

Synthesis and Characterization of Some Phthalic Acid Derivatives Precursors for Phthalocyanine Chromogens

VALENTIN RĂDIȚOIU*, LUMINIȚA WAGNER, ALINA RĂDIȚOIU, PETREA ARDELEANU, VIORICA AMĂRIUȚEI, ANA-ALEXANDRA SORESCU

Research and Development National Institute for Chemistry and Petrochemistry -ICECHIM, 202 Splaiul Independenței, 060021, Bucharest, Romania

The article presents experimental data regarding some organic compounds as chemical intermediates with phthalic acid structure, precursors for new phthalocyanine compounds as : 4-nitrophthalimide, 4-aminophthalimide, 4-nitrophthalonitrile and 4-aminophthalonitrile, synthesized by chemical transformation of phthalimide by a series of successive reactions as : nitration and reduction, or nitration, amidation, dehydration and reduction. Reaction products were purified and characterized by means of elemental analysis, UV-Vis, fluorescence, IR, ¹H-NMR, ¹³C-NMR spectroscopy, and thermal analysis. Structure-property relationship in the organic compounds is discussed with respect to the nature of the substituents.

Keywords: phthalimide, 4-aminophthalimide, 4-aminophthalonitrile, phthalocyanine

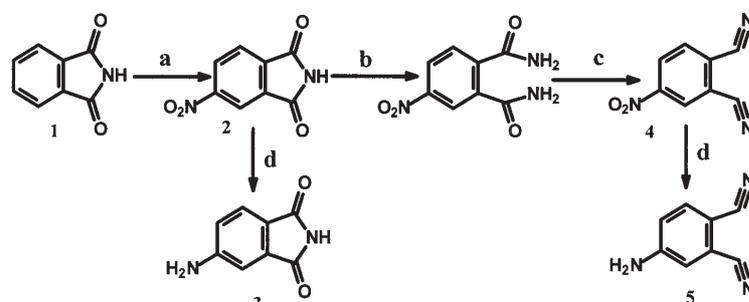
Phthalocyanine chromogens were intensively studied because of their multiple applications as organic pigments and in the last period for unconventional applications in sensors domain, photovoltaic cells or in cancer photodynamic therapy as we can mention some examples.

Phthalocyanines can be obtained by template classical reactions from different precursors such as phthalonitriles, 2-cyanobenzamides, 1,3-diiminoisoindolines, phthalimides, phthalic acid, etc., generally reaction being conducted in no aqueous solvents with high boiling points [1]. Besides the classical method, the electrochemical way [2, 3], and another unconventional synthesis methods for phthalocyanines (laser use [4], UV radiation [5,6],

nitrophthalimide (compound 2) either by reducing with 4-aminophthalimide formation (compound 3) or by forming 4-nitrophthalamide followed by their dehydration at 4-nitrophthalonitrile (compound 4) that by reducing gave 4-aminophthalonitrile (compound 5).

1) obtaining 4-nitrophthalimide (compound 2)

At a quantity of 45 g nitric acid (0.714 moles) under stirring and at a temperature of 0-2°C it was added 324 g sulphuric acid (3.306 moles). Over sulphonic mixture thus obtained and under stirring at a temperature of 2-5°C, it was added 30 g phthalimide (0.203 moles), reaction mass



a –sulponitric mixture;b–ammonia solution;c–thionyl chloride/N,N-dimethylformamide;d–Na₂S₂O₄

Scheme 1

ultrasonic methods [7], or synthesis at microwaves [8-10]) were in attention for scientist for these compounds syntheses optimization.

As it can be seen from consulting enumerated references, the most important intermediates used in these syntheses are phthalimide or phthalonitrile derivatives. Going on from these arguments and having as final scope obtaining phthalocyanine-azomethine joint chromogens, respectively phthalocyanine-quinacridone we have in mind 4-aminophthalimide and 4-aminophthalonitrile synthesis and characterization as key intermediates for suggested synthesis.

