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Bis-(Pyrimidiniumolates)

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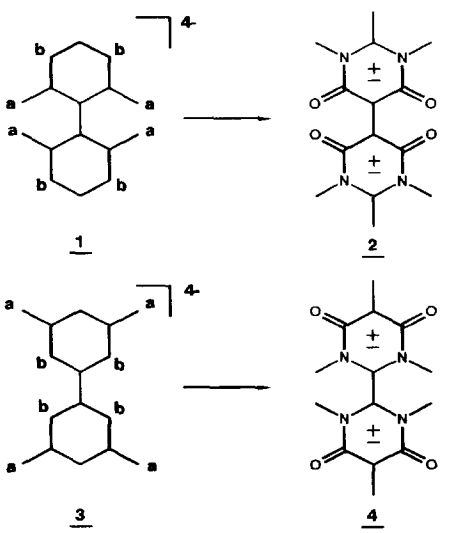
Abstract: The preparation of bis-(pyrimidiniumolates) (**8a-d, 10**) is described. Semiempirical quantum chemical calculations (AM1, PM3) for **2a, 8a, 10, 11** and **12** and an *ab initio* treatment (6-31G*) of **2a** are reported. Copyright © 1996 Published by Elsevier Science Ltd

Introduction

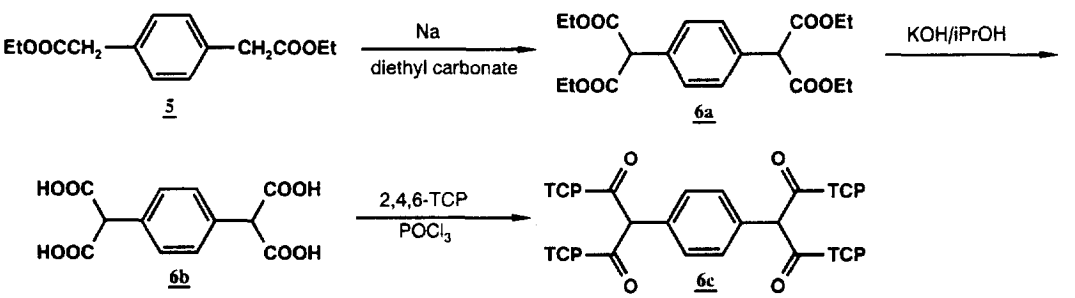
If in tetramethylenbiphenyl tetraanions of type **1** and **3** the centers a and b are substituted against (carbonyl)oxygen and nitrogen atoms, bis-(pyrimidiniumolates)[1] (**2, 4**) are generated. Compounds of this type seem to be unknown, although quite a few examples were described, where mesoionic or other dipolar heterocycles[4] are connected in such a manner[5]. Whereas simple pyrimidiniumolates show a high dipole moment[9], for reasons of symmetry the dipole moments of **2** and **4** must be zero. In connection with our studies on novel liquid crystals with dipolar structure elements[10] it seemed of interest to investigate such systems. In this paper the preparation of phenylogues of **2** and **4** (**8, 10**) is described.

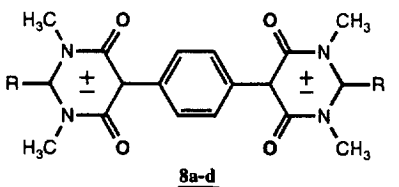


Experimental results

Simple pyrimidiniumolates are known since 1971[3,11,12]. They can be prepared quite conveniently by treatment of N,N'-disubstituted amidines with reactive malonic acid derivatives, e.g., acid chlorides (chlorocarbonylketenes, carbon suboxide[13]) or trichlorophenylesters (TCPM procedure of Kappe and coworkers[3,14]). As starting material for the synthesis of **8** a malonic acid derivative of type **6** was needed. The tetraester **6a** can be prepared either from phenylacetic acid by a known route[8c] or simply by Pd-assisted coupling[15] of diethyl 4-bromophenylmalonate with diethyl malonate. The saponification of **6a** must be conducted under strictly controlled conditions; otherwise decarboxylation takes place.

