# Alkyl-substituted dipyrrylmethenes and their oxa- and thia-analogs: "structure—solvation properties" correlations

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New data on the spectral properties and solution enthalpies of unsymmetrically substituted 2-(alkyl-2-pyrrolylmethylidene)methylpyrrolium bromides (or α,α-dipyrrylmethene hydrobromides), their α,β-, β,β-isomers, as well as their oxa and thia analogs, that is, 2-(2-furylmethylidene)- and 2-(2-thienylmethylidene)-3,4,5-trimethyl-1*H*-pyrrolium bromides, in solutions of organic solvents of different nature are presented. A decrease in the number of substituents, as well as replacement of the heteroatom (N) in one five-membered ring of the dipyrrylmetnehe by oxygen or sulfur atoms cause a monotonic hypsochromic shift of absorption bands in the electronic absorption spectrum and weakening of the chromophore properties of the compounds. The chromophore properties of isomers are weakened from the α,α- to α,β- and β,β-dipyrrylmethenes. Main trends in the influence of structural factors on the specific features of thermooxidative destruction of the above-mentioned compounds were analyzed.

**Key words:** pyrroles, dipyrrylmethenes, solutions, spectrophotometry, calorimetry, thermogravimetry, synthesis.

The so-called dipyrrylmethenes are intermediates in the synthesis of porphyrins in the laboratory experiments and in nature.[1,2] The physicochemical properties of the classical porphyrins and metal porphyrins have been the subject of numerous studies. The physicochemical properties of dipyrrylmethenes (precursors of porphyrins) have been investigated to a much lesser extent; only the electronic absorption spectra (EAS) of these compounds, recorded in a few solvents are usually available. Taking into account the fact that most processes involving porphyrins proceed in the liquid media, the necessity of investigations on the solvation properties, coordination ability, and other properties of not only porphyrins but also simpler fragments the porphyrins are built of (in particular, dipyrrylmethenes and their structural analogs) is obvious.

Earlier,[3,4] we have reported the results of calorimetric measurements of the enthalpies of the interactions between substituted monopyrroles and dipyrroles (dipyrrolylmethanes) and organic solvents of different nature. It was shown that the contribution of solvation to the change in the enthalpy of intermolecular solute—solvent interactions for monopyrroles is primarily determined by the state of the N—H bond. In dipyrrolylmethanes, we deal with the mutual influence of the pyrrole fragments and with their effect on the solvation properties; however, steric factors can also play some role depending on the chain length and nature of substituents in positions 3 and 3´.

Dipyrrylmethenes are conjugated linear chromophores. The field of their applications is more extended compared to dipyrrolylmethanes.[5—7]

The aim of this work was to establish main trends in the influence of successive alkyl substitution on the physicochemical properties of both methyl-substituted α,α-, α,β- and β,β-isomers of dipyrrylmethene and their structural oxa- and thia-analogs in solutions in various organic solvents and in the solid phase.

To this end, we synthesized hydrobromides of various dipyrrylmethenes (structures **1—7**), the oxa- and thia-analogs of compound **6** (structures **8** and **9**, respectively), and hydrobromides of the α,β- and β,β-isomers of compound **1** (structures **10** and **11**, respectively). The spectral characteristics and solvation properties of these compounds in organic solvents of different nature were studied by electronic spectroscopy and solution calorimetry. Dipyrrylmethene hydrobromides were synthesized by condensation of alkylpyrroles having no substituent at one of the four ring carbon atoms with formylpyrroles in metha-

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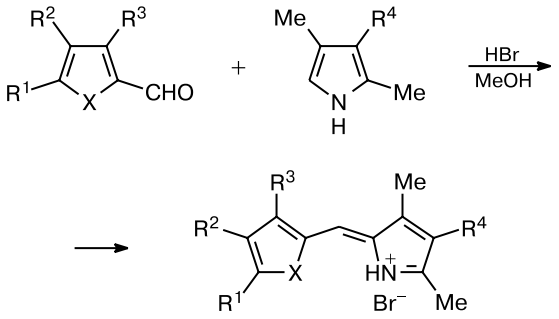
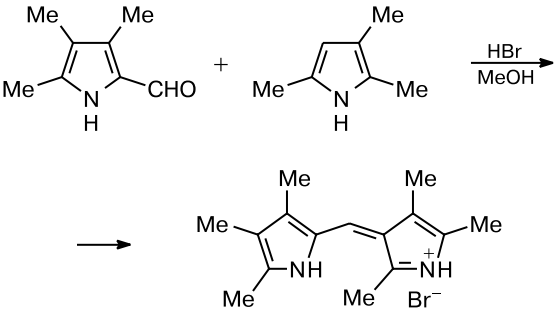
**Scheme 1**

