

Pyrroles, Imidazoles and Poly(vinamidines) from Bis(vinamidinium salts) <sup>1)</sup>

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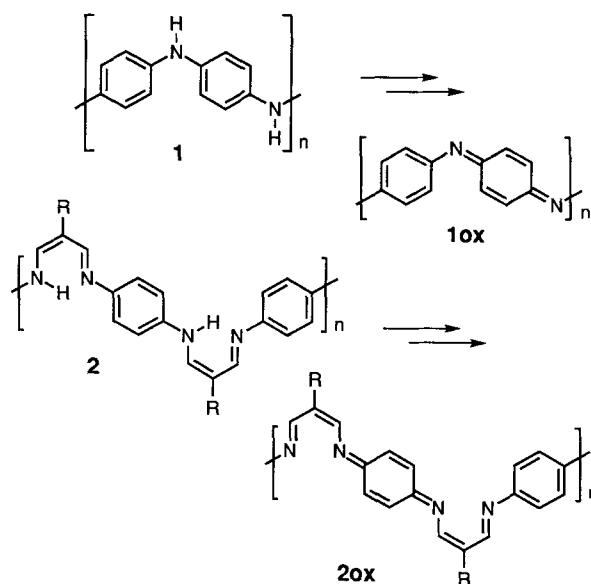
**Abstract.** The reaction of bis(vinamidinium salts) (**5a**, **6**) and amidinium-vinamidinium salts (**7**, **21**) with primary amines was studied. Whereas the condensation of **6** and **7a** with *p*-phenylenediamine and 4,4'-diaminostilbene gave rise to polymeric vinamidines (**12**, **18**), **5a** and **7b** reacted with aromatic amines and diamines to give pyrrole and imidazole derivatives. The reaction of *p*-aminophenylacetic acid with DMF-POCl<sub>3</sub>

produced a new amidinium-vinamidinium salt (**21**) which could be converted into a donor-acceptor substituted diazaterphenyl derivative (**22**) displaying a strong solvatochromism. – The crystal structure analysis of the 2,2'-bis(vinamidinium salt) **5b** revealed a 73° twist angle between the planes of the vinamidinium moieties.

Conjugated polymers [1] such as polyacetylene [2], poly-*para*-phenylene [3], poly-*p*-phenylenesulfide [4], polypyrrole [5], polythiophene [6], and polyaniline **1** [7] show high electrical conductivities after doping with oxidants. We have previously prepared poly(vinamidines) **2** [8] some of which also feature high electrical conductivities. Polymers **2** combine structural features of polyaniline **1**, polyarylenes, polyarylene vinylenes and cyanine dyes. The completely oxidized form **2ox** of **2** is an azabutadienediyl homologue of **1ox**.

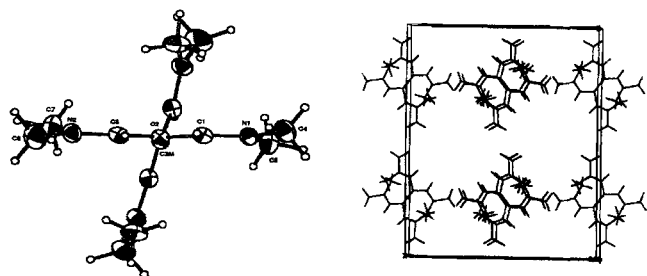
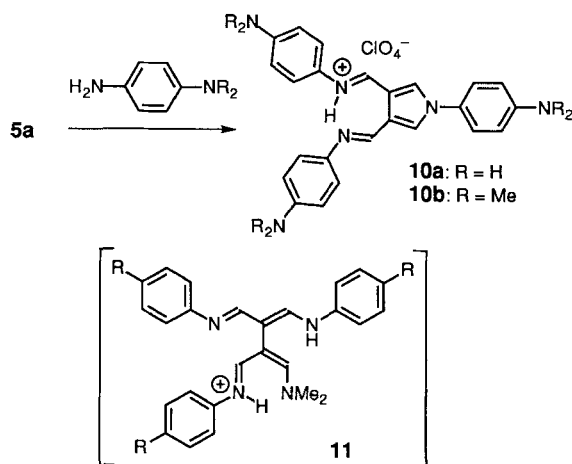
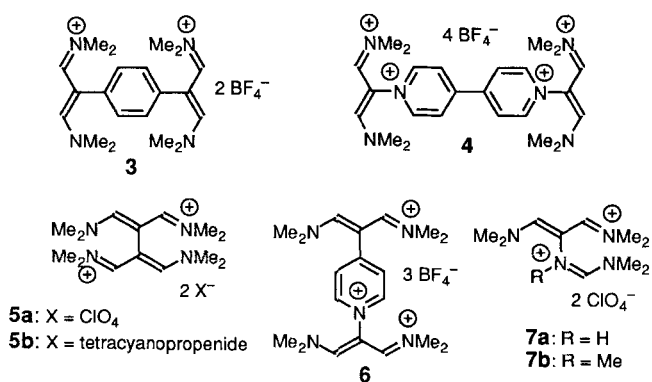
Since vinamidinium salts are readily available and their conversion into polyvinamidines **2** is a straightforward process we set out to study the reactions of bis(vinamidinium salts) **5a** [9], **6** [10] and the amidinium-vinamidinium salt **7** [11] with aromatic amines; the bifunctional phenylene-divinamidinium salt **3** and the bipyridine-derived vinamidinium salt **4** have already been used for the preparation of polyvinamidines [8]).

In order to find out about the steric situation of the cation of **5a** the new salt **5b** was prepared. Its crystal structure (see Figure 1) shows that the planes of the vinamidinium moieties are twisted against each other by 73°. The bond angle C1–C2–C3 (110°) is considerably smaller than the ideal C(sp<sup>2</sup>) angle and the corresponding bond angle in the parent vinamidinium salt (119°) [12]. The bond angles N1–C1–C2 (132°) and N2–C3–C2 (130°) are considerably larger than the ideal C(sp<sup>2</sup>) angle and also larger than the corresponding bond angle in the parent vinamidinium salt (126°).

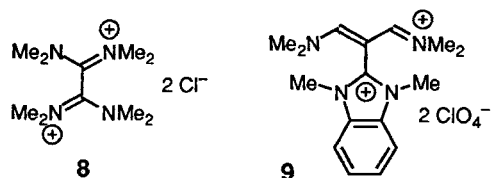
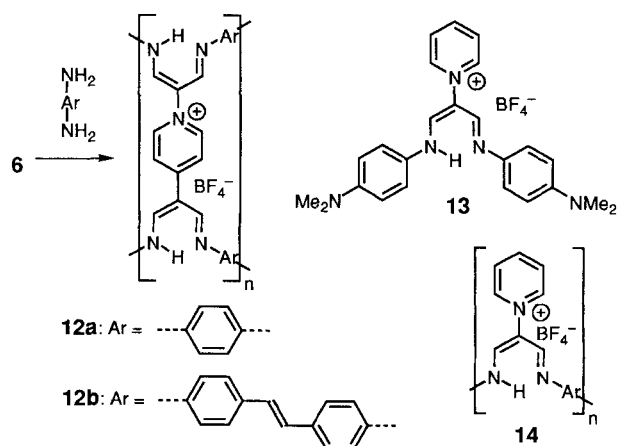


The twist angles in the vinamidinium salts **8** (76°) [14] and **9** (88°) [15] which are electronically different from **5b** – both central carbon atoms in **8** carry a partial positive charge; in **9**, one of the central carbon atoms carries a partial positive, the other one a partial negative charge, and in **5b** both central carbon atoms carry a partial negative charge – are close to twist angle in **5b**, which means that steric factors are the main reason for the twisting.

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**Fig. 1** Structure of **5b** in the crystal (ORTEP) [13]: View down the C2–C2M bond, the tetracyanopropenide anions are omitted for clarity (left); crystal structure (right). Selected bond lengths (pm) and bond angles (°): N1–C1 131.8(5), N1–C4 147.1(6), N1–C5 147.1(6), N2–C3 132.8(6), N2–C6 146.1(6), N2–C7 147.3(7), C1–C2 141.0(6), C2–C2M 149.1(6), C2–C3 139.5(5); N1–C1–C2 131.9(4), C1–C2–C3 109.9(4), N2–C3–C2 130.3(4).



