Macroheterocyclic Compounds with *p*-Diamines of the Diaryl Series

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Abstract—The reactions of indane-1,3-dione with 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfide, and 4,4'-diaminodiphenyl ether were used to synthesize symmetrical macroheterocyclic compounds.

Along with phthalonitrile and isoindoline-1,3-diimine, indane-1,3-dione (I) can undergo cyclizations to form macroheterocyclic compounds [1-4]. Dione I and its derivatives are reactive compounds susceptible to various chemical transformations. The chemical properties of dione I have been exemplified by a great variety of reactions: with acids, halogens, secondary amines, ammonium acetate, etc. [5].

We have synthesized macroheterocyclic compounds on the basis of dione I and *m*-phenylenediamine, 2,6-diaminopyridine, and 2,5-diamino-1,3,4thiadiazole [6–8]. Macroheterocyclic compounds on the basis of *p*-phenylenediamine and benzidine [4] have also been obtained, that differ in their properties from macroheterocycles containing *m*-phenylenediamine, 2,6-diaminopyridine, and 2,5-diamino-1,3,4-thiadiazole residues.

At the same time, of interest are macroheterocyclic compounds in which *p*-diamines of the diphenyl series contain groups that uncouple the phenylene residues. We set ourselves the task to synthesize macroheterocyclic compounds on the basis of dione I and p,p'-diaminobiphenyl and its derivatives and to study their properties.

As objects for synthesis and study we took dione I, as well as *p*-diamines, such as 4,4'-diaminodiphenyl sulfone (II), 4,4'-diaminodiphenyl sulfide (III), and 4,4'-diaminodiphenyl ether (IV). Dione I was prepared by the procedure in [5]. Macroheterocyclic compounds were synthesized by the scheme given below.



 $\mathbf{X} = p \cdot \mathbf{C}_{6}\mathbf{H}_{4} - \mathbf{SO}_{2} - \mathbf{C}_{6}\mathbf{H}_{4} - p' (\mathbf{II}, \mathbf{V}, \mathbf{VIII}, \mathbf{XI}), p \cdot \mathbf{C}_{6}\mathbf{H}_{4} - \mathbf{S} - \mathbf{C}_{6}\mathbf{H}_{4} - p' (\mathbf{III}, \mathbf{VI}, \mathbf{IX}, \mathbf{XII}), p \cdot \mathbf{C}_{6}\mathbf{H}_{4} - \mathbf{O} - \mathbf{C}_{6}\mathbf{H}_{4} - p' (\mathbf{IV}, \mathbf{VII}, \mathbf{X}, \mathbf{XIII}).$

As seen from the scheme, the synthesis involved three stages. First dione I was reacted with sulfone II, sulfide III, or ether IV (molar ratio 2:1) in methanol under reflux for 8 h to synthesize diamines V-VII. They are dark blue or violet powders melting above

150°C. When heated in conc. H_2SO_4 , they hydrolyze into the starting compounds.

Diamines V-VII are soluble in most organic solvents. They also dissolve in conc. H_2SO_4 at room



Fig. 1. Electronic absorption spectra in ethanol of diamines (1) V, (2) VI, and (3) VII.

temperature; therewith, the color of the solution change: Blue and violet substances form orange and yellow solutions. On dilution of the solutions, the compounds are recovered unchanged. Apparently, diamines V-VII take up four protons to form tetracation **A** [9].



The electronic absorption spectra of diamines V-VII in organic solvents show characteristic bands in the UV and visible ranges: 370–400 and 550–600 nm (Fig. 1). The bands at 370–400 nm relate to the conjugated β -aminovinylcarbonyl system HN–C=C–C=O. The long-wave band is responsible for the color of the compounds and is formed by π – π * transitions in the conjugation system. The electronic absorption spectra of diamines V–VII in sulfuric acid display a characteristic band at 400–420 nm.

