyanine ring as function of the electron withdrawing nature of nitron groups on the periphery and other band at 624 nm. The same observation were found in B-band of these compounds, table (2) as shown absorption bands and molar extinction of all prepared compounds. The ^1H NMR spectra as shown in figures (1-5). All the ^1H NMR spectra of nitrones were characterized (28-30) by the presence of protons of at $\delta = 9.115$ ppm were due to proton of imine group, since the CH₃ protons appeared at $\delta = 3.072$ ppm. The OCH₃ protons showed singlet signal within the region 3.072 ppm. The aromatic protons rings showed multiplet signals in the region $\delta = (7.418-7.481)$ ppm.. The proton of NH (a) showed singlet

signals at 4.781 ppm. While proton of NH (b) showed singlet signals at 2.175 ppm.

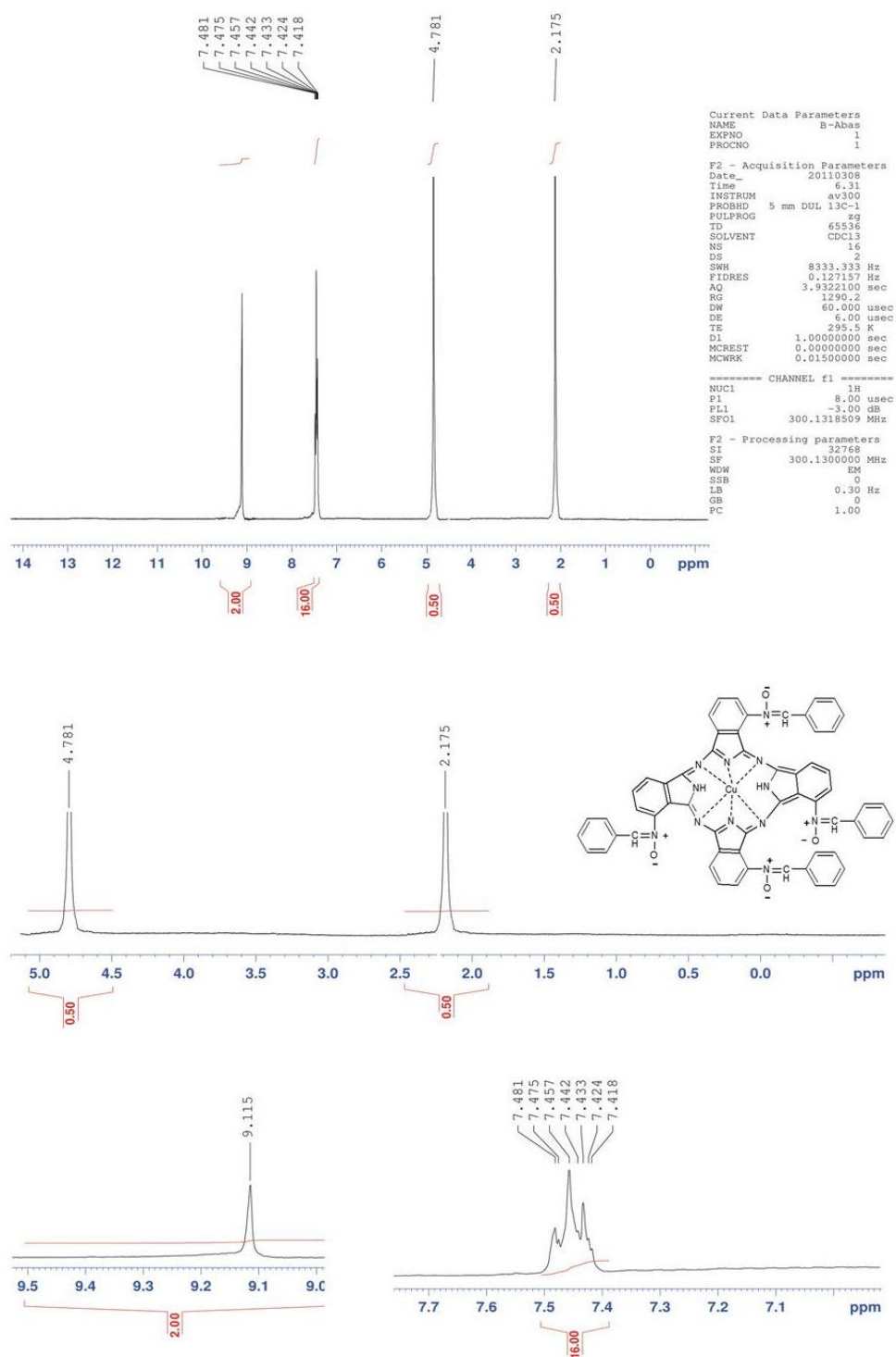
The nitron compounds derived from phthalocyanine are used as catalyst in organic synthesis, biological active, anti oxidants and trapping free radicals.