Experimental part

The paper presents experimental data regarding syntheses and characterization of some compounds (scheme 1) derived from phthalic acid synthesized by phthalimide nitration (compound 1), transforming 4-

being maintained 5 h for concluding the nitration reaction (chromatography testing), interval in which temperature was let free to rise from 5°C to 25°C. Over a mixture of 50 mL water and 350 g ice and under stirring at 0-2°C, it was added the reaction mass thus temperature was maintained under 10°C. The resulting suspension was filtered and after that paste was washed with 200 mL water with ice in portions to pH=4. The isolated 4-nitro-phthalimide paste was dried at 40-50°C, obtaining 31.5 g 4-nitrophthalimide that correspond to an 60% yield.

2) obtaining 4-aminophthalimide (compound 3)

To a solution obtained from 150 mL water and 26 g sodium dithionite (0.15 mole) stirred at 25°C it was added a nitroderivative suspension made from 5.79 g 4-nitrophthalimide (0,03 mole) and 30 mL ammonia solution 25%. The reaction mass was stirred 4 h at normal temperature for finishing reduction reaction (chromato-

* Tel.: 0740043398

graphic test), maintaining at a weak alkaline pH. Amine suspension was filtered and the isolated product was dried at 40-50°C. It was obtained 2.92 g 4-amino-phthalimide that correspond to a 80% yield.

3) obtaining 4-nitrophthalonitrile (compound 4)

To a quantity of 116.55 g ammonia solution 25% (1.714 moles) stirred and exterior cooled it was added 28.95 g 4-nitrophthalimide (0.15 mole) maintaining temperature at 25°C for 24 h for finishing the amidation reaction (chromatographic test). 4-nitrophthalimide suspension was filtered in vacuum and the isolated product was washed with 200 ml cold water in portions to pH=7 and it was dried at 40-50°C in a vacuum drying stove. It was obtained 30 g 4-nitrophthalimide that correspond to a 95% yield.

In 100 mL N,N-dimethylformamide stirred at 0-5°C it was added 41.75 mL thionyl chloride (68 g, 0.572 moles). Over the obtained mixture and under stirring at 0-5°C it was added 30 g 4-nitrophthalimide (0.143 moles) that was maintained 18 h for concluding dehydration reaction, reaction being done in a nitrogen atmosphere. The reaction mass was added to a mixture made from 80 mL water and 80g ice stirred at 0-2°C so that temperature was maintained under 10°C. The resulted suspension was filtered and washed on the filter with 150 mL water with ice to a pH=5. The isolated product was dried in a vacuum drying stove at 40-50°C, obtaining 22.6 g 4-nitrophthalonitrile which correspond to a 86% yield.

4) obtaining 4-aminophthalonitrile (compound 5)

To a solution made from 150 mL water and 26.1 g sodium dithionite (0.151 moles) and under stirring at normal temperature it was added a nitroderivative suspension obtained from 5.54 g 4-nitrophthalonitrile (0.032 moles) and 30 ml ammonia (25%) solution, maintained 4 hours (chromatographic test). Suspension was filtered, and isolated product was dried in a drying stove at 40-50°C. It was obtained 1.83 g 4-aminophthalonitrile, that correspond to a 40% yield.

Purifying of the obtained compounds was made by recrystallization from absolute ethanol. Purified compounds were subject for elemental analysis. Experiments were made with a Carlo-Elba M 1106 apparatus. Results obtained are presented in table 2 and are in good agreement with those theoretically calculated.

UV-Vis absorption spectra and fluorescence emission spectra were made with solutions in ethanol and dimethylsulphoxide, respectively water and dimethylsulphoxide at 10^{-4} molar concentrations, at $25 \pm 0,5^{\circ}\text{C}$, in rectangular quartz cuvettes with a thickness of 1 cm, on a UV-VIS-NIR JASCO V-570 spectrometer, respectively a JASCO FP 6500 spectrofluorometer (results and work conditions being those from tabels 3-4) and IR spectra were made in kalium bromide pellets on a JASCO FT-IR 6300 spectrometer (results and work conditions being those from table 5). ^1H - and ^{13}C -NMR spectra were made on a Bruker Avance 400 MHz spectrometer at 25°C (results and work conditions are presented in table 6). Thermal analysis (DSC) was made with a thermal analysis system Du Pont TA 2000, in air at a heating rate of 0.5 degree / min.

