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Synthesis, Physicochemical and Coordination Properties of 5,15-Diphenyltetramethyltetraethylporphyn Nitro Derivatives

E. M. Kuvshinova, A. S. Semeikin, E. A. Kolodina, S. A. Syrbu, and O. A. Golubchikov

Ivanovo State University of Chemical Technology, Engelsa pr. 7, Ivanovo, 153000 Russia
e-mail: semeikin@isuct.ru

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Abstract—The 5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin nitro derivatives containing the nitro groups in the *meso*-positions of the porphyn ring and/or *para*-positions of phenyl rings were synthesized. Porphyrins were characterized by electron absorption, ^{1}H NMR, and IR spectra. The purity and individuality of the synthesized compounds was proved by TLC and elemental analysis. Kinetic parameters of complexation reactions of the synthesized porphyrins with copper acetate in pyridine and in the mixed solvent benzene–acetic acid (7:3) depend on the degree of deformation of the tetrapyrrole cycle, on the solvation effects and electronic effects of the nitro groups.

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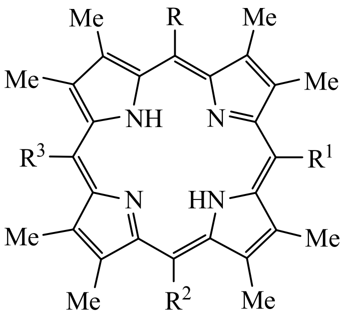
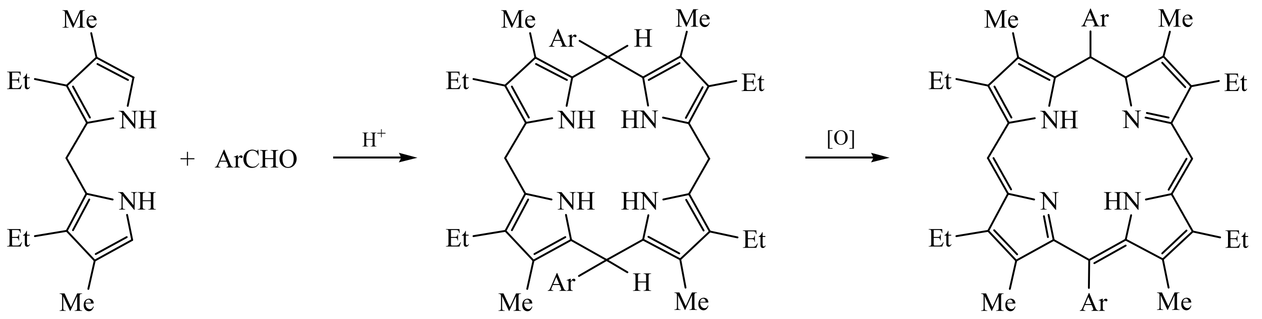
The introduction of a large number of peripheral substituents in the *meso*- and β-position of porphyrin macrocycle is known to lead to a sharp change in its physicochemical properties due to the distortion of the porphyrin ring [1–7]. The nitration reaction is a kind of modification of porphyrins in *meso*- and β-positions, so in order to study the effect of structural features of porphyrin molecules on their physicochemical properties we synthesized 5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyn **I** and its nitro derivatives **II–V**. We studied the kinetics of coordination of porphyrins **IV** by the copper acetate in pyridine and benzene–acetic acid (7:3) binary solvent.



