Synthesis and Study of Macroheterocyclic Compounds Based on 2,6-Dihydro-1*H*-cyclopenta[*cd*]phenalene-5,7-diimine

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Abstract—Previously unknown macroheterocyclic compounds containing cyclopenta[*cd*]phenalene and 1-phenyl-1,2,4-triazole, 1,3,4-thiadiazole, or pyridine fragments were synthesized by reaction of 2,6-dihydro-1*H*-cyclopenta[*cd*]phenalene-5,7-diimine with heteroaromatic diamines.

This study continues our previous works on the synthesis and physical and chemical properties of various macroheterocyclic compounds and metal complexes derived therefrom [1–6]. The present communication reports on the synthesis of water-soluble macroheterocyclic compounds on the basis of 2,6-dihydro-1*H*-cyclopenta[*cd*]phenalene-5,7-diimine, which attract interest as potential biologically active substances.

2,6-Dihydro-1*H*-cyclopenta[*cd*]phenalene-5,7-diimine (**I**) was prepared from acenaphthene and malononitrile [7]. It is an orange–brown substance melting above 300°C. Macroheterocyclic compounds **V**–**VII**

were synthesized by heating equimolar amounts of diimine **I** and heteroaromatic diamines, 3,5-diamino-1,3,4-thiadiazole, 2,6-diaminopyridine, and 3,5-di-amino-1-phenyl-1,2,4-triazole, in boiling butanol (Scheme 1). They were also prepared from 2:1 condensation products **II**–**IV** and the corresponding heteroaromatic diamines. The products obtained by the two methods had identical elemental compositions and properties.

Macroheterocyclic compounds **V**–**VII** are brown powders of different tint, which do not melt up to 400°C. They are weakly soluble in water, methanol, ethanol, and dimethylformamide and are resistant to

Scheme 1.
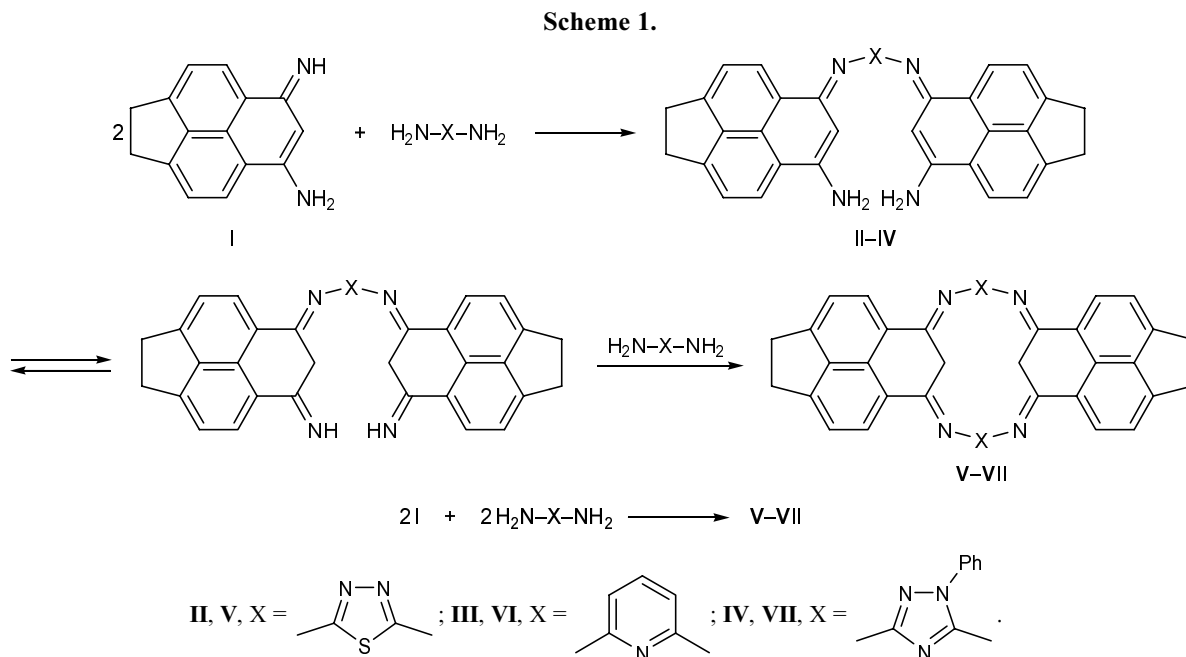
Absorption frequencies (cm^{-1}) in the IR spectra of compounds **I–VII**