Results and discussions

For phthalimide nitration, reaction medium used was sulphuric acid of 96% and 100%, that have a double role, to solvate phthalimide for nitration and binding agent for water that result from nitration, ensuring by charged quantity an optimal dehydration capacity. It was chosen

for using sulphuric acid 100% concentration at a volumetric ratio 6:1 to nitric acid. Concerning the molar ratio phthalimide : nitric acid, it was varied in the range 1:2 to 1:5 correlated with small reactivity of phthalimide. In case of a 1:2 ratio, nitrated product was impurified with phthalimide, for a 1:5 ratio a large excess of nitric acid conduct to impurification with bis nitrated derivative, optimum molar ratio being established to 1:3.5. Ratio water : ice necessary for seaking was varied in the limits 1:1 to 1:10, optimum being established to 1:7, when it was ensured a good stirring and a minimum volume but also a maximum nitroderivative concentration of 6% in the reaction mass.

For the achievement of the reduction reaction of 4-nitrophthalimide with sodium dithionite, molar ratio 4-nitrophthalimide : sodium dithionite was varied in the limits 1:2 to 1:7, for a 1:2 ratio the reduced product being impurified with nitrophthalimide and for 1:7 ratio the large excess of sodium dithionite conduct to formation of large quantities of sodium sulfite and sulphur by decomposition. The best results were obtained at a molar ratio of 1:5, being mentioned that maintaining an alkaline pH during reduction was very important for obtaining a pure product. Molar ratio 4-nitrophthalimide : ammonia was varied between 1:2 and 1:14, optimum being established at 1:9.

For the achievement of 4-nitrophthalimide dehydration reaction, the medium used was N,N-dimethylformamide that had a role in solvation of thionyl chloride and bisamide for maintainig an omogen reaction mass. Molar ratio 4-nitrophthalimide : thionyl chloride was varied in the limits 1:2 to 1:5 correlated with little reactivity of 4-nitrophthalimide. For a 1:2 ratio 4-nitrophthalonitrile was impurified with nitrophthalimide. The optimum molar ratio was established to 1:4.

For the completing of the 4-nitrophthalonitrile reduction reaction with sodium dithionite, nitroderivative was conditioned by suspending or solvating under stirring in pyridine, sodium hydroxide 20% solution, ammonia 25% solution and concentration of the raw material in the reaction mass was varied in 10-25% range. It was selected as optimum alkaline agent ammonia solution 25% and an optimum nitroderivative concentration of about 18%, since as a consequence of the reduction reaction with sodium dithionite result ammonia salts more soluble in the reaction mass that determined a high purity of the reaction product. Molar ratio 4-nitrophthalonitrile : sodium dithionite was varied in the limits 1:2 to 1:7. Optimum molar ratio was established at 1:4.7 from the same reasons exposed in the case of 4-nitrophthalimide reduction.

From the experiments it was concluded that for a good unfolding of the reduction reaction the dithionite solution used must have a maximum concentration, order of adding the reactants was the nitroderivative suspension over the hydrosulfite solution so at the end of the adding reducing reaction was unfolded in omogen medium by nitroderivative solvation. Always maintaining alkaline pH during the reduction was very important for obtaining a pure product.

Purity of the synthesized compounds and controle during the synthesis was made by thin layer chromatography being established fix and mobile phases for each compound and determined specific developing method.

Subsequent experiments were established as optimal separation method, the ascending method on glass plates having as stationary phase Silica gel 60G (Merck) and as mobile phase ethyl acetate p.a.. Probes solubilization was done in ethanol p.a. at a 0.5% concentration and was

Table 1
R_f VALUES FOR SYNTHESIZED INTERMEDIATES

| Compound | 1 | 2 | 3 | 4 | 5 |
|----------------|-----|------|------|------|------|
| R _f | 0.9 | 0.94 | 0.85 | 0.00 | 0.78 |