Table (2) Data of the UV-Visible absorption spectra of prepared compounds

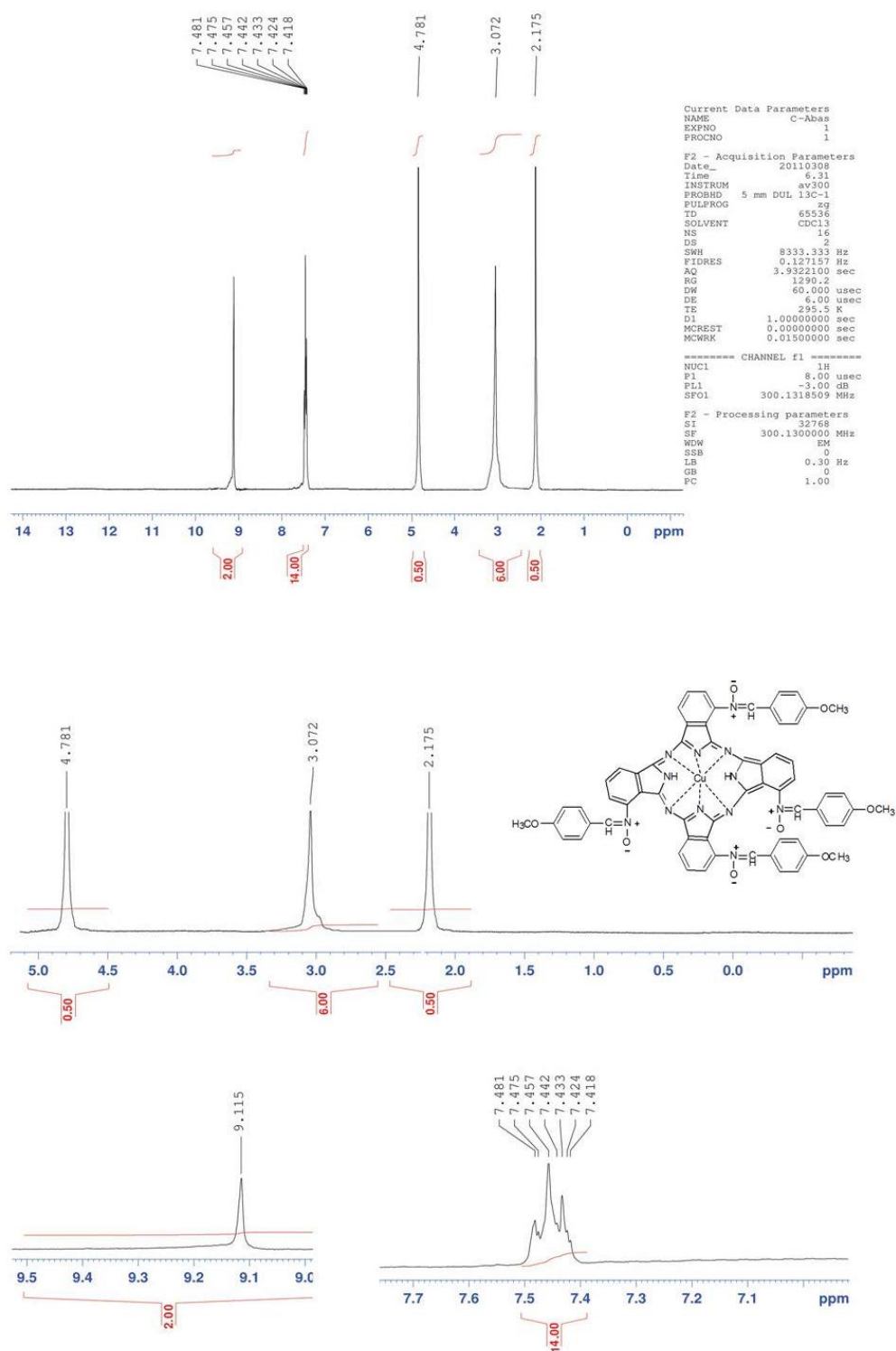
Number of compound	$\lambda_{nm} (\pi \rightarrow \pi^*)$ Q-band	$\epsilon (l.mole^{-1}.cm^{-1})$	$\lambda_{nm} (\pi \rightarrow \pi^*)$ B-band	$\epsilon (l.mole^{-1}.cm^{-1})$
1	660	39000	363	27000
2	640	45000	341	29500
3	648	42250	348	28960
4	665	38500	370	26890
5	652	40800	360	27500



