SYNTHESIS AND CHARACTERISATION OF NEW 2-DIAZO-3-OXO-5,10,15,20-TETRAPHENYLCHLORINS

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Abstract: The Cu and Ni derivatives of β-amino-5,10,15,20-tetraphenylporphyrin react with sodium nitrite in THF by formation of 2-diazo-3-oxo-5,10,15,20-tetraphenylchlorins. The spectroscopic properties and some electrochemical properties of the synthesised compounds were investigated.

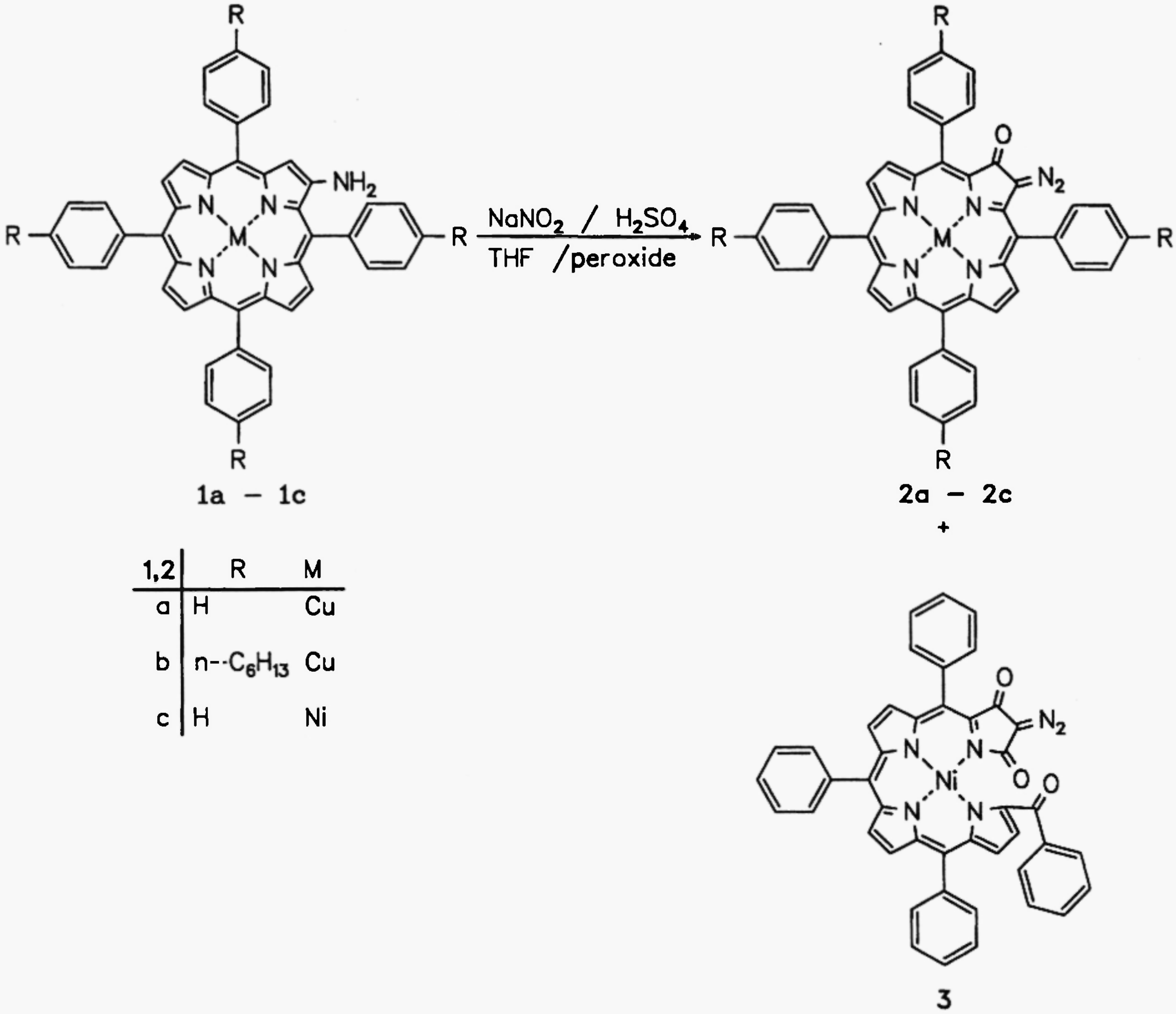
INTRODUCTION

The synthesis of new porphyrin and chlorin derivatives is of considerable interest for the development of biomimetic model systems of the photochemical reaction centre chromophores (1). In these model systems a light induced electron transfer from excited porphyrin systems to electron acceptors takes place (2-4). For studying the electron transfer process it is often necessary to modify the electronic properties of the porphyrinic macrocyle. The electronic properties of a porphyrinic macrocyle can be changed especially by modification of the β-substituents. We therefore became interested in the synthesis of new porphyrin derivatives that may act as versatile starting materials in the synthesis of different β-substituted porphyrins. In earlier publications we reported about the synthesis and reactions of porphyrinic diazonium ions (5-6). Herein we report about the first synthesis and the spectroscopic characterisation of new interesting porphyrinic diazoketones. These compounds may also be of interest as starting materials for the synthesis of new porphyrinic systems.

RESULTS AND DISCUSSION

The porphyrinic diazoketones 2a - 2c were synthesised by reaction of β-amino-5,10,15,20-tetraphenylporphyrin 1a - 1c with $NaNO_2$ and sulphuric acid in hydroperoxide containing THF (Scheme 1). It is very important that hydroperoxide containing THF (CAUTION) is used, otherwise the reaction will lead to a porphyrin diazonium ion and CuTPP (tetraphenylporphyrinato-copper(II)) as main reaction products and a large number of decomposition products. The reaction mixture was stirred in THF at room temperature for 5 - 10 h. The diazoketones were formed in 25 - 54% yield and isolated by column chromatography on