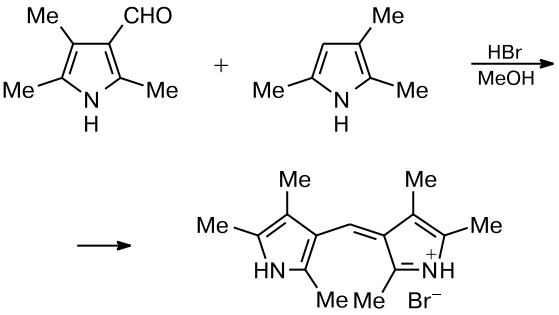



**1—9**

| Compound | $R^1$ | $R^2$ | $R^3$ | $R^4$ | X |
|---|---|---|---|---|---|
| **1** | Me | Me | Me | Me | NH |
| **2** | Me | Et | Me | Et | NH |
| **3** | Me | Bu | Me | Bu | NH |
| **4** | H | Me | Me | Me | NH |
| **5** | Me | H | Me | Me | NH |
| **6** | H | H | H | Me | NH |
| **7** | H | H | H | Me | NMe |
| **8** | H | H | H | Me | O |
| **9** | H | H | H | Me | S |




**10**




**11**

nol in the presence of concentrated hydrobromic acid (Scheme 1).

The yields, elemental analyses data, positions of bands in the EAS, and signal assignment in the $^1$H NMR spectra are listed in Tables 1 and 2.

## Experimental

**3,3′,4,4′,5,5′-Hexamethyl-2,2′-dipyrrylmethene hydrobromide (1).** To a solution of 2,3,4-trimethylpyrrole (0.75 g, 6.9 mmol) and 2-formyl-3,4,5-trimethylpyrrole (0.95 g, 6.9 mmol) in methanol (15 mL), conc. HBr (1 mL) was added and the mixture was stirred for 1 h. The precipitate was filtered off, successively washed with methanol and ether, dried, and recrystallized from a chloroform—methanol mixture to which HBr was added. Hydrobromides **2—9** were obtained analogously. The yields and characteristics of the compounds synthesized are listed in Tables 1 and 2.

**2′,3,4,4′,5,5′-Hexamethyl-2,3′-dipyrrylmethene hydrobromide (10).** To a solution of 2,3,4-trimethylpyrrole (0.80 g, 7.3 mmol) and 3-formyl-2,4,5-trimethylpyrrole (1.00 g, 7.3 mmol) in methanol (10 mL), conc. HBr (1 mL) was added and the mixture was stirred for 2 h. The reaction mixture was diluted with water (1 : 1 v/v), the precipitate was filtered off, dried, boiled with acetone (50 mL) for 15 min, filtered off, and washed with acetone.

**2,2′,4,4′,5,5′-Hexamethyl-3,3′-dipyrrylmethene hydrobromide (11).** To a solution of 2,3,5-trimethylpyrrole (0.95 g, 8.7 mmol) and 3-formyl-2,4,5-trimethylpyrrole (1.20 g, 8.7 mmol) in methanol (5 mL), conc. HBr (2 mL) was added and the mixture was stirred for 2 h. Then ether (50 mL) was added dropwise. The solution was decanted, the precipitate was boiled with benzene (50 mL), filtered off, and dried.

The initial pyrroles and formylpyrroles were obtained following the known procedures.[3]

The $^1$H NMR spectra of pyrroles were recorded on a Tesla BS-497 spectrometer while those of dipyrrylmethenes were recorded on a Bruker AC-200 spectrometer with hexamethyldisiloxane as internal reference. Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer. The solvents for calorimetric measurements were prepared following the known procedures.[8] The experimental data obtained using a precision isothermic-shell calorimeter at 298.15 K [9] are listed in Table 3.

