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Synthesis and Properties of (1,2,3,7,9-Pentamethyldipyrrolylmethen-8-yl)-(1,2,3,7,8-pentamethyldipyrrolylmethen-9-yl)methane and Bis(1,2,3,7,9-pentamethyldipyrrolylmethen-8-yl)trifluoromethylmethane Dihydrobromides

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Abstract—(1,2,3,7,9-pentamethyldipyrrolylmethen-8-yl)(1,2,3,7,8-pentamethyldipyrrolylmethen-9-yl)-methane and bis(1,2,3,7,9-pentamethyldipyrrolylmethen-8-yl)trifluoromethylmethane hydrobromides were synthesized and characterized spectrally (^{1}H NMR, IR, electron absorption spectra). A comparative study was performed of the effect of the bonding site (α- or β-position of the dipyrrolylmethene) with the methane structural fragment connecting two dipyrrolylmethene chromophores, and trifluoromethyl group on the spectral properties of the molecules of compounds dissolved in organic solvents of different nature and their resistance to thermal oxidative degradation.

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Syntheses of new ligands based on pyrrole and its derivatives provide materials with practically useful properties [1, 2]. In this regard linear oligopyrroles are of considerable interest, in particular, dipyrrolylmethenes and bis(dipyrrolylmethenes) [2–5]. The information on the spectral, solvation, coordination, and other properties of symmetrically and unsymmetrically substituted dipyrrolylmethenes available up till now was summarized in [1, 6–8].

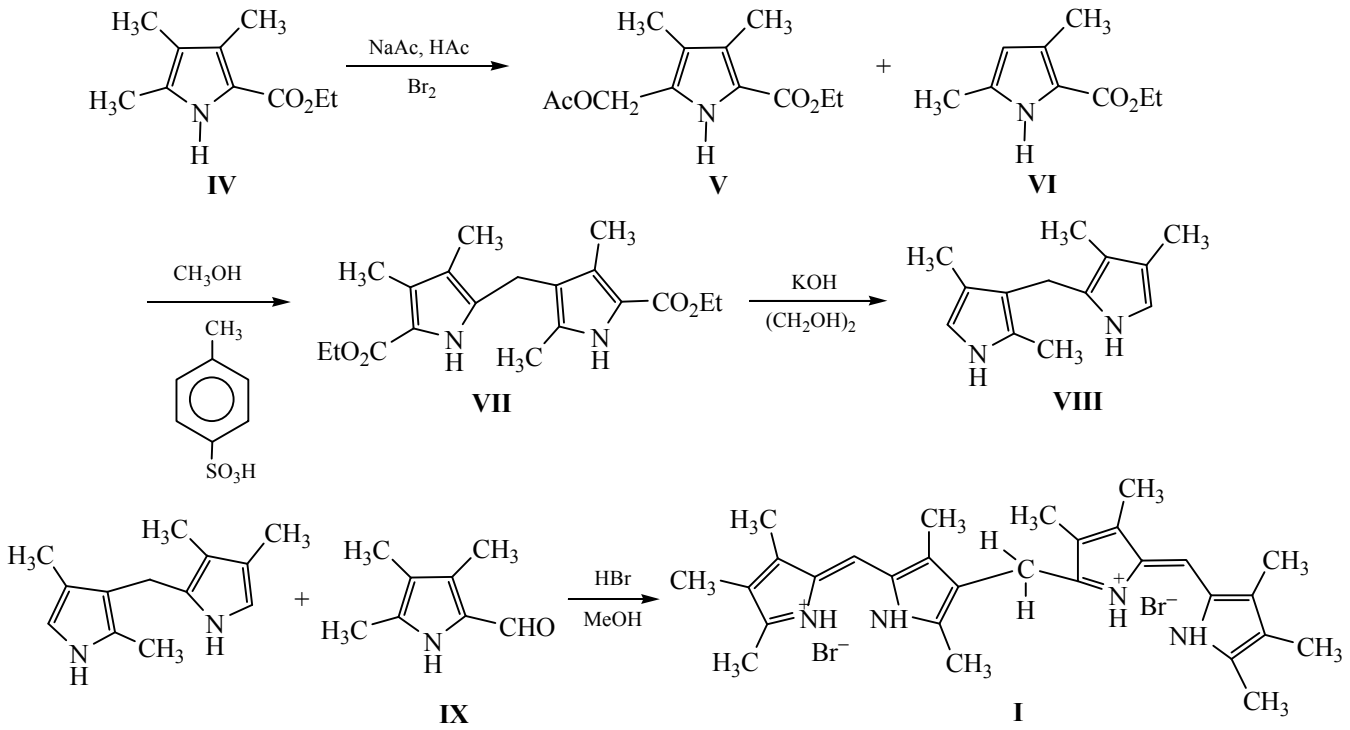
The more complex, and more conformationally labile bis(dipyrrolylmethenes) were poorly studied. Nevertheless, it is obvious that a change in the structure of the molecules of these compounds must have a significant influence on their properties.