silica gel. It is interesting to note, that a diazoketone is formed from β-aminoporphyrins that lack a hydroxy group in α-position. However, there is at least one example of a comparable reaction described in the literature (7). After initial diazotization 1-aminophenazine is oxidised to the corresponding diazoketone via 2-hydroxy-3-diazophenazine. It is most likely for this system that after diazotization attack of water on the highly reactive α-carbon takes place and subsequent oxidation by air or nitrous acids lead to the α-diazoketone (8). However, if the aminoporphyrins 1a - 1c were reacted in peroxide free THF, no formation of a diazoketone was observed. Therefore it is most likely for our systems that the hydroperoxide is the oxidation reagent or may have some catalytic activity. Furthermore, if $NaNO_2$ was used in high excess (10-fold excess), CuTPP was the main reaction product (approx. 70% yield). This might be due to reduction of the intermediately formed porphyrinic diazonium-ion by nitrite. Interestingly, for the nickel complex we obtained a side product (16% yield) to which we assign structure 3. This compound can be formed by attack of oxygen or hydroperoxide on the C-1/C-20-double bond and subsequent ring opening (9). Nevertheless, the synthesised diazoketones are stable compounds and can be kept for more than four weeks at room temperature in the dark without significant decomposition. Furthermore, prolonged heating (48 h) of the synthesised diazoketones in boiling THF or $CHCl_3$ did not lead to any decomposition products.

The structural assignment of diazoketones 2a - 2c was mainly based on MS studies and NMR studies for the Ni-complex 2c. The 300 MHz ^1H NMR spectrum of 2c in $CDCl_3$ showed signals corresponding to the resonance's of six β-H (δ 8.41 - 8.59) and twenty aromatic protons (δ 7.59 - 7.94). The assignment of the pairs of the six pyrrolic protons and corresponding carbons was achieved through 2D NMR experiments (^1H-^1H COSY and ^1H-^{13}C HETCOR). The most noticeable features in the ^{13}C spectrum of 2c were the signals corresponding to the resonance's of C-2 and C-3 carbons that appear at δ 73.3 and δ 185.4, respectively.



