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Synthesis and Properties of Macroheterocyclic Compounds Containing 1-Imino-2-phenyl-1*H*-inden-3-amine Fragments

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Abstract—Reaction of 1-imino-2-phenyl-1*H*-inden-3-amine with 3,3′-dichloro-, 2,2′-disulfo-, and 2,2′-dinitro-biphenyl-4,4′-diamines gave 2 : 1 and 1 : 2 linear condensation products and symmetrical macroheterocycles. The products were characterized by the IR, UV, and ^{1}H NMR data.

Keywords: indandione, arylenediamine, macrocycle, synthesis, properties

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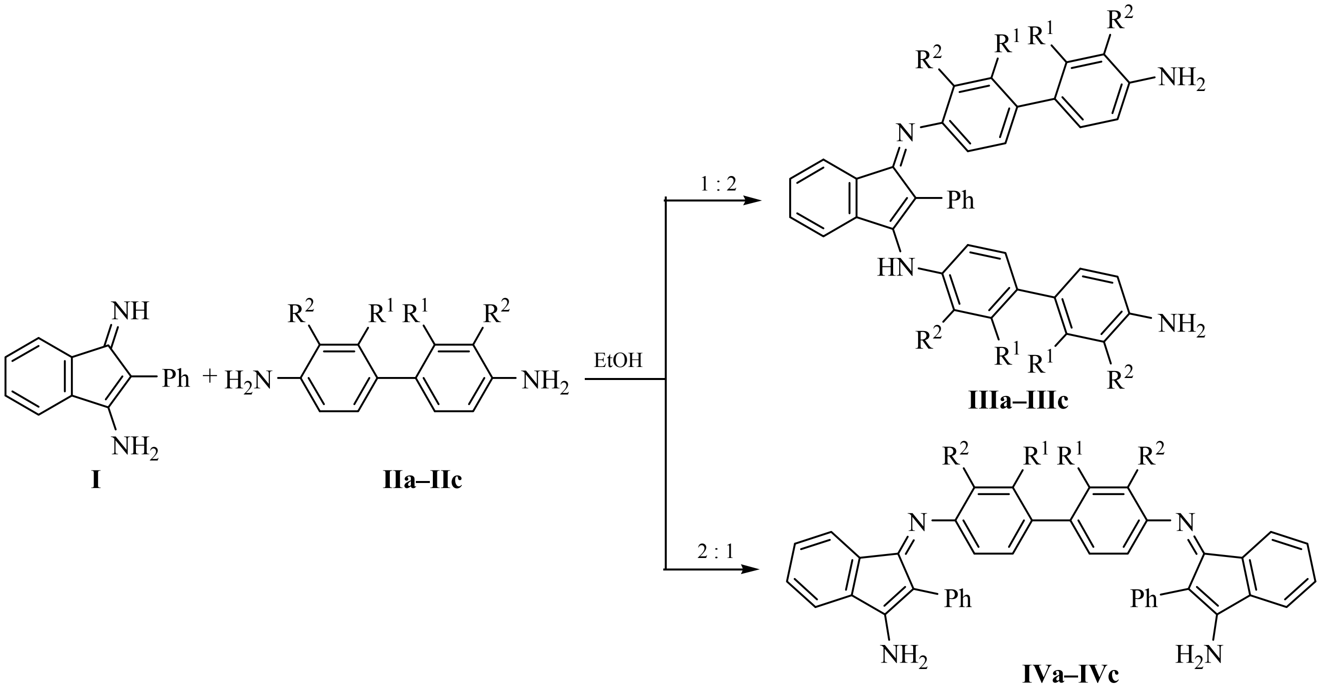
Studies on the synthesis of various macroheterocyclic compounds [1–6] are important due to potential application of such compounds in various fields of science and technology. In keeping with published data [7], macroheterocyclic compounds cannot be obtained from 2-phenylindan-1,3-dione according to the same procedure as from indan-1,3-dione. Therefore, as starting compound we selected 1-imino-2-phenyl-1*H*-inden-3-amine (**I**) [8]. The reaction of amino imine **I** with 3,3′-dichloro-, 2,2′-disulfo-, and 2,2′-dinitro-

Scheme 1.