From **6b** the TCP ester **6c** is available by treatment with 2,4,6-trichlorophenol/$POCl_3$. The condensation of **6c** with the N,N-dimethylamidines **7**[16,17] yields **8a-d** as colorless or faintly yellow high melting crystalline materials.

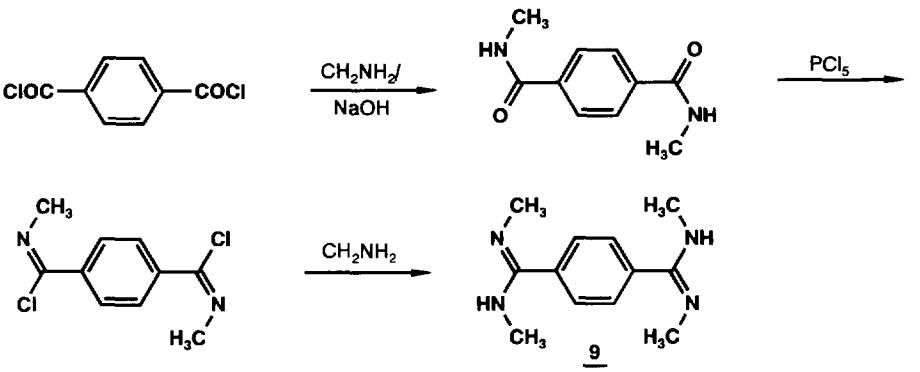




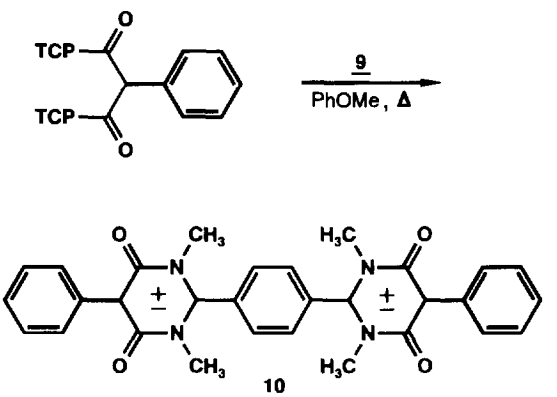
8a-d

7, 8	R
a	phenyl
b	p-methoxyphenyl
c	p-nitrophenyl
d	n-heptyl

Compound **10** is available on a similar route. Treatment of bisamidine **9**, which is in turn accessible from terephthalic acid, with the corresponding trichlorophenylmalonate yields **10** as a colorless solid with high melting point, although in low yields (18%).



It should be remarked that even for those bis-(pyrimidiniumolates) which carry long alkyl side chains (**8d**, mp 295-298° C) liquid crystalline behaviour was not observed, although compounds with high melting points which show such properties are well known[20].



Theoretical Investigations

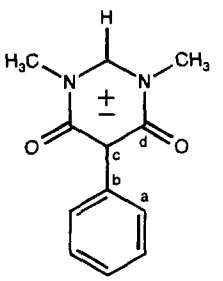
The solution state structures of **8** and **10** are not known with certainty. In order to gain some insight into the geometry of these compounds semiempirical quantum chemical calculations for **8a** and **10**

using the AM1 and PM3 hamiltonians[21,22] have been performed. Both **8** and **10** can adopt several conformations which are minima on the potential hypersurface (PES)[23].

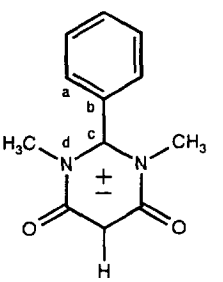
The conformers of **8a** and **10** have been investigated in some detail (see Fig.3,4). In **8a** the phenyl rings A and C are nearly perpendicular to the pyrimidiniumolate system, whereas ring B is twisted in conformer **A** by 36.2° (AM1; PM3: 62.3°) and in conformer **B** by 35.8° (AM1; PM3:63.3°).

For **10** a twist angle ω(a-b-c-d) of 36.2° (AM1; PM3: 72.2°) is found (conformer **B**: ω(a-b-c-d)= 36.2° (AM1; PM3: 71.8°)).

