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Synthesis and Properties of Macrocyclic Compounds Containing 2-Methylindan-1,3-dione and Substituted Biphenyl Fragments

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Abstract—Reaction of 2-methylindan-1,3-dione diimine with diaminobiphenyl (3,3'-dichloro-, 3,3'-dimethoxy-, and 2,2'-disulfo-) derivatives afforded the 2 : 1 cyclization products and symmetric macrocyclic compounds. Structures of compounds were confirmed by IR, UV, and NMR spectroscopy data.

Keywords: diimines, 2-methylindan-1,3-dione, macrocyclic compounds, spectroscopy

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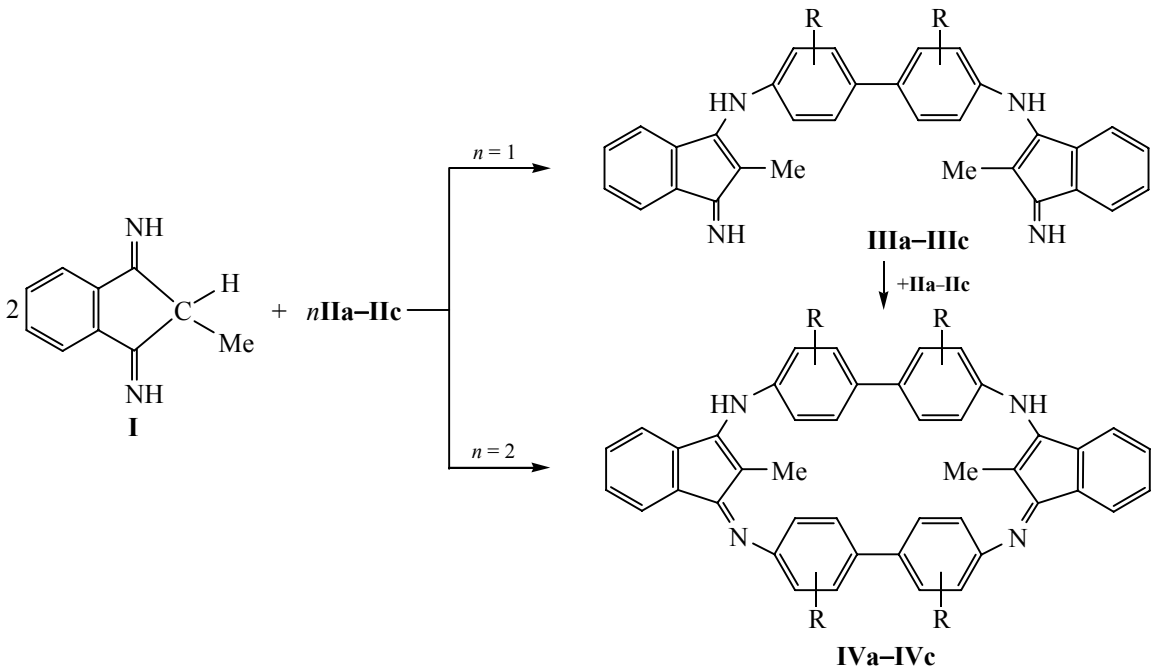
Macromolecular compounds of cyclic structure containing more than twelve atoms (nitrogen, carbon, metal, etc.) in the large inner ring (macrocyclic compounds) are separately considered among the diversity of organic compounds. Such compounds possess unique properties and are applied in various fields of science, engineering, and medicine as pigments and dyes, stabilizers against heat and light, organic semiconductors, catalysts for redox processes, pharmaceuticals and biologically active compounds [1–7].

Scheme 1.



R = 3-Cl (**a**), 3-MeO (**b**), 2-SO_3H (**c**).

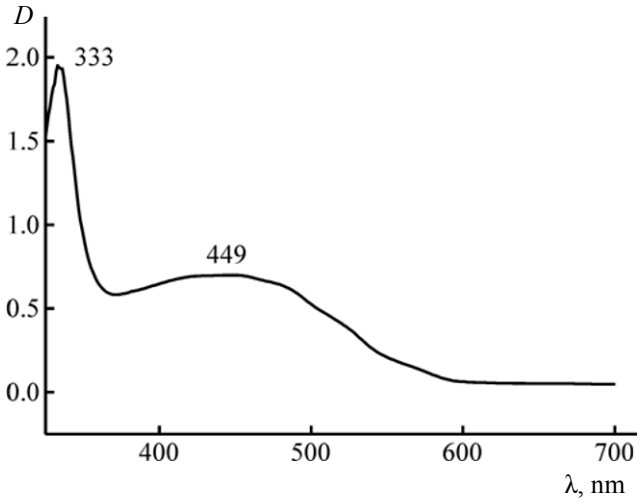


Fig. 1. Electron absorption spectrum of compound **IIIa** in a mixture acetone–chloroform, 1 : 1.