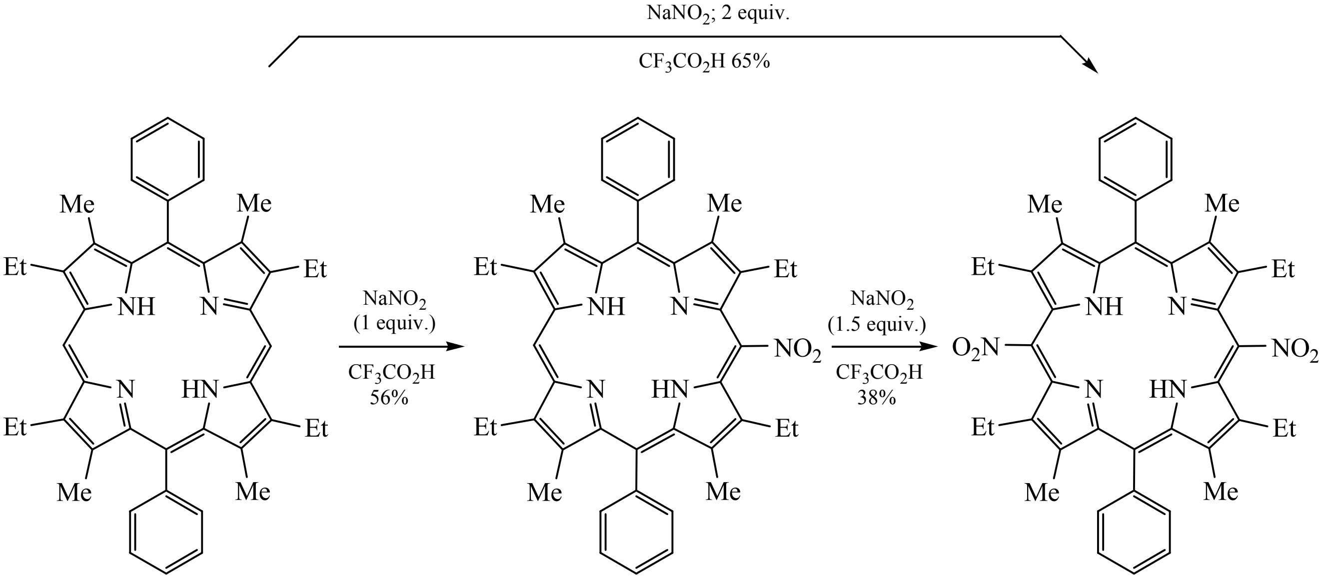
I: R = R^2 = Ph, R^3 = R^1 = H; **II**: R = R^2 = 4-NO_2-Ph, R^1 = R^3 = H; **III**: R = R^2 = Ph, R^3 = H, R^1 = NO_2; **IV**: R = R^2 = Ph, R^1 = R^3 = NO_2; **V**: R = R^2 = 4-NO_2-Ph, R^1 = R^3 = NO_2.

Porphyrins **I** and **II** were obtained by condensation in methylene chloride of 4,4-dimethyl-3,3'-diethyldipyrrolylmethane with the corresponding benzaldehyde derivatives catalyzed by chloroacetic acid, followed by oxidation of the intermediate porphyrinogenes with *p*-chloranil [8]. The introduction of nitro group in the *meso*-position of the macrocycle was performed by the action of sodium nitrite in trifluoroacetic acid. At the equimolecular ratio of porphyrin **I** and sodium nitrite in CF_3COOH *meso*-mononitroporphyrin **III** is formed in a 56% yield. The nitration of **I** with two equivalents of sodium nitrite in CF_3COOH leads to the formation of a single product, *meso*-dinitro-substituted porphyrin **IV** in a yield of 65%. Tetranitroporphyrin **V** was obtained by nitration of porphyrin **II** with a significant excess of $NaNO_2$ in CF_3COOH (see the scheme). Porphyrins **I**–**V** were characterized by EAS, ^{1}H NMR and IR spectra. The purity and individuality of compounds was proved by TLC on Silufol plates [9].