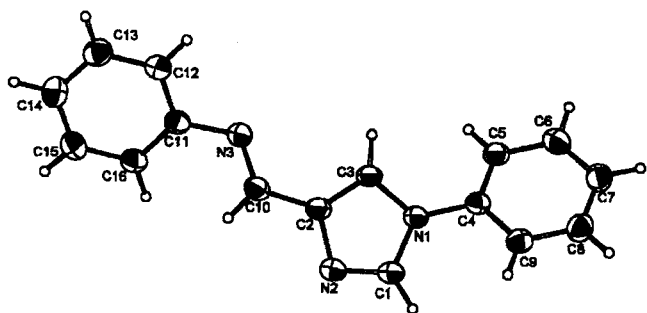
The reaction of **5a** with *p*-phenylenediamine did not lead to a polymer as with **3** and **4** but to the red pyrrole derivative **10b** probably *via* the intermediate **11**; with *N,N*-dimethyl-*p*-phenylenediamine **10a** was obtained. The <sup>1</sup>H NMR spectra of **10** demonstrate that nitrogen atoms of the imino groups are protonated. The C<sub>2</sub> symmetry indicates a rapid prototropic shift (*cf.* the structures of related fulvene derivatives [16]).

The reaction of the pyridinio-bridged bis(vinamidinium salt) **6** [10], which is a pyridinium-homologue of **5**, with *p*-phenylenediamine and 4,4'-diaminostilbene gives rise to the dark red poly-vinamidines **12**. The IR spectra of **12** are very similar to those of **13** [8] and **14** [8]. The longest wavelength absorption maxima of **12a** (λ<sub>max</sub> = 470 nm) and **12b** (λ<sub>max</sub> = 465 nm) appear at

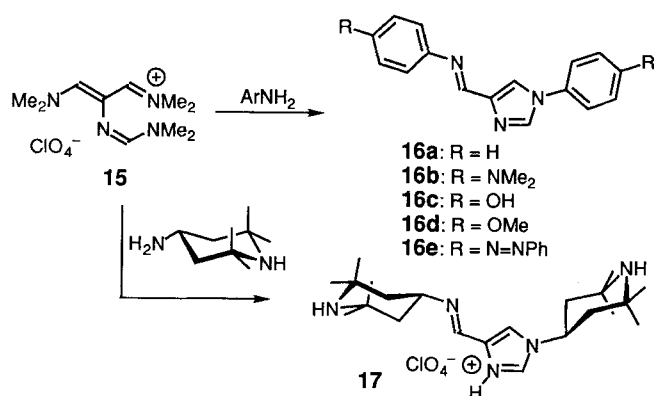
longer wavelengths than λ<sub>max</sub> = 403 nm of **13** which is an indication of a π-conjugation across the phenylene bridges in **12**. The electrical powder conductivities of native samples of **12a** (σ = 0.9 Scm<sup>-1</sup>) and **12b** (σ = 0.01 Scm<sup>-1</sup>) [17] are remarkably high.

The amidinium-vinamidinium salts **7** [11] can be viewed as aza-analogues of **5a**. Thus, if the reaction of bis(vinamidinium salt) **5a** with aromatic amines provides pyrroles, the formation of imidazoles from **7** and aromatic amines is to be expected. In the event, the reaction of **15** [11], obtained from **7a** with triethylamine, with aromatic amines and 4-amino-2,2,4,4-tetramethylpiperidine gave the colourless imidazole derivatives **16** and **17**.

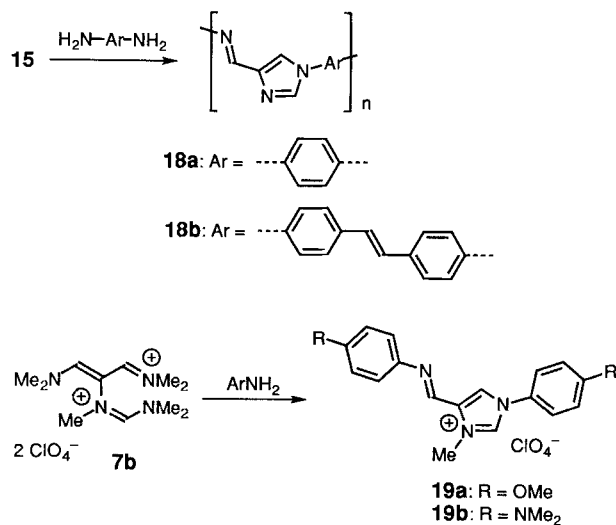
The crystal structure analysis of **16a** (see Figure 2) shows that the plane formed of the imidazole ring and the imino group (C10–N3) and the plane of the N<sup>1</sup>-phenyl ring have a twist angle of 28.24(6)° and the planes of the imidazole and the imino-*N*-phenyl ring a twist angle of 35.30(5)°.



**Fig. 2** Structure of **16a** in the crystal (ORTEP) [18]: Selected bond lengths [pm] and bond angles [°]: N1–C1 136.4(2), N1–C3 136.3(2), N1–C4 142.7(2), N2–C1 129.7(2), N2–C2 137.9(2), N3–C10 127.3(2), N3–C11 140.8(2), C2–C3 135.4(2), C2–C10 144.3(2); C1–N1–C3 106.1(1), N1–C1–N2 112.5(1), N2–C2–N3 110.1(1), N1–C3–C2 106.3(1), C1–N2–C2 104.9(1), N3–C10–C3 124.6(1), C10–N3–C11 106.3(1).

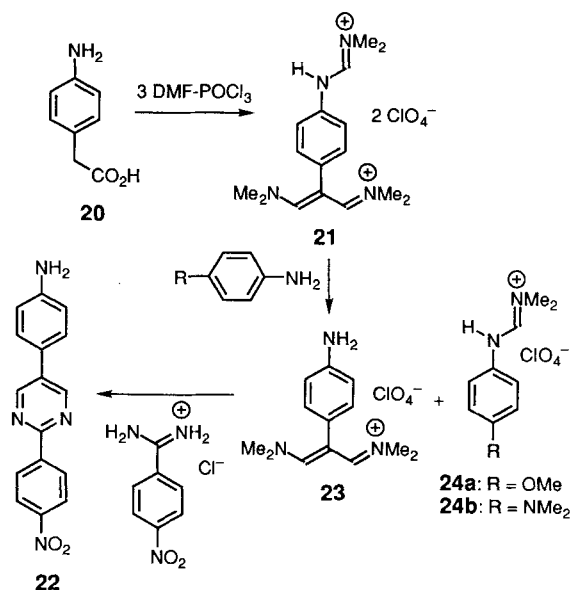


Heating of **15** with *p*-phenylenediamine or 4,4'-diaminostilbene gives rise to the brown polymers **18**. Their IR spectra resemble the spectrum of **16a**. The electrical powder conductivity  $\sigma$  of a native sample of **18b** ( $\sigma = 0.8 \text{ Scm}^{-1}$ ) [17] is as high as that of **12a**.

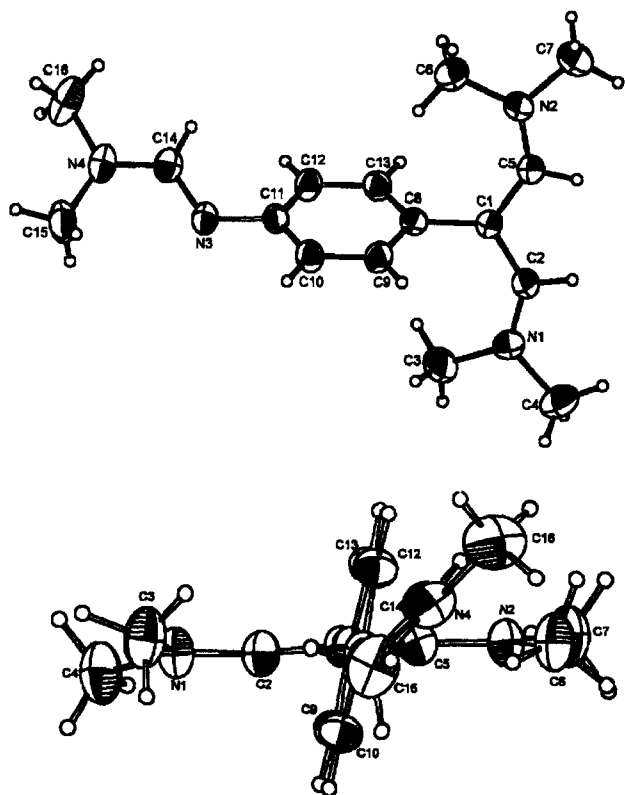


The amidinium-vinamidinium salt **7b** [11] reacts with aromatic amines to give the imidazolium salts **19**.

