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# 3,3'-Bis(dipyrrolylmethenes) as New Chelating Ligands: Synthesis and Spectral Properties

**G. B. Guseva[a], N. A. Dudina[a], E. V. Antina[a], A. I. V'yugin[b], and A. S. Semeikin[b]**

[a] *Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademichskaya 1, Ivanovo, 153045 Russia*
*e-mail: gbg@isc-ras.ru*

[b] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*

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**Abstract**—Hydrobromides of three new alkyl-substituted tetrapyrrole ligands with an open chain, in which the dipyrrolylmethene fragments are linked by a $CH_2$-spacer at the 3,3'-pyrrole carbon atoms, were synthesized and studied by IR, $^1H$ NMR, and electronic absorption spectroscopy. As compared to the 2,2' isomers (alkyl derivatives of biladiene-*a,c*) and monomers (2,2'-, 2,3'-, and 3,3'-dipyrrolylmethenes, the effect of structural factors is manifested in a considerable (up to 19–31 nm) bathochromic shift of the strong band in the electronic spectrum, an increase in the N–H stretching vibration frequency in the IR spectra (by more than 30 $cm^{-1}$), and a decrease in the stability of 3,3'-bis(dipyrrolylmethene) salts. The solvent effect is manifested in small changes in the quantitative characteristics of the electronic absorption spectra of 3,3'-tetrapyrrole hydrobromides in $C_6H_6$, $CCl_4$, $CH_2Cl_2$, $CHCl_3$, and alcohols. In DMF, DMSO, and $C_5H_5N$, the salts undergo solvolytic dissociation to the free ligands and HBr, which accelerates in dilute solutions ($<10^{-4}$ M) and with an increase in the electron-donor power of the solvent. The auxochromic effects of protons in the electronic absorption spectra of the salts, compared to ligands, were estimated quantitatively.

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Synthesis and use of new chelating ligands in coordination and supramolecular chemistry attracts much attention as a promising route to materials with new physicochemical properties [1]. Oligopyridines forming interesting two- and three-dimensional structures (rods, lattices, cages, helices, etc.) are popular ligands for the synthesis of supramolecular metal chelates [2]. However, complexes of neutral oligopyridine ligands contain counterions, which complicates their chromatographic purification and the X-ray diffraction analysis of crystals.

Preparation of a series of complexes of $Co^{II}$ and $Zn^{II}$ with dipyrrolylmethenes, reported in 1998 [3], aroused interest in a new class of chromophore chelating ligands, linear oligopyrroles consisting of dipyrrolylmethene fragments linked by an alkyl spacer, and in the use of their chelates in supramolecular chemistry. In contrast to structurally related porphyrins, linear oligopyrroles exhibit higher flexibility and conformational invariance because of the nonmacrocyclic structure of the molecules. The use of dipyrrolylmethenes and oligodipyrrolylmethenes for metal chelation is advantageous because their complexes, as a rule, do not require counterions, as the ligand in the complex is charged. Therefore, dipyrrolylmethenates have an ordered crystal structure and can be readily purified by standard chromatographic methods [4]. Dipyrrolylmethene complexes found use as laser dyes [5, 6], and the ligands themselves are very promising as highly sensitive analytical reagents. However, the physical chemistry of compounds of this class is in the early step of the development.

Within the framework of studies in the field of porphyrin chemistry [7], we examine the possibilities of using linear oligopyrroles as chelating ligands in coordination and analytical chemistry. The first studies concerned complexes of alkyl-substituted dipyrrolylmethenes and biladiene-*a*,*c* ($H_2L$), which is 2,2'-bis(dipyrrolylmethene), and determination of the prevailing structural and solvation factors controlling the complexation with *d* metals ($Zn^{II}$, $Cd^{II}$, $Cu^{II}$, $Co^{II}$, $Ni^{II}$, $Pb^{II}$, $Hg^{II}$, etc.) [8–10]. It was shown that, in

complexes of 2,2'-bis(dipyrrolylmethenes) with methylene spacer, the metal–ligand ratio strongly depends on the type of the stable ligand conformation determined by the alkyl substituents, metal ion, and solvent [2, 4, 8–12]. For example, the reaction of $Co^{II}$ with biladiene-*a*,*c* in pyridine yields a mononuclear monohelical complex (CoL), and in DMF, binuclear complexes: heteroligand $Co_2LX_2$ or bihelical homoligand $Co_2L_2$ [10]. According to published data [4, 11, 12], 3,3'-bis(dipyrrolylmethenes) form with $Zn^{II}$, $Co^{II}$, and $Cu^{II}$ only binuclear complexes $M_2L_2$, which substantially simplifies their use in supramolecular and analytical chemistry. Therefore, our recent studies are aimed at examining the effects exerted on the physicochemical properties of bis(dipyrrolylmethene) ligands and their metal chelates by solvent properties, structures of alkyl substituents and spacer, and positions of spacer insertion between the dipyrrolylmethene fragments (between 2,2'-, 3,3'-, or 2,3'-C atoms).