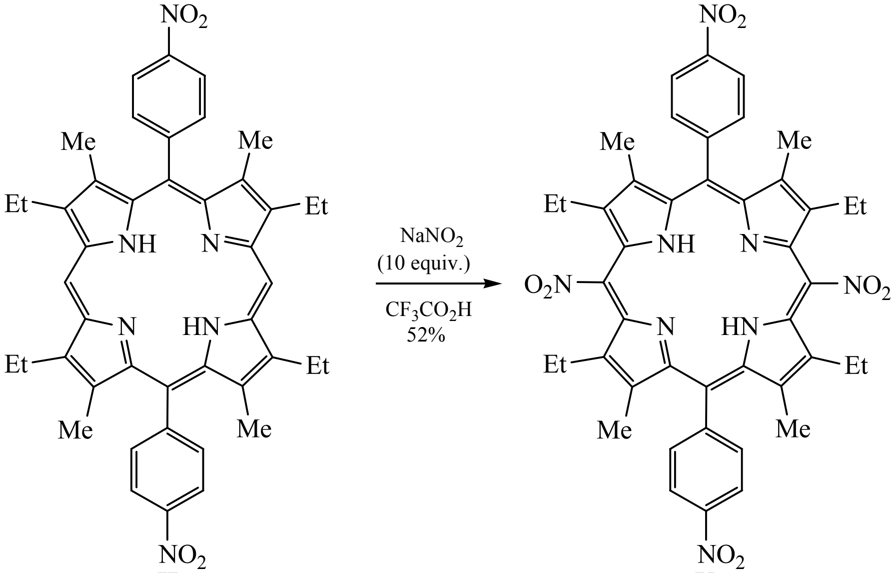
Kinetics of the coordination of obtained porphyrins by copper acetate was studied in pyridine and a binary solvent benzene–acetic acid (7:3). The mixed solvent benzene–acetic acid was used because of the limited solubility of porphyrins **I**–**V** in acetic acid. Spectral changes upon complexation of porphyrins **I**–**V** with copper acetate in pyridine and acetic acid–benzene



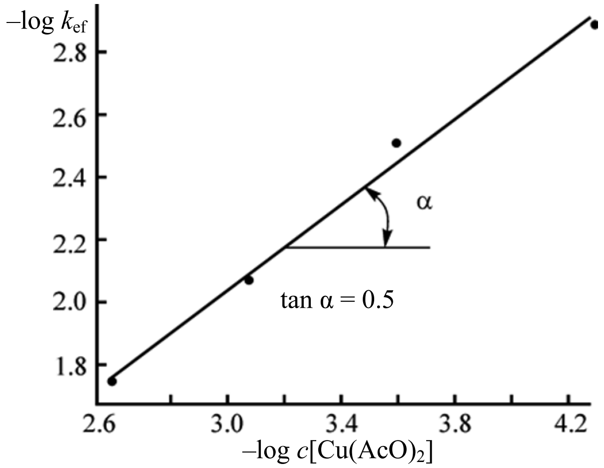
Ar = C_6H_5 (**I**), 4-$NO_2C_6H_4$ (**II**).



I **III** **IV**



II **V**



Dependence of log k_{ef} on log c[Cu(ACO)$_2$] at the formation of CuP complex **II** in the mixed solvent benzene–acetic acid (7:3) at 318 K.

occur with the retention of clear isobestic points. The four-band EAS characteristic of the free porphyrin transform into two-band spectra of the final reaction products. The formation of copper complexes of porphyrins **I−V** has a first kinetic order with respect to the ligand, as evidenced by the linear dependence in the coordinates $c^0(H_2P)/c(H_2P)$–τ, where $c^0(H_2P)$ and c (H_2P) are initial and current concentrations of porphyrin respectively, τ is time. Kinetic experiments were carried out with a significant excess of copper acetate with respect to the porphyrin (more than 100-fold), which enabled us to calculate the effective rate constant (k_{ef}) of reaction (1) by Eq. (2).

$$H_2P + Cu(AcO)_2 \rightarrow CuP + 2AcOH, \quad (1)$$

$$k_{ef} = 1/\tau \ln [A_0 - A_\infty]/[A - A_\infty]. \quad (2)$$

Here A_0, A, and A_∞ are optical densities of solution in the initial moment, at the time τ and at the end of the reaction, respectively.

The activation energy of the formation of CuP compounds **I–V** was calculated with the Arrhenius Eq. (3):

$$k = \mathrm{A}e^{-E/RT}. \quad (3)$$

The preexponential factor (A) was calculated with Eq. (4):

$$\ln A = \ln k_{1+n} + E/RT. \quad (4)$$

To determine the order of the reaction with respect to the metal salt in the mixed solvent benzene–acetic acid (7:3), we investigated the dependence of the rate of CuP **II** formation on the concentration of Cu(AcO)$_2$. The figure shows that the logarithmic dependence of k_{ef} on the concentration of copper acetate has a linear character:

$$\ln k_{ef} = \ln k + n \ln c[Cu(AcO)_2]. \quad (5)$$

The reaction order n with respect to the salt in the benzene–acetic acid mixed solvent, as shows Fig. 1, is 0.5. The reaction order for complexation with respect to Cu(AcO)$_2$ in pyridine is 0.4 [9]. Total rate constants were calculated by Eq. (6):

$$k_{1+n} = k_{ef}/c^n [Cu(AcO)_2]. \quad (6)$$

The effective rate constants and kinetic parameters of the formation of the porphyrin copper complexes **I–V** are listed in Tables 1 and 2.