## Results and Discussion

Compounds **1—11** are complex chromophores, as indicated by the absorption of their solutions in the visible region (see Tables 1 and 4). They differ from one another in position, number, and volume of substituents, as well as in position and nature of the heteroatom and, hence, in the effect of these fragments on the centers of non-specific and specific solvation of the molecules of dipyrrylmethenes and their furan and thiophene analogs. The presence of NH groups in the dipyrrylmethene molecules implies solvation by electron-donor solvents. The tertiary nitrogen atoms (—N=) favor the interaction of the dipyrrylmethene molecules with proton-donor solvents, while the presence of a conjugated system of π-bonds must favor solvation by aromatic solvents. On this basis we chose benzene as inert aprotic solvent, DMF and pyridine as electron-donor solvents, and propanol and chloroform as proton-donor solvents.

**Table 1.** Yields and elemental analysis data for compounds **1**—**11** and their electron absorption spectra (EAS) in methylene chloride

| Compound | Yield (%) | Found / Calculated (%) | | | | Empirical formula | EAS, $\lambda_{max}$/nm (lgε) | |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | Br | | I | II |
| **1** | 70 | 58.26 | 6.84 | 9.06 | 26.84 | $C_{15}H_{21}BrN_2$ | 486 | 362 |
| | | 58.15 | 6.10 | 9.00 | 26.53 | | (4.99) | (4.02) |
| **2** | 69 | 60.54 | 7.47 | 8.31 | 23.69 | $C_{17}H_{25}BrN_2$ | 488 | 370 |
| | | 61.00 | 7.53 | 8.25 | 23.72 | | (5.03) | |
| **3** | 58 | 64.11 | 8.45 | 7.12 | 22.31 | $C_{21}H_{33}BrN_2$ | 490 | 354 |
| | | 64.18 | 8.95 | 7.00 | 22.02 | | (5.05) | |
| **4** | 70 | 56.96 | 6.49 | 9.49 | 27.07 | $C_{14}H_{19}BrN_2$ | 480 | 374 |
| | | 56.38 | 6.29 | 9.01 | 27.58 | | (4.88) | |
| **5** | 79 | 56.96 | 6.49 | 9.49 | 27.07 | $C_{14}H_{19}BrN_2$ | 478 | 373 |
| | | 56.33 | 6.28 | 9.78 | 28.00 | | | (4.98) |
| **6** | 68 | 53.95 | 5.66 | 10.49 | 29.91 | $C_{12}H_{15}BrN_2$ | 465 | 378 |
| | | 53.20 | 5.01 | 10.99 | 29.41 | | (4.88) | |
| **7** | 59 | 55.53 | 6.09 | 9.96 | 28.42 | $C_{13}H_{17}BrN_2$ | 479 | 378 |
| | | 55.12 | 5.85 | 9.43 | 28.91 | | (4.58) | |
| **8** | 63 | 53.75 | 5.26 | 5.22 | 29.80 | $C_{12}H_{14}BrNO$ | 425 | — |
| | | 53.28 | 5.98 | 4.81 | 29.30 | | (4.45) | |
| **9*** | 48 | 50.71 | 4.96 | 4.93 | 28.11 | $C_{12}H_{14}BrNS$ | 429 | — |
| | | 51.15 | 5.41 | 5.25 | 27.85 | | (4.46) | |
| **10** | 70 | 58.26 | 6.84 | 9.06 | 26.84 | $C_{15}H_{21}BrN_2$ | 477 | 403 |
| | | 58.25 | 6.15 | 9.15 | 26.82 | | (4.36) | (4.10) |
| **11** | 56 | 58.26 | 6.84 | 9.06 | 26.84 | $C_{15}H_{21}BrN_2$ | 475 | 376 |
| | | 58.90 | 6.09 | 9.23 | 26.15 | | (4.02) | (4.39) |

* S — 11.28/11.34.