Dipyrrolylmethene, a common building block of porphyrins, corrins, and other macrocyclic tetrapyrroles, appeared also to be an elementary unit for molecules of a new class of linear oligodipyrrolylmethenes, including bis(dipyrrolylmethenes) whose simplest representative is biladiene-*a*,*c*. The capability of dipyrrolylmethenes and biladiene-*a*,*c* to form coordination compounds with *d*-metal ions is the key property for the template synthesis of macrocycles and for preparation of stable macromolecular metal chelates with useful properties [2, 4–6]. In contrast to dipyrrolylmethene whose core is virtually planar because of the conjugation of the pyrrole fragments through the methylene bridge, molecules of bis(dipyrrolylmethenes), including biladiene-*a*,*c*, are three-dimensional because of rotation of the dipyrrole fragments about the alkyl spacer (methylene group in the simplest case) linking them. This gives rise to invariance of molecular conformations of linear tetrapyrroles. In accordance with single crystal X-ray diffraction data [4, 13] and theoretical calculations [14], the most stable conformations are helical (which is close to a macrocycle in shape) and open ridge tile structures (Fig. 1). The conformational isomerism of linear tetrapyrroles is important for the formation of metal complexes of different structures (mono-, bi-, or trinuclear; mono- or bihelical) [2, 4, 7–14]. In addition, owing to the high structural flexibility, linear tetrapyrrole molecules accomplish functions of the most important class of prosthetic groups of highly organized natural chromoproteins, phytochromes, as photomorphogenesis processes are based specifically on light-dependent conformational transformations of pigment molecules [15].

The conformational analysis of unsubstituted biladiene-*a,c* and its alkyl derivatives (the quantum-chemical study was performed using the PCGAMESS program package on an Athlon computer in the Linux environment; the MacMolPlt program was used for data analysis and imaging) [14] showed that the ridge tile and helical conformations are separated by a potential barrier as low as 2.1 kJ $mol^{-1}$, which accounts

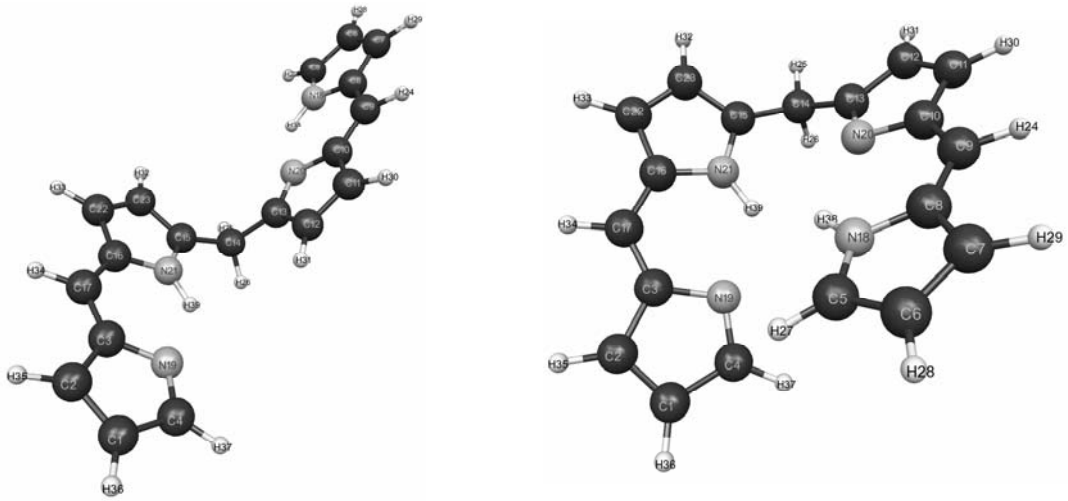



**Fig. 1.** Ridge tile and helical conformations of unsubstituted biladiene-*a*,*c*.

for the easy conformational transitions depending on the solvent, ligand alkylation pattern, and metal ion [8–10, 12, 13]. In accordance with single crystal X-ray diffraction data, 3,3'-bis(dipyrrolylmethenes), in contrast to the 2,2' isomers, occur in the crystals in the ridge tile conformation, which is also, probably, characteristic of solutions [12].

No less important property of natural and synthetic compounds of this class is their chromophore activity and high sensitivity of the electronic spectra to changes in the molecular structure, to coordination and acid–base interactions, and to solvation features. Despite the fact that electronic absorption spectra are widely used for qualitative and quantitative analysis and for monitoring of complexation of oligopyrroles, available data on the quantitative characteristics of the electronic spectra of compounds of this class in various solvents are very limited. For example, data on the electronic absorption spectra of 3,3'-bis(dipyrrolylmethenes) are available from the foreign literature mostly for solutions in methylene chloride, whereas studies of these compounds are performed in alcohols, chloroform, and their mixtures with nonpolar and electron-donor solvents [1–13].

We prepared in the form of hydrobromides three alkyl-substituted 3,3'-bis(dipyrrolylmethenes): compounds **I–III**, of which only for **II** the synthesis and certain properties have been reported previously [12]. Procedures for the synthesis of **I–III**, $^1$H NMR and IR data, and results of elemental analysis are given in Experimental. Based on the results of previous spectroscopic studies of dipyrrolylmethenes and 2,2'-bis(dipyrrolylmethenes) [8, 10, 16] and on the new data for 3,3'-bis(dipyrrolylmethenes), we analyzed how the features of the molecular structure of chromophores and the solvent affect the electronic absorption spectra of the compounds in organic solvents. For comparison, along with 3,3'-bis(dipyrrolylmethenes) we chose structurally related bis(dipyrrolylmethenes) with the methylene spacer linking the dipyrrolylmethene units via 2,2'-pyrrole carbon atoms (biladienes **IV, V**) and dipyrrolylmethenes (compounds **VI–X**), synthesized as hydrobromides or free ligands. The quantitative characteristics of the electronic absorption spectra of compounds **I–X** in nonpolar ($C_6H_6$, $CCl_4$, $CH_2Cl_2$), proton-donor ($CH_3Cl$, EtOH, 1-PrOH, *i*-PrOH), and electron-donor ($C_5H_5N$, DMF, DMSO) solvents are given in Tables 1 and 2.

It was shown previously that, for dipyrrolylmethenes and biladienes, the auxochromic effect of the proton is manifested in a considerable (up to 35–42 nm) bathochromic shift of the strong absorption band and appearance of a weak broadened charge-transfer band in the range 360–400 nm in the electronic absorption spectra of the hydrobromides, compared to the free bases [10, 16, 17]. In Table 1, the corresponding data are given for ligands **VI***–**VIII*** and their salts **VI–VIII**, taken as examples.