Model studies on **11** and **12** show a rotational barrier for the phenyl rings of 2.4 kcal/mol (Fig.1) and 17.9 kcal/mol (Fig.2; AM1 values). Introduction of bulkier substituents in the *ortho*-positions of the phenyl ring of **11** should give rise to atropisomeric pyrimidiniumolates[23].



11



12

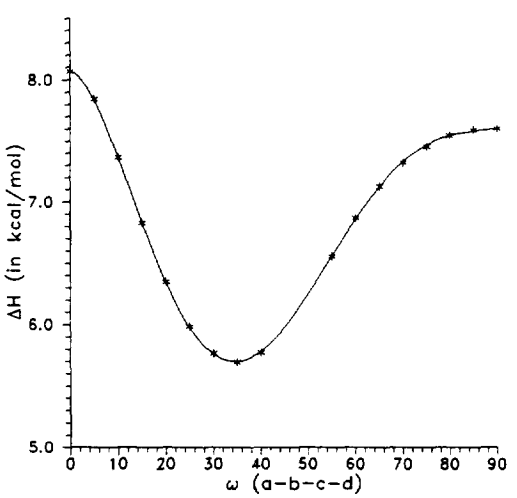


Fig. 1
Rotational barrier for **11** (0 °< ω< 90 °, AM1 values)

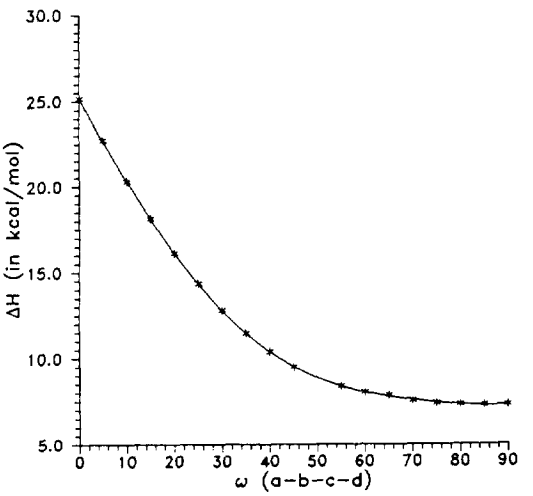
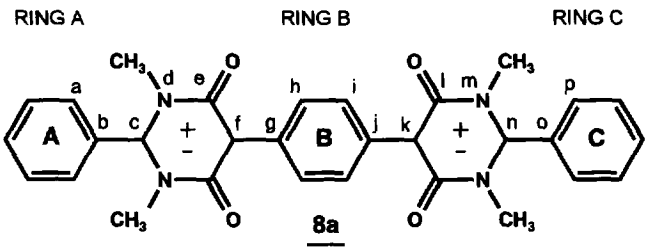


Fig. 2
Rotational barrier for **12** (0 °< ω< 90 °, AM1 values)



CONFORMER A CONFORMER B

dihedral	*AM1*	*PM3*	*AM1*	*PM3*
ω (a-b-c-d)	87.6	90.0	-91.0	-89.8
ω (e-f-g-h)	36.2	62.3	35.8	63.3
ω (i-j-k-l)	36.2	62.3	-35.8	-63.3
ω (m-n-o-p)	87.6	90.0	-91.0	-89.8

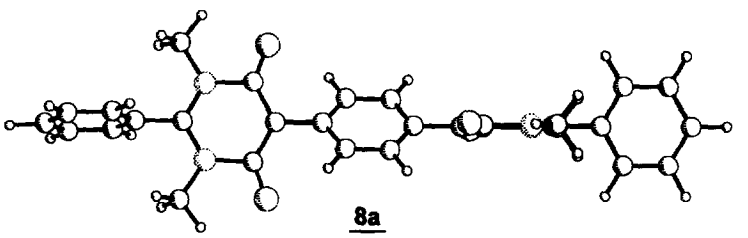
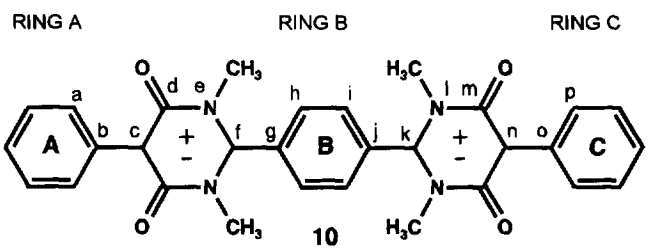
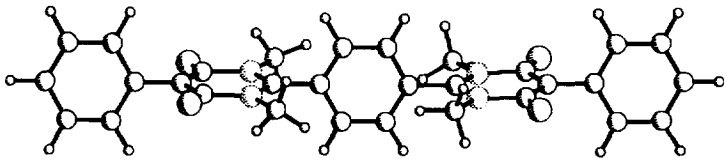