1,2	R	M
a	H	Cu
b	n--C_6H_{13}	Cu
c	H	Ni

Scheme 1

An HMBC experiment optimised for 5 Hz long-range *J* (C/H) coupling giving the connectivity of protons to carbons at two or three bonds away allowed the assignment of several protons. The doublets assigned to the resonance of the protons H-12,13 (δ 8.47, 8.51) have a direct correlation to the signals at δ 141.2 and 143.3 that were due to carbons C-11,14. Similar correlation's can be observed for the other β-protons signals (δ 8.41, 8.52 and 8.50, 8.59) allowing to identify the resonance's at δ 140.0, 144.2 and δ 141.0 and 144.0 to carbons C-6,9, C-16,19. In the same experiment was observed a correlation between the doublet of the ortho protons of phenyl ring at C-20 (δ 7.87) and the signals at δ 109.1 and 129.7, which were due to the resonance's of C-20 and the para-carbon of the phenyl ring at C-20. A similar correlation was also observed between the signal attributed to the ortho protons of the phenyl ring at C-5 and the signal at δ 116.7 that was due to carbon C-5. From the HMBC spectrum of 2c it was not possible to observe any correlation between the signals of carbons of C-2 and C-3 and any proton signals. This was an important data and allowed us to conclude that there are no protons on that pyrrole moiety of the molecule. Furthermore the FAB mass spectra of all diazoketones 2a - 2c gave a peak corresponding to the (M^+ + 1) peak of the compound and a second peak at (M^+ - 28). This finding is also consistent with the proposed structures. Strong IR absorptions were detected for compound's 2a - 2c at 1667 cm^{-1} (CO) and 2086 - 2093 cm^{-1} (CN_2). All porphyrinic diazoketones exhibit shifted Soret absorption bands at 431 - 433 nm (CH_2Cl_2) and four absorption bands in the visible region at 434 - 443, 522 - 524, 558 - 562 and 605 - 609 nm. These data are consistent with the proposed oxochlorine structure of the compounds.

The electrochemical properties of the new porphyrinic systems were investigated by pulse voltammetry and cyclic voltammetry. The obtained electrochemical data are summarised in the table. The cyclic voltammograms of compounds 2a - 2b exhibit two electrochemical processes in the anodic region corresponding to the formation of the radical cation and dication, respectively. These processes can be regarded as reversible or quasi-reversible as indicated by the ΔE_{peak} values ($\Delta E_{peak} = E_{pa} - E_{pc}$) and the peak current ratio i_{pc} / i_{pa} that is close to unity (10). Furthermore, the peak potential of both anodic processes depends only slightly upon the scan rate. It is well known that diazo ketones and diazo compounds undergo dediazoniation upon electrochemical reduction in aprotic solvents (11). For example, if 2-diazo-1,2-diphenylethan-1-one is electrochemically reduced formation of an radical anion takes place. This radical ion reacts slowly by elimination of nitrogen and formation of a carbene radical ion (12). Hydrogen transfer to the carbene radical ion and subsequent electron transfer occurs rapidly.

	$E^{1/2}$ (ox1)	ΔE_{peak}	$E^{1/2}$ (ox2)	ΔE_{peak}	E_{peak} (red1)	$E^{1/2}$ (red2)	ΔE_{peak}
2a	0.51	70	0.72	80	-1.58	-2.11	100
2b	0.49	65	0.69	85	-1.61	-2.10	110
2c	0.50	70	0.62	80	-1.52	-2.15	120

Table 1: Electrochemical data of porphyrinic diazoketones 2a - 2c (10^{-3} M solutions). Potentials given in volt measured at a glassy carbon working electrode measured against a Ag/AgCl reference electrode and referenced against the ferrocene/ ferrocinium system. ΔE values given in mV. Solvent: CH_2Cl_2 ,0.1 M TBATFB. Scan rate 100 mV/s, T = 293 K.

Two electrochemical processes can be easily distinguished in the voltammogram of the porphyrinic diazo ketones in the cathodic region (Figure 1). The main features of the voltammogram are an irreversible peak at -1.58 V and a quasi-reversible process at -2.15 V. The first peak remains irreversible at all scan rates investigated even if the scan is reversed at -1.7 V. The current function (i_{pc} / $v^{1/2}$) decreased with increasing scan rate indicating a chemical reaction following the electrochemical process. Furthermore, the peak potential shifts negatively with increasing scan rate. Thus irreversibility of this process is most propably due to loss of nitrogen. At -2.15 V a second electron transfer takes place leading to a porphyrinic dianion. This process can be regarded as quasi-reversible as indicated by the appearance of a back-peak at -2.05 V in the reverse scan and a ΔE_{peak} value of 100 - 120 mV (Table 1).

