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Synthesis and Physicochemical Properties of Heterocyclic Compounds Based on 5,7-Diimino-2,5,6,7-tetrahydro-1*H*-cyclopenta[*cd*]phenalene

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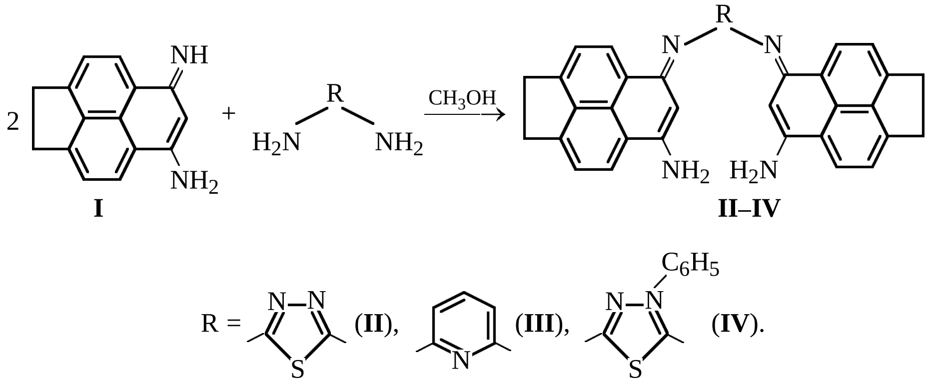
Abstract—*N,N'*-Bis(7-amino-2,5-dihydro-1*H*-cyclopenta[*cd*]phenalen-5-ylidene)-substituted derivatives of 2,5-diamino-1,3,4-thiadiazole, 2,6-diaminopyridine, and 3,5-diamino-1-phenyl-1,2,4-triazole were synthesized. The products are soluble in water, and they attract interest as potential biologically active substances.

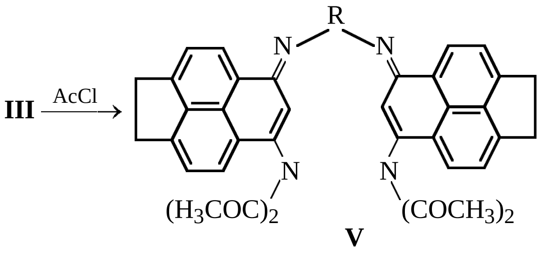
Arylenediamines based on isoindole and 1,3-indandione [1–5] are soluble only in nonaqueous media. Analogous derivatives of 5,7-diimino-2,5,6,7-tetrahydro-1*H*-cyclopenta[*cd*]phenalene are soluble in water. Proceeding with our studies in the field of synthesis and properties of various heterocycles, the present communication reports on arylenediamines which can be used as intermediate products in the preparation of macroheterocyclic compounds. 5,7-Diimino-2,5,6,7-tetrahydro-1*H*-cyclopenta[*cd*]phenalene (**I**) was obtained by reaction of acenaphthene with malononitrile [6]. Compound **I** is an orange–brown substance which does not melt below 300°C. Arylenediamines **II**–**IV** were synthesized by reaction of diimine **I** with aromatic diamines: 2,5-diamino-1,3,4-thiadiazole, 2,6-diaminopyridine, and 3,5-diamino-1-phenyl-1,2,4-triazole, respectively (Scheme 1).

Scheme 1.



The reactions were carried out in boiling methanol at a reactant molar ratio of 2 : 1. Products **II**–**IV** are brown crystalline substances which are soluble in water, methanol, ethanol, and dimethylformamide and insoluble in benzene and acetone. They do not undergo hydrolysis on heating in boiling hydrochloric acid. Acylation of compound **III** with acetyl chloride afforded the corresponding tetraacetyl derivative (Scheme 2).

Scheme 2.



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Characteristic frequencies (cm^{-1}) in the IR spectra of compounds **I**–**IV**

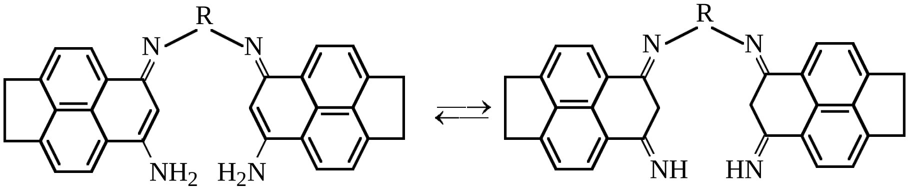
Comp. no.	ν(C=NH)	ν(NH_2)	δ(NH_2)	ν(CH)	δ(CH)	ν(C=C)	ν(C–N)	ν(C=N)	ν(C–S)
I	3408	3425	1600	3120	1440	1560		1638	
II		3330	1512	3190	1408	1500	1160	1650	620, 645
III		3427	1520	3180	1490	1510	1080	1645	
IV		3410	1530	3050	1480	1510	1150	1640	1450[a]

[a] ν(N=N).