*p*-Aminophenylacetic acid **20** is a phenylogue of glycine. In the same way as **7a** (**15**) [11] is formed by reacting glycine with the Vilsmeier-Haack reagent, **20** delivers the amidinium–vinamidinium salt **21**. The crystal structure analysis of **21** (see Figure 3) shows that the angles in the vinamidinium moiety are similar to those in **5b**. The planes of the vinamidinium moiety and the phenyl ring have a twist angle of 74.9°, those of the amidinium moiety and the phenyl ring a twist angle of 32.4°.

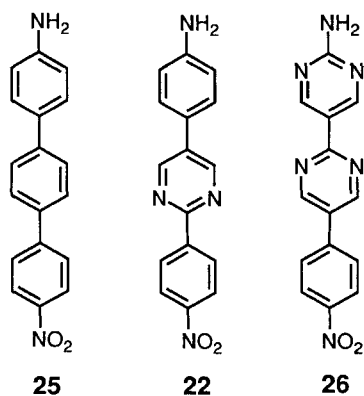


**21** does not react with dimethylamine (in EtOH); with *p*-aminoanisole or *N,N*-dimethyl-*p*-phenylenediamine, however, a mixture of **23** and **24** is formed in good yields. **23** is a poor electrophile as well; there is no reaction with aromatic amines. The condensation of **23** with *p*-nitrobenzamide gives rise to the donor-acceptor substituted diazaterphenyl derivative **22**. In the toluene/DMSO solvent system, **22** has a very strong positive solvatochromism ( $\Delta\tilde{\nu}_{\text{max}}$  (toluene/DMSO) = 2548 cm<sup>-1</sup>) which is indicative of interesting nonlinear optical properties [20]. As compared with the donor-acceptor substituted terphenyl derivatives **25** [21] ( $\lambda_{\text{max}}$  (DMSO) = 360 nm) and **26** [22] ( $\lambda_{\text{max}}$  (DMSO) = 349 nm), **22** absorbs at longer wavelengths ( $\lambda_{\text{max}}$  (DMSO) = 400 nm; ( $\lambda_{\text{max}}$  (toluene) = 363 nm). As a result of the stronger *o,o'*-hydrogen interactions in **25** than in **22** and **26**, **25** is more twisted than **22** and **26** and consequently the resonance interaction of NH<sub>2</sub> and NO<sub>2</sub> is stronger in **22** and **26** than in **25**. On the other hand, the *p*-ami-



**Fig. 3** Structure of **21** in the crystal (ORTEP) [19]; the perchlorate anions are omitted for clarity (top); view down the C10–C9 and C12–C13 bonds (phenyl ring). Selected bond lengths (pm) and bond angles ( $^{\circ}$ ): N1–C2 129.9(7), N2–C5 131.5(6), N3–C14 133.2(6), N4–C14 128.9(6), N3–C11 144.6(6), C1–C2 140.9(6), C1–C5 138.4(5), C1–C8 149.4(6); N1–C2–C1 132.8(4), N2–C5–C1 132.4(4), C2–C1–C5 111.8(4), N3–C14–N4 124.2(5), C11–N3–C14 121.3(4).

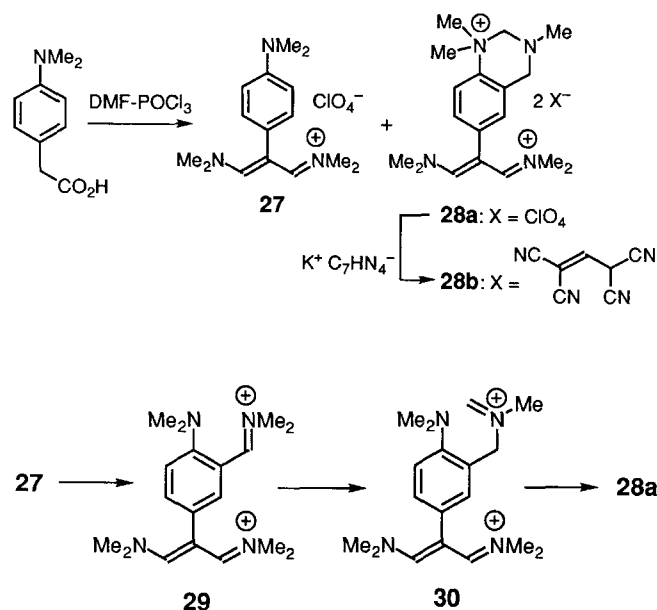
nophenyl group in **22** is a stronger electron donor than the 2-aminopyrimidinyl group in **26** (cf.  $pK_a = 4.58$  of aniline [23] vs.  $pK_a = 3.54$  of 2-aminopyrimidine [24]) and therefore  $\lambda_{\max} \mathbf{22} > \lambda_{\max} \mathbf{26}$ .



When *p*-dimethylaminophenylacetic acid is treated with 2 equivalents of DMF–POCl<sub>3</sub>, a 3:2 mixture of the vinamidinium salts **27** and **28a** is formed (as concluded

from the <sup>1</sup>H NMR spectrum; **27** could not be isolated). **28a** is the sole product, obtained in poor yield, if 3 equivalents of DMF–POCl<sub>3</sub> are used; it can be purified by metathesizing it to the salt **28b**.

We assume that **27** is iminoformylated to form **29**; a prototropic shift leads to **30** which in turn cyclizes to give **28a**.



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## Experimental

NMR spectra were recorded on a Bruker ARX 300 (300MHz) and a Varian VXR 400 S (400 MHz); IR spectra on a Perkin-Elmer 125 and a Bruker IFS 45; UV/Vis spectra on a Zeiss DMR 10 and a Perkin-Elmer model Lambda 3; mass spectra on a AEJ, MS 902, and a MAT 95Q, Cs-Gun). Melting points were obtained on a Büchi SMP-20 and a Reichert Thermovar BHT apparatus.

### 2,2'-Bis(dimethylamino-*N,N*-dimethyl-prop-2-eneiminium) bis(1,1,3,3-tetracyanopropenide) (**5b**)

The vinamidinium salt **5a** [9] (0.20 g, 0.44 mmol) was dissolved in warm water (15 ml). The warm solution of potassium tetracyanopropenide [25] (0.16 g, 0.89 mmol) was added dropwise. After cooling, thin platelets were collected by suction filtration and washed with MeOH and ether. Colorless platelets, yield 0.19 g (80%). Long transparent needles with *m.p.* 189–190  $^{\circ}$ C for the crystallographic analysis were obtained by dissolving 0.07 g in acetonitrile (5 ml) and allowing

ether to diffuse into the solution. – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 2950, 2190, 1590, 1550$ . – UV/Vis (DMSO):  $\lambda_{\text{max}} (\lg \epsilon) = 345 \text{ nm} (4.94)$ . –  $^1\text{H NMR}$  ( $[\text{D}_6]$  DMSO):  $\delta/\text{ppm} = 3.13$  (s, 12H,  $\text{NCH}_3$ ), 3.31 (s, 12H,  $\text{NCH}_3$ ), 6.98 (s, 2H, propenide-H), 7.37 (s, 4H, vinamidinium– $\text{NCH}_2\text{C}$ ). –  $^{13}\text{C NMR}$  ( $[\text{D}_6]$  DMSO):  $\delta/\text{ppm} = 38.20$  (q,  $^1J_{\text{C,H}} = 141.5 \text{ Hz}$ ,  $\text{NCH}_3$ ), 49.31 (s, propenide– $(\text{NC})_2\text{C}$ ), 50.61 (q,  $^1J_{\text{C,H}} = 139.2 \text{ Hz}$ ,  $\text{NCH}_3$ ), 92.65 (s, vinamidinium– $\text{NCH}_2\text{C}$ ), 115.58 (s, CN), 119.04 (s, CN), 154.47 (d,  $^1J_{\text{C,H}} = 157.6 \text{ Hz}$ , propenide–CH), 164.85 (d,  $^1J_{\text{C,H}} = 167.1 \text{ Hz}$ , vinamidinium– $\text{NCH}_2\text{C}$ ).