Scheme 1

Figure (1) : ^1H NMR spectrum of nitronium (1)



Figure (3) : ^1H NMR spectrum of nitrone (3)

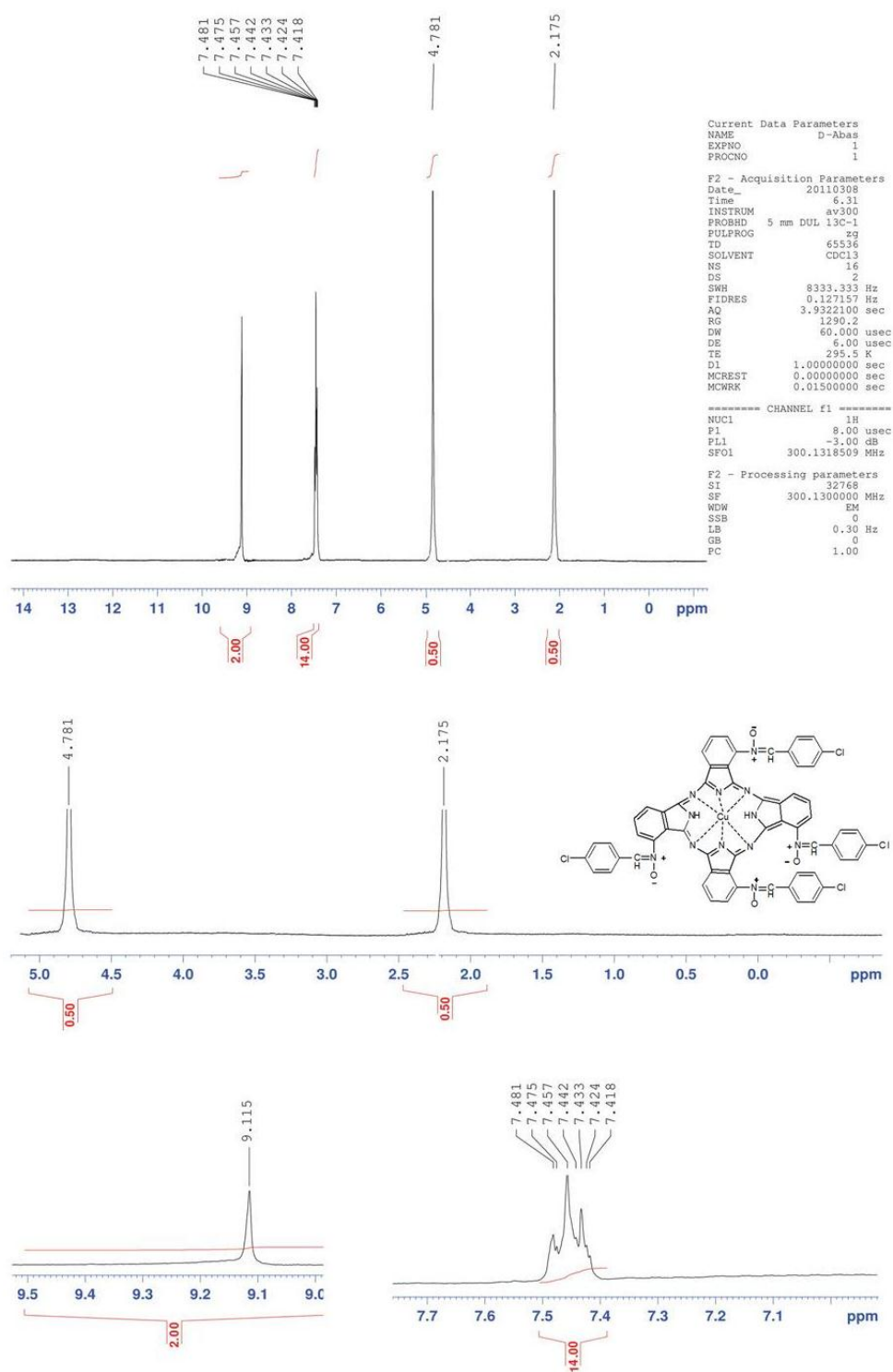
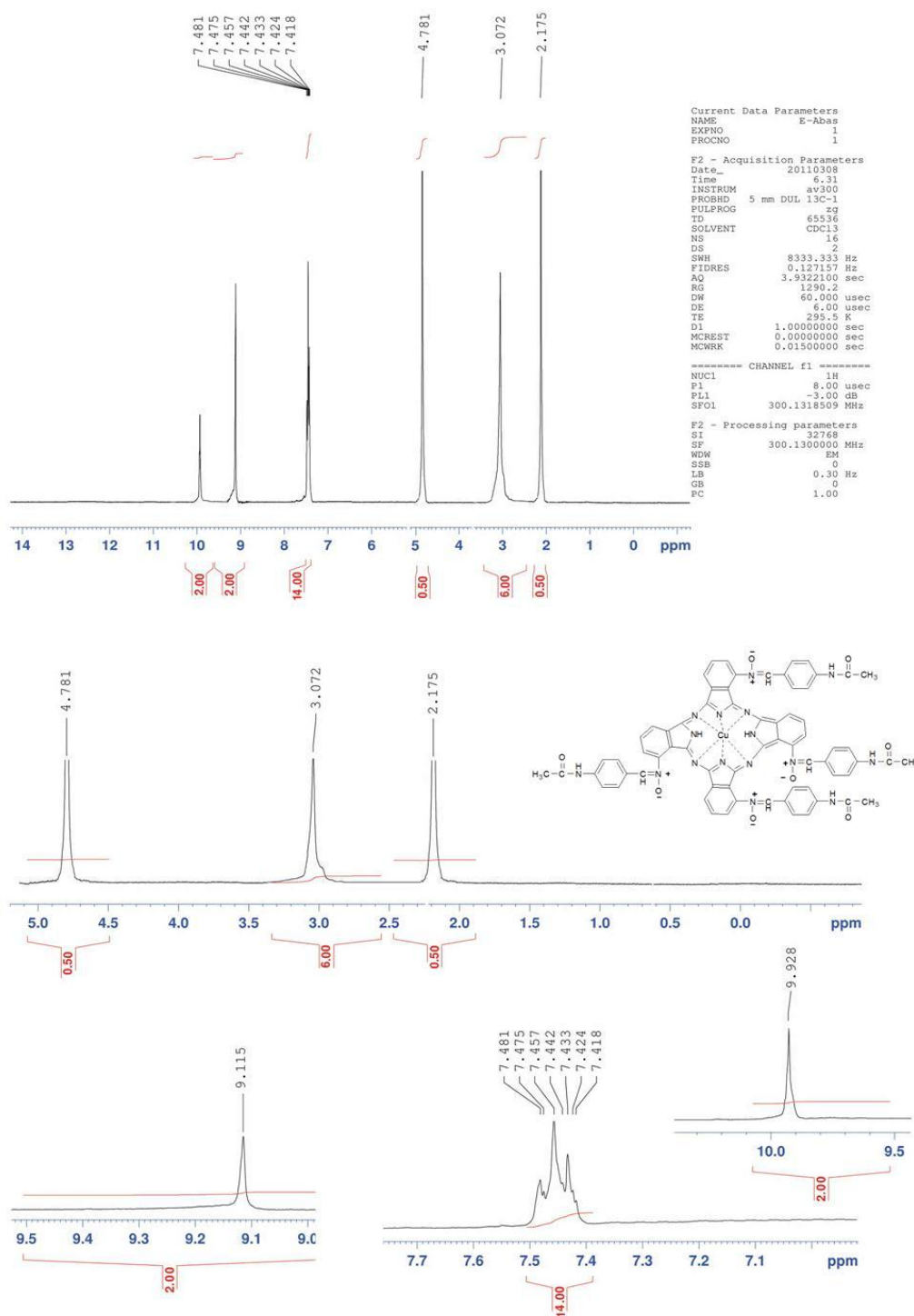


Figure (4) : ^1H NMR spectrum of nitrone (4)

Figure (5) : ^1H NMR spectrum of nitron (5)**References:**

- 1.F.G. Stone and W.A. Graham , " Inorganic Polymer", Academic press, New York, London, (1962).
- 2.R.P. Linstead , *J. Chem. Soc.*, 1016, (1934).
- 3.R.P. Linstead, C.E. Dent and A.R. Lowe , *J. Chem. Soc.*, 1033, (1934).
4. K. Venkataraman , "The Chemistry of Synthesis Dye", Academic press, 1,244,(1952).
- 5.S.M. Ahmad, MSc. Thesis, College of Science , University of Baghdad, (1983).
6. C.S. Marrel and M.M.Martin , *J.Am.Chem.Soc.*,80,1197, (1958).
- 7.J.A. Elvidge and A.B. Lever, *J.Chem.Soc.*,1257, (1961).
- 8.R.D. Joymer and M.E. Kenney, *J.Am.Soc.*,82,5790, (1960).