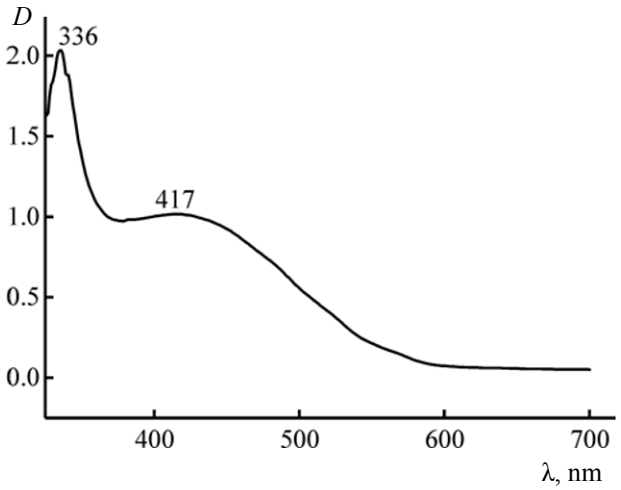


Fig. 2. Electron absorption spectrum of compound **IIIb** in ethanol.

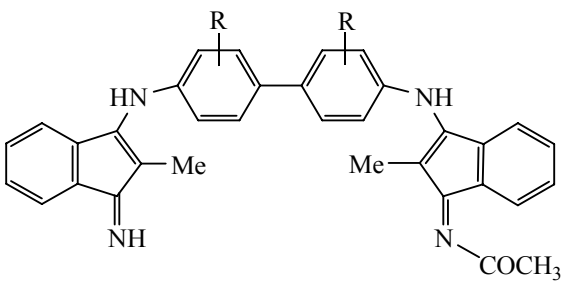
Indan-1,3-dione and its derivatives (2-methyl- and 2-phenylindan-1,3-dione) as well as the other cyclic β-diketones are extremely reactive species taking part in various chemical transformations. Therefore they are used for the synthesis of compounds of different types [8–13].

Thus, reaction of diimine **I** [14] with 3,3'-dichloro-, 3,3'-dimethoxy-, and 2,2'-disulfobiphenyl-4,4'-diamines **IIa**–**IIc** gave rise to biphenylene diamines **IIIa**–**IIIc** and macrocyclic compounds **IVa**–**IVc** (Scheme 1).

Synthesis of compounds **IIIa**–**IIIc** was performed in ethanol at reflux for 10 h until ammonium evolution stopped. Compounds **IIIa**–**IIIc** were red powders, melting with decomposition, soluble in water, ethanol, DMF, and sulfuric acid, hydrolyzed in boiling hydrochloric acid.

Acylation of biphenylene diamines **IIIa**–**IIIc** with acetic acid anhydride afforded the corresponding acyl derivatives (Scheme 2).

Scheme 2.



Macrocyclic compounds **IVa**–**IVc** were synthesized by reacting biphenylene diamines **V**–**VII** with 3,3'-dichloro-, 3,3'-dimethoxy-, and 2,2'-disulfobiphenyls in boiling DMF for 4–6 h. Macrocycles **IVa**–**IVc** are hydrolyzed in conc. hydrochloric acid. Compounds **IVa** and **IVc** decompose without melting; they are soluble in water, DMF, ethanol, acetone–chloroform mixture (1 : 1).

The structure of the macrocycles was confirmed by IR, UV, and NMR spectroscopic data.

IR spectrum of 2-methylindan-1,3-dione diimine **I** contained an absorption band at 3347 cm^{-1} due to intermolecular hydrogen bond of the imino groups and strong absorption band at 3111 cm^{-1} corresponding to C=N bond vibrations. The absorption band at 1522 cm^{-1} originated from bending vibrations of the imino group [15]. An absorption in the range of 1400–850 cm^{-1} is mainly caused by vibrations of C–C and C–N bonds.

In the IR spectra of biphenylene diamines **IIIa**–**IIIc** the absorption bands characteristic of 2-methylindan-1,3-dione diimine **I** was retained, and the absorption of imino group (3107–3411 cm^{-1}), the C–Cl (685 cm^{-1}), C–O (1241 cm^{-1}), and S=O bonds (1041 cm^{-1}) appeared.

In the IR spectra of macrocycles **IVa**–**IVc** the absorption bands of NH-group at 3469–3104 (**IVa**), 3378–2934 (**IVb**), and 3405–3108 cm^{-1} (**IVc**) were registered.