Fig. 3: Calculated structure for 8a (AM1)



CONFORMER A CONFORMER B

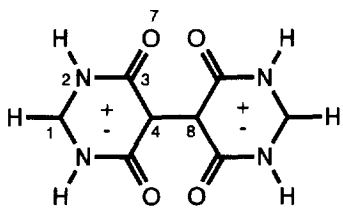
dihedral	*AM1*	*PM3*	*AM1*	*PM3*
ω (a-b-c-d)	36.2	-72.2	36.2	-71.8
ω (e-f-g-h)	91.1	90.0	90.0	90.0
ω (i-j-k-l)	- 91.1	90.0	90.0	90.0
ω (m-n-o-p)	- 36.2	72.2	36.2	-71.8



10

Fig. 4: Calculated structure for **10** (AM1)

Ab initio calculations[25] (6-31G* level)[27] on the parent system **2** show that in the most stable conformation both rings are perpendicular to one another; this result is in accord with AM1 and PM3 studies. The rotational barrier is calculated as 19.2 kcal/mol (AM1), 20.5 kcal/mol (PM3), and 21.9 kcal/mol (*ab initio*, 6-31G*), resp. X-ray investigations of simple pyrimidiniumolates[28] reveal an extraordinary long N-CO bond. This is in accord with expectations[29] and with AM1, PM3 and *ab initio* calculations (Table 1).



2

Table 1: Bond distances of **2** (AM1, PM3 and *ab initio* (6-31 G*)); values in Ångstrøm

method	r_{1-2}	r_{2-3}	r_{3-4}	r_{3-7}	r_{4-8}
AM1	1.342	1.465	1.423	1.243	1.444
PM3	1.352	1.491	1.415	1.223	1.452
6-31G*	1.297	1.462	1.408	1.201	1.475

Appendix

As already mentioned in the **Introduction**, on a simple topological level compounds of type **2** and **4** may be considered as perturbed hydrocarbon tetraanions of type **1** and **3**, resp. It is of interest, that the eigenvalues (and eigenvectors) of these graphs can be expressed in closed form[30].

The characteristic polynomials are obtained as $P(\varepsilon)(1) = \varepsilon^{16} - 17\,\varepsilon^{14} + 112\,\varepsilon^{12} - 368\,\varepsilon^{10} + 644\,\varepsilon^{8} - 580\,\varepsilon^{6} + 244\,\varepsilon^{4} - 16\,\varepsilon^{2} = (\varepsilon - 1)(\varepsilon + 1)(\varepsilon^{4} - 2\,\varepsilon^{3} - 4\,\varepsilon^{2} + 8\,\varepsilon - 2)(\varepsilon^{4} - 2\,\varepsilon^{3} - 4\,\varepsilon^{2} - 8\,\varepsilon - 2)(\varepsilon^{2} - 2)^{2}$ and $P(\varepsilon)(3) = \varepsilon^{16} - 17\,\varepsilon^{14} + 112\,\varepsilon^{12} - 364\,\varepsilon^{10} + 612\,\varepsilon^{8} - 496\,\varepsilon^{6} + 144\,\varepsilon^{4} = \varepsilon^{4}(\varepsilon^{4} + \varepsilon^{3} - 6\,\varepsilon^{2}\,4\,\varepsilon + 6)(\varepsilon^{4} - \varepsilon^{3} - 6\,\varepsilon^{2}\,4\,\varepsilon - 6)(\varepsilon^{2} - 2)^{2}$. The HOMO-LUMO difference for **1** is calculated as $\Delta\varepsilon$ (HOMO-LUMO) = $\varepsilon_{10} - \varepsilon_{11} = -(3 - (5 + 3^{1/2})^{1/2})^{1/2}) + 1.0\,[\beta] = 0.699\,\beta$. The expression for **3** is slightly more complicated.