We synthesized and spectrally characterized (1,2,3,7,9-pentamethyl-dipyrrolylmethen-8-yl)-(1,2,3,7,8-pentamethyldipyrrolylmethen-9-yl)methane (**I**) and bis(1,2,3,7,9-pentamethyl-dipyrrolylmethen-8-yl)-trifluoromethylmethane (**II**) and isolated them as dihydrobromides (Schemes 1 and 2). The results obtained were analyzed using also the data for the symmetrically substituted bis(1,2,3,7,9-pentamethyl-dipyrrolylmethen-8-yl)methane dihydrobromide (**III**), whose synthesis and properties had been described [9].

Electron absorption spectra (EAS) of compounds **I** and **II** in the proton-donor ($CHCl_3$, EtOH, PrOH), nonpolar (CH_2Cl_2), and electron-donor (DMF, DMSO) solvents in the region of working concentrations 1×10^{-6}–1×10^{-4} M are listed in Table 1. In nonpolar aromatic benzene the dihydrobromides **I–II** are poorly soluble, and it has been impossible to obtain their quantitative EAS characteristics.

It follows from the data of Table 1 that for the studied compounds in nonpolar and proton-donor solvents a three-band absorption spectrum is characteristic. In compounds **I, II** dihydrobromides the proton, being delocalized over the aza-groups of the pyrrole ring fragments of dipyrrolylmethenes, acts as an auxochrome polarizing the chromophore molecule, which is manifested in the EAS as a broad charge-transfer band of low intensity in the region of 360–380 nm. A similar effect was observed previously for dipyrromethenes [6, 10] and biladienes-*a,c* [11].

Scheme 1.



Scheme 2.