9. D. Wohrle and G.Meyer, "Phthalocyanine Properties and Application", VCH publishers, Cambridge, (1996).
10. N.B. Mckeown, "Phthalocyanine Materials : Synthesis, Structure and Function", Cabridge University press, (1998).
11. G. Christian , M. Cook, J.M. Nolte and T. Torres, *Monatshefte for chemie,Review*, 132,3-11, (2001).
12. H. Baba, K. Chitoku and K. Natta, Honkaido University, 177,652;C.F., *Chem. Abs.*, 50,11100, (1950).
13. D.D. Eley, *Nature*, 162,819, (1948); C.F., *Chem.Abs.*, 43,3731,(1949).
14. T. Kano, T. Hashimoto and K. Karuoko; *J. Amer. Soc.*, 70, 11926-11927 (2005).
15. A. Banerji, S. Dasgupta, P. Sengupta and A. Neuman; *Indian J. Chem.*, 3B, 135, (2004).
16. A. Banerji, P. Sengupta, *Indian In St. Sei.*; 81, 313 -323, (2001).
17. P. Meino, S. Anora, L. Francisco and T. Tanas; *Molecules*, 5, 132- 152, (2000).
18. P. Meino, S. Anora, E. Cerrada, M. Languna and T. Jejero; *Molecules*, 6, 208-220, (2001).
19. S. Barbat, J. Clement, G. Olive and P. Tordo; *Chem. Bio.*,33,163, (1997).
20. M. O. Zink, A. Kramer and P. Nesvadba; *Macromolecules*, 33, 8106-8108, (2000).
- 21.A. B. David, J. L. James, E. Luis and A. Robert; *J. Am. Chem. Soc.*, 124 ,126,(2002).
22. L. C. Hawkins, J. M. Davies; *Current Topics in Biophysics*, 26(1), 37-144 (2002).
- 23.A.I.Vogel,"Textbook of Practical Organic Chemistry", 4th ed.,839,(1978).
24. A.I.Vogel,"A Text-Book of Practical Organic Chemistry", 3^{ed}, Longman Group Limited, London, (1956).
- 25.K.Nakamotu, "Infrared and Raman Spectra of Organic and Coordination Compounds", 7th ed., John Wiley and Sons, USA, (2009).
- 26.A.E.Gillam and E.S. Stem,"An Introduction to Electronic Absorption Spectroscopy in Organic chemistry", 2nd ed., Edward Amold, London, (1957).
27. A.B.P. Lever, "Inorganic Electronic Spectroscopy", 2nd ed., Elsevier Science, (1984).
28. Silverstien R.M., Webster F.X., Kiemle D.J., "Spectrometric Identification of Organic Compounds", 6th ed., John Wiley and Sons, New Yourk, USA, (2005).
29. Cooper J.W., "Spectroscopic Techniques for Organic Chemistry", John Wiley and Sons, New Yourk, USA, (1980).
30. Shriner R.L., Hermann C.K., "Spectroscopic Techniques for Organic Chemistry", John Wiley and Sons, New Yourk, USA, (2004).

تحضير وتشخيص بعض النايترينات الجديدة المشتقة من الفثالوسيانين

نسرین ناظم مجید ، عباس فاضل عباس ، عادل علي الفرجي

قسم الكيمياء ، كلية العلوم ، جامعة البصرة ، البصرة ، العراق

(تاريخ الاستلام: 28 / 12 / 2011 ---- تاريخ القبول: 13 / 3 / 2012)

الملخص

تم تحضير خمس مركبات جديدة رباعية النايترين من خلال تفاعل 4و4و4و4- رباعي هيدروكسيل امين نحاس فثالوسيانين مع البنزالديهيد ومشتقاته المعوضة في الموقع بارا. وتم تشخيص تلك المركبات باستخدام تحليل العناصر الدقيق ومطيافية الاشعة تحت الحمراء ومطيافية الاشعة فوق البنفسجية ومطيافية الرنين النووي المغناطيسي للبروتون.