$\Delta\varepsilon$ (HOMO-LUMO)(**3**) is calculated as $\Delta\varepsilon = 0.788\,\beta$. That means that on this level of theory compounds of type **1** should absorb at slightly longer wavelength than compounds of type **3**, but after introduction of suitably modified Coulomb integrals at position a ($0 \leq \alpha_a \leq 2$) and b ($0 \leq \alpha_b\ 2$) one obtains $\Delta\Delta\varepsilon$(HOMO-LUMO) = $\Delta\varepsilon$(HOMO-LUMO)(**1**) - $\Delta\varepsilon$(HOMO-LUMO)(**3**) > 0 for all reasonable values of α_a (= α[N]) and α_b (= α[O])[35,36].

Experimental Section

Melting points were taken on a Büchi melting point apparatus and are not corrected. Infrared spectra were measured on a Perkin-Elmer Paragon FFT infrared spectrometer and are reported in wavenumbers (cm^{-1}). ^{1}H and ^{13}C magnetic resonance spectra were measured on a Bruker AM200 or an AM300 magnetic resonance spectrometer and are reported in parts-per-million (ppm) downfield from tetramethylsilane internal standard (δ = 0 ppm) as the reference. Mass spectra were taken with a Finnigan MAT 8230 mass spectrometer.

p-Phenylene-bis-(diethyl malonate) (6a).

To a suspension of potassium t-butoxide (11.20 g, 100 mmol) in 100 ml of 1,2-dimethoxyethane, diethyl malonate (8.00 g, 50 mmol) was added under vigorous stirring at 0 °C. After 10 min diethyl 4-bromophenylmalonate (15.75 g, 50 mmol) and dichlorobis(triphenylphosphine)-palladium (500 mg, 0.70 mmol) were added. The mixture was heated for 20 h at 70 °C under argon. After cooling to rt, the solution was acidified with 1N hydrochloric acid and extracted with ether. The extracts were dried (Na_2SO_4) and after evaporation of the solvent the residue was purified by column chromatography on silica gel using ether/pentane as eluent. Recrystallisation from methanol gives **6a** (12.20 g, 62%) as colorless crystals with mp 74 °C (lit. mp 75 °C[8c]), ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 12H), 4.20 (q, 8H), 4.61 (s, 2H), 7.40 (s, 4H).

p-Phenylene-bis-malonic acid (6b).

To a solution of potassium hydroxide (10.0 g, 0.18 mol) in 100 ml of isopropanol, diethyl-p-phenylenediethyldimalonate (3.95 g, 10 mmol) in 20 ml of ethanol was added dropwise at a

temperature of -20 °C. The mixture was stirred at -8 °C for 48 h. The colorless precipitate was collected, washed with ethanol and ether and dissolved in 50 ml of water. After the addition of 50 ml of 2N hydrochloric acid, the product was extracted with ten portions of 30 ml diethyl ether. After evaporation the residue was recrystallized from methanol giving **6b** as colorless crystals (2.10 g, 74 %) with mp 250 °C (decomp.). - MS m/z (rel intensity) 194 (44), 177 (5), 163 (7), 150 (13), 149 (100), 131 (8), 123 (8), 105 (30), 104 (32), 103 (14), 95 (10), 91 (17), 81 (22). ^{1}H NMR (DMSO-d_6): δ 3.50 (s, 2H), 4.30 (s, 4H), 7.15 (m, 4H). ^{13}C NMR (DMSO-d_6): d 40.37, 129.28, 133.34, 172.76.

p-Phenylene-bis-(di(2,4,6-trichlorophenyl) malonate) (6c).