**Table 2.** $^1$H NMR spectra (δ, *J*/Hz) of the compounds synthesized (deuterated chloroform as solvent, with hexamethyldisiloxane as internal reference)

| Compound | NH (s) | *meso*-H (s) | $R^1$ | $R^2$ | $R^3$ | 3-Me (s) | 4-Me | 5-Me (s) |
|---|---|---|---|---|---|---|---|---|
| **1** | 12.92 | 7.02 | 2.64 s | 1.97 s | 2.25 s | 2.25 | 1.97 s | 2.64 |
| **2** | 12.48 | 7.32 | 2.64 s | 2.52 (q, *J* = 7.6); 1.13 (t, *J* = 7.6) | 2.38 s | 2.38 | 2.52 (q, *J* = 7.6) 1.13 (t, *J* = 7.6) | 2.64 |
| **3** | 12.88 | 7.02 | 2.65 s | 2.35 (t, *J* = 7.1); 1.30 m; 0.93 (t, *J* = 7.1) | 2.26 s | 2.26 | 2.35 (t, *J* = 7.1); 1.30 m; 0.93 (t, *J* = 7.1) | 2.65 |
| **4** | 12.80; 12.93 | 7.15 | 7.52 s | 2.00 s | 2.28 s | 2.29 | 2.06 s | 2.70 |
| **5** | 12.94; 13.08 | 7.05 | 2.67 s | 6.13 s | 2.35 s | 2.26 | 1.99 s | 2.67 |
| **6** | 13.35; 13.53 | 7.20 | 7.70 m | 6.50 m | 7.10 s | 2.29 | 2.02 s | 2.75 |
| **7** | 2.83; 13.02 | 7.30 | 8.81 m | 6.52 s | 7.19 m | 2.35 | 1.97 s | 2.83 |
| **8** | 13.76 | 7.17 | 8.33 s | 6.73 s | 7.63 s | 2.31 | 2.07 s | 3.04 |
| **9** | 13.96 | 7.52 | 9.16 s | 7.45 s | 7.96 s | 2.35 | 2.06 s | 3.01 |
| **10** | 11.73; 11.92 | 7.50 | 2.71 s (5′-Me) | 2.02 s (4′-Me) | 2.14 s (3′-Me) | 2.28 (2-Me) | 2.01 s | 2.74 |
| **11** | 12.39 | 8.15 | 2.28 s (5′-Me) | 2.03 s (4′-Me) | 2.45 s (2′-Me) | 2.45 (2-Me) | 2.03 s | 2.28 |

**Table 3.** Changes in the standard solution enthalpies ($\Delta_{sol}H°$) and enthalpies of transfer ($\Delta_{tr}H°$) of dipyrrylmethene hydrobromides and their structural analogs (kJ mol$^{-1}$)

| Compound | PrOH | $CHCl_3$ | | DMF | | Py | | $C_6H_6$ | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta_{sol}H°$ | $\Delta_{sol}H°$ | $\Delta_{tr}H°$ | $\Delta_{sol}H°$ | $\Delta_{tr}H°$ | $\Delta_{sol}H°$ | $\Delta_{tr}H°$ | $\Delta_{sol}H°$ | $\Delta_{tr}H°$ |
| **1** | 35.1±1.1 | 4.8±0.3 | −30.3 | 18.5±0.5 | −16.6 | 10.7±1.8 | −24.7±0.7 | 20.5 | −14.6 |
| **2** | 40.9±1.5 | 2.5±0.2 | −38.4 | 19.3±0.5 | −21.6 | — | — | 25.3±0.8 | −15.6 |
| **3** | 30.6±1.5 | 6.2±1.8 | −24.4 | 19.2±0.9 | −11.4 | 18.7±0.5 | −11.9 | 32.8±0.8 | 2.2 |
| **4** | — | 4.7±0.7 | — | 9.2±1.0 | — | 13.5±1.4 | — | — | — |
| **5** | 23.3±1.5 | 10.0±1.2 | −13.3 | 3.5±0.3 | −19.8 | 18.9±1.3 | −4.4 | 30.3±3.0 | 7.0 |
| **6** | 16.9±1.1 | 8.3±0.8 | −8.6 | 5.3±0.5 | −11.6 | 18.7±0.5 | 1.8 | 4.0±0.4 | −12.9 |
| **7** | 21.7±2.0 | 0±1.5 | −21.7 | 7.1±0.5 | −14.6 | −16.7±1.2 | −38.4 | 6.7±0.5 | −15.0 |
| **8** | 32.1±1.5 | 14.5±1.2 | −17.6 | 7.8±0.7 | −24.3 | −19.7±1.6 | −51.8 | — | — |
| **9** | 22.1±0.5 | 1.9±0.2 | −20.2 | −40.3±1.5 | −62.4 | −17.6±0.5 | −39.7 | 5.7±1.6 | −16.4 |
| **10** | 25.0±1.5 | 3.2±0.3 | −21.8 | 11.8±0.5 | −13.2 | — | — | — | — |
| **11** | 5.2±0.1 | −9.2±0.9 | −14.4 | −16.7±0.9 | −21.9 | — | — | — | — |