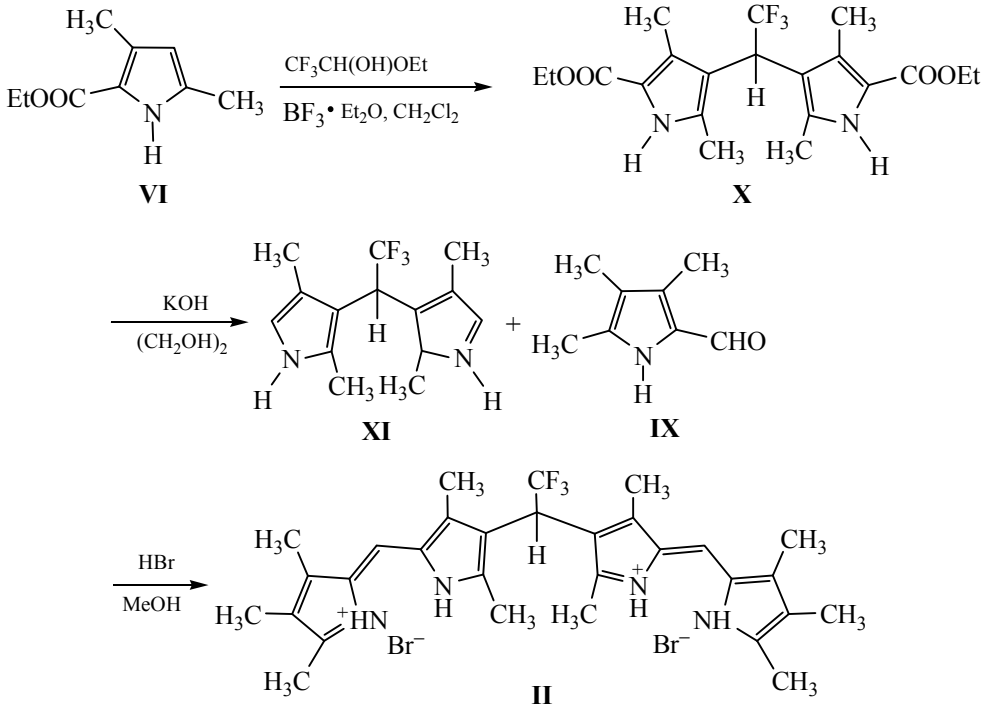


Table 1. Parameters of EAS of compounds **I-III** in organic solvents

Solvent	I		II		III	
	λ_{max}, nm	log ε	λ_{max}, nm	log ε	λ_{max}, nm	log ε
Ethanol	364	4.07	370	3.93	376	–
	454	4.73	453	4.71	458	4.64
	503	5.05	493	4.98	499	4.99
Propanol-1	363	4.09	364	3.76	364	–
	456	4.78	456	4.48	458	4.40
	506	5.13	494	4.79	501	4.78
Chloroform	363	4.11	363	4.06	364	4.15
	462	4.69	459	4.80	461	5.01
	509	5.23	496	5.18	502	5.43
Methylene chloride	364	4.09	363	4.01	362	–
	459	4.74	455	4.81	464	4.83
	507	5.19	497	5.12	504	5.08
N,N-Dimethylformamide[a], c_1	373	4.01	373	3.96	373	3.89
	458	4.56	458	4.66	456	4.64
	505	4.82	493	4.92	496	4.87
c_2	426	–	447	4.72	456	4.67
Dimethylsulfoxide[a], c_1	370	4.06	365	3.88	368	3.95
	459	4.70	460	4.67	465	4.75
	507	5.04	497	4.95	503	5.09
c_2	433	–	453	4.55	463	4.70

[a] c_1 ~1.10^{-4} M, c_2 ~1×10^{-6} M are the concentrations of dihydrobromides and molecular forms, respectively, of bis(dipyrrolylmethenes) in electron-donating solvents.

It is presumable [12] that the change in the solvation of the excited state is a major contributor to the changes in the electronic spectrum. Comparison of the first (long-wavelength) absorption band in nonpolar and polar solvents shows that, depending on the bis(dipyrrolylmethene) dihydrobromide structure, the transition of the molecule in an excited state is almost always accompanied by a decrease in the dipole of its *p*-electron cloud.

Salts **I** and **II**, like the substituted dipyrrolylmethene hydrobromides, are stable in inert proton-donor solvents, as seen from the EAS of the solutions (if kept in the dark) which do not change over time. At adding a strong proton acceptor, e.g., triethylamine, to a solution of a compound **I–III** in methylene chloride, the dihydrobromide EAS is converted in the spectrum of the bis(dipyrrolylmethene) free base, the first absorption band suffers a blue shift by 81, 50 and 48 nm in the spectra of the compounds **I**, **II,** and **III**, respectively. These values indicate a substantial increase in the auxochromic effect of the proton on the chromophore system of 2,3'-bis(dipyrrolylmethene) **I** (shift by 81 nm) compared with 3,3'-tetrapyrroles **II** and **III** caused possibly by the asymmetry of the molecule and as a consequence, by a kind of "individuality" of the NH-groups protons, which is manifested in different shifts of the signals of all four protons of NH-groups in the ^{1}H NMR spectrum.

In the electron-donating solvents (DMF, DMSO), the salt dissociation makes the access of solvent molecules to the proton easier, and specific solvation of the latter gives rise to the processes of solvolytic dissociation of salts [6, 10].

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

where B is a base (the solvent).