The data on the kinetics of the formation of copper complexes with porphyrins **I–V** in pyridine (Tables 1 and 2) show that upon the increasing deformation of the tetrapyrrole ring the rate of the complexation reaction increases, while the activation energy decreases. The most reactive in the formation of the copper complexes are porphyrins **IV** and **V**, whose aromatic macrocycle is distorted maximally due to the presence of the nitro groups in *meso*-positions. Porphyrin **V** is more active in the complexation reaction than porphyrin **IV**. The decisive contribution to the energy of the transition state in this case obviously orogonates from the extension of N–H bonds because of the presence of the electron-acceptor nitro groups in the *para*-positions of the phenyl rings. Another pattern was obtained in the study of the complexation reaction of porphyrins **I−V** with copper acetate in the benzene–acetic acid (7:3) mixed solvent (Tables 1, 2). In this binary solvent the reactivity of porphyrin **IV** toward complexation is extremely low. Here, the effect of deformation contributes to the basicity of the tertiary nitrogen atoms, and they form strong hydrogen bonds with molecules of acetic acid blocking the porphyrin coordination center. A slight increase in the rate of the complexation of porphyrin **V** compared with **IV** is apparently due to the opposite contributions of the deformation and –*I*-effect of the nitro groups in the phenyl rings to the complexation reaction rate.

EXPERIMENTAL

Copper acetate of analytical grade was recrystallized from aqueous acetic acid and dried at 370–390 K. Pyridine of reagent grade was dried with potassium hydroxide and distilled twice [10]. Acetic acid of reagent grade was dried by boiling with a

Table 1. Effective rate constants of porphyrins **I–V** coordination by copper acetate in pyridine and in the benzene–acetic acid mixed solvent[a] (λ is the analytical wavelength)

Comp. no.	Pyridine			Acetic acid–benzene (7:3)		
	λ, nm	T, K	$k_{ef}\times10^5$, s^{-1}	λ, nm	T, K	$k_{ef}\times10^3$, s^{-1}
I	507	318	2.23±0.13	532	298	5.7±0.4
		328	5.2±0.3		308	14±0.6
		338	12±0.6		318	29.5±1.2
II	559	318	1.2±0.07	534	298	10±0.6
		328	2.3±0.11		308	22.5±0.8
		338	4.7±0.3		318	50.3±1.2
III	521	298	44±2.55	606	298	2.49±0.12
		308	79±4.42		308	6.03±0.3
		318	136±7.75		318	13.6±1
IV	573	288	210±10	564	298	1.08±0.04
		298	340±17		308	3±0.15
		308	520±30		318	8.8±0.6
		318	790±50			
V	The reaction occurs at mixing solutions			562	288	0.945±0.056
					298	3±0.12
					308	8.84±0.44

[a] In pyridine, $c[\mathrm{Cu(OAc)_2}] = 2.5\times10^{-3}$ M, in the mixed solvent benzene–acetic acid (7:3) $c[\mathrm{Cu(OAc)_2}] = 2.5\times10^{-4}$ M.

Table 2. Kinetic parameters of the porphyrins **I–V** coordination by copper acetate in the mixed solvent benzene–acetic acid (7:3) and pyridine

Porphyrin	Acetic acid–benzene (7:3)			Pyridine		
	$K^{298}_{1.5}$, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	A, s^{-1}	$K^{318}_{1.4}\cdot10^3$, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	A, s^{-1}
I	0.360±0.014	64±2	5.97	0.245±0.014	74±1	$35\cdot10^7$
II	0.633±0.037	62±2	4.67	0.132±0.009	60±3	$94\cdot10^4$
III	0.157±0.011	66±1	5.82	14.94±0.87	44±1	$25\cdot10^4$
IV	0.068±0.003	85±1	5.42	86.8±5.2	33±2	$22\cdot10^3$
V	0.190±0.008	82±1	4.49	The reaction does not occur instantaneously at mixing solutions		

calculated amount of acetic anhydride and distilled. Benzene of analytical grade was distilled on a column. The water content in solvents was determined using titration by the method of Fisher [11], it was 0.03% in pyridine, 0.02% in acetic acid, and 0.01% in benzene.