**Table 4.** Positions (λ/nm) and intensities (lg ε) of absorption bands in the electronic spectra of dipyrrylmethenes and their structural analogs

| Compounds | PrOH | $CHCl_3$ | DMF | Py | $C_6H_6$ |
|---|---|---|---|---|---|
| **1** | 478 (4.61) | 483 (4.75) | 435 (4.67) | 448 (4.59) | 484 (4.66) |
| | 361 (3.75) | 362 (4.02) | | | 364 (3.41) |
| **2** | 479 | 488 | 438 | 451 | 494 |
| | 362 | 363 | | | 364 |
| **3** | 480 | 490 | 440 | 456 | 498 |
| | 363 | 362 | | | 368 |
| **4** | 463 (4.63) | 477 (4.56) | 415 (4.28) | 421 (4.24) | 479 (3.75) |
| | 371 | 370 | | | 425 |
| **5** | 468 (4.42) | 472 (4.64) | 428 (4.33) | 434 (4.35) | 474 (4.61) |
| | 356 | 354 | | | 361 |
| **6** | 463 (4.58) | 465 (4.62) | 390 (4.07) | 400 (4.09) | 462 (4.58) |
| | 401 | 374 | | | |
| **7** | 474 (4.42) | 476 (4.44) | 402 (4.01) | 433 (3.63) | 485 (3.57) |
| | 376 | 378 | | | 382 |
| **8** | 408 (3.70) | 424 (4.44) | 368 (3.31) | 380 (3.77) | LS* |
| | 370 | | | | |
| **9** | 412 (3.40) | 427 (4.35) | 359 (4.06) | 378 (3.40) | 429 (3.54) |
| **10** | 473 (4.34) | 481 (4.48) | 402 (4.08) | 406 | LS* |
| | 412 (4.07) | 403 (4.10) | | уш. | |
| **11** | 476 (3.98) | 472 (4.43) | 400 (3.86) | 407 | LS* |
| | 378 (3.91) | 376 (4.39) | | | |

* LS is low soluble.

The proton delocalized over the aza groups in the pyrrole rings of the molecules of dipyrrylmethene hydrobromides acts as an auxochrome, which induces polarization of the chromophore molecule.[10] Changes in the volume, number, and positions of substituents in dipyrrylmethenes strongly affects their EAS and other physicochemical properties.

Compounds **1—3** have symmetrical structures in which the excess positive charge of the H atom of the HBr molecule is uniformly delocalized over both pyrrole rings. Replacement of methyl substituent by ethyl and butyl groups (compounds **2** and **3**, respectively) causes a minor improvement of the chromophore properties of dipyrrylmethenes (see Table 1). A decrease in the number of methyl groups in the molecules (compounds **4—6**) is responsible for both the hypsochromic shift (by 21 nm) of the absorption band in the EAS and the changes in the band intensity (given are the data for solutions in chloroform with a concentration of nearly $10^{-5}$ mol L$^{-1}$). The lack of substituent in α- or β-position in one pyrrole ring (compounds **4** and **5**) has little effect on the position but strongly affects the intensity of the absorption band. This

is indicative of nonequivalence of the α- and β-positions in the pyrrole moieties, involved in the common conjugation system of dipyrrylmethene.