Table 2
RESULTS FOR ELEMENTAL ANALYSIS

| Compound | Molecular mass | Elemental analysis (%) | | | | | | Melting point (°C) |
|----------|----------------|------------------------|-------|------------|-------|------------|-------|--------------------|
| | | C | | H | | N | | |
| | | calculated | found | calculated | found | calculated | found | |
| 1. | 147.13 | 65.31 | 65.09 | 3.43 | 3.24 | 9.52 | 9.84 | 241 |
| 2. | 192.13 | 50.01 | 49.88 | 2.10 | 1.97 | 14.58 | 14.72 | 202 |
| 3. | 162.15 | 59.26 | 59.07 | 3.73 | 3.56 | 17.28 | 17.43 | 288 |
| 4. | 173.13 | 55.50 | 55.34 | 1.75 | 1.61 | 24.27 | 24.41 | 140 |
| 5. | 143.15 | 67.13 | 66.95 | 3.52 | 3.44 | 29.35 | 29.53 | 185 |

Table 3
RESULTS FOR UV-VIS SPECTROMETRY

| Compound 1 | Compound 2 | Compound 3 | Compound 4 | Compound 5 |
|---|------------------------|------------------------|------------------------|------------------------|
| c = 1.85 · 10 ⁻⁴ M in water | | | | |
| λ ₁ =298 nm | λ ₁ =327 nm | λ ₁ =302 nm | λ ₁ =299 nm | shoulder at 316 nm |
| lg ε = 2.953 | lg ε = 3.817 | lg ε = 3.689 | lg ε = 2.545 | |
| | λ ₂ =409 nm | λ ₂ =368 nm | | |
| | lg ε = 3.800 | lg ε = 3.757 | | |
| | λ ₃ =430 nm | | | |
| | lg ε = 3.735 | | | |
| | λ ₄ =469 nm | | | |
| | lg ε = 3.308 | | | |
| c = 1.80 · 10 ⁻⁴ M in dimethylsulphoxide | | | | |
| λ ₁ =292 nm | shoulder at 286 nm | λ ₁ =313 nm | λ ₁ =306 nm | λ ₁ =290 nm |
| lg ε = 3.364 | | lg ε = 3.931 | lg ε = 3.388 | lg ε = 3.941 |
| | | λ ₂ =373 nm | | λ ₂ =331 nm |
| | | lg ε = 3.804 | | lg ε = 3.498 |

applied at a 2μL level. Compounds visualizing was done after exposure in a chlorine chamber and sputtering with a mixture 1:1 (vol/vol) made from a kalium iodide aqueous solution 1% and a starch 1% solution, the color obtained being mauve. R_f values for studied compounds are presented in table 1.

The synthesized compounds, in accordance with the resulted methods from laboratory experiments were purified by recrystallization from absolute ethylic alcohol and were characterized by elemental analysis in a Carlo Erba M 1106 apparatus, the obtained results being in accordance with the calculated data (table 2). Melting points were determined with a Mettler SP5 thermal analyzing system at a 5°C/min. heating rate.

Obtaining compounds with necessary purity for spectral characterization need separation of the obtained mixtures by column chromatography, using as stationary phase Silicagel 60G and as mobile phase ethyl acetate.

Analyzing absorption spectra in the UV domain (table 3) it was found that all the synthesized compounds have ethylene characteristic bands (E) and benzene (B) due to some π-π* transitions and also conjugated bands (K) and of radical type (R) due to the presence of the heteroatom's (nitrogen, oxygen) in the molecule, that have nonbonding pairs of electrons. Analyzing molar coefficient and absorption maxima positions as a function of solvent polarities used for experiments for all the compounds presented, it was found that absorption maxima

correspond to overlaying of some permitted transitions of π-π* type having large absorption molar coefficients, with forbidden transitions of n-π* type having small absorption molar coefficients. Presence of grafted substituent's on the benzene nucleus is materialized in the ultraviolet absorption spectrum by a displacement of the absorption maximum expanded between 5-20 nm as a function of the substituent nature and solvent polarity. Grafting a substituent with (-I, -M) effect as it is nitro group leads to a hypsochromic effect under the position of the absorption maxima of 26-29 nm. Appearance in the ultraviolet domain of a band that can be of charge transfer between the aromatic ring as donating and nitro group as accepting, was situated dependent on solvent polarity at 286 nm as a shoulder in the case of the compound 2.

