New Perylene Structures

DELIA ATANASOAIE[1]*, ION SEBE[1], LAVINIA OPRISAN[1], LUCIAN ISCRULESCU [2], ELENA TINTAVEANU[3], CRISTINA MINDRUTA[2]

[1] University Politehnica of Bucharest, Faculty of Industrial Chemistry,149 Calea Victoriei, 010072, Bucharest, Romania

[2] UMF Carol Davila, Faculty of Pharmacy, 4 Traian Vuia, 020956, Bucharest, Romania

[3] Hygiene and Veterinary Public Health Institute, 5 Campul Mosilor, 021201, Bucharest, Romania

The paper presents experimental data regarding five new thermo-resistant pigments synthesized by condensing perylene 3,4,9,10-tetracarboxylic dianhydride with different amines in various molar ratio. Reaction products were purified and characterized by elemental analysis, UV-VIS and IR.

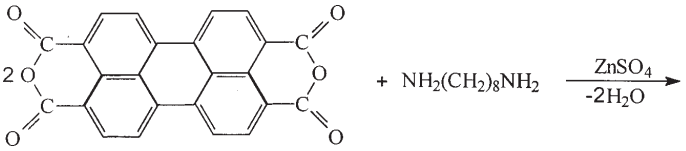
Keywords: Perylene 3,4,9,10-tetracarboxylic dianhydride, amines, thermo-resistant pigments, fluorescence

Perylene dyes are known for their good thermo-resistant properties and their high fluorescence in different media [1]. Some of them are successfully used as crystal growing inhibitors. They are also used for synthesizing fluorescent pigments for liquid crystals devices such as displays and for the colored laser technique [2-4]. Perylene dyes have been used for laser applications since 1961 [5-7].

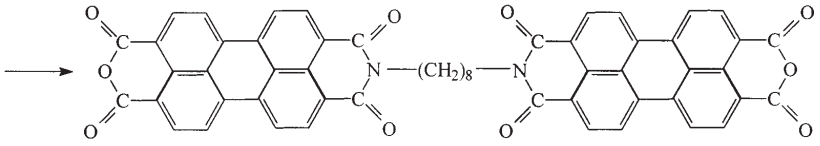
This paper presents the synthesis of new compounds starting from 3,4,9,10-perylenetetracarboxylic 3,4,9,10-dianhydride by condensing it with different amines. The physical and chemical properties of all compounds were analyzed.

Experimental part

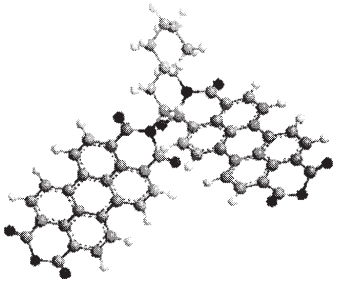
In the condensing reaction perylene 3,4,9, 10-tetracarboxylic dianhydride, different amines (octane-1,6-diamine, hexane-1,6-diamine, 6-amino-hexan-1-ol, 2-amino-5-(3-hydroxy-prop-1-ene-1-sulfonyl)-benzoic acid, 3-(4-amino-benzenesulfonyl)-prop-2-en-1-ol, 3-(4-amino-3-methyl-benzenesulfonyl)-prop-2-en-1-ol), 1,4,6-C_6H_3, $Zn(CH_3COO)_2$ and inorganic compounds (HCl, NaOH) were used, according to the following reactions:



1



P_1



*Synthesis of pigment **1** (P_1)*

200 mL of 1,4,6-trichlorobenzene were introduced into a 3-necked flask with mechanical stirrer, reflux condenser and thermometer and were heated to 100° then 7.84 g (0.2 moles) of perylene 3,4,9, 10-tetracarboxylic dianhydride and 2.16 g moles octane-1,6-diamine (0.015) were added while stirring. After dissolution of the reagents 1.77 g (0.01 moles) of $Zn(CH_3COO)_2$ were added. Reaction mass is heated at 200° for 12 h. The reaction is considered completed when a sample reaction mass no longer displays the characteristic fluorescence of the dianhydride heated with a NaOH solution at the boiling point. After the reaction is completed, the mixture is cooled to 100° and filtered. The precipitate is washed with HCl to remove the traces of the unreacted amine. Finally the precipitate is washed with boiling water to neutral pH . The solid phase is dried at 100°, 8.5 g (yield = 75.3%) of dried product is obtained.