For structural assessment of compounds V-VII we measured their IR spectra. The diketone form of dione I gives a doubled band at 1770–1705 and a band at 1600–1580 cm⁻¹. The first range relates to two carbonyl group and the second, to the aromatic system [9, 10]. The doublet disappears upon reaction of diketone I with diamines II–IV. The IR spectra shows well-defined vibration bands groups intervening the phenylene nuclei of the diamine residues (see Experimental).

We compared the spectral properties of diamines **V–VII** and **XIV–XVIII**.



 $X = m-C_6H_4$ (**XIV**), pyridine-2,6-diyl (**XV**), 1,3,4-thiadiazol-2,5-diyl (**XVI**), $p-C_6H_4$ (**XVII**), $p-C_6H_4-C_6H_4-p'$ (**XVIII**).

Inspection of the electronic absorption spectra of diamines V–VII and XIV–XVIII showed that replacement of the *m*-phenylene (compounds XIV–XVI) by *p*-phenylene (compound XVII) and diphenylene (compounds V–VII and XVIII) fragments produces a strong bathochromic shift (470 \rightarrow 610 nm) of the long-wave bands due to extension of the conjugation chain in the molecule.

The presence between the phenyl rings in the diphenylene residue of the -S-, >S=O, and -O- groups favors more intense coloration of compounds. The principal absorption band in the electronic absorption spectra shifts hypsochromically by 25, 14, and 25 nm for compounds **V–VII**, respectively, compared to compound **XVIII**. This fact is explained by that the >S=O, -S-, and -O- group uncouple the conjugation chain in the molecule.

The ¹H NMR spectra of compounds **XIV** and **XVI** in HMPA display a fairly narrow one–proton signal. Substituents of the benzidine series make this signal to vanish.



The large chemical shift and lack of multiplicity allow this signal to be assigned to the hydroxyl proton in keto–enol form \mathbf{B} or \mathbf{C} stabilized by hydrogen bond.

Introduction of substituents of the benzidine series, i.e. enlargement of the phenylene bridge, gives rise to

steric hindrances or intramolecular hydrogen bonding. Form $\mathbf{B} \longleftrightarrow \mathbf{C}$ is unlikely to exist because of destroyed conjugation; had they been formed, the compounds would have changed their color, but this phenomenon was observed neither visually nor spectrophotometrically.

Benzoylation of diamines V–VII was performed in boiling benzoyl chloride for 6 h. Benzoyl derivatives VIII–X are brown powders, they are not hydrolyzed by conc. H_2SO_4 , and are readily cleaved with sodium ethylate to starting compounds V–VII. Alkaline hydrolysis involve cleavage of the acyl–oxygen bond. By comparing the electronic absorption spectra of diamines V–VIII and benzoyl derivatives V–VII one can see that benzoylation renders compounds stronger colored.

The electronic absorption spectra of benzoyl derivatives **VIII–X** characteristically contain a single absorption band at 300–400 nm (Fig. 2a). The long-wave absorption band of benzoyl derivatives **VIII–X** is shifted hypsochromically compared to compounds **V–VII** (by ~200 nm) (Figs. 1 and 2a). A possible explanation for this fact is that ketone carbonyl stronger withdraws and delocalizes electrons that ester carbonyl, which, in its turn, is associated with the presence of an internal effect in ester carbonyl, adversely affecting the electron-acceptor ability of the C=O group [10]. The elemental analyses and IR spectra provide evidence for the composition and structure of benzolylated diamines **VIII–X**.

Macroheterocycles **XI**-XIII were prepared in glacial acetic acid under reflux. They are variously shaded brown substances. They are soluble in DMF, chloroform, and acetone (under heating). Macrocycle XIII is insoluble in ethanol, unlike macrocycles XI and XII. The electronic absorption spectra characteristically contain a single absorption band at 305, 416, and 293 nm (compounds XI-XIII, respectively]. The formation of a macroheteroring with a lacking conjugation system produces no changes into the electronic absorption spectrum of compounds XI and XIII, whose *p*-phenylene fragments are intervened by an SO₂ group and an oxygen atom, unlike compound XII that has a sulfur bridge (Fig. 2b). This fact can be explained by that the coordinately unsaturated sulfur(II) atom serves to combine the weak chromophores into a single one. The oxygen atom and the SO₂ group do not possess such an ability.