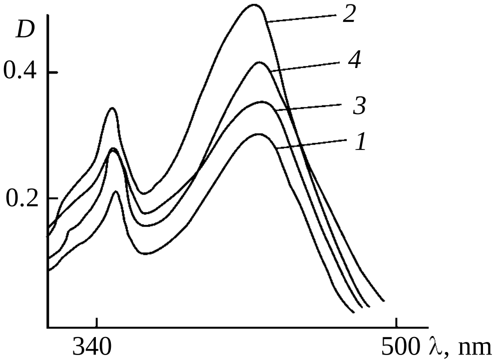
The structure of the products was confirmed by the IR spectra. Some characteristic IR frequencies are listed in the table. The IR spectra of **II**–**IV** preserve the main absorption bands typical of initial diiminocyclopentaphenalene (**I**), which appear at 3425, 3275, and 3100 cm^{-1}. The position of these bands indicates formation of intermolecular hydrogen bonds, but it is difficult to assign them to a particular amino or imino group. The IR spectrum also contains a strong absorption band at 1650 cm^{-1}, which belongs to bending vibrations of primary amino group. Stretching vibrations of the C=N bonds should give rise to a band located in the same region. This band can be distinguished when the β_{NH} band is displaced toward higher frequencies [7]. The $\nu_{C=N}$ band in the spectrum of **I** is located at 1638 cm^{-1} and is the strongest (obviously, due to association). The band at 1580 cm^{-1} arises from bending vibrations of the imino group [8], and strong band at 1560 cm^{-1} was assigned to stretching vibrations of the C=C bond in the cyclohexene ring. Single C–C and C–N bonds give rise to absorption in the region 1400–850 cm^{-1} (see table).

Compounds **II**–**IV** can exist as at least two tautomers (Scheme 3).

Scheme 3.



Like compound **I**, the IR spectra of **II**–**IV** contain absorption bands corresponding to vibrations of the amino and imino groups. The band at 1160–1080 cm^{-1} is typical of stretching vibrations of the C–N bond. In addition, absorption bands arising from stretching vibrations of the C–S bond in the thiadiazole ring (1560 cm^{-1}, compound **II**) and N=N bond in the 1,2,4-triazole ring (1450 cm^{-1}, compound **IV**), and pyridine ring (475 cm^{-1}, compound **III**) are observed (see table).



Electronic absorption spectra of compounds (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV** in water; *c* = 10^{-4}–10^{-5} M.

Compounds **II**–**IV** are characterized by the presence of two absorption maxima in the electronic spectra of their aqueous solutions. The first maximum is located at λ 340–342 nm and is less intense. It belongs to π–π transitions in the acenaphthene core [9]. The second, more intense band at λ 403–410 nm arises from electronic transitions in the NH_2–C=C–C=N bond system (see figure). The electronic absorption spectra of compounds **II**–**IV** resemble that of initial compound **I**. No bands indicating appearance of a new chromophore were found.

EXPERIMENTAL

The electronic absorption spectra were recorded on a Specord M-400 spectrophotometer from solutions in water and DMF at 20°C (quartz cells, *l* = 1 cm). The IR spectra were measured on a Specord M-80 instrument in KBr. The purity of the products was checked by TLC on Silufol UV-254 plates.

2,5-Bis(7-amino-2,5-dihydro-1*H*-cyclopenta[*cd*]-phenalen-5-ylideneamino)-1,3,4-thiadiazole (II). A mixture of 3 g of compound **I** and 0.8 g of 2,5-diamino-1,3,4-thiadiazole in 50 ml of methanol was heated under reflux. When the reaction was complete, the mixture was cooled to room temperature, and the precipitate was filtered off, washed with benzene, alcohol, and acetone, and dried at 100–120°C. Yield 2 g (57%); brown crystalline substance which does not melt below 400°C; R_f 0.45 (DMF); insoluble in benzene and acetone; soluble in water, methanol, ethanol, and DMF. UV spectrum, λ_{max}, nm: DMF: 342, 409 (log ε 4.5); H_2O: 342, 405. Found, %: C 72.9; H 4.1; N 16.4; S 5.9. $C_{32}H_{22}N_6S$. Calculated, %: C 73.6; H 4.2; N 16.1; S 6.1.

