peri-Naphthylenediamines: XL.* Solvatochromism of 1-Methyl-4-[2-(1-naphthyl)ethenyl]pyridinium Salts, Including That Containing "Proton Sponge" Residue

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Abstract—A number of 1-methyl-4-[2-(1-naphthyl)ethenyl]pyridinium salts were synthesized by condensation of 1,4-dimethylpyridinium iodide with naphthalene-1-carbaldehydes containing dimethylamino groups in positions *4* and *5*. The obtained salts are characterized by negative solvatochromism which is the most pronounced for those possessing 1,8-bis(dimethylamino)naphthalene ("proton sponge") and 1,2,2,3-tetramethyl-2,3-dihydroperimidine residues.

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Recent studies on the chemical properties of 1,8-bis(dimethylamino)naphthalene ("proton sponge") showed that *peri*-dimethylamino groups in its molecule not only are responsible for the anomalously high basicity of this compound but also exert a strong electron-donor effect on the naphthalene ring [2]. One of the numerous consequences is a moderate positive solvatochromism of 1,8-bis(dimethylamino)-4-nitro-naphthalene (**IA**) [3]. Its long-wave absorption maximum in the electron spectra in hexane, benzene, chloroform, and DMSO is located at λ 411, 444, 463, and 484 nm, respectively. Obviously, the excited state of **I** has dipolar structures like **B** and **C** which are
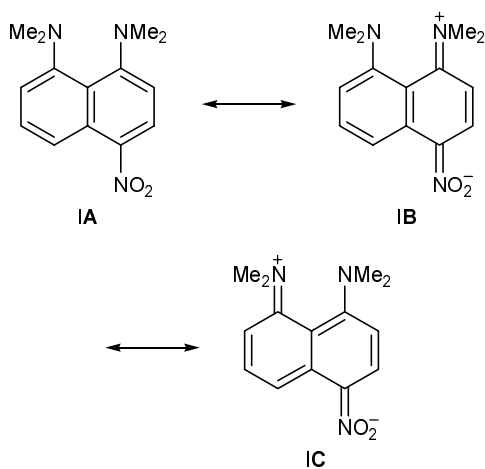
better stabilized by polar solvents. Taking the above stated into account, we believed it feasible to obtain even more effective solvatochromic compounds on the basis of proton sponge.

One of the well known solvatochromic compounds is 4-[2-(1-methyl-4-pyridinio)ethenyl]phenoxide (**IID**) [4, 5]. Its excited state is assumed to be represented best by mesomeric structure **IIF** which may be regarded as intermediate between zwitterionic benzoid structure **IID** and quinoid structure **IIE** with no charge separation. Insofar as transition of **II** to the excited state is accompanied by decrease in polarity, this compound is characterized by negative solvatochromism. The long-wave absorption maximum in ethanol, DMSO, cyclohexane, and chloroform is located at λ 510, 572, 592, and 620 nm, respectively.
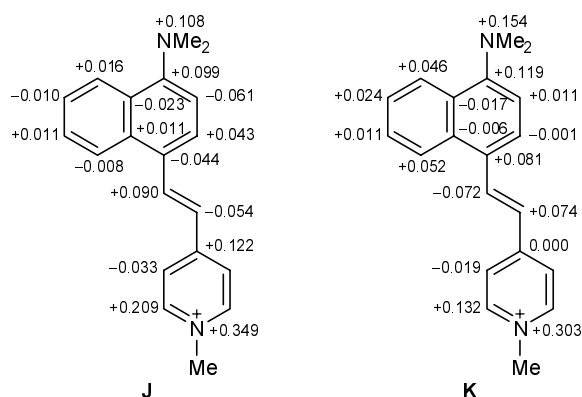
Scheme 1.