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) [ν(N=N)]
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]
V				3200	1404	1512	1275	1624	664, 628
VI				3010	1495	1511	1120	1650	
VII				3080	1485	1513	1110	1600	[1455]

hydrolysis in boiling concentrated hydrochloric acid. Their structure was confirmed by the IR spectra (see table). Diimine **I** displays IR absorption bands at 3425, 3408, and 3120 cm^{-1}, which indicate formation of intermolecular hydrogen bonds but are difficult to assign to amino or imino group. A strong band at 1600 cm^{-1} in the IR spectrum corresponds to bending vibration of the primary amino group. The same region is typical of stretching vibrations of the C=N bond; its absorption may be distinguished when the δ_{NH} band is displaced toward higher frequencies [8]. In our case, the strongest absorption band in the spectrum (1638 cm^{-1}) is that belonging to δ_{NH}; presumably, its intensity is enhanced due to association. The band at 1580 cm^{-1} originates from bending vibrations of the imino group [9].

The IR spectra of compounds **II–IV** contain absorption bands typical of diimine **I**. These compounds can exist as at least two tautomers (Scheme 1). Like initial diimine **I**, compounds **II–IV** showed in the IR spectra absorption bands corresponding to vibrations of the amino and imino groups. The band at 1160–1080 cm^{-1} belongs to stretching vibrations of the C–N bonds. In addition, absorption bands due to vibrations of the thiadiazole (compound **II**, $\nu_{C–S}$ 1560 cm^{-1}), 1-phenyl-1,2,4-triazole (**III**, $\nu_{N=N}$ 1450 cm^{-1}), and pyridine ring (**IV**, 1455 cm^{-1}) were present (see table).

The IR spectra of macroheterocyclic compounds contained absorption bands typical of only NH groups (3300 and 1670–1620 cm^{-1}), but those assignable to primary amino group were absent. Also, one ν(C=N) band appeared at 1650–1600 cm^{-1}. In the spectrum of **VII**, the δ_{CH} band was stronger due to the presence in its molecule of one more 1-phenyl-1,2,4-triazole fragment. On the whole, the IR spectral patterns of compounds **II–IV** and macrocyclic derivatives **V–VII** are similar.

The electron absorption spectra of **V–VII** in methanol, DMF, and water are characterized by absorption in both ultraviolet and visible regions. Unlike macroheterocyclic compounds on the basis of diimino-isoindole and 1,3-indandione [5, 10], compounds **V–VII** are soluble in water. Aqueous solutions of compounds **II–IV** and **V–VII** display two absorption bands. The first band has its maximum at λ 403–410 nm and is more intense. It originates from electron transitions in the H$_2$N–C–C–C=N bond sequence (cyclohexene ring conjugated with diamine residue). The second less intense band (λ_{max} 340–342 nm) corresponds to the acenaphthene chromophore [11]. Presumably, the electron absorption spectra of **II–IV** and macroheterocycles **V–VII**, as well as the spectrum of the initial diimine, reflect electron transitions in particular structural fragments. We observed no bands indicating appearance of a new chromophore in the macroring. Thus introduction of thiadiazole, phenyltriazole, and pyridine fragments into molecules **II–IV** does not affect the position of absorption maxima in the electron spectra to an appreciable extent, i.e., no closed conjugation system is formed as a result of macroring closure.

EXPERIMENTAL

The electron absorption spectra were recorded on a Specord M 400 spectrophotometer from solutions in methanol, DMF, and water at 20°C. The IR spectra were measured in KBr on a Specord M80 instrument. The purity of the products was checked by TLC on Silufol UV-254 plates.

2,5-Bis(7-amino-1,2-dihydro-5*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-di-amino-1,3,4-thiadiazole in 50 ml of methanol was

heated under reflux. The mixture was cooled, and the precipitate was filtered off, washed with benzene, alcohol, and acetone, and dried at 100–120°C. Yield 2 g (57%), R_f 0.45 (DMF). UV spectrum (DMF, water), λ_{max}, nm (logε): 342, 409 (4.51); 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-1,2-dihydro-5H-cyclopenta[cd]-phenalen-5-ylideneamino)pyridine (III) was synthesized in a similar way. Yield 1.82 g (52%), R_f 0.55 (DMF). Electron absorption spectrum (DMF, water), λ_{max}, nm (logε): 342, 406 (4.0); 342, 404. Found, %: C 80.7; H 4.8; N 11.9. $C_{32}H_{25}N_5$. Calculated, %: C 81.6; H 4.9; N 13.5.