II–IV: R^1 = SO$_3$H, R^2 = H (**a**), R^1 = H, R^2 = Cl (**b**), R^1 = NO$_2$, R^2 = H (**c**).

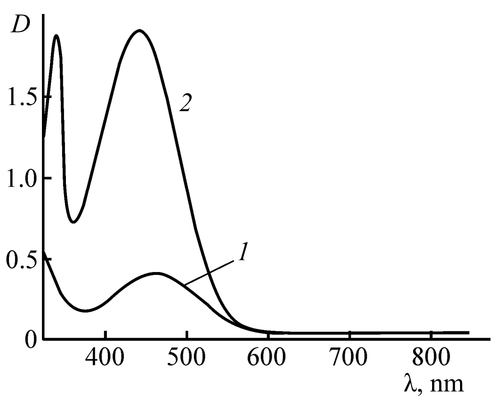


Fig. 1. Electronic absorption spectra of compounds (*1*) **IIIa** and (*2*) **Va** in acetone–chloroform (1 : 1); $c = 10^{-3}$ to 10^{-4} M.

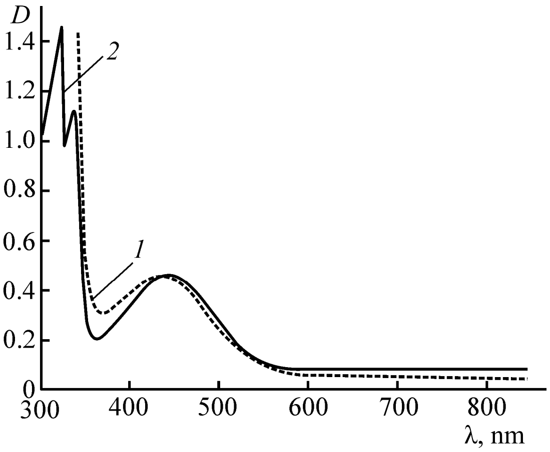


Fig. 2. Electronic absorption spectra of compounds (*1*) **IIIb** and (*2*) **Vb** in acetone–chloroform (1 : 1); $c = 10^{-3}$ to 10^{-4} M.

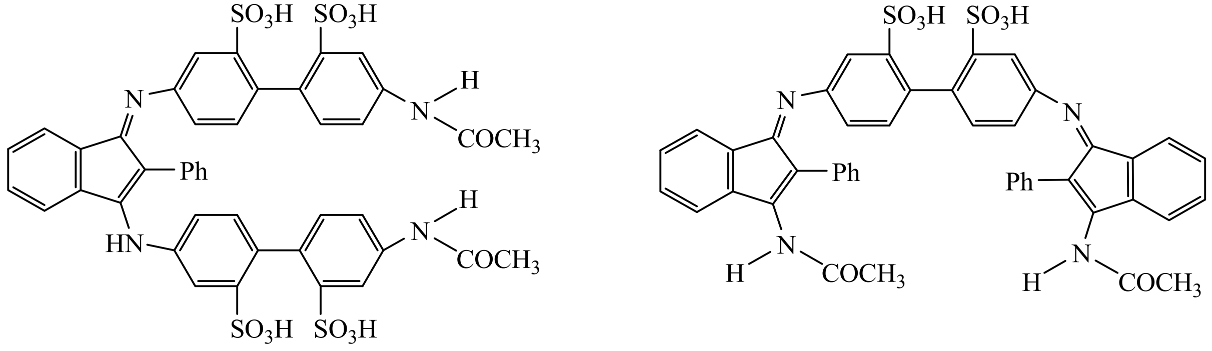
biphenyl-4,4′-diamines **IIa**–**IIc** at molar ratios of 1 : 2 and 2 : 1 in boiling ethanol (until ammonia no longer evolved from the reaction mixture; 40 and 46 h, respectively) afforded arylenediamines **III** and **IV**, respectively (Scheme 1).