X = I, ClO$_4$.
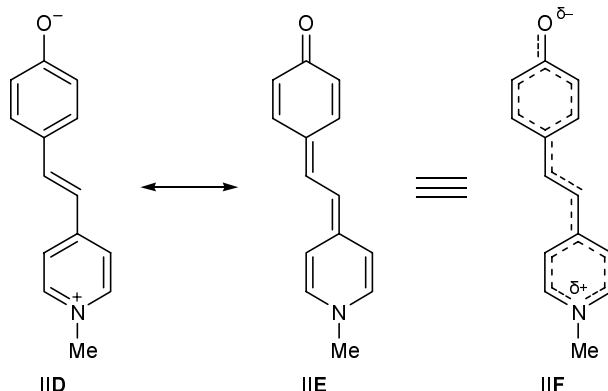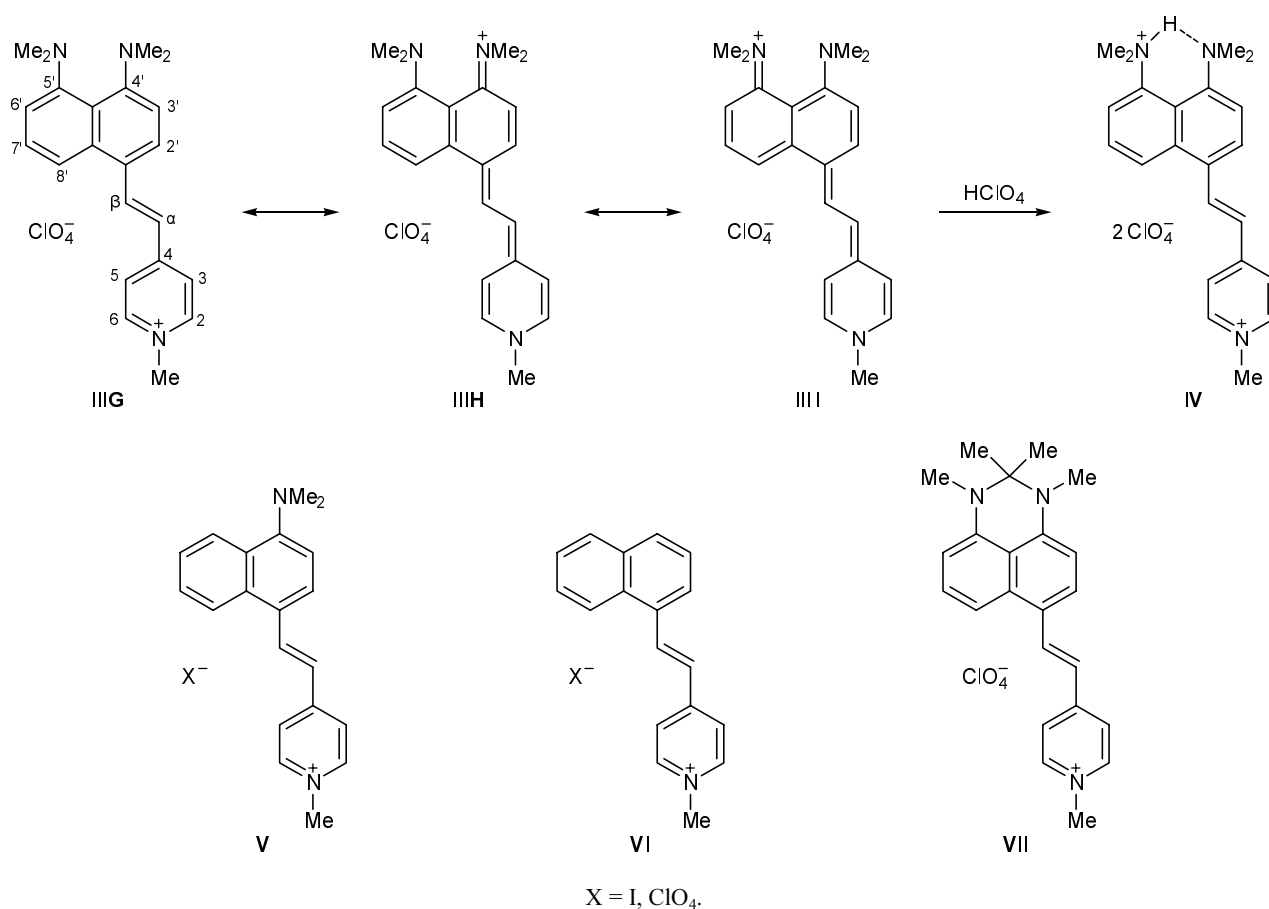
The goal of the present study was to synthesize an analog of **II** containing a 1,8-bis(dimethylamino)naphthalene residue instead of the phenoxide group. For this purpose, 1,8-bis(dimethylamino)naphthalene-4-carbaldehyde was reacted with 1,4-dimethylpyridinium iodide in the presence of piperidine. We thus obtained pyridinium salt **III** which was isolated as perchlorate. Salt **III** is capable of undergoing further protonation, e.g., by the action of perchloric acid, to give diperchlorate **IV** (Scheme 1). In addition, we examined structurally related salts **V–VII** which were synthesized by a similar procedure from the corresponding naphthalenecarbaldehydes. It was interesting to reveal whether the obtained compounds show positive (like nitro derivative **I**) or negative solvatochromism (like pyridinium phenoxide **II**).