$\text{C}_{28}\text{H}_{30}\text{N}_{12}$  Calcd.: C 62.90 H 5.66 N 31.44  
(534.6) Found: C 62.82 H 5.84 N 31.39.

*1-(4-Aminophenyl)-3-[N-(4-aminophenyl)-iminiummethyl]-4-[N-(4-aminophenyl)-iminomethyl]-pyrrole perchlorate (10a)*

A suspension of **5a** [9] (2.00 g, 4.4 mmol) and *p*-phenylenediamine (1.33 g, 13.4 mmol) in MeOH (50 ml) was refluxed for 24 h. The hot mixture was suction filtered and the solid material was washed with MeOH and ether. Orange powder, *m.p.* 145 °C, yield 1.75 g (80%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 3400, 3371, 1668, 1625, 1545, 1519, 1100, 830, 625$ . – UV/Vis (DMSO):  $\lambda_{\text{max}} (\lg \epsilon) = 305 \text{ nm} (4.51), 467 (4.44)$ . –  $^1\text{H NMR}$  ( $[\text{D}_6]$  DMSO):  $\delta/\text{ppm} = 5.55$  (br. s, 2H,  $\text{NH}_2$ ), 5.65 (br. s, 4H,  $\text{NH}_2$ ), 6.71 (d,  $J = 8.6 \text{ Hz}$ , 4H, phenylene-H), 6.72 (d,  $J = 8.9 \text{ Hz}$ , 2H, phenylene-H), 7.30 (d,  $J = 8.9 \text{ Hz}$ , 2H, phenylene-H), 7.36 (d,  $J = 8.9 \text{ Hz}$ , 2H, phenylene-H), 8.31 (s, 2H, CH=N), 8.97 (s, 2H, pyrrole-2,5-H).

$\text{C}_{24}\text{H}_{23}\text{ClN}_6\text{O}_4$  Calcd.: C 58.24 H 4.68 N 16.98  
(494.9) Found: C 57.83 H 4.76 N 16.83.

*1-(4-Dimethylaminophenyl)-3-[N-(4-dimethylaminophenyl)-iminiummethyl]-4-[N-(4-dimethylaminophenyl)-iminomethyl]-pyrrole perchlorate (10b)*

A solution of *N,N*-dimethyl-*p*-phenylenediamine (1.8 g, 13.3 mmol) in MeOH (25 ml) was added to the warm solution (55 °C) of **5a** [9] (1.0 g, 2.2 mmol) in MeOH (100 ml) and the mixture refluxed for 20 h (the solution turned turbid after 1 h). The precipitate was collected by suction filtration and washed with ether. Hygroscopic red powder, *m.p.* 230–232 °C, yield 1.23 g (93%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 2896, 2855, 1666, 1612, 1544, 1524, 1095, 817, 623$ . – UV/Vis (DMSO):  $\lambda_{\text{max}} (\lg \epsilon) = 313 \text{ nm} (4.51), 480 (4.41)$ . –  $^1\text{H NMR}$  ( $[\text{D}_6]$  DMSO):  $\delta/\text{ppm} = 2.96$  (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 2.98 (s, 12H,  $\text{N}(\text{CH}_3)_2$ ), 6.83 (d,  $J = 9.0 \text{ Hz}$ , 6H, phenylene-H), 7.38 (d,  $J = 9.0 \text{ Hz}$ , 4H, phenylene-H), 7.45 (d,  $J = 9.0 \text{ Hz}$ , 2H, phenylene-H), 8.31 (s, 2H, CH=N), 8.94 (s, 2H, pyrrole-2,5-H). – MS (70 eV):  $m/z$  (%): 478 (9) [ $\text{M}^+ - \text{HClO}_4$ ], 343 (9) [ $\text{M}^+ - \text{HClO}_4 - \text{N,N}$ -dimethyl-*p*-phenylene-diamine], 69 (100).

$\text{C}_{30}\text{H}_{35}\text{ClN}_6\text{O}_4 \times \text{H}_2\text{O}$  Calcd.: C 60.34 H 5.91 N 14.07  
(597.1) Found: C 60.67 H 5.91 N 14.31.

*Poly-{1,4-pyridinium-di-[3-amino-prop-2-ene-N-(p-phenylene)imine]tetrafluoroborate} (12a)*

Acetic acid (10 drops) was added to a warm solution (60 °C) of **6** [10] (1.0 g, 1.7 mmol) in MeOH (50 ml). *p*-Phenylenediamine (0.37 g, 3.4 mmol), dissolved in MeOH (25 ml), was added under stirring to warm solution and the mixture was

refluxed for 24 h. After cooling, the precipitate was collected by suction filtration and washed with water, MeOH and ether. Dark red powder, *m.p.* > 350 °C, yield 0.66 g (87%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1647, 1608, 1507, 1084, 835$ .

$(\text{C}_{23}\text{H}_{18}\text{BF}_4\text{N}_5 \times 1.5 \text{ H}_2\text{O})_n$   
(478.3)<sub>n</sub> Calcd.: C 57.76 H 4.43 N 14.64  
Found: C 58.17 H 5.18 N 15.17.

*Poly-{1,4-pyridinium-di-[3-amino-prop-2-ene-N-(p-phenylene)vinylphenylene]imine} tetrafluoroborate} (12b)*

A suspension of **6** [10] (1.2 g, 2.0 mmol) and 4,4'-diaminostilbene (0.84 g, 4.0 mmol) in MeOH (50 ml) was refluxed for 24 h after adding acetic acid (10 drops). The precipitate was collected by filtration and washed with water, MeOH and ether. Dark red powder, *m.p.* > 350 °C, yield 1.09 g (83 %). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1653, 1616, 1506, 1084, 835$ .

$(\text{C}_{39}\text{H}_{30}\text{BF}_4\text{N}_5 \times 3 \text{ H}_2\text{O})_n$  Calcd.: C 66.02 H 5.11 N 9.87  
(708.6)<sub>n</sub> Found: C 66.17 H 5.43 N 11.59.

*1-Phenyl-4-[(N-phenyl)-iminomethyl]-1H-imidazole (16a)*

A solution of aniline (1.12 g, 12.0 mmol) in MeOH (10 ml) was added dropwise to a solution of **15** [11] (0.59 g, 2.0 mmol) in MeOH (10 ml) and the mixture was refluxed for 20 h. After cooling the solution to –20 °C and scratching, colourless crystals were formed. Transparent rectangular platelets, *m.p.* 159–160 °C, yield 0.25 g (51%). Crystals for the X-ray were obtained by recrystallizing 0.18 g from EtOH (22 ml). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 3071, 1631, 1601, 1590, 1554, 1510, 1198, 1069, 965, 860, 762, 756, 701, 690$ . – UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}/\text{nm} (\lg \epsilon) = 288(4.24), 312 (4.22)$ . –  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 7.23$ – $7.52$  (m, 10H, phenyl-H), 7.93 (s, 2H, imidazole-2,5-H), 8.52 (s, 1H, N=CH). – MS (70 eV);  $m/z$  (%): 247 (86) [ $\text{M}^+$ ], 246 (100) [ $\text{M}^+ - \text{H}$ ], 220 (9) [ $\text{M}^+ - \text{HCN}$ ].  
 $\text{C}_{16}\text{H}_{13}\text{N}_3$  Calcd.: C 77.71 H 5.30 N 16.99  
(247.3) Found: C 77.04 H 5.28 N 16.36.

*1-(4-Dimethylaminophenyl)-4-[N-(4-dimethylaminophenyl)-iminomethyl]-1H-imidazole (16b)*

A solution of *N,N*-dimethyl-*p*-phenylenediamine (0.54 g, 4.0 mmol) in MeOH (35 ml) was added dropwise to a solution of **15** [11] (0.59 g, 2.0 mmol) in MeOH (10 ml) and the mixture refluxed for 18 h. After cooling the solution to –25 °C, the green precipitate was collected by suction filtration and recrystallized from MeOH (40 ml). – Greenish powder, *m.p.* 250 °C, yield 0.25 g (37%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 2810, 1621, 1594, 1525, 1515, 1206, 1070, 946, 817$ . – UV/Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}/\text{nm} (\lg \epsilon) = 278 (4.47), 313 (4.40)$ . –  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta/\text{ppm} = 2.97$  (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 3.00 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 6.76 (d,  $J = 9.1 \text{ Hz}$ , 4H, phenylene-H), 7.28 (d,  $J = 9.1 \text{ Hz}$ , 4H, phenylene-H), 7.78 (s, 1H, imidazole-H), 7.85 (s, 1H, imidazole-H), 8.56 (s, 1H, N=CH). – MS (70 eV);  $m/z$  (%): 333 (100) [ $\text{M}^+$ ], 318 (6) [ $\text{M}^+ - \text{CH}_3$ ].