Insofar as the azomethine CH=N group in neutral medium is less reactive than carbonyl, the addition of aromatic amine **II** to 2-phenylindan-1,3-dione diimine **I** required 40–46 h against 8 h in the reaction with indan-1,3-dione. The condensation products were purified by column chromatography on aluminum oxide using acetone–chloroform (1 : 1) as eluent. Compounds **III** and **IV** were isolated as red powders with different tints; they melted above 350°C and were soluble in water, DMF, ethanol, acetone, chloroform, sulfuric acid, and alkalies. Their hydrolysis in concentrated aqueous HCl on heating for 4 h at the boiling point led to the formation of 2-phenylindan-1,3-dione (mp 145°C). By acylation of compounds **III** and **IV** with acetic anhydride we obtained the corresponding diacetyl derivatives (Scheme 2).

Compounds **III** and **IV** were identified by elemental analyses and spectral data. The IR spectra of diamines **III** and **IV** contained absorption bands in the region 3356–3313 cm^{-1}, which are typical of stretching vibrations of amino groups involved in intermolecular hydrogen bonds. The band at 3103 cm^{-1} arises from N–H stretching vibrations of the secondary amino group. A strong band belonging to the C=N stretching vibrations was present. Absorption bands in the region 1237–1030 cm^{-1} originate mainly from vibrations of single C–C and C–N bonds. In addition, absorption bands corresponding to stretching vibrations of O–H (2639, 3076 cm^{-1}), C–O (826, 706, 759 cm^{-1}), C–S (621, 627 cm^{-1}), S=O [**III**: 1402 (asym.), 1195 cm^{-1} (sym.); **IV**; 1472 cm^{-1}], and C–Cl bonds (754 cm^{-1}) and NO$_2$ group (1358, 1352 cm^{-1}) and bending vibrations of C–H bonds (706, 701 cm^{-1}) were observed [9–11]. Thus, the IR spectra confirm the presence of the above listed fragments in molecules **III** and **IV**.

The electronic absorption spectra of diamines **III** and **IV** were recorded in water, ethanol, DMF,

Scheme 2.



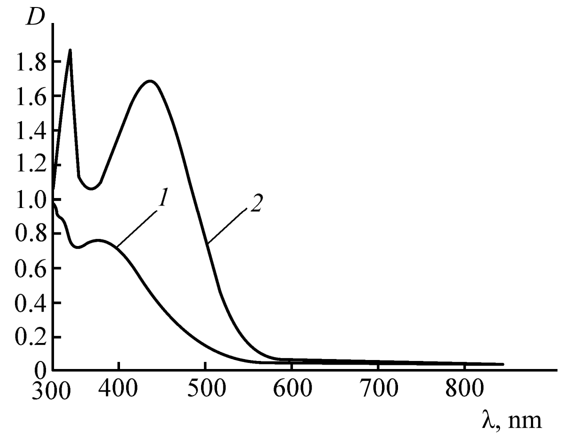


Fig. 3. Electronic absorption spectra of compounds (*1*) **IIIc** and (*2*) **Vc** in acetone–chloroform (1 : 1); $c = 10^{-3}$ to 10^{-4} M.

acetone–chloroform (1 : 1), chloroform, and concentrated sulfuric acid. The absorption in the region λ 250–350 nm corresponds to electronic transitions involving the 2-phenylindene fragments. The band with its maximum at λ 430–470 nm, which is responsible for the color of compounds **III** and **IV**, arises from π–π electronic transitions in the conjugation chain covering the entire molecule (Figs. 1–3). The long-wave absorption band shifts to the blue region (λ 320–400 nm) in going from organic solvents to sulfuric acid due to protonation.