^{1}H NMR spectra of the macrocycles obtained contained the signals of aromatic protons at 7.21–

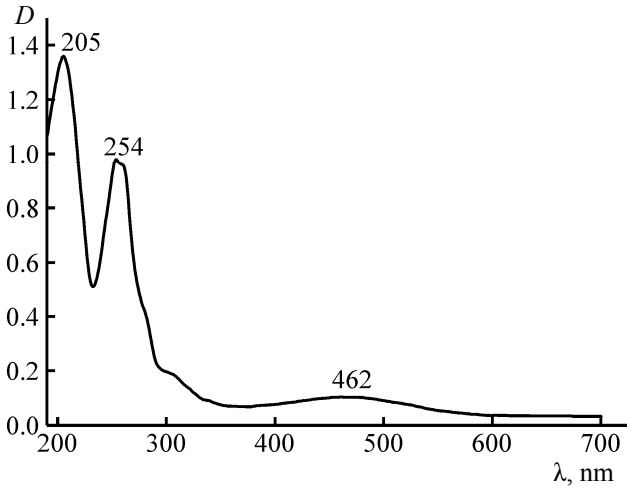


Fig. 3. Electron absorption spectrum of compound **IIIc** in water.

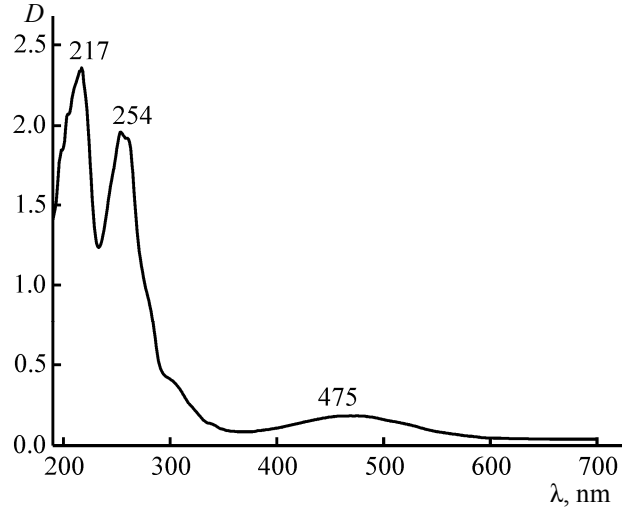


Fig. 4. Electron absorption spectrum of compound **IVc** in DMF.

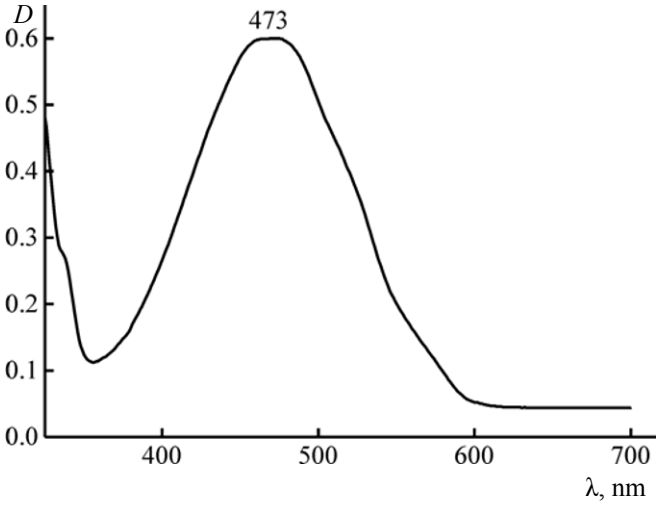


Fig. 5. Electron absorption spectrum of compound **IVc** in water.

7.75 ppm. The protons of the methyl groups at the phenyl ring resonated as singlet signals at 1.95–2.50 ppm.

The electron absorption spectra of the compounds obtained were measured in water, ethanol, hydrochloric acid, DMF, acetone–chloroform mixture (1 : 1), and acetone (Figs. 1–5). An absorption in the range of 200–300 nm corresponded to the electron transfer with the participation of 2-methylindan-1,3-dione diimine **I** fragments. An absorption band at 417–472 nm was caused by π–π-electron transfer along the conjugation chain in the biphenylene diamine molecule. The appearance of the long-wave bands at 417–472 nm was due to the electron transfer along the whole molecule that also governed the compounds coloration.

The electron absorption spectrum of water solution of **IIIc** (Fig. 3) was characterized by the appearance of three absorption bands at 205, 254, and 462 nm. A similar picture was observed for compound **IIIa** (Fig. 1). Ring closure did not led to any significant changes in the spectrum except for increase in the absorption intensity and a small red shift of the long-wave band.