In proton-donor solvents, the spectra of free bases **VI***–**VIII*** resemble the spectra of the corresponding hydrobromides, which is due to the solvatochromic effect caused by donor–acceptor interactions of tertiary nitrogen atoms of dipyrrolylmethene with chloroform molecules ($>N\cdots HCCl_3$) and is indicative of the high ligand basicity. The similar solvatochromic effect is lacking in alcohols (1-PrOH) because of their strong association and lower proton-donor power of the solvent.

Oligomerization by linking of two dipyrrolylmethene groups with a methylene bridge at the 2,2'-positions of the pyrrole rings is accompanied, as a rule, by appearance in the spectra of the corresponding biladienes **IV** and **V** of additional weak bands or shoulders on the wings of the strong long-wave band, with $\lambda_{max}$ of the latter undergoing a slight bathochromic shift relative to the corresponding monomeric analogs (compounds **VI–VIII**). Whereas 2,3'- and 3,3'-bipyrroles **IX** and **X** are characterized by a small hypsochromic shift of the long-wave band relative to the 2,2' analog (compound **VI**), in the spectra of 3,3'-bis(dipyrrolylmethene) salts $\lambda_{max}$ undergoes a large bathochromic shift compared to the structurally related 2,2'-bipyrroles and 2,2'-bis(dipyrrolylmethenes). For example, the differences in $\lambda_{max}$ in the spectra of alkylated analogs (compounds **I, IV, VI; II, III, VII**) range from 19 to 31 nm. The observed considerable enhancement of the chromophore properties may be due to increased conjugation in the π system as a result of weaker distortion of the planar structure of the dipyrrole fragments in the 3,3' analogs compared to the 2,2' isomers, as indicated by X-ray structural data [4, 12]. However, the main structural effect in this case is apparently due to differences in the polarization of the conjugated π system of the dipyrrolylmethene fragment on introducing a substituent, (dipyrrolylmethene)methylene group, into the α- or β-position of the pyrrole ring [18].

Salts **I–III**, like symmetrically substituted dipyrrolylmethenes and 2,2'-tetrapyrroles, are stable in inert and proton-donor solvents, and the electronic

**Table 1.** Electronic absorption spectra [λ, nm (log ε)] of hydrobromides of dipyrrolylmethenes and bis(dipyrrolylmethenes) in nonpolar and proton-donor solvents[a]

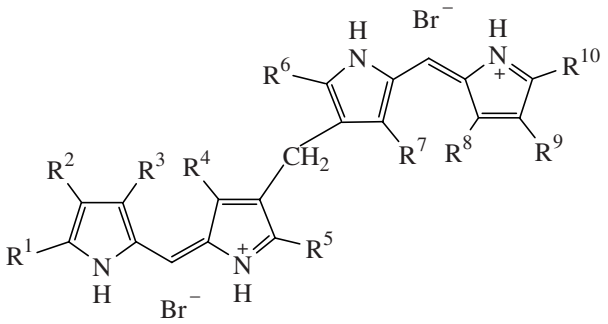
| Comp. no. | Solvent | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_6H_6$ | $CCl_4$ | $CH_2Cl_2$ | $CHCl_3$ | EtOH | 1-PrOH | *i*-PrOH |
| **VI**[b] | 442 | sp. sol. | – | 380–450 w, 480 | – | 441 | – |
| **VII**[b] | 442 | sp. sol. | – | 380–450 w, 481 | – | 442 | – |
| **VIII**[b] | 445 | sp. sol. | – | 380–450 w, 484 | – | 446 (4.42) | – |
| **VI** | 364 (3.41), 484 (4.66) | sp. sol. | 486 (4.994) | 362 (4.02), 483 (4.75) | – | 361 (3.73), 478 (4.61) | – |
| **VII** | 368 w, 482 | sp. sol. | – | 363 w, 473 | – | 362 w, 479 | – |
| **VIII** | 366 w, 486 | sp. sol. | – | 363 w, 484 | – | 365 (3.83), 481 (4.83) | – |
| **IX** | sp. sol. | sp. sol. | 477 (4.36) | 403 (4.10), 481 (4.48) | – | 412 (4.07), 473 (4.34) | – |
| **X** | sp. sol. | sp. sol. | 475 (4.02) | 376 (4.39), 472 (4.43) | – | 378 (3.91), 476 (3.98) | – |
| **IV**[c] | 366 w, 485 | 370 w, 484 | – | 363 w, 482, 521 w | – | – | – |
| **V** | 375 w, 466 sh, 499, 527 w | – | – | 371 w, 452 sh, 498, 523 w | – | 370 (4.17), 449 (4.75), 490 (4.72), 520 sh | – |
| **I** | 365, 466, 507 | sp. sol. | 362 (4.29), 464 (4.83), 504 (5.08) | 364 (4.22), 461 (5.01), 502 (5.43) | 376 (3.87), 458 (4.64), 499 (4.99) | 364 (3.74), 458 (4.40), 501 (4.78) | 364 (3.74), 458 (4.40), 500 (4.79) |
| **II** | 365–375, 465 w, 508 | sp. sol. | 360 (4.27), 461 (4.89), 505 (5.20) | 363 (4.25), 462 (5.04), 504 (5.45) | 362–385, 459 (4.69), 500 (5.09) | 367, 462 (4.65), 502 (5.06) | 369, 458, 502 |
| **III** | 370, 466, 508 | sp. sol. | 365 (4.22), 465 (4.90), 504 (5.17) | 363 (4.28), 463 (5.05), 504 (5.45) | 360–382, 459 (4.68), 500 (5.06) | 367 (4.02), 461 (4.65), 502 (5.01) | 369, 462, 500 |

[a] (sp. sol.) Compound is sparingly soluble. [b] Spectrum of the free base. [c] Data for **IV–X** were taken from [16, 17–19]; the same for Table 2.