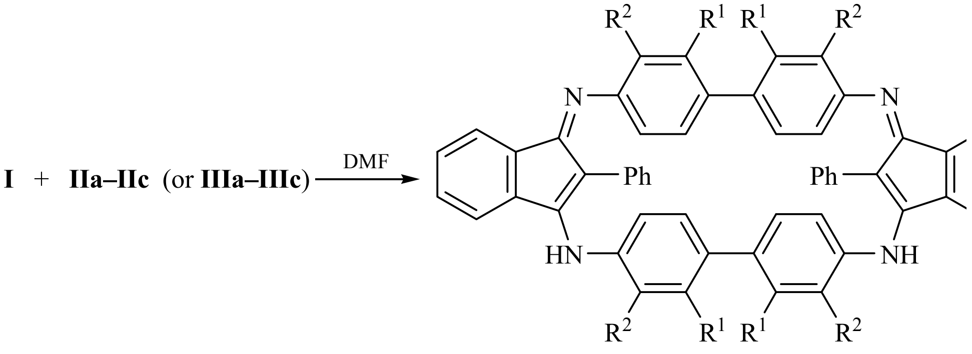
Macroheterocyclic compounds were synthesized in two ways: by reaction of compounds **III** with 1-imino-2-phenyl-1*H*-inden-3-amine (**I**) and by reaction of compound **I** with an equimolar amount of substituted diaminobiphenyls **II** (Scheme 3). In both cases, the reactants were heated in boiling DMF until ammonia no longer evolved. Macroheterocyclic compounds **Va**–**Vc** were isolated as red powders with different tints; they did not melt on heating up to 350°C and were soluble in DMF, water, ethanol, acetone–chloroform (1 : 1), and chloroform.

The IR spectra of **Va**–**Vc** retained absorption bands typical of initial diamines **IIIa**–**IIIc**. Compounds **Va**–**Vc** displayed two bands in the electronic absorption spectra (Figs. 1–3). Closure of the macrocycle was accompanied by a blue shift and increase in intensity of the long-wave absorption band of **Va** as compared to initial diamine **IIIa**, while the short-wave band (λ 300–350 nm) was displaced toward longer wavelengths. Compounds **Vb** and **Vc** showed a red shift of the long-wave absorption band. Broadening of the absorption bands in the visible region indicates that molecules **V** are nonplanar; therefore, there is no common conjugation chain.

EXPERIMENTAL

The electronic absorption spectra were measured at 20°C on a Hitachi U-2010 spectrophotometer from solutions in organic solvents and concentrated sulfuric acid which were placed into quartz cells. The IR spectra were recorded in KBr on a Nicolet Avatar 360 FT-IR ESP instrument. The ^{1}H NMR spectra were obtained on a Bruker AMD 500 spectrometer using acetone-d_6 as solvent and tetramethylsilane as internal reference. The elemental compositions were determined on a FlashEA 1112 Series CHNS-O analyzer. The products were purified by column chromatography on aluminum oxide (Brockmann activity grade II) using acetone–chloroform (1 : 1 by volume) as eluent. Their purity was checked by TLC on Silufol UV-254 plates using acetone–chloroform (1 : 1 by volume).

Scheme 3.



$R^1 = SO_3H$, R^2 = H (**a**), R^1 = H, R^2 = Cl (**b**), $R^1 = NO_2$, R^2 = H (**c**).