$\text{C}_{20}\text{H}_{23}\text{N}_5$  Calcd.: C 72.04 H 6.95 N 21.00  
(333.4) Found: C 71.94 H 6.86 N 21.14.

*1-(4-Hydroxyphenyl)-4-[N-(4-hydroxyphenyl)-iminomethyl]-1H-imidazole (16c)*

A suspension of **15** [11] (1.19 g, 4.0 mmol) and *p*-aminophenol (0.87 g, 8.0 mmol) in MeOH (30 ml) was refluxed for 30 h.

The hot mixture was suction, filtered and the precipitate, formed after cooling to  $-20\text{ }^{\circ}\text{C}$ , collected by filtration. Colourless shining crystals, *m.p.*  $235\text{ }^{\circ}\text{C}$ , yield 0.30 g (24%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1631, 1519, 1506, 1189, 1083, 970, 833$ . – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 289 (4.22), 336 (4.24). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 3.19$  (s, 3H,  $\text{CH}_3\text{OH}$ ), 6.80 (d,  $J = 8.7$  Hz, 2H, phenylene-H), 6.91 (d,  $J = 9.0$  Hz, 2H, phenylene-H), 7.14 (d,  $J = 8.7$  Hz, 2H, phenylene-H), 7.52 (d,  $J = 9.0$  Hz, 2H, phenylene-H), 8.15 (s, 1H, imidazole-H), 8.22 (s, 1H, imidazole-H), 8.45 (s, 1H, N=CH). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 48.54$  ( $\text{CH}_3\text{OH}$ ), 115.66, 116.07, 119.58, 121.93, 122.33, 128.35, 136.63, 140.98, 143.10, 151.38, 155.79, 156.81. – MS (70 eV);  $m/z$  (%): 279 (100)  $[\text{M}^+]$ , 251 (10), 109 (25)  $[\text{HOC}_6\text{H}_4\text{NH}_2]$ .

$\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2 \times \text{CH}_3\text{OH}$  Calcd.: C 65.58 H 5.50 N 13.50 (311.3) Found: C 65.39 H 5.29 N 13.48.

*1-(4-Methoxyphenyl)-4-[N-(4-methoxyphenyl)-iminomethyl]-1H-imidazole (16d)*

A solution of *p*-anisidine (0.74 g, 6.0 mmol) in MeOH (10 ml) was added dropwise to a solution of **15** [11] (0.59 g, 2.0 mmol) in MeOH (10 ml). The mixture was refluxed for 16 h, cooled to  $-20\text{ }^{\circ}\text{C}$ , and the precipitate was collected by suction filtration. Yellow-brown shining crystals, *m.p.*  $143\text{--}146\text{ }^{\circ}\text{C}$ , yield 0.69 g (76%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1628, 1595, 1542, 1519, 1502, 1187, 1089, 1075, 969, 835, 625$ . – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 288 (4.11), 332 (4.11). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 2.57$  (s, 6H, N( $\text{CH}_3$ )<sub>2</sub>), 3.78 (s, 3H,  $\text{OCH}_3$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ), 6.97 (d,  $J = 8.9$  Hz, 2H, phenylene-H), 7.10 (d,  $J = 9.0$  Hz, 2H, phenylene-H), 7.24 (d,  $J = 8.9$  Hz, 2H, phenylene-H), 7.67 (d,  $J = 9.0$  Hz, 2H, phenylene-H), 8.25 (s, 1-H, imidazole-H), 8.32 (s, 1H, imidazole-H), 8.48 (s, 1H, N=CH). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 34.33$  (N( $\text{CH}_3$ )<sub>2</sub>), 55.19 ( $\text{OCH}_3$ ), 55.44 ( $\text{OCH}_3$ ), 114.37, 114.88, 120.07, 121.91, 122.14, 129.63, 136.82, 140.90, 144.54, 152.31, 157.52, 158.40. – MS (70 eV);  $m/z$  (%): 307 (100)  $[\text{M}^+]$ , 292 (31)  $[\text{M}^+ - \text{CH}_3]$ .

$\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_2 \times (\text{CH}_3)_2\text{NH}_2\text{ClO}_4$  (452.9)  $\ddot{\text{E}}$  Calcd.: C 53.04 H 5.56 N 12.37 Found: C 53.04 H 5.50 N 12.23.

*1-(4-Phenylazophenyl)-4-[N-(4-(phenylazophenyl)-iminomethyl)-1H-imidazol (16e)*

A suspension of **15** [11] (0.59 g, 2.0 mmol) and 4-aminoazobenzene (1.18 g, 6.0 mmol) in MeOH (35 ml) was refluxed for 17 h; the orange precipitate was collected by suction filtration and recrystallized from dichloromethane (50 ml). Orange powder, *m.p.*  $230\text{ }^{\circ}\text{C}$ , yield 0.23 g (25%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1627, 1602, 1587, 1549, 1517, 1197, 1069, 966, 846, 767, 687$ . – UV/Vis ( $\text{CDCl}_3$ ):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 363 (4.11), 450 (sh). – MS (70 eV);  $m/z$  (%): 455 (55)  $[\text{M}^+]$ , 350 (100)  $[\text{M}^+ - \text{C}_6\text{H}_5\text{N}_2]$ .

$\text{C}_{28}\text{H}_{21}\text{N}_7$  Calcd.: C 73.83 H 4.65 N 21.52 (455.5) Found: C 73.69 H 4.73 N 21.60.

*1-(2,2,6,6-Tetramethylpiperidine-4-yl)-4-[N-(2,2,6,6-tetramethylpiperidine-4-yl)iminomethyl]-1H-imidazolium perchlorate (17)*

A warm solution of **15** [11] (0.59 g, 2.0 mmol) and 4-amino-

2,2,6,6-tetramethylpiperidine (0.63 g, 4.0 mmol) in MeOH (20 ml) was refluxed for 18 h. The hot mixture was suction-filtered; after cooling, the colorless precipitate was collected by suction filtration, washed with MeOH and ether and recrystallized from MeOH (35 ml). Transparent colourless crystals, *m.p.*  $291\text{ }^{\circ}\text{C}$ , yield 40 mg (4%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 2970, 2930, 1653, 1109, 626$ . – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 260 (4.20). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 1.18$  (s, 6H,  $\text{CH}_3$ ), 1.29 (s, 6H,  $\text{CH}_3$ ), 1.35 (s, 6H,  $\text{CH}_3$ ), 1.41 (s, 6H,  $\text{CH}_3$ ), 1.60 (sept,  $J = 12.6$  Hz, 4H), 1.72 (dd,  $J = 13.5, 3.9$  Hz, 2H), 1.92 (dd,  $J = 12.4, 3.1$  Hz, 2H), 3.75 (m, 1H, piperidine-4-H), 4.69 (m, 1H, piperidine-4-H), 7.69 (s, 1H, imidazole-H), 7.83 (s, 1H, imidazole-H), 8.30 (s, 1H, N=CH). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 25.20, 26.91, 30.50, 32.83, 42.58, 43.80, 49.39, 52.53, 55.41, 59.20, 118.60$  (d,  $^1J_{\text{C,H}} = 193$  Hz, imidazole-C-5), 136.63 (d,  $^1J_{\text{C,H}} = 208$  Hz, imidazole-C-2), 139.15 (s, imidazole-C-4), 155.49 (d,  $^1J_{\text{C,H}} = 157$  Hz, N=CH). – MS (70 eV);  $m/z$  (%): 373 (3)  $[\text{M}^+ - \text{HClO}_4]$ , 358 (51)  $[\text{M}^+ - \text{HClO}_4 - \text{CH}_3]$ , 124 (100).

$\text{C}_{22}\text{H}_{40}\text{ClN}_5\text{O}_4$  Calcd.: C 55.74 H 8.50 N 14.77 (474.1) Found: C 54.73 H 8.30 N 14.56.