The presence of methyl group at the N atom in molecule **7** has virtually no effect on the energy of absorbed light quantum. At the same time it causes a significant decrease in the absorption probability, thus indicating that the charge of $H^+$ is still delocalized over the *N*-methyl-substituted dipyrrylmethene. Replacement of the heteroatom (nitrogen) in one pyrrole moiety by oxygen or sulfur atoms (compounds **8** and **9**, respectively) causes a shift of the maximum of the absorption band by 40 nm toward the boundary of the visible region compared to dipyrrylmethene **6** and a strong decrease in the band intensity. So significant changes in the EAS are likely due to a decrease in the extent of delocalization of the positive charge over these atoms.

Thus, the absorption band in the EAS experiences a bathochromic shift as the number of methyl groups increases in the order **6** < **7**, **5**, **4** < **1**. Replacement of the H atom by a methyl group at the nitrogen atom in one pyrrole ring causes a larger shift of the absorption band as compared to the effect of methyl substituent at the C atom. Replacement of the pyrrole ring by the furan or thiophene ring weakens the chromophore properties. Weakening of π-conjugation in these compounds is likely due to electronic rather than steric factors.

In the α,α-, α,β-, and β,β-isomers, the effect of planarity distortion of dipyrrylmethene molecules (estimated by calculations) changes as follows: **1** < **10** < **11**. This structural distortion has little effect on the position of the spectral band (hypsochromic shift is only ~10 nm) but strongly affects the absorption probability, which substantially decreases (see Table 1). Besides, the absorption band is broadened (probably, due to activation of vibrational states).

An analogous, though less pronounced, effect is observed in the case of *N*-methyl substitution in dipyrrylmethene **7**. Here, the absorption band experiences a bathochromic shift relative to dipyrrylmethene **6** and its intensity substantially decreases, which is probably due to steric hindrances produced by the methyl group at the nitrogen atom.

No less specific is the effect of the solvent nature on the EAS of compounds studied (see Table 4). A characteristic feature of the EAS of hydrobromides is the presence of two absorption bands. The first, long-wavelength, band is intense while the second band is weak and, as a rule, disappears in the proton-acceptor solvents (DMF, pyridine) responsible for (this is our hypothesis) elimination and solvation of HBr molecule. The last-mentioned process must cause a decrease in the polarity of the dipyrrylmethene molecule, weakening of its interaction with the solvent and, as a consequence, a hypsochromic shift of the first absorption band, which is indeed observed experimentally.

It is assumed[10] that the change in solvation of the excited state makes the major contribution to the changes in the electronic spectrum. Comparison of positions of the first absorption bands in the non-polar solvent and in polar solvents (see Table 4) shows that, depending on the structure of the dipyrrolylmethene molecule, transition to the excited state is almost without exception accompanied by a decrease in the dipole moment of its π-electron cloud. Dissolution of dipyrrylmethene hydrobromides in proton-acceptor solvents (pyridine, DMF) is accompanied by elimination of HBr molecule. As a result, the electronic spectra observed are characteristic of free dipyrrylmethene bases.[11]

Analysis of the EAS recorded in DMF and pyridine revealed a characteristic feature of dipyrrylmethene bases and their analogs, namely, a marked solvatochromic effect even in the electron-donor solvents of similar nature. In pyridine solutions, the absorption bands experience a bathochromic shift as compared to DMF, which is probably due to π,π*-solvation interactions between dipyrrylmethenes and their analogs and π-deficient pyridine.

By and large, positions of absorption bands in the EAS of compounds **1—11** depend on the molecular structure in a complex manner due to superimposition of the electronic and steric effects of functional substituents and to the effect of the nature of the heteroatom. This requires further investigations.

Our study of changes in the molal solution enthalpies, $\Delta_{sol}H^m = f(m)$, of compounds **1—11** showed that, within the limits of experimental error, the $\Delta_{sol}H^m$ values are independent of the solute concentration (all compounds possess the properties of very weak electrolytes in the chosen range of operating concentrations, $10^{-5}$—$10^{-4}$ mol $kg^{-1}$ [12]).