In the case of grafting amino group having (-I, +M) effects in the same position of the compound 2, produced a bathochromic shift on the absorption maximum of 70 nm. Appearance in the spectrum of a supplementary band at 302-313 nm for compound 3, respectively at 290 nm for compound 5, can be due to an electronic transition with charge transfer. The amino group was acting as donating group and benzene ring as accepting group.

Absorption maxima shifting to larger wavelengths by increasing solvent polarity demonstrate that by interaction with light are favoured polar structures that are also responsible on the other hand for luminescence phenomena.

Table 4
RESULTS FOR EMISSION OF FLUORESCENCE SPECTROMETRY

| Com- pound | solid | | | | water | | | | | dimethylsulphoxide | | | | | |
|---------------|------------------------|------------------------|---------------|------------------|------------------------|------------------------|---------------|-----------------------------------|------------------|------------------------|------------------------|---------------|-----------------------------------|------------------|------|
| | λ_{ex} (nm) | λ_{em} (nm) | I_f a.u. | Sensi- bility | λ_{ex} (nm) | λ_{em} (nm) | I_f a.u. | Conc., mole/l $\times 10^4$ | Sensi- bility | λ_{ex} (nm) | λ_{em} (nm) | I_f a.u. | Conc., mole/l $\times 10^4$ | Sensi- bility | |
| 1. | - | - | - | 11x 1/10 | - | - | - | - | 11x 1/10 | 365 | 472 | 1023 | 2.3 | 11x 1/10 | |
| 2. | - | - | - | | - | - | - | - | | - | 365 | 468 | 90 | | 0.52 |
| 3. | 365 | 511 | 4761 | | 365 | 545 | 426 | 1.85 | | 365 | 472 | 22635 | 0.77 | | |
| 4. | - | - | - | | - | - | - | - | | - | 365 | 472 | 1492 | | 1.8 |
| 5. | 365 | 504 | 3693 | | 300 | 398 | 1304 | 2 | | 300 | 393 | 5051 | 1.9 | | |

Table 5
RESULTS FOR ABSORPTION IR SPECTROMETRY

| Com- pound | Frequencies (cm^{-1}) |
|---------------|--|
| 1 | 3518 ; 3197 ; 3060 ; 2717 ; 2185 ; 2002 ; 1971 ; 1904 ; 1868 ; 1774 ; 1751 ; 1604 ; 1467 ; 1387 ; 1307 ; 1288 ; 1184 ; 1140 ; 1089 ; 1070 ; 1053 ; 975 ; 817 ; 794 ; 745 ; 715 ; 668 ; 647 ; 549 ; 534 ; 407 |
| 2 | 3329 ; 3105 ; 3056 ; 2348 ; 1957 ; 1792 ; 1702 ; 1621 ; 1546 ; 1433 ; 1412 ; 1349 ; 1308 ; 1172 ; 1110 ; 1078 ; 1031 ; 937 ; 900 ; 865 ; 801 ; 761 ; 719 ; 689 ; 651 ; 606 ; 556 ; 519 ; 417 |
| 3 | 3853 ; 3838 ; 3735 ; 3675 ; 3648 ; 3445 ; 3362 ; 3243 ; 2361 ; 1762 ; 1718 ; 1645 ; 1616 ; 1589 ; 1558 ; 1541 ; 1507 ; 1473 ; 1392 ; 1346 ; 1325 ; 1244 ; 1134 ; 1041 ; 970 ; 836 ; 748 ; 631 ; 565 ; 494 |
| 4 | 3419 ; 3098 ; 3086 ; 3050 ; 2880 ; 2241 ; 1956 ; 1856 ; 1831 ; 1713 ; 1610 ; 1587 ; 1538 ; 1480 ; 1410 ; 1355 ; 1298 ; 1214 ; 1177 ; 1128 ; 1075 ; 931 ; 917 ; 855 ; 801 ; 744 ; 716 ; 647 ; 599 ; 525 ; 490 |
| 5 | 3852 ; 3734 ; 3445 ; 3288 ; 2226 ; 1716 ; 1635 ; 1599 ; 1558 ; 1541 ; 1496 ; 1436 ; 1397 ; 1331 ; 1234 ; 1135 ; 1043 ; 963 ; 842 ; 625 ; 523 ; 397 |

Compounds 3-5 had absorption maxima shifted bathochromic and hyperchromic passing from polar solvents (water) to dimethylsulphoxide while compounds 1-2 presented shifting hypsochromic and hypochromic.