**Table 2.** Electronic absorption spectra [λ, nm (log ε)] of hydrobromides of dipyrrolylmethenes and bis(dipyrrolylmethenes) in solutions in electron-donor solvents. Concentrations: $C_1 < 5 \times 10^{-5}$ and $C_2 > 1 \times 10^{-4}$

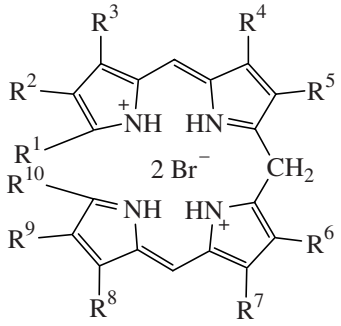
| Comp. no. | Solvent | | | | | |
|---|---|---|---|---|---|---|
| | $C_5H_5N$ | | DMF | | DMSO | |
| | $C_1$ | $C_2$ | $C_1$ | $C_2$ | $C_1$ | $C_2$ |
| **VI**[b] | 448 (4.59)[a] | – | 437 | 437 | – | – |
| **VII**[b] | – | – | 439 | 439 | – | – |
| **VIII**[b] | 445 | 445 | 440 (4.44)[a] | 440 (4.44) | – | – |
| **VI** | 448 (4.59)[a] | 363 w, 484 | 435 (4.67)[a] | – | – | – |
| **VII** | – | 364 w, 474 | 438[a] | – | – | – |
| **VIII** | 445[a] | 364 w, 485 | 440 (4.62)[a] | – | – | – |
| **IX** | 406[a] | 401 w, 483 | 402 (4.08)[a] | – | – | – |
| **X** | 407[a] | 377 w, 473 | 400 (3.86)[a] | – | – | – |
| **IV** | 435 (4.61)[a] | 370 w, 483 | 431 (4.61)[a] | 366 w, 480 | 442 (4.43)[a] | 369 w, 481 |
| **V** | 441[a] | 380–400 w, 493 | 438[a] | 380–400 w, 488 | 438[a] | 380–400 w, 490 |
| **I** | 462 (4.64)[a] | 373–375, 462 sh, 499 (4.84) | 456 (4.67)[a] | 372–375, 456 sh, 496 (4.87) | 463 (4.70)[a] | 367–380, 465 sh, 503 (5.09) |
| **II** | 467 (4.80)[a] | 373–375, 467 sh, 500 (5.01) | 463 (4.79)[a] | 374–380, 463 sh, 500 (5.01) | 465 (4.81)[a] | 370 (4.05), 465 sh, 505 (5.18) |
| **III** | 462 (4.73)[a] | 368–375, 462 sh, 497 (4.89) | 459 (4.73)[a] | 370–376, 459 sh, 494 (4.82) | 462 (4.78)[a] | 375 (4.07), 462 sh, 505 (5.14) |

[a] Spectrum of the free base. [b] One-band spectra are given for nonprotonated ligand species, which are formed by complete dissociation of the corresponding hydrobromides in dilute ($<1 \times 10^{-5}$ M) solutions in electron-donor solvents.



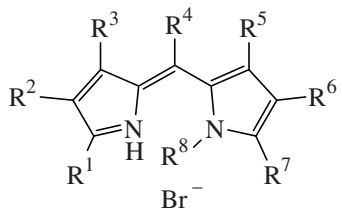
**I–III**
3,3'-Bis(dipyrrolylmethene) dihydrobromide

**I**: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = R^9 = R^{10} =$ Me; **II**: $R^1 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = R^{10} =$ Me, $R^2 = R^9 =$ Et; **III**: $R^1 = R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{10} =$ Me, $R^4 = R^7 =$ Et.



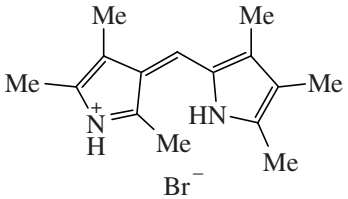
**IV, V**
2,2'-Bis(dipyrrolylmethene) hydrobromide

**IV**: $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = R^9 = R^{10} =$Me; **V**: $R^1 = R^3 = R^4 = R^7 = R^8 = R^{10} =$ Me, $R^2 = R^5 = R^6 = R^9 =$ Bu.

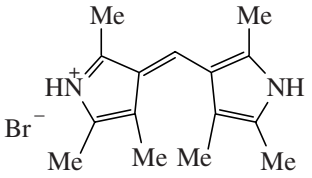


**VI–VIII**
2,2'-Dipyrrolylmethene hydrobromide

**VI**: $R^4 = R^8 =$ H, $R^1 = R^2 = R^3 = R^5 = R^6 = R^7 =$Me; **VII**: $R^4 = = R^8 =$ H, $R^1 = R^3 = R^5 = R^7 =$ Me, $R^2 = R^6 =$ Et; **VIII**: $R^4 = R^8 =$ H; $R^1 = R^3 = R^5 = R^7 =$ Me, $R^2 = R^6 =$ Bu.