The solvolytic dissociation process can be traced by observing the characteristic transformation of the spectrum of salt into the spectrum of free base: the first absorption band suffers a blue shift, and the charge

Table 2. The change in chemical shift of the proton signals (Δδ, ppm) of NH groups in the ^{1}H NMR spectra of compounds **I–III**

Comp. no.	Δδ	1/4ΣΔδ
I	13.20 br.s, 13.14 br.s, 13.12 br.s, 12.98 br.s (4H, NH)	13.11
II	13.46 br.s (2H, NH), 13.11 br.s (2H, NH)	13.28
III	13.14 s (2H, NH), 13.01 s (2H, NH)	13.08

Table 3. Thermooxidative degradation of bis(dipyrrolylmethenes) **I–III** dihydrobromides[a]

Comp. no.	Process stage		
	t_b	t_{max}	t_{end}
I	182	204	499
II	199	212	503
III	260	300	590

[a] Heating from 15 to 600°C, error (ΔT ± 2.3°C), heating rate 2.5 deg min^{-1}; t_b, and t_{end} are the temperatures of beginning and end of the process of degradation, t_{max} is the temperature of the maximum exothermic effect, °C.

transfer band disappears. In basic media at low (~1×10^{-6} M) concentrations of salt the process is irreversible, in a relatively weakly basic media or at high (~1×10^{-4} M) concentrations of salt an equilibrium may occur between the protonated form of the ligand and the dissociation products, because in the linear tetrapyrroles there is an additional factor of stabilization of the protonated form in the rather "closed" (helical) conformation, characteristic of bis(dipyrrolylmethenes) with a short spacer [1]. In the proton-acceptor DMF at low concentrations (~1×10^{-6} M) of compounds **I, II** in the electronic spectrum a blue shift (by 50–81 nm) of the first band is observed relative to the corresponding salt with HBr. In DMSO, the pattern is similar, but the blue shift of the first absorption band is by 6–7 nm less than in DMF.

The first (and single) absorption band of the deprotonated form of compound **II** in DMF suffers a blue shift by 9 nm compared to the free base **III**, indicating a decrease in chromophoric properties of the molecule with the electron-withdrawing CF_3 group in the methylene fragment. The absorption band of α,β-decamethyl-substituted bis(dipyrrolylmethene) **I** in DMF suffers 30 nm blue shift compared with **III**. Apparently, due to the distortion of the free base **I** molecule, its chromophore is considerably weaker than **III**.

At adding auxochrome (proton) to a free base molecule of **I** the situation changes. The position of the first absorption band of 2,3'-bis(dipyrrolylmethene) **I** dihydrobromide in nonpolar methylene chloride and in alcohol suffers a red shift by about 3–5 nm, with a simultaneous increase in the probability of a photon absorption (cf. log ε, Table 1) compared with 3,3'-bis-(dipyrrolylmethene) dihydrobromide **III**. This is probably due not only to increase in the planarity of the molecule as a whole, but also owing to its polarization due to unequal mutual influence of dipyrrolylmethene fragments as evidenced by the splitting of the proton signals in the ^{1}H NMR spectrum (Table 2). In the proton-donor solvent, chloroform, there is an additional solvatochromic effect, owing to specific interactions.

The decrease in the electron density on the contact nitrogen atoms due to the introduction of electron-acceptor CF_3 groups in the methylene fragment of the compound **II** apparently leads to the polarization of the NH bonds of the molecule. Consequently, the dihydrobromide **II** stability to the thermooxidative degradation is substantially reduced (by 61°C) in comparison with **III**, which leads to the removal of two molecules of HBr. A similar but stronger effect (up to 78°C) induces the symmetry violation of the molecule **I** (Table 3). After removal of the stabilizing hydrobromide molecules the thermo-oxidative degradation of organic parts of the synthesized compounds continues. The temperature of the maximum exothermic effect of oxidation of compounds **I** and **II** lies by about 90–100°C lower than that of **III**.

EXPERIMENTAL

^{1}H NMR spectra of the synthesized compounds in deuterated chloroform were recorded on a Bruker 500 NMR spectrometer (internal reference TMS). IR spectra from the KBr pellets were recorded on an Avatar 360 FT-IR EAS instrument. Electron absorption spectra of samples in organic solvents were taken on an SF-56 spectrophotometer and a CM 2203 spectrofluorimeter. MALDI mass spectra[1] of bis-(dipyrrolylmethene) dihydrobromides were registered on a Ultraflex III Bruker mass spectrometer in the mode of positive ions on the metal target, the matrix was *p*-nitroaniline (100:1). Thermogravimetric studies

[1] Recorded in the laboratory of the physicochemical analysis of Arbuzov Institute of Organic and Physical Chemistry.

were performed on a MOM 1000D derivatograph (Hungary) in the non-isothermal mode, the heating rate 2.5 deg min^{-1} in the temperature range 15–600°C. The sample weight was 17–19 mg, the derivatogram reproducibility was checked by triple repetition of the experiment with each compound.