It is evidently that wavelength of the emission maximum was influenced by the possible intermolecular interactions by hydrogen bonds with solvent, the structure of compounds being decisive. Because of the phthalimide residue able to give hydrogen bonds, colors of the fluorescence emission for 4-aminophthalimide were from blue to green while for 4-aminophthalonitrile are from violet to green.

Fluorescence was observed in case of those derivatives having donating groups (compounds 3 and 5), when absorption and emission properties are associated with intramolecular charge transfer implying electron donating group (amino) and electron withdrawing groups (carbonyl and nitrile).

There were explained differences between wavelengths of these two amines emission maxima (manifested in solution and in solid state 78/46/7 nm) mostly in dimethylsulfoxide solution (more nonpolar solvent) when solvent-compound interactions are more weak.

Stokes shifts are more important for 4-amino-phthalonitrile being over 100 nm, while for the phthalimide derivative because of the molecule polarity and groups capable to associate intermolecular by hydrogen bonds, in solution and also in solid state, Stokes shifts are only of 30 nm.

The other compounds had weak fluorescence only in the nonpolar solvent. Fluorescence intensity, four times higher for phthalimide derivative than for phthalonitrile derivative recorded in dimethylsulfoxide was explained by weak interactions nonpolar solvent - polar molecules, while in water phthalonitrile derivative had a fluorescence intensity three times higher than that of phthalimide

compound because of strong interactions polar solvent - polar molecules. In solid state where such interactions are comparative, compounds present roughly the same fluorescence intensity.

In IR spectra bands situated at 1650 cm^{-1} and 1350 cm^{-1} are assigned to benzene skeleton vibrations. Their positions is not determined so much by the substituent nature but by its position in the nucleus. Thus for compound 1 bands at 1604 cm^{-1} respectively 1468 cm^{-1} may be assigned to stretching vibrations of the C=C group. Cycle breathing vibrations are, for compound 1, situated at 1053 cm^{-1} respectively 817 cm^{-1} while for in plane deformation vibrations these are situated at 716 cm^{-1} and 647 cm^{-1} and for out of plane at 534 cm^{-1} .

Vibrations of the CH bond were found for compound 1 at 3060 cm^{-1} and they were not affected by the substituent's nature, for the other compounds being situated at $3050\text{--}3100\text{ cm}^{-1}$. In plane and outer plane deformation vibrations are founded at $1184\text{--}1031\text{ cm}^{-1}$, respectively $970\text{--}900\text{ cm}^{-1}$.

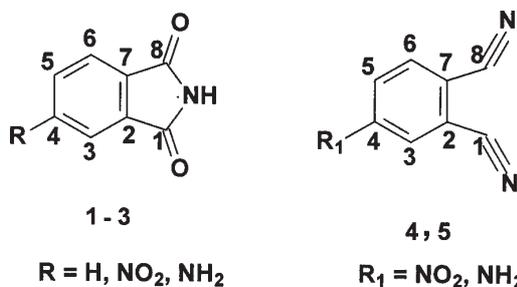
Stretching vibrations of the CN bond was situated at 1184 cm^{-1} , while in plane deformation being at 407 cm^{-1} . Stretching vibration frequencies for the carbonyl group was situated in $2000\text{--}1500\text{ cm}^{-1}$ region, but in the same range it was founded also deformation vibration of the N-H bond or stretching vibrations for C=C and CN bonds. Yet this group gave more intense absorption, position depending of conjugation, hydrogen bonds, and the cycle size of which it was attached. For cyclic imides there were observed two stretching bands in $1790\text{--}1740\text{ cm}^{-1}$, respectively $1730\text{--}1700\text{ cm}^{-1}$ zone. In plane and outer plane oscillation vibrations are situated at 550 cm^{-1} , respectively 408 cm^{-1} and had weak intensity. Stretching frequency for NH group was found at 3197 cm^{-1} for phthalimide, in plane deformation at 1468 cm^{-1} and out of plane at 647 cm^{-1} .