Since compounds **4**, **8**, **10**, and **11** are virtually insoluble in benzene, we calculated the enthalpies of transfer ($\Delta_{tr}H^\circ$) from 1-propanol (see Table 3). The results obtained show a strong dependence of the change in the enthalpy of the solute—solvent interaction on the structure, up to insolubility of some compounds in benzene (see above). Apparently, a nearly 100% insolubility of dipyrrylmethenes **10** and **11** in benzene is due to distortion of planarity in the molecules of these compounds. As a result, the π—π-solvation interactions between benzene and dipyrrylmethene become sterically hindered by substituents.

Propanol possesses the weakest solvation properties toward most of the compounds studied; therefore, the corresponding solution enthalpies have the largest positive values. Among methyl-substituted dipyrrylmethenes (**1** and **4—7**), the largest and smallest effective molecular volumes have hexamethyl-substituted dipyrrylmethene **1**

and compound **6**, respectively, the latter having one unsubstituted pyrrole moiety. In this connection the endothermicity of solution of α,α-dipyrrylmethenes in propanol decreases as follows: **1** > **5** > **7** > **6**. The hypsochromic shift of $\lambda_1$ in the EAS increases (*i.e.*, the chromophore properties of the molecules weaken) in the same order. Loosening of the lattice in the molecular crystals of the α,α-, α,β-, and β,β-isomers of hexamethyl-substituted dipyrrylmethenes (**1**, **10**, **11**) due to increasing molecular distortion (α,α < α,β < β,β) causes a decrease in the endothermicity of solution in the order **1** > **10** > **11** in all the proton-donor and proton-acceptor solvents.

Thanks to the proton-donor nature of chloroform, additional solvation of dipyrrylmethene hydrobromide molecules due to the formation of hydrogen bonds, $Br^-...HCCl_3$, is possible in this case. This requires the bromide ion and proton to be delocalized over the pyrrole rings. Analysis of the enthalpies of transfer to chloroform (see Table 3) suggests that the degree of proton delocalization over the pyrrole rings in the α,α-dipyrrylmethene molecules decreases in the order **1** > **7** > **5** > **6**.

As mentioned above, the interaction of hydrobromides of dipyrrylmethenes and their analogs with proton-acceptor solvents is accompanied by elimination of HBr molecule and by π—π-interactions in the case of pyridine. High enthalpy of transfer of *N*-methyl-substituted dipyrrylmethene **7** to pyridine is likely due to electron-donor effect of the methyl group bound to the nitrogen atom and to strengthening of the π—π-interactions between **7** and pyridine.

Structurally similar compounds **6**, **8**, and **9** differ in heteroatom (N, O, S) in one five-membered ring. The corresponding changes in the solution enthalpies depend on the solvent nature in a complex manner. As follows from the EAS, the degree of delocalization of the positive charge over the five-membered heterocycles in these compounds appreciably decreases due to weakening of conjugation. As a result, the molecular fragments become much less conjugated than the symmetrically substituted dipyrrylmethene **1**. The endothermicity of solution in propanol decreases in the order **8** > **9** > **6**. One can assume that solvation of these compounds in propanol enhances in the same order.

Three methyl substituents in the same ring of dipyrrylmethene **6** to some extent compensate the effect of positive charge on the nitrogen atom in aprotic and proton-donor solvents. In DMF and pyridine, where elimination of HBr occurs, the pyrrolenine ring acts as acceptor toward the adjacent ring. This causes weakening of solvation of dipyrrylmethene **6** in electron-donor solvents and especially pyridine (positive enthalpy of transfer).

In compound **8**, the electron density is shifted to the furan ring due to high electronegativity of oxygen atom. This should cause enhancement of solvation by proton-donor solvents (propanol and chloroform). The endothermicity of solution of **8** in propanol is nearly doubled as compared to the corresponding value for dipyrrylmethene **6**. Simultaneously, solvation by chloroform enhances ($\Delta_{tr}H°$, see Table 3), which is likely due to the formation of hydrogen bonds between $HCCl_3$ and the oxygen atom. At the same time a dramatic enhancement of solvation by electron-donor solvents (especially pyridine) occurs because of an increase in the positive charge of the adjacent pyrrolenine moiety.