EXPERIMENTAL

The electronic absorption spectra were measured on a Specord M-400 instrument in DMF, acetone,



Fig. 2. Electronic absorption spectra. (a) Benzoylated diamines (1) **VIII**, (2) **IX**, and (3) **X** (ethanol); and (b) macroheterocyclic compounds (1) **XI**, (2) **XII**, and (3) **XIII** (DMF).

benzene, and chloroform in quartz cells $(l \ 1 \ cm)$ at 20°C. IR spectra were obtained on an Avatar-360 FT-IR-ESP in KBr.

Purity control was performed by TLC on Silufol UV-254 plates (eluent methanol-chloroform, 1:19 v/v).

3-[4-(4-[(1-Oxo-1*H***-inden-3-yl)amino]phenylsulfonyl)anilino]-1***H***-inden-1-one (V). A mixture of 0.01 mol of dione I and 0.005 mol of sulfone II was heated in 20 ml of methanol under reflux for 8 h. After cooling, a precipitate formed and was filtered off, washed with ethanol, and dried in air. Product V was purified by column chromatography on alumina (Brockmann II), eluent methanol–chloroform, 1:1 \text{ v/v}, yield 86%, dark blue crystals, mp 228°C, R_f 0.87,**

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soluble in benzene, ethanol, DMF, chloroform, and acetone; insoluble in hexane, heptane, and 20% alkali. UV spectrum, v_{max} , nm (ethanol): 376, 585; (benzene): 382, 558; (DMF): 536; (chloroform): 378, 562; (acetone): 381, 569. IR spectrum, cm⁻¹: δ (NH) 3382, δ (NH) 1505, v(C=O) 1658, v(CN) 1208, v(CC) 1106, v(CS) 728, v(CH) 2921, δ (CH) 833, v(S=O) 1145. Found N, %: 5.3. C₃₀H₂₀N₂O₄S. Calculated N, %: 5.6.

Compounds VI, VII, and XIV–XVIII were prepared in a similar way.

3-[4-(4-[(1-Oxo-1*H***-inden-3-yl)amino]phenylsulfanyl)anilino]-1***H***-inden-1-one (VI), yield 75%, dark green crystals, mp 176°C, R_f 0.6. UV spectrum, \lambda_{max}, nm (ethanol): 385, 596; (benzene): 376, 575; (DMF): 385,585; (acetone): 377, 582; (chloroform): 378, 512, 584. IR specrum, cm⁻¹: v(NH) 3373, δ(NH) 1547, v(C=O) 1649, v(CN) 1207, v(CC) 1102, v(CS) 735, v(CH) 2918, δ(CH) 817. Found N, %: 6.1. C₃₀H₂₀· N₂O₂S. Calculated N, %: 5.9.**

3-(4-4-[(1-Oxo-1*H***-inden-3-yl)amino]phenoxyanilino)-1***H***-inden-1-one (VII), yield 77%, violet crystals, mp 256°C, R_f 0.77. UV spectrum, \lambda_{max}, nm (DMF): 394 (log \epsilon 4.5), 585 (log \epsilon 4.2). IR spectrum, cm⁻¹: v(NH) 3437, \delta(NH) 1549, v(C=O) 1654, v(CN) 1448, v(CC) 1093, v(CH) 2921, \delta(CH) 833, v(CO) 1204. Found N, %: 5.5. C_{30}H_{20}N_2O_3. Calculated N, %: 6.1.**