Before proceeding to the discussion on solvatochromic properties of compounds **III** and **V–VII**, let us consider first some parameters of their ^{1}H NMR spectra, which could elucidate electron density distribution in their molecules in the ground state. The cationic fragments of salts **III** and **V–VII** are charac-

terized by large and approximately similar coupling constants for protons at the exocyclic double C=C bond, $J_{\alpha\beta}$ = 15.8–16.1 Hz. On the one hand, the $J_{\alpha\beta}$ values indicate *trans* orientation of substituents at the C$^\alpha$=C$^\beta$ bond and, on the other, weak antibonding character of that bond, i.e., localization of the positive charge on the pyridine nitrogen atom. This also follows from the chemical shifts of N-methyl protons in the pyridinium (δ 4.2–4.3 ppm) and 1,8-bis(dimethylamino)naphthalene fragments (δ 2.7–2.9 ppm). The observed values approach those typical of pyridinium salts [6] and proton sponge derivatives [2] taken separately, though some tendency for the electron density to shift toward the pyridine ring in the series **III**, **VII** > **V** > **VI** may be noted (cf., δ values for the N-methyl-pyridinium fragment in DMSO-d_6). We can conclude that the ground state of salts **III** and **V–VII** is closer to structures like **IIIG** with small contributions of canonical structures **H** and **I**. Probable reasons are nonplanar arrangement of the naphthalene and pyridine ring and (what is more important) rupture of aromaticity of the cyclic systems in going to structures **IIIH**

and **III I**. An indirect support of the above assumption may be obtained by quantum-chemical calculations of charge distribution in the cations under study. According to the Hückel calculations performed for cation **V**, the most part of positive charge in the ground state (**J**) is localized on the pyridine nitrogen atom (+0.349) rather than on the dimethylamino group (+0.108); moreover, the exocyclic ethylene bond connecting the cyclic fragments is characterized by the largest π-order (0.771). As might be expected, the first excited state (**K**) is characterized by considerable electron density transfer from the naphthalene fragment (including the dimethylamino group) to the pyridine ring, which leads to additional charge delocalization.