Primary aromatic amines gave two intense absorption bands at 3500 cm^{-1} asymmetric and at 3400 cm^{-1} symmetric.

For compounds, 3 and 5 the first band was situated at 3445 cm^{-1} and the second at 3360 cm^{-1} . In plane deformation vibrations are observed at 1616 cm^{-1} , respectively 1599 cm^{-1} and for the out of plane are in the range 700-850 cm^{-1} .

For compound 4 vibrations of the CN groups from nitriles is situated at 2241 cm^{-1} and for compound 5 at 2226 cm^{-1} their positions being influenced by conjugation.

Aromatic nitro derivatives gave two characteristic very intense vibrations in IR spectrum at 1560 cm^{-1} the asymmetric and at 1370 cm^{-1} the symmetric one. For compound 2 these are situated at 1546 cm^{-1} , respectively 1349 cm^{-1} and for compound 4 at 1538 cm^{-1} , respectively 1355 cm^{-1} .



Scheme 2. Atoms localization for ^1H and ^{13}C -NMR spectra

Phthalimide was characterized by ^1H -NMR, its spectrum having the signal that correspond to four equivalent protons situated as a singlet at 7.81 ppm. At 11.32 ppm was situated the imide proton as large singlet. ^{13}C -NMR spectra had four signals that correspond to the equivalent carbon atoms.

4-nitrophthalimide was characterized by ^1H -NMR spectrometry, spectrum having signals that correspond to four protons. At 8.07-8.08 ppm it was observed as a doublet H-6 proton. This was situated in meta position strong electronoaccepting nitro group. H-3 proton appeared at 8.44 ppm, small splitting of the signal showing that in the neighbourhood doesn't exist protons. Due to this fact it was concluded that nitration take place in position 4 and H-5 proton was situated as doublet at 8.60-8.62 ppm. Imide proton appeared as large singlet at 11.83 ppm. Its position was slightly shifted to lower field with 0.5 ppm, showing that it was deshielded by the presence of an electron accepting group. ^{13}C -NMR spectrum contain signals for the carbonyl carbon atoms at 167 ppm and at 151.34 ppm appeared the carbon atom linked to the nitro group. The other carbon atoms were situated at usual values for aromatic carbon atoms being influenced by vecinities.

By ^1H -NMR spectrometry was established the signal accordingly to primary aromatic amine group from 4-aminophthalimide situated as singlet at 3.59 ppm and imide proton as large singlet at 11.86 ppm. At 7.42-7.44 ppm it was observed as doublet of singlets H-6 proton. This was situated in meta position of strong electronodoning amino group. H-3 proton appeared at 6.87 ppm, small splitting of the signal showing that in its vicinity doesn't exist protons and H-5 was situated at 6.79-6.81 ppm as doublet. ^{13}C -NMR spectrum contained signals that correspond to carbonyl atom at 169 ppm and at 154.88 ppm appeared the carbon atom linked to amino group.

We found that ^1H -NMR spectrum for 4-nitrophthalonitrile present distinct signals for the three aromatic protons, having chemical shifting to the lower values of the field. H-3 proton became the most deshielded having a value of the shift of 8,98 ppm. Shifting of the values with 0.7 ppm to those recorded for 4-nitrophthalimide was large enough for proving formation of the newest compound and for checking reaction promotion (synthesis control). Amide proton that corresponds to precursor (4-nitrophthalimide) disappeared from the spectrum that indicated total transforming of the amidic groups in nitriles. In ^{13}C -NMR spectrum are viewed signals corresponding to carbon atoms from the nitrile groups situated at 115.12-114.81 ppm and those of the carbon atom linked to the nitro group situated at 149.92 ppm.

As it was observed from the ^1H -NMR spectrum after nitro group reduction and formation of the aromatic amino group it was produced a shifting to higher field of the aromatic protons. In the spectrum H-3 proton vicinal to amino group was founded as a singlet shifted to 7.03 ppm while H-5 proton was founded as a doublet at 6.87-6.89 ppm. A small shielding effect was recorded for the H-6 proton that appeared in the spectrum as a doublet at 7.61-7.63 ppm. For the proton from the aromatic amino group signal in the spectrum was an intense singlet situated at 3.41 ppm. ^{13}C -NMR spectrum had as main characteristics the presence of the carbon atom from nitrile groups at 116.45-115.47 ppm values and finding the carbon atom linked to the amino group at 153.09 ppm.