1-(4-[(4-[3-(Benzoyloxy)-1*H*-inden-1-yliden]aminophenyl)sulfonyl]phenylimino)-1H-inden-3-yl benzoate (VIII). A mixture of 0.02 mol of compound V, 13 ml of benzoyl chloride, and 5 ml of pyridine was heated under reflux for 6 h. After cooling, a precipitate formed and was filtered off, washed with benzene, dissolved in 5% alkali, filtered off, and dried at 100°C. Organic admixtures were extracted in a Soxhlet apparatus with benzene. Yield 52%, brown crystals, does not melt up to 250°C, R_f 0.9, soluble in chloroform, acetone, and DMF (under heating), and insoluble in benzene. UV spectrum, λ_{max} , nm (chloroform): 299. IR spectrum, cm^{-1} : v(C=O) 1720, v(CC) 1072, v(C=N) 1664, v(CS) 710, v(CH) 2918, δ (CH) 794, v(S=O) 1152. Found N, %: 3.8. $C_{44}H_{28}N_2O_6S$. Calculated N, %: 33.9.

Compounds **IX** and **X** were prepared in a similar way.

1-(4-[(4-[3-(Benzoyloxy)-1*H*-inden-1-yliden]aminophenyl)sulfanyl]phenylimino)-1*H*-inden-3-yl benzoate (IX), yield 44%, brown crystals, does not melt up to 250°C, R_f 0.85. UV spectrum, .max, nm (ethanol): 401. IR spectrum, cm⁻¹: v(C=O) 1713, v(CC) 1084, v(C=N) 1656, v(CS) 752, v(CH) 2973, δ (CH) 826. Found N, %: 3.6. C₄₄H₂₈N₂O₄S. Calculated N, %: 4.1.

1-(4-[(4-[3-(Benzoyloxy)-1H-inden-1-yliden]aminophenoxy]phenylimino)-1H-inden-3-yl benzoate (X), yield 22%, brown crystals, does not melt up to 300°C, R_f 0.92. UV spectrum, λ_{max} , nm (DMF): 300 (log ε 4.5). IR spectrum, cm⁻¹: v(C=O) 1716, v(CC) 1093, .(C=N) 1616, v(CH) 2920, v(CH) 842, v(CO) 1236. Found N, %: 4.4. C₄₄H₂₈N₂O₅. Calculated N, %: 4.2.

1,7(1,3)-Di-1*H*-indena-3,5,9,11(1,4)-tetrabenzola-2,6,8,12-tetraaza-4,10-dithiacyclododecaphane-1,6diene-4,10-dione (XI). A mixture of 0.0003 mol of compound V and 0.002 mol of sulfone II was heated in 15 ml of glacial acetic acid under reflux for 3 h. After cooling, the reaction mixture was poured into hexane. A precipitate formed and was filtered off and dried at 100°C, yield 87%, light brown crystals, mp 225°C, R_f 0.6, soluble in DMF, acetone, ethanol and chloroform (under heating), and insoluble in hexane and HCl. UV spectrum, λ_{max} , nm· (ethanol): 305. IR spectrum, cm⁻¹: v(NH) 3373, δ(NH) 1522, v(CN) 1401, v(CC) 1073, v(C=N) 1675, v(CS) 734, v(CH) 2920, δ(CH) 833, v(S=O) 1148, 1320. Found N, %: 8.2. $C_{42}H_{28}N_4O_4S_2$. Calculated N, %: 7.8.

1,7(1,3)-Di-1*H*-indena-3,5,9,11(1,4)-tetrabenzola-2,6,8,12-tetraaza-4,10-dithiacyclododecaphane-1,6diene (XII), yield 29%, dark brown crystals, does not melt up to 250°C, R_f 0.65, soluble in acetone, ethanol, and chloroform. UV spectrum, λ_{max} , nm (DMF): 416 (log ε 4.7). IR spectrum, cm⁻¹: v(NH) 3415, δ(NH) 1540, v(CN) 1398, v(CC) 1049, v(C=N) 1606, v(CS) 747, v(CH) 2923, v(CH) 830. Found N, %: 7.9. C₄₂H₂₈N₄S₂. Calculated N, %: 8.6.