yellow substances. These variations are illustrated by the data in table where long-wave absorption maxima for zwitterionic compound **II** are also given for comparison. Compound **II** shows especially good correlation between λ_{max} and generalized Reichardt parameter E_T^N which characterizes solvent polarity. The absorption maximum of **II** in water and alcohols is located at shorter wavelengths, while it sharply shifts to the long-wave region in going to weakly polar chloroform, so that the difference between λ_{max} in water and chloroform reaches 178 nm. Unfortunately, some of the examined salts were poorly soluble in water, and we failed to determine the corresponding parameters. Nevertheless, the obtained data clearly indicate that salts **III**, **V**, and **VII**, as well as zwitterionic compound **II**, are characterized by pronounced negative solvatochromism. This means that their excitation is accompanied by electron density transfer from the amino nitrogen atoms to the antibonding π orbital of the conjugated system in the cation, which leads to delocalization of positive charge (i.e., increase in the contribution of canonical structures **H** and **I** to the excited state). Salt **VI** having no amino groups in the naphthalene ring shows a very weak solvatochromism. Solvatochromic properties also weaken in going from salt **III** to its analog **V** possessing only one dimethylamino group (cf., e.g., λ_{max} of **III** and **V** in CHCl₃). By contrast, the range of variation of λ_{max} for salt **VII** is larger than that observed for salt **III**. Presumably, this is the result of greater coplanarity of the dihydroperimidine and pyridinium π systems in cation **VII**, which favors positive charge delocalization in the excited state.

Despite considerable solvatochromism of salts **III** and **VII** (their color is especially deep in methylene

Salts containing amino groups in the naphthalene ring are violet (**III**, **VII**) or red substances (**V**). Their color is likely to reflect the degree of conjugation between the amino groups and the pyridinium fragment. In fact, salt **VI** having no amino group and diperchlorate **IV** (in which the dimethylamino groups are forced out from conjugation due to protonation) are

Long-wave absorption maxima λ_{max} (nm) in the electron spectra of compounds **II**, **III**, and **V–VII**

Solvent	E_T^N [7]	II	III		V		VI		VII	
		λ_{max}	λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$	λ_{max}	$\log\varepsilon$
Water	1.00	442	–	–	418	–	–	–	506	3.84
Methanol	0.76	509	–	–	458	4.31	–	–	568	3.88
Ethanol	0.65	510	528	4.41	463	4.30	391	4.34	573	3.92
Acetonitrile	0.46	–	528	4.41	–	–	–	–	–	–
DMSO	0.44	572	522	4.40	458	4.21	387	4.38	560	3.98
DMF	0.40	–	526	4.35	458	4.29	–	–	556	3.93
Acetone	0.36	577	524	4.20	462	4.31	–	–	565	3.91
Methylene chloride	0.31	–	613	4.29	510	4.42	–	–	645	3.92
Chloroform	0.26	620	570	4.51	506	4.26	403	4.30	608	3.58

chloride), compound **II** nevertheless ranks first in this respect. Obviously, transition from the ground to excited state of molecule **II** involves at least partial charge neutralization which leads to sharp reduction in the polarity. Excitation of cations **III** and **VII** is accompanied by only some dispersion of positive charge, while no charge neutralization occurs.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Unity-300 instrument (300 MHz) using TMS as internal reference. The electron absorption spectra were measured on a Specord M-40 spectrophotometer. The melting points were determined on a PTP device in a sealed capillary and were not corrected. The solvents were purified and dehydrated by standard procedures.