Organic solvents of chemically pure grade were prepared according to known methods [14]. The water content in the solvents by Fisher titration did not exceed 0.02%.

3,4-Dimethyl-2-acetoxymethyl-5-ethoxycarbonylpyrrole (V). To a solution of 5.0 g (27.6 mmol) of 2,3,4-trimethyl-5-ethoxycarbonylpyrrole **I** [15] and 5.0 g (61.0 mmol) of sodium acetate in 50 ml of acetic acid at vigorous stirring was added gradually 1.5 ml (29.1 mmol) of bromine. The mixture was stirred for 0.5 h and poured into 200 ml of water. The precipitate formed was filtered off, washed with water, and dried in air at room temperature. Yield 5.0 g (76%). ^{1}H NMR spectrum, δ, ppm: 4.97 s (2H, C$\underline{H_2}$OAc); 4.26 q (2H, OC$\underline{H_2}$CH$_3$); 2.20 s, 2.02 s (2×3H, CH_3); 1.97 s (3H, Ac); 1.33 t (3H, CH_2CH_3). Found, %: C 60.35, H 7.22; N 5.98. C_{12} $H_{17}NO_4$. Calculated, %: C 60.24; H 7.16; N 5.85.

2',3,4,4'-Tetramethyl-5,5'-diethoxycarbonyldipyrrolylmethane-2,3' (VII). In 40 ml of methanol was dissolved while stirring 3.8 g (15.8mmol) of 3,4-dimethyl-2-acetoxymethyl-5-ethoxycarbonylpyrrole **V** and 2.7 g (16.1 mmol) of 2-ethoxycarbonyl-3,5-dimethylpyrrole **VI** [15], 0.2 g of *p*-toluenesulfonic acid was added, and the mixture was stirred for 4 h at 40ºC. Then the solvent was evaporated in a vacuum to half volume, cooled to room temperature, the precipitate was filtered off, washed with methanol, and dried at room temperature. Yield 4.5 g (82%). ^{1}H NMR spectrum, δ, ppm: 8.78 br.s, 8.14 br.s (2×1H, NH); 4.24 m (4H, C$\underline{H_2}$CH$_3$); 3.63 c (2H, *ms*-H); 2,24 s (3H, 4-CH_3) ; 2.17 s (3H, 4'-CH_3); 2.14 s (3H, 2'-CH_3); 1,97 s (3H, 3-CH_3); 1.35 m (6H, $CH_2C\underline{H_3}$). Found, %: C 66.01, H 7.82; N 8.28. $C_{19}H_{26}N_2O_4$. Calculated, %: C 65.88; H 7.56; N 8.09.

2',3,4,4'-Tetramethyldipyrrolylmethane-2,3 (VIII). 2.5 g (7.22 mmol) of 2',3,4,4'-tetramethyl-5,5'-diethoxycarbonyldipyrrolylmethane-2,3 **VII** was refluxed for 1 h with 2.5 g (44.6 mmol) KOH in 25 ml of ethylene glycol. The solution was poured into 200 ml of water, sodium acetate was added, the precipitate was filtered off, and dried in air at room temperature to a constant weight. Yield 1.1 g (75%). The product was used without further purification because of its instability.