4-Amino-4′-{[3-(4′-amino-2,2′-disulfobiphenyl-4-ylamino)-2-phenyl-1*H*-inden-1-ylidene]amino}biphenyl-2,2′-disulfonic acid (IIIa). A mixture of 1.4 mmol of 1-imino-2-phenyl-1*H*-inden-3-amine (**I**) and 0.87 mmol of 4,4′-diaminobiphenyl-2,2′-disulfonic acid (**IIa**) in 10 mL of ethanol was heated for 40 h under reflux. After cooling, the precipitate was filtered off and dried in air. Yield 0.4 g (98%), red–brown crystalline substance which did not melt up to 350°C, R_f 0.48; the product is soluble in water, DMF, and sulfuric acid and moderately soluble in ethanol and acetone–chloroform (1 : 1). IR spectrum, ν, cm^{-1}: 3356, 3327 (NH_2); 3103 (NH), 2639 (OH); 1634, 1607 (C=N); 1557, 1523 (C=C); 1401 (S=O), 1237 (C–N); 1043, 1030 (C–C); 826 (S–O), 621 (C–S). UV spectrum, λ_{max}, nm: in water: 463; in EtOH: 463; in acetone–chloroform (1 : 1): 462; in DMF: 459; in H_2SO_4: 331, 393. Found, %: C 50.95; H 3.33; N 7.13; O 24.22; S 15.26. $C_{39}H_{30}N_4O_{12}S_4$. Calculated, %: C 53.54; H 3.46; N 6.40; O 21.94; S 14.66.

Acyl derivative of compound IIIa. A mixture of 0.12 g of compound **IIIa** and 10 mL of acetic anhydride was heated for 3 h under reflux with continuous stirring. After cooling, the precipitate was filtered off, the filtrate was diluted with 10 mL of distilled water and neutralized with a 10% solution of alkali, and the precipitate was filtered off and dried in air. Yield 0.09 g (69%), decomp. point 235°C. Found, %: C 51.97; H 3.48; N 5.31; O 21.96; S 12.67. $C_{43}H_{34}N_4O_{14}S_4$. Calculated, %: C 53.86; H 3.57; N 5.84; O 23.36; S 13.37.

Compounds **IIIb** and **IIIc** were synthesized as described above for **IIIa**.

***N*-[3-(4′-Amino-3,3′-dichlorobiphenyl-4-ylamino)-2-phenyl-1*H*-inden-1-ylidene]-3,3′-dichlorobiphenyl-4,4′-diamine (IIIb).** Yield 0.25 g (79.4%), red–orange crystalline substance which did not melt up to 350°C, R_f 0.39; the product is soluble in most organic solvents. IR spectrum, ν, cm^{-1}: 3409 (NH_2), 2974 (NH), 1632 (C=N), 1237 (C–N), 1049 (C–C), 754 (C–Cl). UV spectrum, λ_{max}, nm (log ε): in DMF: 426; in chloroform: 282 (4.54), 421 (3.82); in acetone: 433; in acetone–chloroform (1 : 1): 436. Found, %: C 61.54; H 3.21; Cl 19.2; N 7.28. $C_{39}H_{30}Cl_4N_4$. Calculated, %: C 67.2; H 4.3; Cl 20.4; N 8.05.

***N*-[3-(4′-Amino-2,2′-dinitrobiphenyl-4-yl)amino]-2-phenyl-1*H*-inden-1-ylidene]-2,2′-dinitrobiphenyl-4,4′-diamine (IIIc).** Yield 0.2 g (80%), brick red crystalline substance which did not melt up to 350°C, R_f 0.7; the product is soluble in most organic solvents. IR spectrum, ν, cm^{-1}: 3987 (NH_2), 3202 (NH), 1631 (C=N), 1557 (C=C); 1516, 1369 (NO_2); 1236 (C–N), 1080 (C–C). UV spectrum, λ_{max}, nm (log ε): in acetone: 379; in DMF: 397; in chloroform: 250 (4.84), 379 (3.95). Found, %: C 60.75; H 3.77; N 14.20. $C_{39}H_{26}N_8O_8$. Calculated, %: C 63.76; H 3.5; N 15.26.