A mixture of **6b** (280 mg, 1 mmol), 2,4,6-trichlorophenol (780 mg, 4 mmol) and phosphorus oxychloride (800 mg, 5 mmol) was heated to 100 °C for 2 h. The reaction mixture was cooled to rt, poored on 50 g ice/water and extracted with diethyl ether. The organic layers were washed with water, dried (Na_2SO_4) and evaporated. Recrystallization from ether/pentane gave **6c** (880 mg, 88%) as colorless crystals with mp 193 °C (decomp.). - ^{1}H NMR ($CDCl_3$): δ 5.38 (s, 2H), 7.41 (m, 4H), 7.76 (m, 4H); IR (KBr, cm^{-1}) 1790, 1774, 1566, 1447, 1386, 1323, 1235, 1191, 1158, 1131, 1101, 855, 820, 792, 593. This product must be stored at low temperatures to avoid decomposition.

General procedure for the synthesis of bis(pyrimidiniumolates).

TCP-ester 6c (0.2 mmol) and the corresponding N,N´-dimethylamidine 7 (0.4 mmol) were dissolved in 5 ml of anisole. The reaction mixture was refluxed for 5 min. After cooling to rt 50 ml of diethyl ether were added. In case of spontaneous crystallization the crystals were filtered, washed with diethyl ether and recrystallized from methanol. If no precipitation occurred, the compounds were separated by silica gel column filtration using diethyl ether to eluate TCP, anisole and by-products and hot methanol to eluate crude products 8, which were recrystallized from methanol.

8a: colorless crystals (32 mg, 31 %) with mp 350 °C (decomp.); MS m/z (%): 506 (3), 378 (35), 350 (27), 305 (20), 198 (56), 196 (61), 150 (15), 134 (19), 132 (29), 118 (100). IR (KBr, cm^{-1}) 1780 (w), 1734 (w), 1640 (s), 1516 (w), 1446 (w), 1415 (w), 1377 (w), 1258 (m), 1097 (w), 1024 (w), 785 (w), 450 (w). UV (acetonitrile, λ_{max} (nm), log ε): 219 (4.489), 258 (3.818), 345 (3.607). HRMS Calcd for $C_{30}H_{26}N_4O_4$: 506.1950. Found: 506.1950.

8b: Faintly yellow crystals (46 mg, 41%) with mp. 330 °C (decomp); MS m/z (%): 324 (19), 323 (79), 242 (18), 241 (73), 186 (10), 185 (69), 167 (12), 159 (68), 149 (50), 135 (30), 125 (26), 123 (24), 121 (25). IR (KBr, cm^{-1}) 1646 (s), 1608 (w, sh), 1490 (m), 1408 (w), 1368 (w), 1298 (w), 1252 (m), 1182 (w), 1024 (w), 830 (w). UV (acetonitrile, λ_{max} (nm), log ε): 220 (4.363), 268 (3.829), 370 (3.7833). Anal. Calcd for $C_{32}H_{30}N_4O_6$: C, 67.83; H, 5.34. Found: C, 68.4; H, 4.9 %.

8c: Yellow crystals (47 mg, 40%) with mp. 350 °C (decomp.); MS m/z (%): 200 (25), 198 (34), 192 (100), 163 (64), 162 (11), 160 (17), 149 (30), 146 (21), 134 (20), 133 (19), 132 (40), 17 (79). IR (KBr, cm^{-1}) 1650 (s), 1602 (w, sh), 1526 (m), 1452 (w), 1431 (w, sh), 1350 (m), 1256 (w), 866 (w). UV (acetonitrile, λ_{max} (nm), log ε): 200 (4.700), 260 (4.151), 345 (3.607). Anal. Calcd for $C_{30}H_{24}N_6O_8$: C, 60.40; H, 4.05 %. Found: C, 61.7; H, 4.8 %.