*Poly[4-iminomethyl-1-(1,4-phenylene)-1H-imidazole] (18a)*

A solution of **15** [11] (1.19 g, 4.0 mmol), *p*-phenylenediamine (0.43 g, 4.0 mmol) and acetic acid (10 drops) in MeOH (30 ml) was refluxed for 24 h. The precipitate was collected by suction filtration and washed with water and MeOH. Brown powder, *m.p.*  $> 350\text{ }^{\circ}\text{C}$ , yield 0.69 g (92%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1630, 1600, 1514, 1201, 1071, 968, 872, 837, 792$ . ( $\text{C}_{10}\text{H}_7\text{N}_3 \times \text{H}_2\text{O}$ )<sub>n</sub> Calcd.: C 64.16 H 4.84 N 22.45 (187.2)<sub>n</sub> Found: C 62.46 H 4.57 N 21.98.

*Poly[4-iminomethyl-1-(4,4'-phenylenevinylphenylene)-1H-imidazole] (18b)*

A suspension of **15** [11] (2.37 g, 8.0 mmol) and 4,4'-diaminostilbene (1.68 g, 8.0 mmol) and acetic acid (10 drops) in MeOH (55 ml) was warmed to  $60\text{ }^{\circ}\text{C}$  for 19 h. The precipitate was collected from the warm mixture by suction filtration and washed with water, MeOH, and ether. Brown powder, *m.p.*  $> 350\text{ }^{\circ}\text{C}$ , yield 2.0 g (86%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 1626, 1606, 1519, 1199, 967, 834$ .

( $\text{C}_{18}\text{H}_{13}\text{N}_3 \times \text{H}_2\text{O}$ )<sub>n</sub> Calcd.: C 74.72 H 5.22 N 14.52 (289.3)<sub>n</sub> Found: C 75.58 H 5.32 N 13.97.

*1-(4-Methoxyphenyl)-4-[N-(4-methoxyphenyl)-iminomethyl]-3-methyl-imidazolium perchlorate (19a)*

A suspension of **7b** [11] (0.82 g, 2.0 mmol) and *p*-anisidine (0.49 g, 4.0 mmol) in MeOH (30 ml) was refluxed for 18 h. The precipitate was collected from the hot mixture by suction filtration and washed with MeOH and ether. Colourless powder, *m.p.*  $240\text{--}241\text{ }^{\circ}\text{C}$ , yield 0.60 g (71%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1} = 2840, 1641, 1616, 1595, 1518, 1090, 835, 626$ . – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 341 (4.22). –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta/\text{ppm} = 3.81$  (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ), 4.21 (s, 3H, N $\text{CH}_3$ ), 7.05 (d,  $J = 8.9$  Hz, 2H, phenylene-H), 7.23 (d,  $J = 9.0$  Hz, 2H, phenylene-H), 7.43 (d,  $J = 8.9$  Hz, 2H, phenylene-H), 7.76 (d,  $J = 9.0$  Hz, 2H, phenylene-H), 8.71 (s, 1H, imidazolium-H), 8.72 (s, 1H,

N=CH), 9.81 (s, 1H, imidazolium-H). –  $^{13}\text{C}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 36.09 (NCH<sub>3</sub>), 55.33 (OCH<sub>3</sub>), 55.74 (OCH<sub>3</sub>), 114.54, 115.17, 122.86, 123.33, 123.40, 127.48, 131.31, 137.92, 142.41, 144.77, 158.98, 160.13.

C<sub>19</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>6</sub> Calcd.: C 54.10 H 4.78 N 9.96 (421.8) Found: C 54.04 H 4.87 N 9.77.

*1-(4-Dimethylaminophenyl)-4-[N-(4-dimethylaminophenyl)-iminomethyl]-3-methyl-imidazolium perchlorate (19b)*

A suspension of **7b** [11] (0.82 g, 2.0 mmol) and *N,N*-dimethyl-*p*-phenylenediamine (0.54 g, 4.0 mmol) in MeOH (35 ml) was refluxed for 17 h. The precipitate was collected from the hot mixture by suction filtration. Pale brown powder, *m.p.* 218 °C, yield 0.34 g (38%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 2810, 1634, 1611, 1594, 1523, 1095, 821, 625. – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  (lg  $\epsilon$ ) = 307 (4.22), 401 (4.35). –  $^1\text{H}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 2.96 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.99 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 4.17 (s, 3H, NCH<sub>3</sub>), 6.79 (d, *J* = 9.1 Hz, 2H, phenylene-H), 6.89 (d, *J* = 9.2 Hz, 2H, phenylene-H), 7.37 (d, *J* = 9.1 Hz, 2H, phenylene-H), 7.58 (d, *J* = 9.2 Hz, 2H, phenylene-H), 8.54 (s, 1H, imidazolium-H), 8.67 (s, 1H, N=CH), 9.67 (s, 1H, imidazolium-H). –  $^{13}\text{C}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 35.97 (NCH<sub>3</sub>), 39.87 (N(CH<sub>3</sub>)<sub>2</sub>), 112.19, 112.22, 122.09, 122.34, 122.82, 123.12, 131.65, 136.79, 137.76, 140.81, 150.15, 150.81.

C<sub>21</sub>H<sub>26</sub>ClN<sub>5</sub>O<sub>4</sub> Calcd.: C 56.31 H 5.85 N 15.64 (447.9) Found: C 56.65 H 5.91 N 15.52.

*3-Dimethylamino-N,N-dimethyl-2-[4-(N,N-dimethyliminioformylamino)-phenyl]-prop-2-eneiminium bis(perchlorate) (21)*

Phosphoryl chloride (61.08 g, 0.40 mol) was added dropwise to dimethylformamide (81.7 g, 1.12 mol) at 0 °C. After 1 h, *p*-aminophenylacetic acid (20.0 g, 0.13 mol) was added to the mixture at room temperature (evolution of heat and a gas). The solution was maintained at 90 °C for 17 h and then at 125 °C for 2 h. After cooling to room temperature, a black oil was formed. Water (200 ml) was added and the mixture filtered. Perchloric acid (70%; 22.8 ml, 0.26 mmol) was added to the filtrate, the suspension was stirred at –35 °C for 1 h. The precipitate was collected by suction filtration and washed with cold MeOH. Brown powder, *m.p.* 270 °C, yield 45.5 g (74%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 2933, 1700, 1590, 1090, 784, 626. – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  (lg  $\epsilon$ ) = 319 (4.62). –  $^1\text{H}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 2.47 (s, 6H, NCH<sub>3</sub>), 3.23 (s, 3H, NCH<sub>3</sub>), 3.26 (s, 6H, NCH<sub>3</sub>), 3.36 (s, 3H, NCH<sub>3</sub>), 7.40 (d, *J* = 9.0 Hz, 2H, phenylene-H), 7.45 (d, *J* = 9.0 Hz, 2H, phenylene-H), 7.71 (s, 2H, vinamidinium–NCHC), 8.71 (s, 1H, amidinium–NCHN), 10.94 (s, 1H, NH). –  $^{13}\text{C}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 36.95 (q,  $^1J_{\text{C,H}}$  = 142 Hz, NCH<sub>3</sub>), 39.29 (q,  $^1J_{\text{C,H}}$  = 140 Hz, NCH<sub>3</sub>), 43.31 (q,  $^1J_{\text{C,H}}$  = 141 Hz, NCH<sub>3</sub>), 48.47 (q,  $^1J_{\text{C,H}}$  = 140 Hz, NCH<sub>3</sub>), 103.96 (s, vinamidinium–NCHC), 118.68 (d,  $^1J_{\text{C,H}}$  = 177 Hz, phenylene–C<sup>3,5</sup>), 129.70 (s), 133.24 (d,  $^1J_{\text{C,H}}$  = 163 Hz, phenylene–C<sup>2,6</sup>), 138.19 (s), 153.53 (d,  $^1J_{\text{C,H}}$  = 195 Hz, amidinium–NCHN), 162.91 (d,  $^1J_{\text{C,H}}$  = 171 Hz, vinamidinium–NCHC).

C<sub>16</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>8</sub> Calcd.: C 40.60 H 5.54 N 11.84 (473.3) Found: C 40.96 H 5.63 N 11.53.