4,4′-Bis[3-amino-2-phenyl-1*H*-inden-1-ylideneamino]biphenyl-2,2′-disulfonic acid (IVa). A mixture of 9.1 mmol of compound **I** and 0.44 mmol of 4,4′-diaminobiphenyl-2,2′-disulfonic acid (**IIa**) in 10 mL of ethanol was heated for 46 h under reflux. After cooling, the precipitate was filtered off and dried in air. Yield 0.2 g (58.8%), red–brown crystalline substance which did not melt up to 350°C, R_f 0.45; the product is soluble in DMF and moderately soluble in water, ethanol, and acetone–chloroform (1 : 1). IR spectrum, ν, cm^{-1}: 3419, 3313 (NH_2); 3076 (OH); 1632, 1607 (C=N); 1513 (C=C); 1472 (S–O); 1188 (C–N); 1097, 1044 (C–C); 706, 759 (S–O); 627 (C–S). UV spectrum, λ_{max}, nm: in water: 465; in ethanol: 458; in acetone–chloroform (1 : 1): 448; in DMF: 457; in H_2SO_4: 325, 344. Found, %: C 64.93; H 3.93; N 6.33; S 6.69. $C_{42}H_{32}N_4O_6S_2$. Calculated, %: C 67.19; H 4.03; N 7.46; S 8.54.

Acyl derivative of compound IVa. A mixture of 0.12 g of compound **IVa** and 10 mL of acetic anhydride was heated for 3 h under reflux with continuous stirring. The mixture was cooled, the precipitate was filtered off, the filtrate was diluted with 10 mL of distilled water and neutralized with a 10% solution of alkali, and the precipitate was filtered off and dried in air. Yield 0.1 g (75%), decomp. point 245°C. Found, %: C 64.81; H 4.45; N 6.32; O 13.8; S 6.85. $C_{47}H_{38}N_4O_8S_2$. Calculated, %: C 66.34; N 4.5; N 6.58; O 15.04; S 7.54.

Compounds **IVb** and **IVc** were synthesized as described above for **IVa**.

***N*,*N*′-Bis[3-amino-2-phenyl-1*H*-inden-1-ylidene]-3,3′-dichlorobiphenyl-4,4′-diamine (IVb).** Yield 0.1 g (66.7%), red crystalline substance which did not melt up to 350°C, R_f 0.6; the product is soluble in organic solvents and moderately soluble in water. IR spectrum, ν, cm^{-1}: 3426, 3311 (NH_2); 1631 (C=N), 1543 (C=C), 1079 (C–C), 754 (C–Cl). UV spectrum, λ_{max}, nm: in acetone: 342, 417; in DMF: 439. Found, %: C 73.33; H 3.5; Cl 9.45; N 6.66. $C_{42}H_{30}Cl_2N_4$. Calculated, %: C 76.25; H 4.54; Cl 10.74; N 8.47.

***N*,*N*′-Bis[3-amino-2-phenyl-1*H*-inden-1-ylidene]-2,2′-dinitrobiphenyl-4,4′-diamine (IVc).** Yield 0.08 g (53.3%), brick red crystalline substance which did not melt up to 350°C, R_f 0.4; the product is soluble in organic solvents and moderately soluble in water. IR spectrum, ν, cm^{-1}: 3417 (NH_2), 1616 (C=N), 1514 (C=C, NO_2), 1352 (NO_2), 1188 (C–N), 1082 (C–C). UV spectrum, λ_{max}, nm: in acetone: 385; in DMF: 395; in acetone–chloroform (1:1): 385. Found, %: C 67.86; H 3.13; N 14.14; O 8.56. $C_{42}H_{28}N_6O_4$. Calculated, %: C 74.12; H 4.12; N 12.35; O 9.41.