**IX**
2,3'-Dipyrrolylmethene hydrobromide



**X**
3,3'-Dipyrrolylmethene hydrobromid

absorption spectra of the corresponding solutions (when stored in the dark) do not change for a long time (Fig. 2). In solvents with pronounced electron-donor properties (Py, DMSO, DMF, mixed solvents based on them), salts **I–III** are very unstable. It was shown previously that, owing to proton delocalization on pyrrole fragments, hydrobromides of dipyrrolylmethenes and biladienes in polar organic solvents (e.g., 1-PrOH) behave as weak electrolytes [17], although equilibria (1) and (2) of salt dissociation are strongly shifted to the left.

$$[H_2L]Br_{(Solv)} \rightleftarrows [H_2L]^+_{(Solv)} + Br^-_{(Solv)}, \quad (1)$$

$$[H_4L]Br_{2(Solv)} \rightleftarrows [H_4L]^{2+}_{(Solv)} + 2Br^-_{(Solv)}. \quad (2)$$

In proton-donor solvents, owing to solvation of the $Br^-$ anions, the stability of protonated oligopyrrole species increases, whereas in electron-donor media, owing to salt dissociation, the access of solvent molecules to the protons is facilitated, and specific solvation of the proton leads to solvolytic dissociation of the salts [10, 16, 17]:

$$[H_2L]Br_{(Solv)} + B_{(Solv)} \rightarrow HL_{(Solv)} + [B{\cdot}HBr]_{(Solv)}, \quad (3)$$

$$[H_4L]Br_{2(Solv)} + 2B_{(Solv)} \rightarrow H_2L_{(Solv)} + 2[B{\cdot}HBr]_{(Solv)}, \quad (4)$$

where B is a base (solvent or cosolvent).

The solvolytic dissociation can be monitored by characteristic transformations of the salt spectrum into the spectrum of the nonprotonated ligand: The first long-wave band is shifted hypsochromically, and the charge-transfer band disappears. In strongly basic media, processes (3) and (4) are irreversible, and in

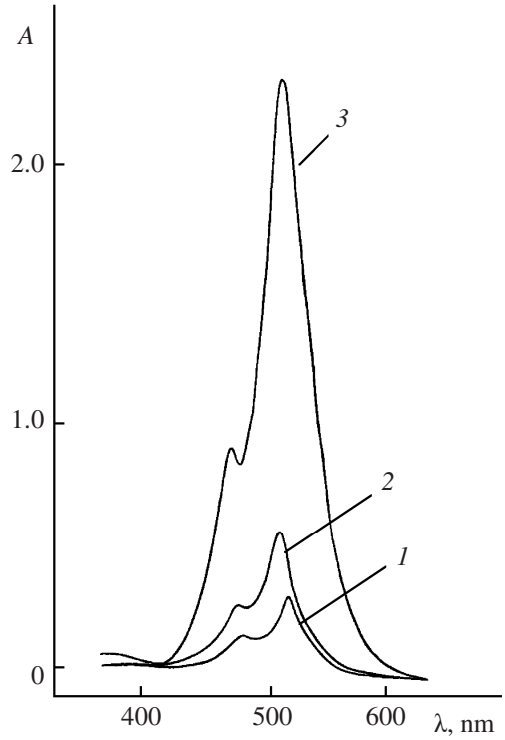



**Fig. 2.** Electronic absorption spectra of **I**: (*1*) $C_6H_6$, *c* 5 × $10^{-6}$ M; (*2*) 1-PrOH, *c* 1.2 × $10^{-4}$ M; and (*3*) $CHCl_3$, *c* 9.4 × $10^{-5}$ M. (*A*) Optical density; the same for Fig. 3.

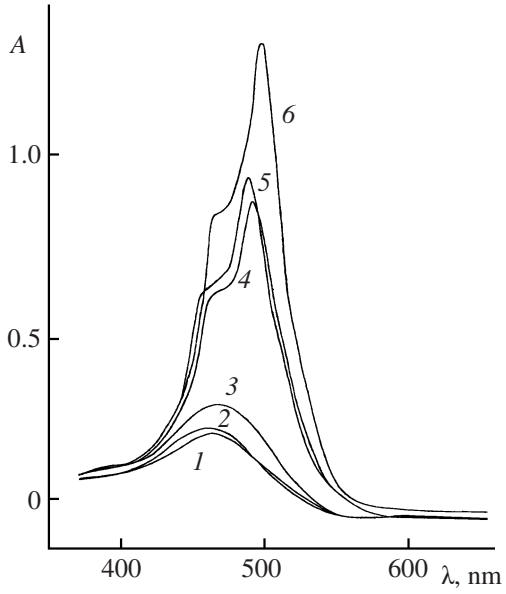



**Fig. 3.** Electronic absorption spectra of **I**: (*1*) Py, (*2*) DMF, (*3*) DMSO, *c* 5 × $10^{-6}$ M; (*4*) Py, (*5*) DMF, *c* 1.2 × $10^{-4}$ M; (*6*) DMSO, *c* 1.05 × $10^{-4}$ M.

relatively weakly basic media there can be an equilibrium between the protonated ligand form and dissociation products. In the general case, the rate of the solvolytic dissociation depends on the electron-donor power, polarity, and dielectric constant of the medium, on the solution concentration, and on the ligand structure. The conditions for the contact of the proton with the solvent and for the irreversible solvolytic dissociation of salts are the most favorable in dipyrrolylmethenes, especially in their 2,3' and 3,3' isomers. As a result, in electron-donor solvents with a high dielectric constant (DMF, ε 43.9; DMSO, ε 45.1) deprotonation of dipyrrolylmethenes **VI–X** is very fast (it occurs during the time of solution preparation), irrespective of the salt concentration. In weakly polar Py (ε 12.3) at high concentrations, self-association of salts is observed [13] and the stability of salts increases, as follows from the appearance of the band of the protonated ligand in the region of 470–480 nm, whose intensity increases with the solution concentration, simultaneously with a decrease in the intensity of the short-wave band of the nonprotonated ligand, owing to the shift of equilibrium (3) to the left. Nevertheless, as a result of solvolytic dissociation of the salt, even the spectra of concentrated solutions gradually transform into the spectrum of the ligand.