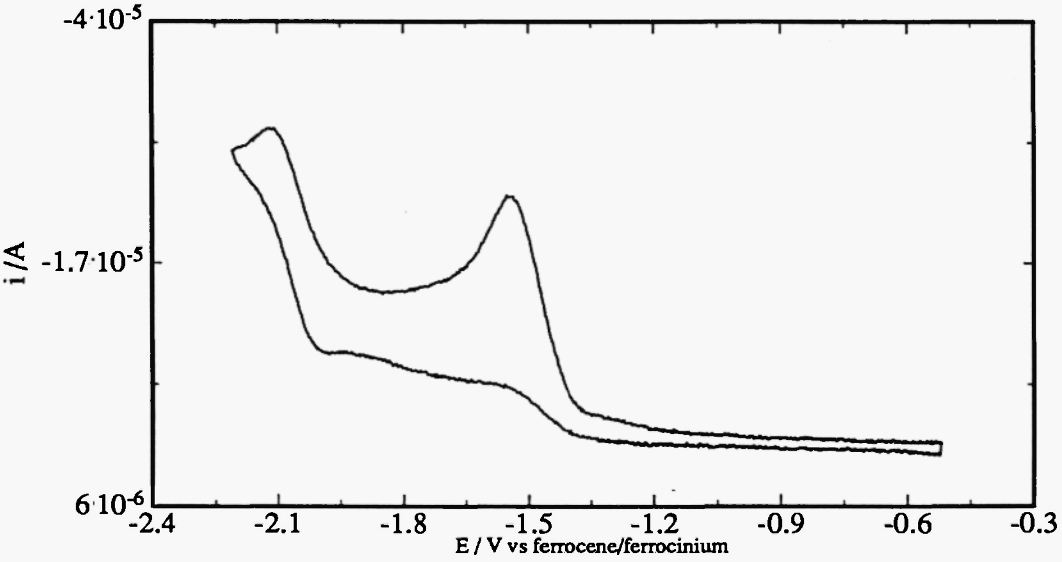


Figure 1: Cyclic voltammogram for the reduction of 2a (10^{-3} M) in CH_2Cl_2 / TBATFB (0.1 M) measured at a glassy carbon electrode against a Ag/AgCl reference electrode, referenced against the ferrocene / ferrocinium system. Scan rate 100 mV/s, T = 293 K.

Interestingly, for compound 2a a new peak appears in the reverse scan at -0.38 V vs the ferrocene / ferrocinium system (Figure 2). For 2b and 2c this peak appears at -0.40 V. The appearence of this peak can be attributed to oxidation of a new compound formed by H-abstraction reaction after dediazoniation of starting diazoketones. However, these are only preliminary results and more detailed electrochemical investigations are necessary to clarify the behaviour of the porphyrinic diazoketones.

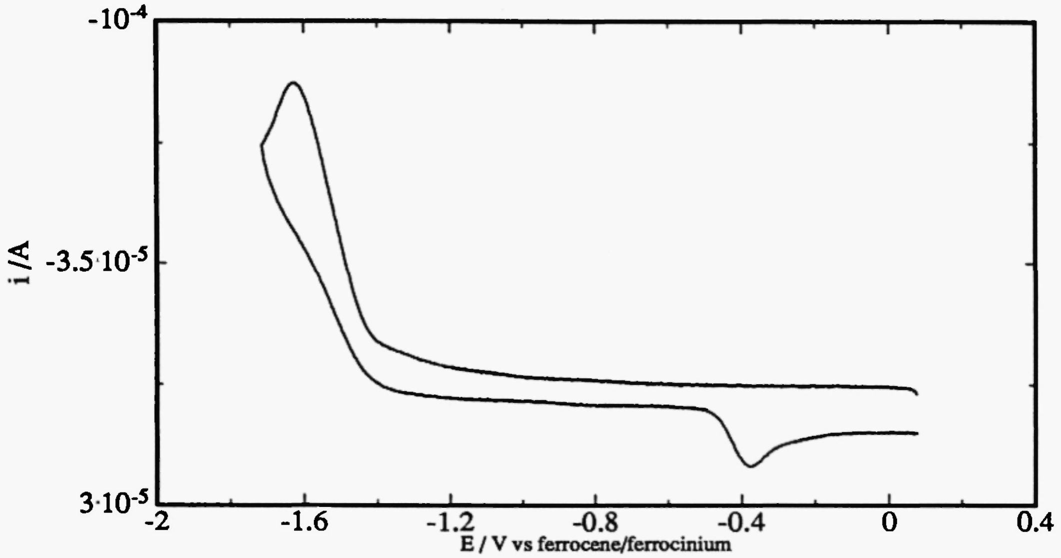


Figure 2: Cyclic voltammogram for the reduction of 2a (10^{-3} M), scan rate 1V/s, T = 293 K in CH_2Cl_2 (0.1 M TBATFB).

As a conclusion we have synthesised and characterised new porphyrinic diazoketones that may be interesting starting materials for the synthesis of other β-substituted porphyrin and chlorin derivatives. Work is underway in our laboratories to investigate the chemical, electrochemical and photochemical reactivity of the synthesised porphyrinic diazoketones.