EXPERIMENTAL

Electron absorption spectra were measured on a Hitachi U-2010 instrument using quarts cells at 20°C. IR spectra were recorded on a Nicolet Avatar 360 FT-IR ESP spectrometer from KBr pellets. ^{1}H NMR spectra of acetone-d_6 solutions were registered on a Bruker AMD 500 spectrometer, internal reference TMS. Elemental analysis was performed on a CHNS-O Analyzer FlashEA 1112 Series instrument. The products purity was controlled by TLC (Silufol UV-254), eluting with a mixture acetone–chloroform, 1 : 1.

***N*-[3-(4'-Amino-3,3'-dichlorobiphenyl-4-ylamino)-2-methyl-1*H*-inden-1-ylidene]-3,3'-dichlorobiphenyl-4,4'-diamine (IIIa)**. A mixture of 1.9 mmol of compound **I** and 1.0 mmol of compound **IIa** in 7 mL of ethanol was refluxed for 10 h. The obtained deep-red solution was evaporated to precipitate formation. The precipitate formed at cooling was filtered off and dried in air. Yield 0.5 g (90.9%), red-brownish powder, mp 193°C, R_f 0.22 (acetone–chloroform, 1 : 1), soluble in water, ethanol, acetone, chloroform. IR spec-trum, ν, cm^{-1}: 3454 (NH), 3346 (C–H), 1626 (C=C), 1602, 1607 (C=N), 1400 [δ(C–H)], 1269 (C–N), 1046 (C–C),

685 (C–Cl). UV spectrum, λ_{max}, nm (log ε): water, 262 (4.3), 460 (3.4); acetone–chloroform (1 : 1), 333, 449. Found, %: C 70.48; H 4.50; N 9.18; Cl 12.56. $C_{32}H_{24}N_4Cl_2$. Calculated, %: C 71.78; H 4.49; N 10.46; Cl 13.27.

Compounds **IIIb** and **IIIc** were prepared similarly.

***N*-[3-(4'-Amino-3,3'-dimethoxybiphenyl-4-ylamino)-2-methyl-1*H*-inden-1-ylidene]-3,3'-dimethoxybiphenyl-4,4'-diamine (IIIb)**. Yield 0.37 g (70%), red-orange powder, mp 185°C, R_f 0.2 (DMF), soluble in water at heating and in common organic solvents. IR spectrum, ν, cm^{-1}: 3546 (NH), 3411 (C–H), 1617 (C=C), 1504 (C=N), 1271 (C–N), 1241 (C–O), 1362 [δ(C–H)], 1033. UV spectrum, λ_{max}, nm: ethanol, 336, 417; acetone, 341, 401; acetone–chloroform (1 : 1), 347, 414. Found, %: C 71.33; H 5.10; N 9.67. $C_{34}H_{30}N_4O_2$. Calculated, %: C 73.12; H 5.38; N 10.04; O 11.46.

4-Amino-4'-{[(3-(4'-amino-2,2'-disulfobiphenyl-4-ylamino)-2-methyl-1*H*-inden-1-ylidene]amino}biphenyl-2,2'-disulfonic acid (IIIc). Yield 0.3 g (51%), red powder, mp 295°C (decomp.), R_f 0.6 (DMF), soluble in water and common organic solvents. IR spectrum, ν, cm^{-1}: 3405 (NH), 3107 (C–H), 1607 (C=C), 1528 (C=N), 1361 [δ(C–H)], 1273 (C–N), 1056 (C–C), 1024 (S=O), 627 (C–S). UV spectrum, λ_{max}, nm (log ε): water, 205, 254 (4.5), 301 (3.8), 462 (3.5); acetone–chloroform (1 : 1), 240, 299, 456, 472. Found, %: C 60.82; H 3.59; N 8.74; S 10.19. $C_{32}H_{26}N_4O_6S_2$. Calculated, %: C 61.34; H 4.15; N 8.94; O 15.34; S 10.23.

Acyl derivative of compound (IIIa). A mixture of 0.12 g of compound **IIIa** and 10 mL of acetanhydride was refluxed at stirring for 3 h. After cooling the precipitate obtained was filtered off, dissolved in 10 mL of distilled water, and neutralized with 10% aqueous alkali solution. The precipitate was filtered off and dried in air. Yield 0.1 g (79%), mp 205°C (decomp). Found, %: C 68.97; H 5.45; Cl 11.2; N 9.11; O 2.96. $C_{34}H_{26}Cl_2N_4O$. Calculated, %: C 70.71; H 4.51; Cl 12.3; N 9.71; O 2.77.