2,6-Bis(7-amino-2,5-dihydro-1*H*-cyclopenta[*cd*]-phenalen-5-ylideneamino)pyridine (III) was synthesized in a similar way from 3 g of compound **I** and 0.7 g of 2,6-diaminopyridine. Yield 1.82 g (52%); brown crystalline substance which does not melt below 400°C; R_f 0.55 (DMF); insoluble in benzene and acetone; soluble in water, methanol, ethanol, and DMF. UV spectrum, λ_{max}, nm: DMF: 342, 406 (log ε 4.0); H_2O: 342, 404. Found, %: C 80.7; H 4.8; N 11.9. $C_{35}H_{25}N_5$. Calculated, %: C 81.5; H 4.9; N 13.6.

3,5-Bis(7-amino-2,5-dihydro-1*H*-cyclopenta[*cd*]-phenalen-5-ylideneamino)-1-phenyl-1,2,4-triazole (IV) was synthesized in a similar way from 3 g of compound **I** and 1.2 g of 3,5-diamino-1-phenyl-1,2,4-triazole. Yield 2 g (51%); brown crystalline substance which does not melt below 400°C; R_f 0.67 (DMF); insoluble in benzene and acetone; soluble in water, methanol, ethanol, and DMF. UV spectrum, λ_{max}, nm: DMF: 342, 405; H_2O: 341, 405 (log ε 4.4). Found, %: C 77.9; H 4.6; N 16.8. $C_{38}H_{27}N_7$. Calculated, %: C 78.4; H 4.7; N 16.9. Products **II**–**IV** showed a positive test for amino group with phthalic anhydride. Also, they were subjected to hydrolysis.

Qualitative test for amino group. A mixture of 1 g of compound **I** and 1.2 g of phthalic anhydride in 20 ml of glacial acetic acid was heated under reflux. When the reaction was complete, the mixture was diluted with 20 ml of distilled water and neutralized with a 10% solution of alkali. The precipitate was filtered off, washed with acetone, and dried in air. Yield 1 g (48%); brown substance which does not melt below 400°C. UV spectrum, λ_{max}, nm: DMF: 342, 401; H_2O: 342, 377. Found N, %: 7.1. $C_{64}H_{38}N_6O_{12}S$. Calculated N, %: 7.6.

Acylation of compound III. A mixture of 2 g of compound **III** and 60 ml of acetic anhydride was heated under reflux. The precipitate was filtered off, washed with dilute acetic acid, alcohol, and water, and dried in air. Yield 2 g (71%); brown substance which does not melt below 400°C. Found N, %: 10.7. $C_{46}H_{47}N_7O_8$. Calculated N, %: 11.9.

Determination of the composition of the acyl derivative. A 0.00674-g portion of the acylated product was added to 30 ml of 0.1 N NaOH (*k* = 1.3869), and the mixture was heated for 1.5 h at 60°C. The mixture was diluted with 100 ml of distilled water and was titrated with 0.1 N hydrochloric acid (32.2 ml; *k* = 1.1326) in the presence of phenolphthalein as indicator. The number of the acyl groups was calculated by the formula

$$n = \frac{(V_1N_1k_1 - V_2N_2k_2)M}{1000a},$$

where *V* is the volume of the alkali and hydrochloric acid (ml), *N* is the normality of the solutions, *k* is a correction factor, *M* is the assumed molecular weight of the acylated product, and *a* is the sample weight (g).

$$n = \frac{30\times0.1\times1.3869 - 32.2\times0.1\times1.1326}{1000\times0.0674} = 4.16.$$

Hydrolysis. A mixture of 0.1 g of compound **III** and 20 ml of concentrated hydrochloric acid was heated at the boiling point. The mixture was cooled, poured into distilled water, and neutralized with a 10% solution of NaOH. The precipitate was filtered off and washed with alcohol and acetone. Yield 0.08 g, the product does not melt below 400°C. UV spectrum (DMF), λ_{max}, nm: 342, 401. Compound **III** hydrochloride is insoluble in water. Found, %: Cl 10.1; N 13.8. Calculated, %: Cl 10.86; N 15.0.

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