The others compounds were obtained using the similar procedure

Fig. 1. Space configuration of the P_1 molecules

* *Tel.: (+40) 021 402 91 00*

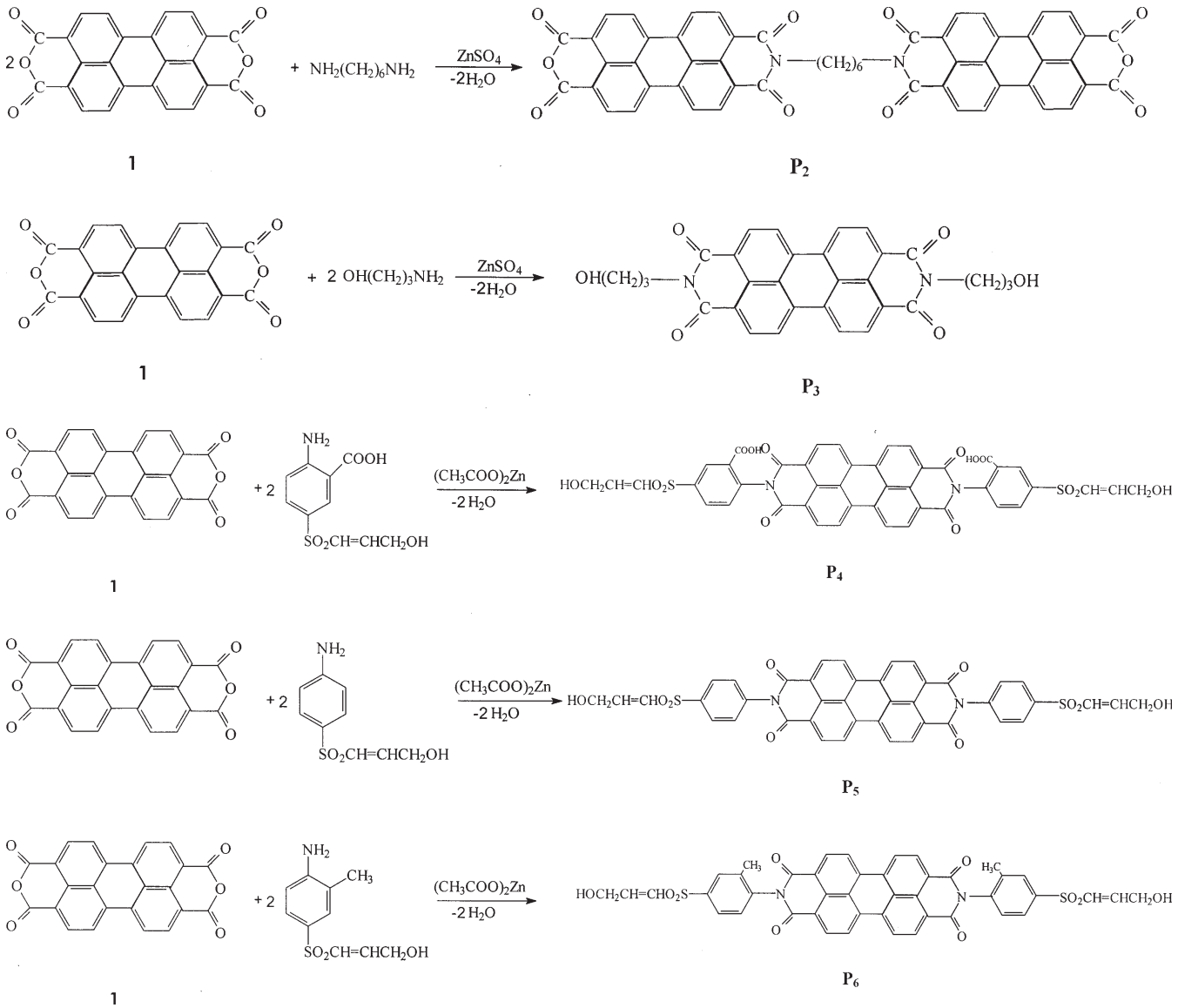


Fig. 2. Space configuration of the $\mathbf{P_6}$ molecules

Results and discussions

In order to confirm the proposed structures the main physical and chemical characteristics were determined for the prepared compounds.