^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer, solvent deuterochloroform, internal reference TMS. IR spectra were taken on a Fourier transform Avatar 360 FT-IR EAS spectrometer from tablets with potassium bromide.

The electron absorption spectra and the rate of porphyrins **I–V** complexing with Cu(AcO)$_2$ were measured on a Hitachi U-2000 spectrophotometer in temperature-controlled cells with polished caps, in the temperature range from 298 K to 338 K. The temperature fluctuations did not exceed ±0.1 K.

5,15-Diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphine (I). To a solution of 1.2 g (5.21 mmol) of 3,3'-diethyl-4,4'-dimethylpyrrolylmethane [3] and 0.6 ml (7.75 mmol) of benzaldehyde in 400 ml of methylene chloride in an argon atmosphere while stirring was added a solution of 1.0 g (10.6 mmol) of monochloroacetic acid in 20 ml of methylene chloride. The mixture was stirred in the dark for 4 h, then 1.9 g (7.8 mmol) of *p*-chloranil was added, and the mixture was kept for 12 h at room temperature. The solvent was evaporated and the residue was washed with 5% solution of sodium hydroxide and water, and dried. For purification, the product was dissolved in chloroform, chromatographed on alumina of III degree of activity by Brockmann eluting with chloroform, the solvent was then evaporated and the porphyrin was recrystallized from chloroform–methanol. Yield 1.25 g (38%). R_f = 0.28 (benzene). EAS λ_{max}, nm (log ε): 625 (3.30) 574 (3.85) 542 (3.70) 508 (4.23) 409 (5.34). ^{1}H NMR spectrum, δ, ppm: 10.22 s (2H, 10,20-H), 8.05 m (4H, *o*-H, Ph); 7.75 m (6H, *m,p*-H, Ph); 2.47 s (12H, 3,7,13,17-CH_3); 3.96 q (8H, 2,8,12,18-C H_2 CH_3); 1.75 t (12H, 2,8,12,18-$CH_2C\underline{H}_3$), –2.43 br.s (NH).

5,15-bis(4'-Dinitrophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyn (II). To a solution of 0.6 g (2.6 mmol) of 3,3'-diethyl-4,4'-dimethylpyrrolylmethane [3] and 0.4 g (2.6 mmol) of *p*-nitrobenzaldehyde in 200 ml of methylene chloride in CO_2 atmosphere while stirring was added a solution of 0.5 g (3.9 mmol) of monochloroacetic acid in 20 ml of methylene chloride. The mixture was stirred in the dark for 4 h, then 0.95 g (3.9 mmol) of *p*-chloranil was added, and the mixture was kept for 12 h at room temperature. The solvent was evaporated, and the residue was washed with 5% solution of sodium hydroxide and water, and dried. For purification the product was dissolved in chloroform and chromatographed on alumina of III degree of activity by Brockman eluting with chloroform. The solvent was evaporated and the porphyrin was crystallized from a chloroform–methanol mixture. Yield 0.45 g (24%). R_f = 0.5 (benzene). EAS, λ_{max}, nm (log ε): 626 (3.4), 575 (3.9), 542 (3.8), 508 (4.2), 408 (5.2). ^{1}H NMR spectrum, ($CDCl_3$–CF_3COOH, external TMS), δ, ppm: 10.29 s (2H, 10,20-H); 8.78 q (4H, *o*-H, Ph); 8.54 q (4H, *m*-H, Ph); 2.24 s (12H, 3,7,13,17-CH_3); 3.74 q (8H, 2,8,12,18-$C\underline{H}_2CH_3$), 1.36 t (12H, 2,8,12,18-$CH_2C\underline{H}_3$); –2.28 br.s (4H, NH).