1,7(1,3)-Di-1*H*-indena-3,5,9,11(1,4)-tetrabenzola-2,6,8,12-tetraaza-4,10-dioxacyclododecaphane-1,6diene (XIII), yield 38%, dark brown crystals, does not melt up to 300°C, R_f 0.7, soluble in DMF and insoluble in ethanol, acetone, and chloroform. UV spectrum, λ_{max} , nm (DMF): 293 (log ε 4.6). IR spectrum, cm⁻¹: v(NH) 3416, δ (NH) 1538, v(CN) 1405, v(CC) 1093, .(C=N) 1614, v(CH) 2920, δ (CH) 834, v(CO) 1219. Found N, %: 8.5. C₄₂H₂₈N₄O₂. Calculated N, %: 9.03.

N,*N*'-**Bis(1-oxo-1***H*-inden-3-yl)-*m*-phenylenediamine (**XIV**), yield 88%, red crystals, mp 291–293°C, R_f 0.7. UV spectrum, λ_{max} , nm (ethanol): 470 (log ε 3.77). IR spectrum, cm⁻¹: v(NH) 3370, δ(NH) 1540, v(C=O) 1680, v(CN) 1240, v(CC) 1120, v(CH) 2920, v(CH) 796. Found N, %: 8.0. C₂₄H₁₆N₂O₂. Calculated N, %: 7.7.

N,N'-Bis(1-oxo-1H-inden-3-yl)pyridine-2,6-di-

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amine (XV), yield 85%, dark brown crystals, mp 259–260°C, R_f 0.8. UV spectrum, λ_{max} , nm (ethanol): 480 (log ε 3.61). IR spectrum, cm⁻¹: v(NH) 3340, δ (NH) 1530, v(C=O) 1680, v(CN) 1280, v(CC) 1150, v(CH) 3160, δ (CH) 825, v(piridin) 475. Found N, %: 11.1. C₂₃H₁₅N₃O₂. Calculated N, %: 11.5 [7].

N,*N*'-**Bis**(1-oxo-1*H*-inden-3-yl)-1,3,4-thiadiazole-2,5-diamine (XVI), yield 63%, yellow crystals, mp 197°C, *R*_f 0.4. UV spectrum, λ_{max} , nm (ethanol): 328, 358, 527. IR spectrum, cm⁻¹: v(NH) 3320, δ (NH) 1510, v(C=O) 1650, v(CN) 1150, v(CC) 1130, v(CH) 2950, δ (CH) 850, v(CS) 692. Found, %: N 13.9; S 8.5. C₂₀H₁₂N₄O₂S. Calculated, %: N 15.0; S 8.6.

N,*N*'-**Bis**(1-oxo-1*H*-inden-3-yl)-*p*-phenylenediamine (**XVII**), yield 81%, dark green crystals, does not melt up to 350°C, *R_f* 0.6. UV spectrum, λ_{max} , nm (ethnol): 600 (log ε 3.73). IR spectrum, cm⁻¹: v(NH) 3180, δ (NH) 1550, v(C=O) 1640, v(CN) 1280, v(CC) 1140, v(CH) 2980, δ (CH) 737. Found N, %: 7.4. C₂₄H₁₆N₂O₂. Calculated N, %: 7.7.

N, *N*'-**Bis**(1-oxo-1*H*-inden-3-yl)benzidine (**XVIII**), yield 85%, dark green crystals, does not melt up to 350°C, *R*_f 0.5. UV spectrum, λ_{max} , nm (ethanol): 610 (log ε 4.1). IR spectrum, cm⁻¹: v(NH) 3330, δ(NH) 1540, v(C=O) 1640, v(CN) 1250, v(CC) 1190, v(CH) 2990, δ(CH) 814. Found N, %: 6.1. C₃₀H₂₀· N₂O₂. Calculated N, %: 6.3.

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