The reaction conditions are presented in table 1.

The purity of the obtained products was tested by TLC using Silica Gel F_{254} plates and DMF as eluent.

The elemental analysis was done through combustion method. The results are given in tabel 2. The obtained percentages are comparable with the calculated ones.

The UV-VIZ spectroscopic measurements were performed with SPECORD 40 apparatus in the range of 200-800 nm in H_2SO_4 95%. Compounds were characterized by the wavelength of their absorption maximum. Results of spectral analysis are presented in table 2.

The I.R. absorption spectra were recorded using a VERTEX 70 apparatus in KBr pellets in the range of 500-3500 cm^{-1}. Results of IR spectra are presented in table 3.

The data obtained from the study of the spectra shows that there is a concordance between the proposed and actual structures. It can be noted that the vibration bands of the C=O bond (characteristic for aromatic anhydrides) at 1024 cm^{-1}(vc-o asim) no longer appear. Opposite split bands characteristic of the cyclic imides can be noted at about 1700 cm^{-1} (sym. C=O frequency) Similarly, each compound displays the characteristic bands of the amines with which the condensation took place.

Fluorescent spectra were recorded using a CARY 10 (VARIAN) apparatus in the λ =190-1000 nm range. The

Table 1
REACTION PARAMETERS

Comp.	Molar ratio (anhydride/ amine)	Catalyst	Reaction medium	Time (h)	Temp (°C)	Color	Yield (%)
P_1	0.01:0.004	$(CH_3COO)_2Zn$	$C_6H_3Cl_3$	8	180	Brown-red	75.4
P_2	0.01:0.004	$(CH_3COO)_2Zn$	$C_6H_3Cl_3$	8	180	Brown-red	78.36
P_3	0.01:0.03	$(CH_3COO)_2Zn$	$C_6H_3Cl_3$	8	180	Brick-red	87.7
P_4	0.01:0.025	$(CH_3COO)_2Zn$	$C_6H_3Cl_3$	12	200	Brick-red	79
P_5	0.01:0.025	$(CH_3COO)_2Zn$	$C_6H_3Cl_3$	12	200	Brick-red	82
P_6	0.01:0.025	$(CH_3COO)_2Zn$	$C_6H_3Cl_3$	12	200	Red	85

Table 2
ELEMENTAL ANALYSIS

Comp	Molecular formula	$M_{1*/2*}$	C%		H%		N%	
			1*	2*	1*	2*	1*	2*
P_1	$C_{56}H_{32}O_{10}N_2$	892/890	75.33	75.32	3.58	3.47	3.13	3.08
P_2	$C_{54}H_{28}O_{10}N_2$	864/862	75	74.89	3.24	3.18	3.24	3.21
P_3	$C_{30}H_{22}O_6N_2$	506/504	71.14	71.1	4.34	4.31	5.53	5.49
P_4	$C_{44}H_{26}0_{14}N_2S_2$	870/868	60.68	58.94	2.98	2.83	3.21	3.18
P_5	$C_{42}H_{26}O_{10}N_2S_2$	782/778	64.45	63.62	3.32	3.26	3.58	3.47
P_6	$C_{44}H_{30}O_{10}N_2S_2$	810/808	65.18	64.93	3.7	3.63	3.45	3.37