Nitration of porphyrins (general procedure). To a solution of about 50 mg of porphyrin in 3 ml of trifluoroacetic acid at room temperature while stirring was added the required amount of sodium nitrite. The mixture was stirred at room temperature monitoring its composition by TLC on Silufol plates. After completing the reaction, the mixture was poured into 50 ml of water, neutralized with 25% solution of ammonia till the change in color from green to red-brown. The nitroporphyrin precipitate was filtered off, washed with water, and dried in air at room temperature to a constant weight. To purify, the nitroporphyrin was dissolved in 30 ml of benzene and chromatographed on a column (1.5×25 cm) with silica gel 60 (230–400) eluting with benzene. The eluate was evaporated to a minimum volume, and the reaction product was precipitated with methanol, filtered, washed with methanol, and dried at room temperature to a constant weight.

10-Nitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyn (III). An equimolar amount (5.45 mg, 0.079 mmol) of sodium nitrite was added to a solution of 49.55 mg (0.079 mmol) of porphyrin **I** in trifluoroacetic acid. The reaction time was 10 min. Yield 29.83 mg (56.2%). R_f = 0.26 (benzene). EAS λ_{max}, nm (log ε): 665 (3.41) 595 (3.78) 524 (4.04) 418 (5.04). ^{1}H NMR spectrum, (δ, ppm): 9.84 s (1H, *meso*-H), 8.08 m (4H, *o*-H, Ph); 7.75 m (6H, *m,p*-H, Ph); 3.8 q (4H, $C\underline{H}_2CH_3$); 3.35 q (4H, $C\underline{H}_2CH_3$); 2.28 s (6H, CH_3); 2.16 s (6H, CH_3); 1.59 t (6H, $CH_2C\underline{H}_3$); 1.27 t (6H, $CH_2C\underline{H}_3$); –2.69 s (2H, NH). IR spectrum, cm^{-1}: 1531 (δ_{as} NO_2), 1368 [δ_s (NO_2)].

10,20-Dinitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyn (IV). 1.5-Fold excess (3.06 mg, 0.044 mmol) of sodium nitrite was added to a solution of 20 mg (0.0296 mmol) of nitroporphyrin **III** in trifluoroacetic acid. The reaction time was 90 min. Yield 8.04 mg (37.7%). R_f = 0.63 (benzene). EAS λ_{max}, nm (log ε): 696 (3.78) 607 (3.91) 541 (4.06) 447 (4.99). ^{1}H NMR spectrum, (δ, ppm): 8.08 m (4H, *o*-H, Ph); 7.81 m (6H, *m,p*-H, Ph); 1.96 s (12H, 3,7,13,17-CH_3); 3.11 q (8H, 2,8,12,18-$C\underline{H}_2CH_3$); 1.18 t (12H, 2,8,12,18-$CH_2C\underline{H}_3$); –2.41 br.s (2H, NH). IR spectrum, cm^{-1}: 1533 (δ_{as} NO_2), 1361 [δ_s(NO_2)].

The dinitro-substituted compound **IV** was also obtained by one-step nitration of 51.05 mg (0.079 mmol) of porphyrin **I** with two equivalents (10.9 mg, 0.16 mmol) of sodium nitrite in trifluoroacetic acid medium. The reaction time was 90 min. Yield 38 mg (65.2%). The products were identical.

10,20-Dinitro-5,15-bis(4'-dinitrophenyl)-3,7,13,17-tetramethyl-2 ,8,12,18-tetraethylporphyn (V). Ten equivalents (47.85 mg, 0.69 mmol) of sodium nitrite were added to a solution of 50.0 mg (0.069 mmol) of porphyrin **II** in trifluoroacetic acid. The reaction time was 90 min. Yield 29.02 mg (51.6%). R_f = 0.54 (benzene). EAS λ_{max}, nm (log ε): 689 (3.45) 616 (3.80) 545 (4.05) 457 (4.99). ^{1}H NMR spectrum, (δ, ppm): 8.69 q (2H, *o*-H, Ph); 8.41 q (2H, *m*-H, Ph); 3.17 q (8H, 2,8,12,18-$C\underline{H_2}CH_3$), 1.99 m (12H, 3,7,13,17-CH_3), 1.28 m (12H, 2,8,12,18-$CH_2C\underline{H_3}$); –2.47 br.s (2H, NH). IR spectrum, cm^{-1}: 1532 (δ_{as} NO_2), 1353 [δ_s (NO_2)].

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