2,5-Bis(7-amino-1,2-dihydro-5H-cyclopenta[cd]-phenalen-5-ylidene)-1,2,4-triazole-3,5-diamine (IV) was synthesized in a similar way. Yield 2 g (51%), R_f 0.67 (DMF). Electron absorption spectrum (DMF, water), λ_{max}, nm (logε): 342, 405; 341, 405 (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.

Qualitative test for primary 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 of the acylated derivative 1 g (48%); brown substance which did not melt below 400°C. Electron absorption spectrum (DMF, water), λ_{max}, nm: 432, 401; 342, 377. Found, %: N 7.1. $C_{64}H_{38}N_6SO_4$. 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. After cooling, the precipitate was filtered off, washed with dilute acetic acid, alcohol, and water, and dried in air. Yield 2 g (71%); brown substance which did 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 mixture of about 70 mg of the acylated product and 30 ml of a 0.1 N solution of sodium hydroxide was heated for 1.5 h at 60°C. It was then diluted with 100 ml of distilled water and titrated with 0.1 N hydrochloric acid in the presence of phenolphthalein. The number of acyl groups was calculated by the formula $n = (V_1N_1k_1 - V_2N_2k_2)M/1000\,a$, where V stands for volume, N for normality, and k for correction coefficients of the alkali and hydrochloric acid (indexed with subscripts "1" and "2", respectively); M is the presumed molecular weight of the acylated product; and a its weight (g). We thus determined that the acyl derivative of **III** contained 4 acetyl groups.

Diacenaphtheno[5,5a,6-i,j:5,5a,6-t,u]-24,26-dithia-2,4,5,7,13,15,16,18-octaazapentacyclo-[17.3.1.1^{3,6}.1^{8,12}.1^{14,17}]hexacosa-1,3,5,7,12(25),14,16,-19(23)-octaene (V). A mixture of 1 g of compound **I** in 15 ml of 1-butanol and 0.8 g of 2,5-diamino-1,3,4-thiadiazole in 15 ml of 1-butanol was heated for 30 h under reflux. The mixture was cooled, and the precipitate was filtered off, washed on a filter with alcohol and acetone, and dried at 150°C. The product was purified by Soxhlet extraction with acetone. Yield 1.7 g (65%), mp >400°C, R_f 0.55 (DMF). Electron absorption spectrum (water, methanol, DMF), λ_{max}, nm (logε): 404 (4.34); 406 (4.56); 408 (4.47). Found, %: C 65.4; H 3.9; N 17.4; S 9.5. $C_{34}H_{20}N_8S_2$. Calculated, %: C 67.6; H 3.3; N 18.5; S 10.6.

Diacenaphtheno[5,5a,6-d,e:5,5a,6-p,q]-2,8,14,-20,25,27-hexaazapentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]-octacosa-1(25),2,7(28),9(27),10,12,15(26),19,21,23-decaene (VI) was synthesized in a similar way. Yield 1.4 g (55%), mp >400°C, R_f 0.3 (DMF). Electron absorption spectrum (water, methanol, DMF), λ_{max}, nm (logε): 407 (3.17); 382, 398 (4.04); 409 (3.51). Found, %: C 80.8; H 4.3; N 12.2. $C_{40}H_{26}N_6$. Calculated, %: C 81.4; H 4.4; N 14.2.

5,23-Diphenyldiacenaphtheno[5,5a,6-i,j:5,5a,6-t,u]-2,4,5,7,13,15,16,18,24,26-decaazapentacyclo-[17.3.1.1^{3,6}.1^{8,12}.1^{14,17}]hexacosa-1,3,6(26),7,12(25),14,-17(24),19(23)-octaene (VII) was synthesized in a similar way. Yield 0.8 g (48%), mp >400°C, R_f 0.4 (DMF). Electron absorption spectrum (water, methanol, DMF), λ_{max}, nm (logε): 405 (4.85); 404 (5.3); 407 (4.4). Found, %: C 75.9; H 4.3; N 19.3. $C_{46}H_{30}N_{10}$. Calculated, %: C 76.4; H 4.2; N 19.4.

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