The endothermicity of solution of thienyl derivative **9** in propanol is intermediate between the corresponding values for compounds **6** and **8**. The electronegativity of sulfur is lower than that of oxygen; however, the 3d-orbital of sulfur atom is a kind of electron density "reservoir." The enthalpy of transfer to chloroform ($\Delta_{tr}H°$) for **9** is close to that of compound **8**, while the enthalpy of transfer to DMF for **9** is the largest ($\Delta_{tr}H° = -62$ kJ mol$^{-1}$). The reason is still to be clarified.

By and large, changes in the nature of heteroatom manifest themselves as enhancement of solvation of compounds by organic solvents in the order **6** < **8** < **9**.

The results of our study[13] on thermooxidative destruction of dipyrrylmethenes and their hydrobromides (Table 5) are also of interest. The nature and arrangement of substituents were found to have a strong effect on the thermal stability of these compounds. Among α,α-isomers, hexamethyl-substituted dipyrrylmethene in the form of both hydrobromide **1** and free base is the most stable toward thermooxidative destruction. Pyrolysis of hydro-

**Table 5.** Parameters of thermooxidative destruction of dipyrrylmethene hydrobromides, their structural analogs, and some free bases

| Compound | $T_e^0$ | $T_d^0$ | $T_{max}$ | $T_t^d$ |
|---|---|---|---|---|
| | °C | | | |
| **1** | 255 | 310 | 490 | 565 |
| **2** | 210 | 318 | 541 | 663 |
| **3** | 200 | 300 | 460 | 570 |
| **4** | 240 | 290 | 520 | 610 |
| **5** | 200 | 320 | 552 | 651 |
| **6** | 130 | 300 | 510 | 550 |
| **7** | 195 | 265 | 290 | 675 |
| **8** | 127 | 208 | 306 | 637 |
| **9** | 168 | 320 | 570 | 660 |
| **10** | 195 | 305 | 520 | 635 |
| **11** | 145 | 300 | 630 | 727 |
| **1**·HBr | | 190 | 500 | 560 |
| **2**·HBr | | 160 | 535 | 580 |
| **3**·HBr | | 140 | 520 | 600 |

*Note.* $T_e^0$ is the temperature at which elimination of HBr begins, $T_d^0$ is the temperature at which thermooxidative destruction of the free base begins, $T_{max}$ is the temperature corresponding to the maximum exothermic effect, and $T_t$ is the temperature at which the process is completed.

bromide **1** involves two stages in the temperature interval 190—560 °C with the maximum exothermic peak at 560 °C and consists in elimination of HBr (first stage) followed by oxidation of the free base, which is accompanied by a 100% loss of the sample mass. As the chain length of alkyl substituents in positions 4 and 4′ increases, the thermal stability of the compounds is markedly reduced in the order **1** > **2** > **3**. Successive decrease in the number of methyl groups in one pyrrole ring of the molecule also reduces the stabilities of the corresponding salts as follows: **1** > **4** > **5** > **6**.

Among isomeric hexamethyl-substituted dipyrrylmethenes, the stability of hydrobromides toward thermooxidative destruction (elimination of HBr) is significantly (by 100 °C on the average) reduced in the order **1** > **10** > **11**. This is likely due to distortion of the planar structure of the α,β- and β,β-isomers (**10** and **11**, respectively) compared to dipyrrylmethene **1**.

The second factor affecting the stability of compounds toward thermooxidative destruction is the nature of the heteroatom in one fragment. A decrease in aromaticity and in the degree of delocalization of positive charge over the five-membered rings as compared to dipyrrylmethene **1** reduces the thermal stability of compounds in the order **9** > **6** > **8**.

Thus, solvation of the compounds synthesized in this work is determined by the solvent nature, positions, number, and size of alkyl substituents, as well as by the nature and position of the heteroatom in the chromophore molecule. The stability of the above-mentioned compounds toward thermooxidative destruction is due to the same factors, except for the solvent effect.

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