*2-(4-Aminophenyl)-3-dimethylamino-N,N-dimethyl-prop-2-eneiminium perchlorate (23)*

The vinamidinium salt **21** (4.74 g, 10.0 mmol) was added in portions to the solution of *p*-anisidine (1.85 g, 15.0 mmol) in EtOH (150 ml) and the suspension was warmed to 70 °C for 20 h. The warm mixture mixture was suction-filtered. After cooling, the precipitate was collected by suction filtration and washed with EtOH. Pale brown powder, *m.p.* 229 °C (dec.), yield 2.43 g (77%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 3378, 2932, 1583, 1529, 1109, 825, 784, 625. – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  (lg  $\epsilon$ ) = 315 (4.53). –  $^1\text{H}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 2.53 (s, 6H, NCH<sub>3</sub>), 3.21 (s, 6H, NCH<sub>3</sub>), 5.34 (br. s, 2H, NH<sub>2</sub>), 6.58 (d, *J* = 8.4 Hz, 2H, phenylene-2,6-H), 6.86 (d, *J* = 8.4 Hz, 2H, phenylene-3,5-H), 7.61 (s, 2H, vinamidinium–NCHC). –  $^{13}\text{C}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 38.31 (NCH<sub>3</sub>), 48.29 (NCH<sub>3</sub>), 105.92 (vinamidinium–NCHC), 113.41 (phenylene–C<sup>3,5</sup>), 117.77 (phenylene–C<sup>1</sup>), 132.36 (phenylene–C<sup>2,6</sup>), 148.90 (phenylene–C<sup>4</sup>), 163.34 (vinamidinium–NCHC).

C<sub>13</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>4</sub> Calcd.: C 49.14 H 6.34 N 13.22 (317.8) Found: C 49.46 H 6.40 N 13.17.

*N-(4-Methoxyphenylamino)-N',N'-dimethyl-methaneiminium perchlorate (24a)*

Ether (300 ml) was added to the filtrate of the preparation of **23**. After 10 min, crystals were collected by filtration. Yellow crystals, *m.p.* 159 °C, yield 1.60 g (58%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 1703, 1512, 1109, 831, 770, 625. – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  (lg  $\epsilon$ ) = 267 (4.17), 304 (sh). –  $^1\text{H}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 3.19 (s, 3H, NCH<sub>3</sub>), 3.33 (s, 3H, NCH<sub>3</sub>), 3.77 (s, 3H, OCH<sub>3</sub>), 7.03 (d, *J* = 6.8 Hz, 2H, phenylene-H), 7.34 (d, *J* = 6.8 Hz, 2H, phenylene-H), 8.56 (s, 1H, amidinium–NCHN), 10.80 (br. s, 1H, NH). –  $^{13}\text{C}$  NMR ([D<sub>6</sub>] DMSO):  $\delta$  = 36.77 (NCH<sub>3</sub>), 43.16 (NCH<sub>3</sub>), 55.35 (OCH<sub>3</sub>), 114.68 (phenylene–C<sup>3,5</sup>), 121.05 (phenylene–C<sup>2,6</sup>), 130.45 (phenylene–C<sup>1</sup>), 153.57 (amidinium–NCHN), 157.47 (phenylene–C<sup>4</sup>).

C<sub>10</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>5</sub> Calcd.: C 43.10 H 5.43 N 10.05 (278.7) Found: C 43.56 H 5.39 N 10.10.

*N-(4-Dimethylaminophenylamino)-N',N'-dimethyl-methaneiminium perchlorate (24b)*

The vinamidinium salt **21** (4.74 g, 10.0 mmol) was added in portions to a solution of *N,N*-dimethyl-*p*-phenylenediamine (1.36 g, 10.0 mmol) in EtOH (150 ml) and the suspension was maintained at 70 °C for 22 h. The warm mixture was suction filtered. After cooling, the precipitate was collected by suction filtration and washed with EtOH (**23**). The filtrate was cooled to –20 °C, the crystals were collected by filtration and washed with EtOH. Yellow powder, *m.p.* 165 °C, yield 0.28 g (10%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 1700, 1616, 1528, 1109, 819, 625. – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  (lg  $\epsilon$ ) = 299 (4.21). –  $^1\text{H}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 2.90 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.16 (s, 3H, NCH<sub>3</sub>), 3.30 (s, 3H, NCH<sub>3</sub>), 6.78 (d, *J* = 6.8 Hz, 2H, phenylene-H), 7.22 (d, *J* = 6.8 Hz, 2H, phenylene-H), 8.48 (s, 1H, amidinium–NCHN), 10.70 (br. s, 1H, NH). –  $^{13}\text{C}$  NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 36.63 (NCH<sub>3</sub>), 40.08 (N(CH<sub>3</sub>)<sub>2</sub>), 43.02 (NCH<sub>3</sub>), 112.64 (phenylene–C<sup>3,5</sup>), 120.78 (phenylene–C<sup>2,6</sup>), 126.41 (phenylene–C<sup>1</sup>), 148.87 (phenylene–C<sup>4</sup>), 153.09 (amidinium–NCHN).

$C_{11}H_{18}ClN_3O_4$  Calcd.: C 45.29 H 6.22 N 14.40  
(291.7) Found: C 45.63 H 6.05 N 14.10.

#### 5-(4-Aminophenyl)-2-(4-nitrophenyl)-pyrimidine (22)

The vinamidinium salt **23** (0.32 g, 1.0 mmol) was added to a suspension of *p*-nitrobenzamidinium chloride (0.22 g, 1.1 mmol) in pyridine (30 ml) and the mixture maintained at 80 °C for 24 h (formation of a yellow solution). After cooling the solution to -20 °C, the crystals were collected by filtration. Yellow needles, *m.p.* > 250 °C, yield 0.17 g (58%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 3395, 1629, 1608, 870, 858, 830, 744. – UV/Vis (DMSO):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 288 (4.25), 400 (4.20). – UV/Vis (toluene):  $\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 363 (4.33). – <sup>1</sup>H NMR ([D] TFA):  $\delta/\text{ppm}$  = 7.90 (d, *J* = 8.6 Hz, 2H, phenylene-H), 8.07 (d, *J* = 8.6 Hz, 2H, phenylene-H), 8.62 (d, *J* = 8.9 Hz, 2H, phenylene-H), 8.70 (d, *J* = 8.9 Hz, 2H, phenylene-H), 9.72 (s, 2H, pyrimidine-H), 11.65 (br. s, 3H, NH<sub>3</sub><sup>+</sup>). – <sup>13</sup>C NMR ([D] TFA):  $\delta/\text{ppm}$  = 126.96, 127.11, 131.58, 132.40, 133.54, 134.15, 136.35, 136.44, 153.49 (C–NO<sub>2</sub>), 158.00 (pyrimidine–CHN), 158.68 (pyrimidine–NCN). – MS (70 eV); *m/z* (%): 292 (100) [M<sup>+</sup>], 262 (12) [M<sup>+</sup>–NO], 246 (31) [M<sup>+</sup>–NO<sub>2</sub>], 117 (26) [*p*-aminophenylacetylene].  
 $C_{16}H_{12}N_4O_2$  Calcd.: C 65.75 H 4.14 N 19.17  
(292.3) Found: C 65.63 H 4.24 N 19.25.

#### Synthesis of the Vinamidinium salts 27 and 28a

##### 2-(4-Dimethylamino)-3-dimethylamino-*N,N*-dimethyl-prop-2-eneiminium perchlorate (27)

Phosphoryl chloride (7.67 g, 50.0 mmol) was added to dimethylformamide (14.25 g, 195.0 mmol) under ice cooling. After 1 h, *p*-dimethylaminophenylacetic acid (4.48 g, 25.0 mmol) was added at 0 °C and the solution was maintained at 65 °C for 17 h and at 125 °C for 3 h (evolution of a gas). After cooling the black product to room temperature, water (25 ml) was added and the mixture filtered. Perchloric acid (70%; 2.16 ml, 25.0 mmol) was added to the filtrate at -10 °C. After cooling to -40 °C, the precipitate was collected by suction filtration, washed with cold EtOH and dried at 100 °C. Pale brown powder, yield 2.25 g. – <sup>1</sup>H NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 2.48 (s, 6H, NCH<sub>3</sub>), 3.00 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.23 (s, 6H, NCH<sub>3</sub>), 6.98 (d, *J* = 8.4 Hz, 2H, phenylene-H), 7.14 (d, *J* = 8.4 Hz, 2H, phenylene-H), 7.67 (s, 2H, vinamidinium–NCHC).