ACKNOWLEDGEMENTS

This work was supported by the INIDA Program (JNICT-DAAD). Financial support by the Fonds der Chemischen Industrie is also gratefully acknowledged. The generous gift of a BD 91 recorder by Kipp & Zonen Deutschland is also gratefully acknowledged.

EXPERIMENTAL

NMR-spectra were obtained in $CDCl_3$ and recorded with a Bruker AMX 300 spectrometer. Mass spectra were measured with a VG-Analytical VG70:250 E instrument. Electronic spectra were recorded on a Kontron Uvikon 860 instrument. Column chromatography was carried out with Merck silica gel mesh size 0.06 - 0.2 mm. IR-spectra were recorded on a Shimadzu 435 spectrometer. Melting points were determined with a Büchi 510 apparatus and are uncorrected. Cyclic voltammetry and pulse voltammetry were carried out with a Tacussel Potentiostat PJT 24-1 equipped with an IMT-1 interface, connected to an IBM-AT computer and a Siemens Oscillar D 1015 oscilloscope or with a Bank POS 73 Potentiostat equipped with a Kipp & Zonen BD 91 recorder. Ohmic drop compensation was performed electronically by positive feed back. Cyclic voltammetry and pulse voltammetry experiments were carried out in a oven dried electrochemical cell at 20 °C under nitrogen using freshly distilled and degassed solvents. All voltammetric experiments were performed using a standard three-cell configuration with a glassy carbon working electrode, a platinum wire counter electrode and a Saturated Calomel Electrode (SCE) as the reference electrode. Ferrocene was added as internal standard after the last measurement. All solvents used for electrochemical measurements were carefully dried and cleaned. Tetrabutyl ammonium tetrafluorborate (Merck) was used as supporting electrolyte.

Synthesis of (2-diazo-3-oxo-tetraphenylchlorinato)copper(II) 2a:

To a solution of 0.24 g (0.35 mmol) 1a in 10 ml THF containing approx. 20 ppm peroxide (Merck Peroxide Test, Merckoquant 10011) were added 0.12 g (1.7 mmol) $NaNO_2$ and 0.3 ml conc. H_2SO_4. The reaction mixture was stirred at room temperature for 16 h. The mixture was poured into 250 ml water, and extracted with $CHCl_3$. The organic layer was dried (Na_2SO_4) and the solvent evaporated. The residue was chromatographed on a silica gel column (5 x 30 cm) using CH_2Cl_2/ hexane (3:1) as eluent. Yield: 0.135 g (54%). Fp > 220°C.- FAB-MS: *m/z* = 720 (M^+ + 1 for ^{65}Cu), 718 (M^+ + 1 for ^{63}Cu), 692 (100 %), 690 (90 %).- UV-Vis (CH_2Cl_2) λ (lg ε) = 430 (5.36), 522 (2.83), 543 (3.18), 562 (3.96), 609 (4.41) nm.- IR (KBr): ν = 2093.5, 1667.5 cm^{-1}. Anal. calc. for $C_{44}H_{28}N_6OCu$ (718.28): C 73.58 H 3.65 N 11.70. Found: C 73.36 H 3.89 N 11.21.

Synthesis of (2-diazo-3-oxo-5,10,15,20-tetra(p-hexylphenyl)chlorinato)copper(II) 2b:

0.30 g (0.28 mmol) 1b were reacted as described for the synthesis of 2a. Yield: 0.08 g (24%).- Fp > 220°C.- FAB-MS: *m/z* = 1057 (M^+ + 1 for ^{65}Cu), 1055 (M^+ + 1 for ^{63}Cu), 1029 (M^+ - N_2).- UV-Vis (CH_2Cl_2): λ (lg ε) = 430 (5.16), 522 (3.03), 543 (3.93, shoulder at 563), 563 (4.03), 609 (4.28).- IR (KBr): ν = 2094.0, 1667.5 cm^{-1}.- Anal. calc. for $C_{68}H_{74}N_6OCu$ (1054.92): C 77.42 H 7.07 N 7.97. Found: C 77.18 H 6.97 N 7.75.