1*=calculated; 2*=determined

Table 3
PHYSICAL AND CHEMICAL PARAMETERS OF THE SYNTHESIZED COMPOUNDS

Compound	λ(nm)	Type of bond	Frequency (cm^{-1})	R_f
P_1	247,6 555,5 601,8	$-CH_{2sim}$ $-CH_{2asim}$ -CH=CH- $C=O_{sim}$ $C-O_{sim}$ $C-O_{asim}$	2860,37 2927,01 1593,59 1701,36 939,1 1122,16	0.85
P_2	247 310 555 600	$C=O_{sim}$ $C=O_{asim}$ $-CH_{2sim}$ $-CH_{2asim}$ $C-O_{sim}$ $C-O_{asim}$	1772,03 1704,57 2860,37 2927,32 939,26 1122,13	0,8
P_3	250.46 550.38 600.58	-OH $-CH_{2sim}$ $-CH_{2asim}$ C=C $C=O_{sim}$	1197,8 2852,24 2926,14 1590,78 1773,5	0,75
P_4	220,7 245,4 511.2 578.6	-OH $-SO_{2asim}$ $-SO_{2sim}$ $C=O_{sim}$ $C=O_{asim}$ COOH C-N	1198,56 1365,04 1559,35 1771,32 1703,81 3325,29 1250,8	0,79
P_5	225,7 245.01 485,6 520,6 587,9	-OH $-SO_{2asim}$ $-SO_{2sim}$ C=C $C=O_{sim}$ $C=O_{asim}$ C-N	1193,32 1367,72fi 1569,12fi 1591,23 1772,48 1701,02 1360,58	0,83
P_6	221,9 246,3 510,8 584.4	-OH $-SO_{2asim}$ $-SO_{2sim}$ C=C $C=O_{sim}$ $C=O_{asim}$	1197,32 1359,24 1546,12 1592 1770,38 1701,3	0.84

recorded absorbtion maxima (in dioxane) for the studied compounds were in the range of 485-519 nm. The tests were performed at *p*H = 9 and at *p*H = 12.

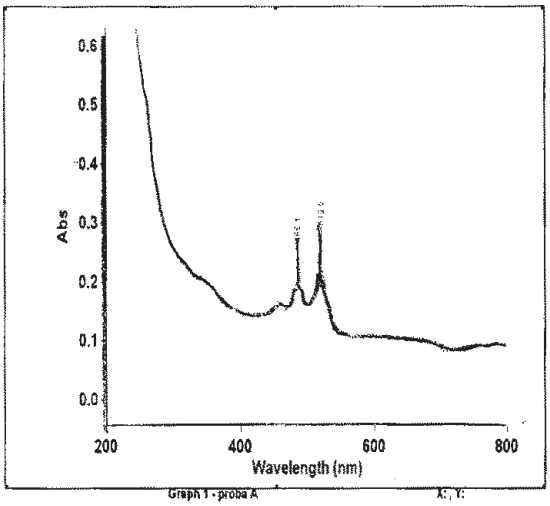


Fig. 3 Fluorescent spectra of P_1

The obtained compounds were insoluble in water- and they could be used as pigments. The melting points are over 300^0.

Conclusion

The 6 new pigments having perylene structure were synthesized by condensing 3,4,9,10-perylenetetracarboxylic 3,4,9,10-dianhidryde with various amines. Reactions were performed in 1,2,4-trichlorobenzene using $(CH_3COO)_2Zn$ as catalyst.

The analysis for the determination of the structures for this type of pigments is particularly difficult due to their insolubility. The obtained pigments are insoluble in HCl, but they are soluble in H_2SO_4 yielding fluorescent solutions with red-violet to violet-blue coloration.

References

1.ATĂNĂSOAIE D.,EBE, I., OPRIŞAN, L., ISCRULESCU, L., Mat. Plast., **44**, no. 4, 2007, p. 303
2. NAGAO, YUKINOU, MISONO, TOKAHISA, TONATE, YORIKO „Nippon Kogaku Kaishi" 1980, (9), 1391-6, cf. Chem. Abstr. 98, 116816y, 1983
3. SCHULZ, G.R., Patent US ,21 may 2002 , 6391104,C07D221/18,Cl 106/494
4. NOWIASKI, P.,Patent US 2.668.815,cf. Chem. Abstr. 48, 11802 e, f, g
5. KOROSIL, A., (American Cynamid Co) Eur. Pat. Apply. Ep. 227.086 (Cl C09411/07), 01 Jul 1987 ,US Appl. 831 .346 , 26 Dec 1985 , 5pp ,cf. CA 1987 ,107, 280525k
6. REISFELD, R., JURGENSEN, C. K., Structure and Chem . Physs Lett. 1989 ,160 ,43. cf. H. Zollinger "Color Chemistry",Weinhein New-York ,Basel-Cambridge,1991
7. IRVING F., WILLIAM DONALD G., US. 3,546,222, (Cl. 260-249G; C07d) 08 Dec 1970, Apr 15, cf. Chem. Abstr. 1970, 70, 38872u.]

Manuscript received: 28.11.2008