1-Methyl-4-{2-[4,5-bis(dimethylamino)-1-naph-thyl]ethenyl}pyridinium perchlorate (III) and diper-chlorate IV. Piperidine, 4–5 drops, was added to a solution of 0.194 g (0.80 mmol) of 4,5-bis(dimethyl-amino)naphthalene-1-carbaldehyde [8] and 0.194 g (0.83 mmol) of 1,4-dimethylpyridinium iodide in 2.5 ml of anhydrous ethanol, and the mixture was kept for 2 weeks at room temperature (on heating, the reaction was accompanied by strong tarring). The solvent was distilled off on a rotary evaporator, and the unctuous residue was ground first with diethyl ether and then with warm toluene to remove the unreacted aldehyde and traces of piperidine. The crude product was dissolved in a minimal amount of ethanol, and several drops of 30% perchloric acid were added to the solution to precipitate diperchlorate **IV**. The product was filtered off, washed on a filter with ethanol acidified with a small amount of perchloric acid, and dried in air. Yield of **IV** 0.132 g (31%), yellow–brown crystalline substance, mp 178–179°C. ^{1}H NMR spectrum (30°C, DMSO-d_6), δ, ppm: 3.13 s (6H, 4'-NMe$_2$), 3.16 s (6H, 5'-NMe$_2$), 4.29 s (3H, MeN$^+$), 7.63 d (1H, α-H, J_{trans} = 15.9 Hz), 7.87 d.d (1H, 7'-H, $J_{7',6'}$ = 7.4, $J_{7',8'}$ = 7.8 Hz), 8.21 m (3H, 3'-, 6'-, 8'-H), 8.44 d (2H, 3-H, 5-H, $J_{3,2}$ = $J_{5,6}$ = 5.49 Hz), 8.69 d (1H, 2'-H, $J_{2',3'}$ = 8.3 Hz), 8.78 d (1H, β-H, J_{trans} = 15.9 Hz), 8.94 d (2H, 2-H, 6-H, $J_{2,3}$ = $J_{6,5}$ = 5.49 Hz), 18.64 br.s (1H, NH). Found, %: C 49.35; H 4.99; Cl 13.01. C$_{22}$H$_{27}$Cl$_2$N$_3$O$_8$. Calculated, %: C 49.63; H 5.11; Cl 13.32.

Treatment of diperchlorate **IV** with excess 1 N potassium hydroxide (3 ml), followed by extraction with an ethanol–chloroform mixture (1:3, 6×4 ml) and removal of the solvent, gave perchlorate **III** as a violet

crystalline substance. Yield 95%, mp 163°C. ^{1}H NMR spectrum, δ, ppm: in CDCl$_3$: 2.78 s (6H, 5'-NMe$_2$), 2.92 s (6H, 4'-NMe$_2$), 4.38 s (3H, MeN$^+$), 6.87 d (1H, 6'-H, $J_{6',7'}$ = 8.35 Hz), 6.93 d (1H, 3'-H, $J_{3',2'}$ = 8.02 Hz), 6.99 d (1H, α-H, J_{trans} = 15.5 Hz), 7.42 d.d (1H, 7'-H, $J_{7',6'}$ = 8.35, $J_{7',8'}$ = 8.28 Hz), 7.69 d (1H, 8'-H, $J_{8',7'}$ = 8.28 Hz), 7.79 d (1H, 2'-H, $J_{2',3'}$ = 8.02 Hz), 7.83 d (2H, 3-H, 5-H, $J_{3,2}$ = $J_{5,6}$ = 6.78 Hz), 8.37 d (1H, β-H, J_{trans} = 15.5 Hz), 8.66 d (2H, 2-H, 6-H, $J_{2,3}$ = $J_{6,5}$ = 6.78 Hz); in CD$_3$CN: 2.79 s (6H, 5'-NMe$_2$), 2.92 s (6H, 4'-NMe$_2$), 4.15 s (3H, MeN$^+$), 7.01 d (1H, 6'-H, $J_{6',7'}$ = 8.39 Hz), 7.02 d (1H, 3'-H, $J_{3',2'}$ = 8.02 Hz), 7.23 d (1H, α-H, J_{trans} = 15.80 Hz), 7.45 d.d (1H, 7'-H, $J_{7',6'}$ = 8.39, $J_{7',8'}$ = 8.35 Hz), 7.84 d (1H, 8'-H, $J_{8',7'}$ = 8.35 Hz), 7.91 d (1H, 2'-H, $J_{2',3'}$ = 8.02 Hz), 7.98 d (2H, 3-H, 5-H, $J_{3,2}$ = $J_{5,6}$ = 6.88 Hz), 8.34 d (2H, 2-H, 6-H, $J_{2,3}$ = $J_{6,5}$ = 6.88 Hz), 8.51 d (1H, β-H, J_{trans} = 15.80 Hz); in DMSO-d_6: 2.73 s (6H, 5'-NMe$_2$), 2.86 s (6H, 4'-NMe$_2$), 4.19 s (3H, MeN$^+$), 6.96 d (1H, 6'-H, $J_{6',7'}$ = 7.66 Hz), 6.97 d (1H, 3'-H, $J_{3',2'}$ = 8.39 Hz), 7.32 d (1H, α-H, J_{trans} = 15.82 Hz), 7.40 d.d (1H, 7'-H, $J_{7',6'}$ = 7.66, $J_{7',8'}$ = 8.21 Hz), 7.93 d (1H, 8'-H, $J_{8',7'}$ = 8.21 Hz), 7.98 d (1H, 2'-H, $J_{2',3'}$ = 8.39 Hz), 8.25 d (2H, 3-H, 5-H, $J_{3,2}$ = $J_{5,6}$ = 6.42 Hz), 8.63 d (1H, β-H, J_{trans} = 15.82 Hz), 8.72 d (2H, 2-H, 6-H, $J_{2,3}$ = $J_{6,5}$ = 6.42 Hz). Found, %: C 60.86; H 6.01; Cl 8.05. C$_{22}$H$_{26}$ClN$_3$O$_4$. Calculated, %: C 61.18; H 6.07; Cl 8.23.