Melting points depend on the molecular structure and rise when imides residues are present grafted on to the structure. This was may be due to the molecular symmetry and more good packing in the crystal lattice and may be attributed to the intermolecular hydrogen bonds.

Melting point for compound 1 determined by DSC at 0.5 degree/minute heating rate was 241 $^{\circ}\text{C}$, DSC curve

Table 6
RESULTS FOR ^1H -NMR AND ^{13}C -NMR SPECTROMETRY

| Compound | ^1H NMR δ (ppm) $(\text{D}_3\text{C})_2\text{SO}$ | ^{13}C NMR δ (ppm) CDCl_3 |
|----------|--|---|
| 1 | NH : 11.32 s, 1H H-3;H-4;H-5;H-6 : 7.81 s, 4H | C-1;C-8 : 169.17; C-2;C-7 : 132.56 C-3;C-6 : 122.86; C-4;C-5 : 134.24 |
| 2 | NH : 11.83 s, 1H H-3 : 8.44 s 1H; H-5 : 8.60-8.62 d 1H H-6 : 8.07-8.08 d, 1H | C-8 : 167.51; C-1 : 167.22; C-4 : 151.34; C-7 : 137.27; C-2 : 134.02; C-3 : 117.73; C-5 : 124.44; C-6 : 129.41 |
| 3 | NH ₂ : 3.59 s, 2H; NH : 11.86 s, 1H H-3 : 6.87-6.87 sd 1H H-5 : 6.79-6.81 dd 1H H-6 : 7.42-7.44 ds, 1H | C-1 : 169.81; C-8 : 169.52; C-4 : 154.88; C-7 : 118.06; C-2 : 135.57; C-3 : 106.91; C-5 : 117.02; C-6 : 124.90 |
| 4 | H-3 : 8.98-8.98 sd 1H H-5 : 8.64-8.67 dd 1H H-6 : 8.38-8.40 ds, 1H | C-1 : 115.12; C-8 : 114.81; C-4 : 149.92; C-7 : 120.37; C-2 : 116.77; C-3 : 128.70; C-5 : 129.00; C-6 : 135.82 |
| 5 | NH ₂ : 3.41 s, 2H H-3 : 7.03 sd 1H H-5 : 6.87-6.89 dd 1H H-6 : 7.61-7.63 ds, 1H | C-1 : 116.45; C-8 : 115.47; C-4 : 153.09; C-7 : 97.72; C-2 : 117.54; C-3 : 116.98; C-5 : 117.27; C-6 : 134.93 |

presenting two neighboring peaks, first at 241°C that represent the melting point and the second at 249°C probable associated to starting of the thermal decomposition. For compound 2 was recorded a transformation that correspond to melting at 197-202°C, heat of the transformation measured being 117 J/g. Melting point for compound 3 was recorded at 278-288°C, heating of the transformation being 36.6 J/g.

DSC analysis for 4-nitrophthalonitrile present an endothermic transformation that correspond to melting at 140°C, heating of the transformation being 124 J/g. The last compound 4-aminophthalonitrile was the most unstable at heating in air, taking place additions and oxidation reactions, the melting process superposed to those processes in the range 162-187°C.

Conclusions

The synthesis methods approached for obtaining the organic compounds derivatives of phthalic acid consist of traversing some successively reaction steps, established work conditions leading to obtaining reaction products with good purity and high yields.

Each product obtained was isolated for characterization and after purifying was submitted to elemental analysis, spectrometric analysis (absorption and emission UV-VIS, IR, ¹H and ¹³C-NMR) and thermal analysis.

For all four studied compounds were established correlations between chemical structure and spectral behavior, distinguishing structural particularities for each case.

Studied compounds constitute base of raw materials for obtaining azomethine chromogens designated for new organic compounds with condensed structure and joint chromogen phthalocyanine-azomethine, usable in unconventional and tinctorial applications.

Financial support: Study was achieved as part of the project CEEEX 21/2005 - AMCSIT Politehnica.

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Manuscript received. 2.06.2008