In tetrapyrroles, the protonated form can be additionally stabilized in the "closer" helical conformation characteristic, as noted above, of biladienes-*a*,*c* and 2,2'-bis(dipyrrolylmethenes) with a short spacer [12, 13], especially in concentrated solutions and low-polarity media (owing to association processes). As a result, the deprotonation rates observed with biladienes-*a*,*c* (compounds **IV, V**) are lower, and in concentrated solutions the protonated forms prevail (Table 2). The electronic spectra of 3,3'-bis(dipyrrolylmethenes) in electron-donor solvents suggest that these salts are the least stable, as even in the spectra of freshly prepared concentrated solutions of **I–III** the band of the nonprotonated ligand appears as a shoulder on the wing of the long-wave band (Fig. 3).

Analysis of the shifts $\Delta\lambda_{max} = \lambda_{max}^{salt} - \lambda_{max}^{ligand}$ (in electron-donor solvents) shows that the auxochromic effect of proton on the chromophore system of 3,3'-tetrapyrroles (41–49 nm) is appreciably weaker compared to biladienes and dipyrrolylmethenes (48–52 nm),

which may be due to differences in the efficiency of acid–base interactions.

Previous studies [19, 20] showed that the decrease in the stability of salts of dipyrrolylmethenes and biladienes can be judged from the long-wave shift of the N–H stretching vibration band in the IR spectra of solid compounds (in KBr). This shift correlates with a decrease in the enthalpy of thermal dissociation of the salt, determined by thermal gravimetric analysis. Dipyrrolylmethenes and biladienes-*a*,*c* have vibration spectra characteristic of secondary amines. Absorption in the range 3400–3500 $cm^{-1}$ corresponds to stretching vibrations of the NH bonds, and that in the range 1590–1650 $cm^{-1}$, to their bending vibrations. Data on stretching and bending vibrations of NH bonds in the IR spectra of pyrrole and compounds **I–X** are given in Table 3. The IR spectra of **I–III** (Fig. 4) are similar to those of dipyrrolylmethenes and biladienes. However, in the IR spectra of **I–III** (compared to **IV–X**), the N–H stretching vibration band ($\nu_{N-H}$) is significantly shifted toward higher frequencies. The shift exceeds 30 $cm^{-1}$ on the average and is maximal for **III** in comparison with **IV** and **VI** (65–63 $cm^{-1}$), which may be due to considerably decreased stability of dihydrobromides of the 3,3' isomers.

Thus, the main differences in the examined spectral characteristics of 3,3'-bis(dipyrrolylmethenes), biladienes-*a*,*c*, and dipyrrolylmethenes consist in significant bathochromic shifts of the long-wave band in the electronic absorption spectra, weakening of the auxochromic effect of the proton, and long-wave shifts of the N–H stretching vibration bands in the IR spectra. All these facts are indicative of a decrease in the stability of salts and in the extent to which the proton of the inorganic acid is delocalized on the π systems of the dipyrrole fragments of the 3,3' isomers of bis(dipyrrolylmethenes). It is known that nonprotonated ligands enter into coordination with metal ions more readily [21]; therefore, in complexation experiments and for preparative synthesis of complexes of 3,3'-bis(dipyrrolylmethenes) it is appropriate to use electron-donor solvents or their additions.

## EXPERIMENTAL

3,3'-Bis(dipyrrolylmethenes) **I–III** in the form of dihydrobromides were prepared as follows.

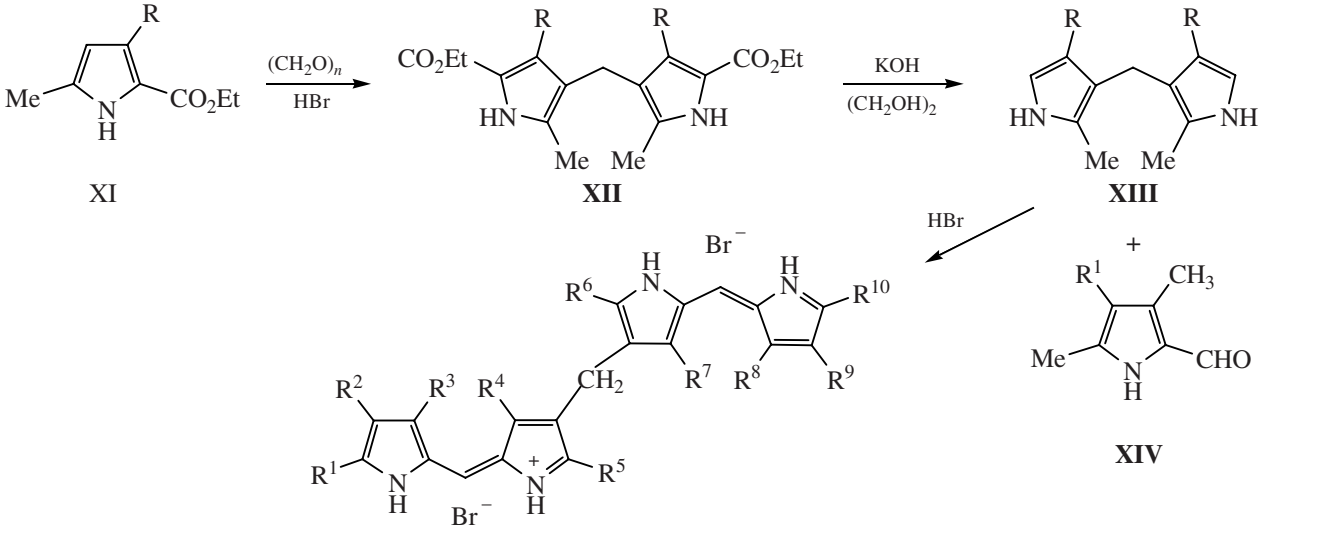



**Table 3.** Stretching ($\nu_{N-H}$, $cm^{-1}$) and bending ($\delta_{N-H}$, $cm^{-1}$) vibrations of NH bonds in IR spectra of pyrrole [19, p. 336] and compounds **I–X**