1-Methyl-4-[2-(4-dimethylamino-1-naphthyl)-ethenyl]pyridinium perchlorate (V). Piperidine, 3 drops, was added to a solution of 0.128 g (0.64 mmol) of 4-dimethylaminonaphthalene-1-carbaldehyde and 0.151 g (0.64 mmol) of 1.4-dimethylpyridinium iodide in 2 ml of anhydrous ethanol, and the mixture was stirred, kept for a week at room temperature, heated for 4 h at 75°C, and kept for 12 h in a refrigerator. The precipitate was filtered off and washed on a filter in succession with warm toluene (2×3 ml) and cold ethanol (2×4 ml). Yield of iodide **V** 0.142 g (53%), bright red crystals, mp 186°C. Found, %: C 57.37; H 4.90; I 30.32. C$_{20}$H$_{21}$IN$_2$. Calculated, %: C 57.70; H 5.08; I 30.48.

Iodide **V** was dissolved in a minimal amount of ethanol, and a saturated solution of lithium perchlorate in ethanol was added dropwise. Yield of perchlorate **V** 91%, mp 193°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.92 s (6H, NMe$_2$), 4.25 s (3H, MeN$^+$), 7.19 d (1H, 3'-H, $J_{3',2'}$ = 8.14 Hz), 7.49 d (1H, α-H, J_{trans} = 15.9 Hz), 7.62 m (2H, 6'-H, 7'-H), 8.06 d (1H, 2'-H, $J_{2',3'}$ = 8.14 Hz), 8.20 m (1H, 8'-H), 8.38 d (2H, 3-H, 5-H, $J_{3,2}$ = $J_{5,6}$ = 6.7 Hz), 8.57 m (1H, 5-H), 8.75 d

(1H, β-H, J_{trans} = 15.9 Hz), 8.84 d (2H, 2-H, 6-H, $J_{2,3}$ = $J_{6,5}$ = 6.7 Hz). Found, %: C 61.52; H 5.60; Cl 8.97. $C_{20}H_{21}ClN_2O_4$. Calculated, %: C 61.78; H 5.44; Cl 9.12.