##### 2-[6-(1,2,3,4-Tetrahydro-1,1,3-trimethylquinazolinio)]-3-dimethylamino-*N,N*-dimethyl-prop-2-eneiminium bis(perchlorate) (28a)

Phosphoryl chloride (11.5 g, 75.0 mmol) was added to dimethylformamide (21.4 g, 293 mmol) under ice cooling. After 1 h, *p*-dimethylaminophenylacetic acid (4.48 g, 25.0 mmol) was added at room temperature and the solution was maintained at 85 °C for 22 h (evolution of a gas) and at 125 °C for 4 h. After cooling to room temperature, the black product was poured into water (50 ml). Perchloric acid (70%; 9.2 ml, 104 mmol) was added at -10 °C and the mixture cooled to -40 °C. The precipitate was collected by suction filtration, washed with cold EtOH and dried at 100 °C. Pale brown powder, *m.p.* > 250 °C, yield 4.23 g (17%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 2950, 1590, 1100, 815, 625. – UV/Vis (DMSO):

$\lambda_{\text{max}}/\text{nm}$  ( $\lg \epsilon$ ) = 271 (4.40), 316 (4.63).

$C_{18}H_{30}Cl_2N_4O_8$  Calcd.: C 43.12 H 6.03 N 11.18  
(501.4) Found: C 42.14 H 5.93 N 10.97.

##### 2-[6-(1,2,3,4-Tetrahydro-1,1,3-trimethylquinazolinio)]-3-dimethylamino-*N,N*-dimethyl-prop-2-eneiminium bis(1,1,3,3-tetracyanopropenide) (28b)

A solution of potassium tetracyanopropenide [25] in water (15 ml) was added to **28a** (0.15 g, 0.30 mmol), dissolved in water (50 ml) under warming. After 20 h, crystals were collected by filtration. Transparent, thin colourless platelets, *m.p.* 141 °C, yield 90 mg (51%). – IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 2934, 2192, 1589, 1551, 814. – <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta/\text{ppm}$  = 2.49 (s, 6H, vinamidinium–NCH<sub>3</sub>), 3.08 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.13 (s, 3H, NCH<sub>3</sub>), 3.24 (s, 6H, vinamidinium–NCH<sub>3</sub>), 4.61 (s, 2H, CH<sub>2</sub>), 4.70 (s, 2H, CH<sub>2</sub>), 6.98 (d, *J* = 8.4 Hz, 1H, quinazolinium–H), 6.99 (s, 1H, quinazolinium–5-H), 7.19 (d, *J* = 8.4 Hz, 1H, quinazolinium–H), 7.21 (s, 2H, propenide-2-H), 7.68 (s, 2H, vinamidinium–NCHC). – <sup>13</sup>C NMR ([D<sub>6</sub>] DMSO):  $\delta/\text{ppm}$  = 37.73 (NCH<sub>3</sub>), 39.27 (NCH<sub>3</sub>), 48.17 (NCH<sub>3</sub>), 48.49 (NCH<sub>3</sub>), 50.64 (C(CN)<sub>2</sub>), 62.07 (CH<sub>2</sub>), 76.19 (CH<sub>2</sub>), 104.35 (vinamidinium–NCHC), 112.67 (CH), 114.04 (CN), 115.50 (CN), 119.03, 122.40, 130.48 (CH), 132.61 (CH), 140.73, 154.48 (propenide–CH), 163.23 (vinamidinium–NCHC).

$C_{32}H_{32}N_{12}$  Calcd.: C 65.74 H 5.52 N 28.75  
(584.7) Found: C 65.77 H 5.59 N 28.48.

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- [13] Crystal data for **5b**:  $C_{28}H_{30}N_{12}$ ,  $M = 534.63$ , orthorhombic, space group  $Pbcn$  (# 60),  $a = 17.461(6)$  Å,  $b = 8.254(2)$  Å,  $c = 20.723(7)$  Å,  $\alpha = 90.00(2)^\circ$ ,  $\beta = 90.00(2)^\circ$ ,  $\gamma = 90.00(2)^\circ$ ,  $Z = 4$ ,  $D_c = 1.189$  g cm $^{-3}$ ,  $\mu = 0.077$  mm $^{-1}$ ,  $F(000) = 1128$ . Data collection: ENRAF-NONIUS CAD4-diffractometer,  $\omega$ -scan, scan width  $(0.60 + 0.35 \tan \Theta)^\circ$ ,  $\Theta_{max} = 22.98^\circ$ ,  $\Theta_{min} = 2.03^\circ$ , crystal dimensions  $33 \times 40 \times 60$  mm, maximum measuring time 60 s, graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). 2733 measured, 2074 independent reflections, 1819 classed as observed ( $I > 2\sigma I$ ); refined parameters: 185/0. Solution of structure: SHELXS86, refinement with SHELXS93. Final  $R1 = 0.0440$  and  $wR2 = 0.1525$  for  $2\sigma I$ ;  $R1 = 0.0498$  and  $wR2 = 0.1650$  for all data; largest/smallest residual electron density  $\rho = 0.160/-0.180$  e Å $^{-3}$ . Supplementary material on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408534, the names of the authors and the journal citation.
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- [18] Crystal data for **16a**:  $C_{16}H_{13}N_3$ ,  $M = 247.29$ , monoclinic, space group  $P2_1/C$  (# 14),  $a = 15.334(5)$  Å,  $b = 11.167(4)$  Å,  $c = 7.536(2)$  Å,  $\alpha = 90.00(2)^\circ$ ,  $\beta = 93.27(2)^\circ$ ,  $\gamma = 90.00(2)^\circ$ ,  $Z = 4$ ,  $D_c = 1.275$  g cm $^{-3}$ ,  $\mu = 0.078$  mm $^{-1}$ ,  $F(000) = 520$ . Data collection: ENRAF-NONIUS CAD4-diffractometer,  $\omega$ -scan, scan width  $(0.50 + 0.35 \tan \Theta)^\circ$ ,  $\Theta_{max} = 22.97^\circ$ ,  $\Theta_{min} = 2.26^\circ$ , crystal dimensions  $40 \times 47 \times 53$  mm, maximum measuring time 60 s, graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). 2061 measured, 1785 independent reflections, 1616 classed as observed ( $I > 2\sigma I$ ); refined parameters: 173/0. Solution of structure: SHELXS86, refinement with SHELXS93. Final  $R1 = 0.0328$  and  $wR2 = 0.1025$  for  $2\sigma I$ ;  $R1 = 0.0359$  and  $wR2 = 0.1088$  for all data; largest/smallest residual electron density  $\rho = 0.141/-0.135$  e Å $^{-3}$ . Supplementary material on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408535, the names of the authors and the journal citation.
- [19] Crystal data for **21**:  $C_{16}H_{26}Cl_2N_4O_8$ ,  $M = 473.31$ , triclinic, space group  $P1$  (# 2),  $a = 9.135(2)$  Å,  $b = 9.491(2)$  Å,  $c = 13.319(5)$  Å,  $\alpha = 82.37(2)^\circ$ ,  $\beta = 84.81(2)^\circ$ ,  $\gamma = 80.35(2)^\circ$ ,  $Z = 2$ ,  $D_c = 1.394$  g cm $^{-3}$ ,  $\mu = 0.337$  mm $^{-1}$ ,  $F(000) = 494$ . Data collection: ENRAF-NONIUS CAD4-diffractometer,  $\omega$ -scan, scan width  $(0.85 + 0.35 \tan \Theta)^\circ$ ,  $\Theta_{max} = 22^\circ$ , crystal dimensions  $0.17 \times 0.40 \times 0.47$  mm, maximum measuring time 60 s, graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). 2884 measured, 2739 independent reflections, 2332 classed as observed ( $I > 2\sigma I$ ); refined parameters: 334/122. Solution of structure: SHELXS86, refinement with SHELXS93. Final  $R1 = 0.0573$  and  $wR2 = 0.1548$  for  $2\sigma I$ ;  $R1 = 0.0667$  and  $wR2 = 0.1625$  for all data; largest/smallest residual electron density  $\rho = 0.421/-0.283$  e Å $^{-3}$ . Supplementary material on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408536, the names of the authors and the journal citation.
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