Synthesis of (2-diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 2c:

In a round bottom flask 0.057 g (0.083 mmol) 1c were added to a mixture of 5 ml THF and 1 ml methanol. Then 44.5 mg (0.64 mmol) $NaNO_2$ and 0.1 ml conc. H_2SO_4 were added and the reaction mixture stirred overnight. The mixture was poured into water and extracted with $CHCl_3$. The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate, followed by water and dried. The dried organic layer was concentrated and chromatographed on a silica gel column using CH_2Cl_2/ petrol ether (2:1) as eluent to give mainly NiTPP (9.1 mg, 16%), followed by green 2c and yellow 3. 2c:Yield: 0.017 g (30%).- Fp > 220°C.- ^{1}H NMR ($CDCl_3$): δ = 7.59 - 7.73 (m, 14 H, H_m and H_p of C-5,10,15,20 phenyl groups and H_o, phenyl at C-5); 7.87 (d, 2 H, *J* = 7.5 Hz, H_o, phenyl at C-20), 7.90 - 7.94 (m, 4 H, H_o, phenyl at C-10, C-15), 8.41 and 8.52 (2d, *J* = 4.7 Hz, 2 H, Hβ), 8.47 and 8.51 (2d, *J* = 4.9 Hz, H-12, H-13), 8.50 and 8.59 (2d, *J* = 4.9 Hz, 2 H, Hβ).- ^{13}C NMR ($CDCl_3$): δ = 73.3 (C-2), 109.1, 116.7, 120.7 and 123.7 (C-5, C-10, C-15, C-20), 127.1, 127.3, 127.8, 128.0, 128.1 and 129.7 (C_m, C_p at phenyls), 127.6 (C-1), 130.0, 130.2, 130.7, 131.7, 132.3 and 134.2 (6s, Cβ), 131.5, 133.2, 133.3 (C_o at phenyls), 138.9, 139.9 and 140.0 (C-1 at phenyls), 135.4 (C-4) 140.0, 141.1, 141.2, 143.3, 144.0 and 144.2 (C-6, C-9, C-11, C-14, C-16, C-19), 185.4 (C-3).- FAB-MS: *m/z* = 713 (M^+ + 1), 684 (M^+ - N_2).- UV-Vis ($CHCl_3$): λ (lg ε) = 433 (5.15), 523 (3.19), 534 (3.42), 560 (3.88), 605 (4.34) nm.- IR (KBr): ν = 1631, 2086 cm^{-1}.- Anal. calc. for $C_{44}H_{28}N_6ONi$ (713.43): C 74.08 H 3.67 N 11.78. Found: C 74.25 H 3.53 N 11.29.

3: Yield: 7.6 mg (16%).- ^{1}H NMR ($CDCl_3$): δ = 7.09 and 7.26 (2d, *J* = 4.4 Hz, 2 H, H-18 and H-17), 7.13 and 7.62 (2d, *J* = 4.8 Hz, 2 H, Hβ), 7.18 and 7.41 (2d, *J* = 5.1 Hz, 2 H, Hβ), 7.42 (t, *J* = 7.7 Hz, 2 H, H_m phenyl at C-20), 7.48 - 7.63 (m, 14 H, H_o phenyls at C-10, C-15, H_m phenyls at C-5, C-10, C-15, H_p phenyls at C-5, C-10, C-15, C-20), 7.85 (bs, 2 H, H_o phenyl at C-5), 8.13 (d, *J* = 7.7 Hz, 2 H, H_o phenyl at C-20).- ^{13}C NMR ($CDCl_3$): δ = 64.8 (C-2), 117.3 (C-4), 124.8, 127.6, 130.5, 133.1, 135.2 (6 Cβ), 127.8, 127.9, 128.0, 129.3, 130.4, 131.8, 132.3, 132.5, 133.1 (C_o, C_m,

C_p at phenyls C-5, C-10, C-15, C-20), 132.6, 135.6, 136.9, 137.2, 137.2, 141.2, 141.2 (4 C-1 phenyls at C-5, C-10, C-15, C-20 and C-5, C-10, C-15), 142.6, 143.6, 144.6, 150.7, 159.4, 166.0 (C-6, C-9, C-11, C-14, C-16, C-19), 168.2 and 178.6 (C-1, C-3), 186.5 (C-20).- FAB-MS: *m/z* = 745 (M^+ + 1).- UV-Vis (CH_2Cl_2): λ = 440, 680 nm.

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(10) The peak current ratio i_{pa}/i_{pc} for the anodic processes is close to unity (0.98 - 1.02) and independent from scan rate (scan rate varried between 0.02 V/s and 5 V/s). Furthermore, the current function $i_{pa}/v^{1/2}$ is independent from scan rate at low scan rates (0.01 - 0.5 V/s). For the second cathodic process we obtained a peak current ratio i_{pc}/i_{pa} of 1.05 - 1.20. This value depends slightly from scan rate.

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Received on October 19, 1996