1-Methyl-4-[2-(1-naphthyl)ethenyl]pyridinium iodide and perchlorate (VI). A solution of 0.2 ml (1.47 mmol) of naphthalene-1-carbaldehyde, 0.345 g (1.47 mmol) of 1,4-dimethylpyridinium iodide, and 5 drops of piperidine in 5 ml of anhydrous ethanol was heated for 10 h under reflux. After cooling, brown crystals of iodide **VI** were filtered off, washed with warm toluene (6 ml) and ethanol (3 ml), and dried in air. Yield 0.450 g (82%), mp 275–276°C. Iodide **VI** was dissolved in 13 ml of anhydrous ethanol, and a solution of 0.193 g of lithium perchlorate in 4 ml of anhydrous ethanol was added. The golden yellow precipitate of perchlorate **VI** (0.318 g, 92%) was filtered off, washed with cold ethanol (2×2 ml), and dried in a vacuum desiccator. mp 263°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.30 s (3H, MeN$^+$), 7.62 d (1H, α-H, J_{trans} = 16.1 Hz), 7.64 m (3H, 3'-H, 6'-H, 7'-H), 8.05 m (3H, 2'-H, 4'-H, 5'-H), 8.43 d (2H, 3-H, 5-H, $J_{3,2}$ = $J_{5,6}$ = 6.8 Hz), 8.58 m (1H, 8'-H), 8.81 d (1H, β-H, J_{trans} = 16.1 Hz), 8.91 d (2H, 2-H, 6-H, $J_{2,3}$ = $J_{6,5}$ = 6.8 Hz). Found, %: C 62.23; H 4.69; Cl 10.01. $C_{18}H_{16}ClNO_4$. Calculated, %: C 62.52; H 4.66; Cl 10.25.

1-Methyl-4-[2-(1,2,2,3-tetramethyl-2,3-dihydroperimidin-6-yl)ethenyl]pyridinium perchlorate (VII). Piperidine, 5 drops, was added to a solution of 138 mg (0.54 mmol) of 1,2,2,3-tetramethyl-2,3-dihydroperimidine-6-carbaldehyde [9] and 127 mg (0.54 mmol) of 1,4-dimethylpyridinium iodide in 5 ml of ethanol, and the mixture was kept for 2 weeks at room temperature. The solvent was evaporated, the residue was washed with 4 ml of diethyl ether and dissolved in a minimal amount of chloroform, and the solution was passed through a small layer of Al_2O_3, the unreacted aldehyde being washed off with chloroform. The violet zone remaining at the start was cut off and washed with a small amount of ethanol containing 2–3 drops of $HClO_4$, and the sorbent was filtered off.

Diethyl ether (1/4 of the overall volume) was added to the filtrate, and the mixture was kept for 24 h in a freezing chamber. The brown precipitate of diperchlorate (80 mg, 27%) was filtered off, dried in air, and converted into perchlorate **VII** by treatment with 2 ml of 1 N aqueous potassium hydroxide. Salt **VII** was extracted into methanol–chloroform (1:4, 5×5 ml), and the extracts were combined and evaporated to obtain 64 mg (96%) of perchlorate **VII** as violet crystals with mp ~140°C (decomp). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.30 s (6H, NMe$_2$), 2.90 s (3H, 1-NMe), 3.01 s (3H, 3-NMe), 4.20 s (3H, MeN$^+$), 6.67 m (2H, 4-H, 9-H), 7.30 d (1H, α-H, J_{trans} = 15.6 Hz), 7.44 d.d (1H, 8-H, $J_{8,7}$ = 8.6, $J_{8,9}$ = 7.9 Hz), 7.79 d (1H, 7-H, $J_{7,8}$ = 8.6 Hz), 8.01 d (1H, 5-H, $J_{5,4}$ = 8.6 Hz), 8.22 d (2H, 3'-H, 5'-H, $J_{3',2'}$ = $J_{5',6'}$ = 6.9 Hz), 8.63 d (1H, β-H, J_{trans} = 15.6 Hz), 8.70 d (2H, 2'-H, 6'-H, $J_{2',3'}$ = $J_{6',5'}$ = 6.9 Hz). Found, %: C 61.88; H 5.69; Cl 7.63. $C_{23}H_{26}ClN_3O_4$. Calculated, %: C 62.23; H 5.90; Cl 7.99.

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