1^2,2^2,6^3,7^2-Tetrasulfo-4^1*H*,9^3*H*-3,5,8,10-tetraaza-4,9(1,3)-diindena-1,2,6,7(1,4)-tetrabenzenacyclodecaphane-3(4^1),9^3(10)-diene (Va). A mixture of 9.1 mmol of compound **I** and 0.87 mmol of 4,4′-diaminobiphenyl-2,2′-disulfonic acid (**IIa**) or 36 mmol of compound **IIIa** in 10 mL of DMF was heated for 55 h under reflux. The mixture was cooled, and the precipitate was filtered off, dried in air, and purified by clumn chromatography on aluminum oxide using acetone–chloroform (1 : 1) as eluent. Yield 0.2 g (41.67%), bright red crystalline substance which did not melt up to 350°C, R_f 0.58. IR spectrum, ν, cm^{-1}: 3454, 3309 (NH); 3051 (OH); 1631, 1608 (C=N); 1543 (C=C), 1430 (S=O), 1155 (C–N), 1080 (C–C), 755 (C–O), 614 (C–S). ^{1}H NMR spectrum, δ, ppm: 7.66 d (4H, *J* = 7.5 Hz), 7.59 d (4H, *J* = 7.7 Hz), 7.35–7.5 m (7H), 7.34 d (2H, NH, *J* = 4.95 Hz), 7.18 t (2H, *J* = 7.4 Hz). UV spectrum, λ_{max}, nm (log ε): in water: 451; in DMF: 342, 444; in ethanol: 341, 450; in acetone–chloroform (1 : 1): 340, 444; in chloroform: 274 (5.14), 435 (4.24); in H_2SO_4: 359. Found, %: C 63.20; H 4.73; N 5.68; O 16.55; S 11.57. $C_{54}H_{36}N_4O_{12}S_4$. Calculated, %: C 61.12; H 3.42; N 5.28; O 18.09; S 12.09.

Compounds **Vb** and **Vc** were synthesized in a similar way.

1^3,2^3,6^2,7^3-Tetrachloro-4^1*H*,9^3*H*-3,5,8,10-tetraaza-4,9(1,3)-diindena-1,2,6,7(1,4)-tetrabenzenacyclodecaphane-3(4^1),9^3(10)-diene (Vb). Yield 0.1 g (25%), dark red crystalline substance which did not melt up to 350°C, R_f 0.8; the product is readily soluble in organic solvents and moderately soluble in water. IR spectrum, ν, cm^{-1}: 3454, 3312 (NH); 1544 (C=C), 1632 (C=N), 1159 (C–N), 1077 (C–C), 756 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 7.69 d (4H, *J* = 7.69 Hz), 7.61 d (6H, *J* = 7.6 Hz), 7.28–7.5 (14H), 7.26 d (2H, NH, *J* = 5.11 Hz), 7.18 t (2H, *J* = 7.3 Hz), 6.93 t (6H, *J* = 8.27 Hz). UV spectrum, λ_{max}, nm (log ε): in acetone: 435; in DMF: 424; in chloroform: 276 (5.21), 430 (4.17). Found, %: C.94; H 4.40; Cl 15.24; N 7.07. $C_{54}H_{32}Cl_4N_4$. Calculated, %: C 73.8; H 3.64; Cl 16.17; N 6.38.

1^2,2^2,6^3,7^2-Tetranitro-4^1*H*,9^3*H*-3,5,8,10-tetraaza-4,9(1,3)-diindena-1,2,6,7(1,4)-tetrabenzenacyclodecaphane-3(4^1),9^3(10)-diene (Vc). Yield 0.2 g (31.7%), red crystalline substance which did not melt up to 350°C, R_f 0.7; the product is soluble in organic solvents and moderately soluble in water. IR spectrum, ν, cm^{-1}: 3455, 3158 (NH); 1633 (C=N), 1544 (NO_2), 1078 (C–C). ^{1}H NMR spectrum, δ, ppm: 7.68 d (2H, *J* = 6.9 Hz), 7.6 d (4H, *J* = 7.5 Hz), 7.35–7.49 m (9H), 7.33 d (2H, NH, *J* = 4.98 Hz), 7.18 t (2H, *J* = 7.4 Hz). UV spectrum, λ_{max}, nm (log ε): in acetone: 406; in DMF: 407; in acetone–chloroform (1 : 1): 344, 438; in chloroform: 275 (5.02), 440 (4.08). Found, %: C 67.56; H 4.41; N 11.55. $C_{54}H_{32}N_8O_8$. Calculated, %: C 70.4; H 3.48; N 12.17.

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