| Compound | $\nu_{N-H}$ | $\delta_{N-H}$ | Compound | $\nu_{N-H}$ | $\delta_{N-H}$ |
|---|---|---|---|---|---|
| Pyrrole | 3496 | – | **VII** | 3426 | 1618 |
| **I** | 3480 | 1611 | **VIII** | 3408 | 1608 |
| **II** | 3460 | 1614 | **IX** | 3414 | 1593 |
| **III** | 3450 | 1615 | **X** | 3415 | 1618 |
| **VI** | 3415 | 1601 | **IV** | 3417 | 1609 |

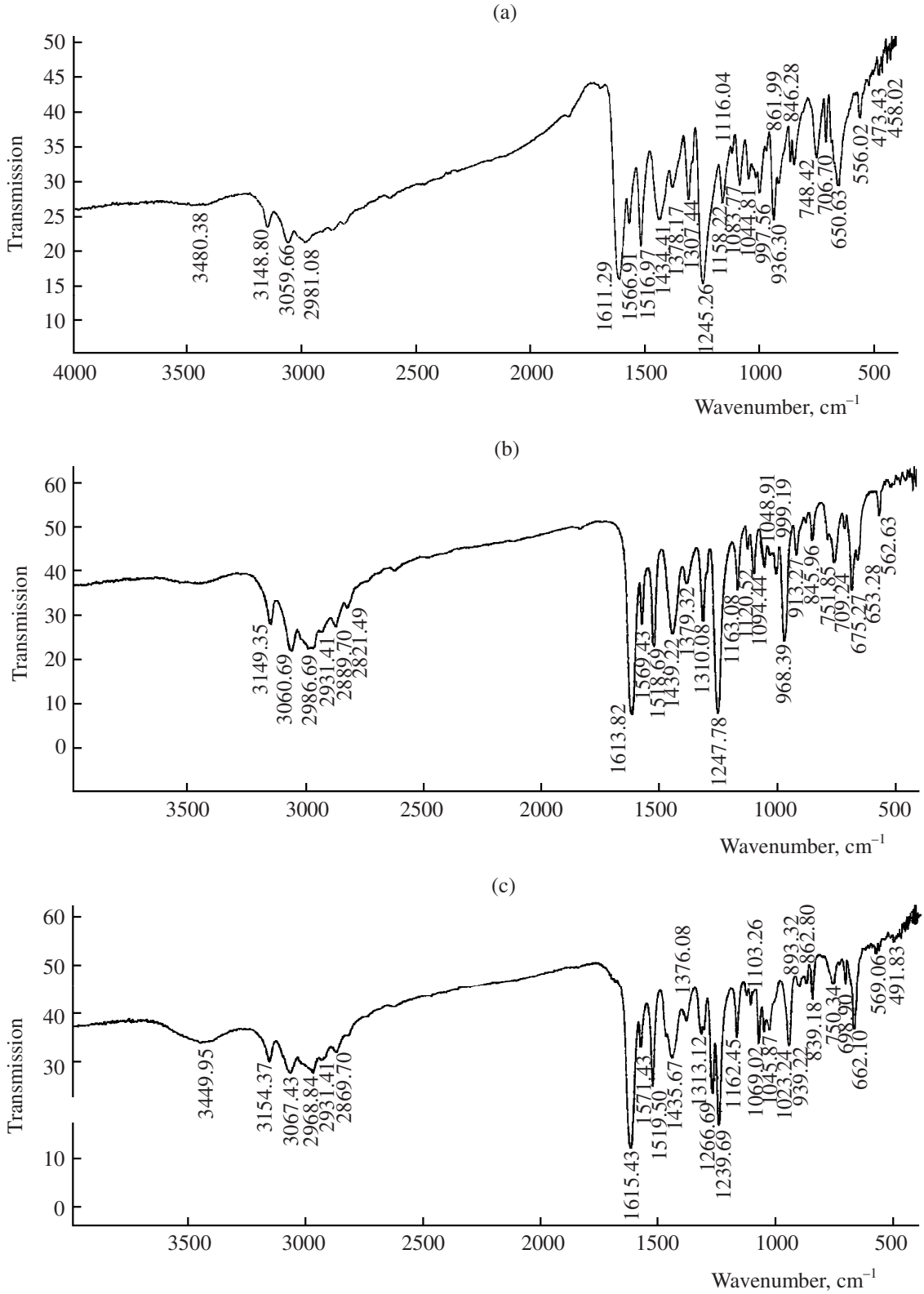



**Fig. 4.** IR spectra of 3,3'-bis(dipyrrolylmethene) dihydrobromides in KBr pellets. Compound: (a) **I**, (b) **II**, and (c) **III**.

**Bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl) methane dihydrobromide I** (*M* 602.46). A mixture of 1.0 g of 5,5'-bis(ethoxycarbonyl)-2,2',4,4'-tetramethyl-3,3'-dipyrrolylmethane (**XII**, R = $CH_3$) and 1.0 g of KOH was refluxed for 1 h in 30 ml of ethylene glycol. The mixture was poured into 200 ml of water, and the precipitate of 2,2',4,4'-tetramethyl-3,3'-dipyrrolylmethane (**XIII**, R = $CH_3$) was filtered off, washed with water, and dried at room temperature in air. Yield 0.51 g (87%). The product without purification was dissolved in 20 ml of methanol, 0.7 g of 2-formyl-3,4,5-trimethylpyrrole (**XIV**, $R^1$ = $CH_3$) was added, and, after its dissolution, 1 ml of concentrated hydrobromic acid was added. The mixture was stirred for 2 h at room temperature. The precipitated product was filtered off, washed with methanol and ether, and dried at room temperature in air. Yield 1.12 g (74%). $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$): 362 (4.29), 464 (4.83), 504 (5.08) ($CH_2Cl_2$). $^1$H NMR spectrum, δ, ppm: 13.11 s (2H, NH), 12.99 s (2H, NH), 7.02 s (2H, *ms*-CH), 3.55 s (2H, *ms*-$CH_2$), 2.67 s (6H, 9-$CH_3$), 2.59 s (6H, 7-$CH_3$), 2.25 s (6H, 2-$CH_3$), 2.15 s (6H, 4-$CH_3$), 1.98 s (6H, 8-$CH_3$) ($CDCl_3$, internal reference TMS). Found, %: C 57.96; H 6.40; N 9.35. $C_{29}H_{38}Br_2N_4$. Calculated, %: C 57.82; H 6.36; N 9.30.

**Bis(8-ethyl-2,4,7,9-tetramethyldipyrrolylmethen-3-yl)methane dihydrobromide II** (*M* 630.51). A mixture of 0.9 g of 5,5'-bis(ethoxycarbonyl)-2,2',4,4'-tetramethyl-3,3'-dipyrrolylmethane (**XII**, R = $CH_3$) and 1.0 g of KOH was refluxed for 1 h in 30 ml of ethylene glycol. Then the mixture was poured into 200 ml of water, and the precipitate of 2,2',4,4'-tetramethyl-3,3'-dipyrrolylmethane (**III**, R = $CH_3$) was filtered off, washed with water, and dried at room temperature in air. Yield 0.46 g (87.3%) (*M* 202). The product without purification was dissolved in 20 ml of methanol, 0.69 g of 4-ethyl-2-formyl-3,5-dimethylpyrrole (**XIV**, $R^1$ = $C_2H_5$, *M* 151) was added, and, after its dissolution, 1.0 ml of concentrated hydrobromic acid was added. The mixture was stirred for 2 h at room temperature, and the precipitate was filtered off, washed with methanol, and dried at room temperature in air. Yield 1.2 g (84%). $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$): 462 (87.3), 505 (235.4) (chloroform). $^1$H NMR spectrum, δ, ppm: 13.09 s (2H, NH), 13.00 s (2H, NH), 7.02 s (2H, *ms*-CH), 3.55 s (2H, *ms*-$CH_2$), 2.68 s (6H, 9-$CH_3$), 2.58 s (6H, 7-$CH_3$), 2.48 q (4H, C*H*$_2$CH$_3$), 2.26 s (6H, 2-$CH_3$), 2.12 s (6H, 4-$CH_3$), 1.06 t (6H, $CH_2CH_3$) ($CDCl_3$, internal reference TMS). Found, %: C 59.25; H 6.96; N 9.30. $C_{31}H_{42}N_4Br_2$. Calculated, %: C 59.05; H 6.71; N 9.14.

**Bis(4-ethyl-2,7,8,9-tetramethyldipyrrolylmethen-3-yl)methane dihydrobromide III** (*M* 630.51). A mixture of 2.0 g of 5,5'-bis(ethoxycarbonyl)-4,4'-diethyl-2,2'-dimethyl-3,3'-dipyrrolylmethane (**XII**, R = $C_2H_5$) and 2.0 g of KOH was refluxed for 1 h in 60 ml of ethylene glycol. The reaction mixture was poured into 200 ml of water, and the precipitate of 4,4'-diethyl-2,2'-dimethyl-3,3'-dipyrrolylmethane (**XIII**, R = $C_2H_5$) was filtered off, washed with water, and dried at room temperature in air. Yield 1.0 g (82%) (*M* 230). The product without purification was dissolved in 20 ml of methanol, 0.6 g of 2-formyl-3,4,5-trimethylpyrrole (**XIV**, $R^1$ = $CH_3$, *M* 137) was added, and, after its dissolution, 1.0 ml of concentrated hydrobromic acid was added. The mixture was stirred for 2 h at room temperature, and the precipitate was filtered off, washed with methanol and ether, and dried at room temperature in air. Yield 1.5 g (54%). $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$): 463 (67.9), 505 (188.1) (chloroform). $^1$H NMR, δ, ppm: 13.15 s (2H, NH), 12.98 s (2H, NH), 6.73 s (2H, *ms*-CH), 3.58 s (2H, *ms*-$CH_2$), 2.67 c (6H, 9-$CH_3$), 2.58 c (6H, 7-$CH_3$), 2.52 κ (4H, C*H*$_2$CH$_3$), 2.24 c (6H, 2-$CH_3$), 1.98 c (6H, 8-$CH_3$), 1.04 t (6H, $CH_2CH_3$) ($CDCl_3$, internal reference TMS). Found, %: C 59.19; H 6.93; N 9.31. $C_{31}H_{42}N_4Br_2$. Calculated, %: C 59.05; H 6.71; N 9.14.

The $^1$H NMR spectra were recorded in deuterochloroform on a Bruker 200 NMR spectrometer. The IR spectra of 3,3'-bis(dipyrrolylmethene) hydrobromides in KBr pellets were measured on an Avatar 360 FT-IR ESP device. The electronic absorption spectra of the samples in organic solvents were taken on SF-103 and Cary 100 spectrophotometers. Organic solvents (chemically pure grade) were additionally purified by standard procedures [22]. The moisture content of the solvents, determined by Fischer titration, did not exceed 0.02%.

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