Macrocycle (IVa). A mixture of 0.37 mmol of compound **I** and 0.4 mmol of compound **IIa** was refluxed in 15 mL of acetic acid for 4 h. After cooling, 15 mL of distilled water was added, and the obtained mixture was neutralized with 10% aqueous alkali solution followed by evaporation to precipitate formation. The precipitate was filtered off and dried in air. Yield 0.8 g (84%), pink powder, mp 258°C (decomp.), R_f 0.5 (DMF), soluble in water (2.8×10^{-4} mol L^{-1}), ethanol, H_2SO_4, hydrochloric acid. IR spectrum, ν, cm^{-1}: 3378 (NH), 2833 (C–H), 1660 (C=C), 1505 (C=N), 1361 [δ(C–H)], 1272 (C–N), 1242 (C–O), 1029 (C–C). ^{1}H NMR spectrum, δ, ppm: 7.71 d (8H, *J* 7.82 Hz), 7.65–7.4 m (8H), 7.26 d (2H, NH, *J* 5.25 Hz), 7.21 t (4H, *J* 6.89 Hz), 2.5 s (6H, 2-CH_3). UV spectrum, λ_{max}, nm (log ε): water, 262 (3.79), 340, 459 (3.58); acetone–chloroform (1 : 1), 330, 459; ethanol, 210, 260, 275, 459. Found, %: C 69.54; H 3.52; Cl 17.97; N 7.11. $C_{44}H_{28}Cl_4N_4$. Calculated, %: C 70.03; H 3.71; Cl 18.83; N 7.43.

Macrocycle (IVb) was obtained similarly from 0.19 mmol of **IIIb** and 0.19 mmol of **IIb**. After the reaction completion the mixture was cooled, 10 ml of distilled water was added, and the mixture was evaporated till precipitate formed. The solid was filtered off and dried in air. Yield 0.12 g (93%), red powder, mp 170°C, R_f 0.6 (DMF), soluble in water (5×10^{-5} mol L^{-1}), ethanol, acetone, chloroform. IR spectrum, ν, cm^{-1}: 3469 (NH), 3376 (C–H), 1665 (C=N), 1620 (C=C), 1384 [δ(C–H)], 1270 (C–N), 1045 (C–C), 700 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 7.75 d (8H, *J* 6.9 Hz), 7.6–7.4 m (8H), 7.3 d (2H, NH, *J* 5.35 Hz), 7.21 t (4H, *J* 7.6 Hz), 2.1 s (6H, 2-CH_3). UV spectrum, λ_{max}, nm (log ε): water, 200, 301 (4.72); acetone–chloroform (1 : 1), 331, 405; DMF, 240, 374, 434. Found, %: C 77.42; H 5.24; N 8.83; O 7.85. $C_{48}H_{40}N_4O_4$. Calculated, %: C 78.26; H 5.43; N 7.61; O 8.70.

Macrocycle (IVc). *a*. A mixture of 0.2 mmol of **IIIc** and 0.37 mmol of **IIc** was refluxed in 7 mL of DMF for 6 h. After cooling, 10 mL of distilled water was added to the mixture. The precipitate was filtered off and dried in air. Yield 0.2 g (90.9%), red powder, mp 260°C (decomp.), R_f 0.2 (DMF), soluble in water (1.44×10^{-3} mol L^{-1}), ethanol, acetone, DMF. IR spectrum, ν, cm^{-1}: 3405 (NH), 3108 (C–H), 1651 (C=C), 1522 (C=N), 1208 (C–N), 1182 (C–C), 1043 (S=O), 629 (C–S). ^{1}H NMR spectrum, δ, ppm: 7.7 d (8H, *J* 7.8 Hz), 7.65 d (4H, *J* 7.3 Hz), 7.35 d (2H, NH, *J* 5.15 Hz), 7.5–7.4 m (8H), 7.19 t (4H, *J* 7.2 Hz), 1.95 s (6H, 2-CH_3). UV spectrum, λ_{max}, nm (log ε): water, 204, 253 (4.54), 473 (4.01); ethanol, 248, 473; DMF, 217, 254, 475; HCl, 204, 243, 276. Found, %: C 55.83; H 4.18; N 5.41; O 19.77; S 11.36. $C_{44}H_{32}N_4O_{12}S_4$. Calculated, %: C 56.41; H 3.42; N 5.98; O 20.51; S 13.68.

b. A mixture of 0.32 mmol of **I** and 0.49 mmol of **IIc** was refluxed in 10 mL of butanol for 10 h. After

cooling the precipitate was filtered off and dried in air. Yield 0.26 g (87%).

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