(1,2,3,7,9-Pentamethyldipyrrolylmethen-8-yl)-(1,2,3,7,8-pentamethyldipyrrolylmethen-9-yl)-methane dihydrobromide (I). In 20 ml of methanol was dissolved 0.6 g (2.96 mmol) of 2',3,4,4'-tetramethyldipyrrolylmethane-2',3 **VIII**, 0.81 g (5.93 mmol) of 2,3,4-trimethyl-5-formylpyrrole **IX** [15] was added, and after the dissolution was added 1 ml of conc. HBr. The mixture was stirred for 2 h at room temperature, the precipitate was filtered off, washed with methanol and ether, and dried at room temperature in air. Yield 1.76 g (99%). IR spectrum, ν_{NH} 3415 cm^{-1} . ^{1}H NMR spectrum, δ, ppm): 13.20 br.s, 13.14 br.s, 13.12 br.s, 12.98 br.s (4×1H, NH); 7.11 s (2H, *ms*-CH); 7.06 s (2H, *ms*-CH_2); 2.71 s, 2.68 s, 2.61 s, 2.31 s, 2.30 s, 2.26 s, 2.24 s, 2.02 s, 2.00 s, 1.71 s (30H, CH_3). Mass spectrum (2HBr split off), *m/z* 441 [M^+ + H]. Found, %: C 58.05, H 6.45; N 9.48. C 29 $H_{38}N_4Br_2$. Calculated, %: C 57.82; H 6.36; N 9.30.

***ms*-(Trifluoromethyl)-2,2',4,4'-tetramethyl-5,5'-diethoxycarbonyldipyrrolylmethane-3,3' (X)**. To a solution of 5 g (29.9 mmol) of 2,4-dimethyl-5-ethoxycarbonylpyrrole **VI** [15] in 50 ml of anhydrous methylene chloride was added 2 ml (15.9 mmol) of boron trifluoride etherate and 1.95 ml (15 mmol) of 90% trifluoroacetic aldehyde hemiacetal ($C_4H_7O_2F_3$, d = 1.23). The solution was stirred at room temperature for 28 h. The mixture was poured into water and boiled to remove methylene chloride and coagulate the sludge. The precipitate was filtered off, washed with water, and dried in air. Then it was dissolved in methylene chloride and chromatographed on silica gel eluting with methylene chloride–hexane. Yield 7.0 g (56.5%). ^{1}H NMR spectrum, δ, ppm: 9.13 s (2H, NH); 5.81 s (1H, *ms*-CH); 4.31 q (4H, C$\underline{H_2}$CH$_3$); 2.21 s, 2.18 s (2×6H, CH_3); 1.36 t (6H, $CH_2C\underline{H_3}$). Found, %: C 58.15, H 6.22; N 6.98. C 20 $H_{25}F_3N_2O_4$. Calculated, %: C 57.96; H 6.08; N 6.76.

***ms*-Trifluoromethyl-2,2',4,4'-tetramethyldipyrrolylmethane-3,3' (XI)**. 3 g (7.23 mmol) of *ms*-trifluoromethyl-2,2',4,4'-tetramethyl-5,5'-diethoxycarbonyldipyrrolylmethane-3,3' **X** was heated at reflux with 3 g (53.6 mmol) of KOH in 30 ml of ethylene glycol for 1 h. The solution was then cooled and poured into 300 ml of water, sodium acetate was added, the precipitate was filtered off, washed with water, and dried in air to a constant weight. Yield 1.0 g (51.1%). The product was used without further purification because of its instability.

Bis(1,2,3,7,9-pentamethyldipyrrolylmethen-8-yl)-trifluoromethylmethane dihydrobromide (II). In 20 ml of methanol was dissolved 1.0 g (3.7 mmol) of *ms*-trifluoromethyl-2,2',4,4'-tetramethyldipyrrolylmethane-3,3' **XI**, then was added 0.97 g (7.4 mmol) of 2,3,4-trimethyl-5-formilpyrrole **IX** and after its dissolution was added 1 ml of conc. HBr. The mixture was stirred for 2 h at room temperature, the precipitate formed was filtered off, washed with methanol and ether, and dried at room temperature in air. Yield 2.07 g (83%). IR spectrum, ν_{NH} 3439 cm^{-1}. ^1H NMR spectrum, δ (ppm): 13.46 br.s, 13.11 br.s (2×2H, NH); 7.10 s (1H, *ms*-CH); 7.10 s (2H, 5-*ms*-CH); 2.73 s, 2.68 s, 2.29 s, 2.18 s, 2.02 s (30H, CH_3). Mass spectrum (2HBr split off), *m/z* 509 [M^+ + H]. Found, %: C 53.91, H 5.69; N 8.58. $C_{30}H_{37}Br_2F_3N_4$. Calculated, %: C 53.74; H 5.56; N 8.36.

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