8d: colorless crystals (23 mg, 21%); mp: 295-298 °C (decomp). MS m/z (%) 550 (13, M^+) , 479 (26), 314 (25), 191 (22), 111 (38), 104 (50), 83 (84), 69 (100). IR (KBr, cm^{-1}) 2926 (w), 1772 (w), 1636 (s), 1558 (w), 1505 (w), 1447 (w), 1404 (w), 1240 (w), 1091 (w), 856 (w), 767 (w), 446 (w). UV (acetonitrile, λ_{max} (nm), log ε): 218 (3.930), 265 (3.481), 355 (3.342). HRMS Calcd for $C_{32}H_{46}N_4O_4$: 551.3557. Found: 551.3553.

N,N′,N″,N‴-Tetramethyl-p-phenylene-bis-amidine (9).

Phosphorus pentachloride (8.4 g, 40 mmol) was dissolved in 50 ml of benzene. The solution was heated to reflux under argon. N,N′-Dimethylterephthaldiamide (3.8 g, 20 mmol) was added in portions of approximately 150 mg each over an interval of 8 hours. The mixture was refluxed for an additional 6 h. After cooling to rt, the mixture was filtered with a sintered glass filter and the solvent was evaporated. The residue was dissolved in 50 ml of dry benzene. This solution was added dropwise under vigorous stirring to 80 ml of a 40% solution of methylamine in water. The temperature was kept below 0 °C . Water (100 ml) was added to the mixture, which then was extracted with benzene. The organic layers were separated and dried (Na_2SO_4). The solvent was evaporated below 50 °C, and the residue was recrystallized from benzene. Pale reddish crystals (1.30-1.96 g, 30-45%) with mp 80 °C (decomp.). - **9:** MS m/z (%) 227 (42), 226 (14), 225 (42), 219 (9), 218 (41) M^+, 217 (100), 203 (14), 198 (34), 196 (37), 188 (39), 185 (13), 184 (12), 183 (16), 174 (23), 172 (23), 157 (20), 155 (17), 144 (20), 143 (56), 129 (25). IR (KBr,cm^{-1}: 3255 (br, w), 2866 (w), 1621 (s), 1534 (s), 1402 (m), 1321 (w), 1031 (m), 854 (m), 492 (w).

General procedure for the synthesis of bis-(pyrimidiniumolates) (10).

p-Phenylen-bis-(N,N′-dimethylamidine) (110 mg, 0.05 mmol) and 0.1 mmol of TCP ester were dissolved in 5 ml of anisole. The reaction mixture was refluxed for 5 min. After cooling to rt, 20 ml of diethyl ether were added. The compounds were separated by silica gel column chromatography using diethyl ether to eluate TCP, anisole and by-products and hot methanol to eluate 10, which was recrystallized from methanol. - **10:** Pale yellow crystals, 45 mg (18%) with mp: 343-347 °C (decomp.); MS m/z (%): 506 (12, M^+), 289 (24), 143 (43), 141 (8), 132 (14), 131 (16), 130 (11), 129 (15), 128 (15), 119 (14), 118 (49), 117 (35), 116 (25), 115 (17), 105 (33), 104 (44), 103 (39), 102

(20), 98 (25), 97 (23), 95 (21), 91 (61), 89 853), 77 (56), 64 (100). IR (KBr, cm^{-1}): 1646 (s), 1545 (m), 1443 (m), 1256 (m), 1019 (w), 862 (w), 779 (w), 607 (w). UV (acetonitrile, λ_{max} (nm), log ε): 223 (4.181), 255 (3.634), 350 (3.403). HRMS calcd for $C_{30}H_{26}N_4O_4$: 506.1950. Found: 506.1954.

Acknowledgement

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36. It should be remarked, that the analytical solutions of the generalized polynomials of **1** and **3** (α_a, $\alpha_b > 0$) can be obtained only for distinct values of α. The characteristic polynomials of the isoconjugate parent systems of **8a** (P(ε)(**8**)) and **10** (P(ε)(**10**)) have also been calculated. One obtains: $P(\varepsilon)(\mathbf{8}) = \varepsilon^{34} - 38\,\varepsilon^{32} + 649\,\varepsilon^{30} - 6600\,\varepsilon^{28} + 44646\,\varepsilon^{26} - 212608\,\varepsilon^{24} + 735810\,\varepsilon^{22} - 1883628\,\varepsilon^{20} + 3594821\,\varepsilon^{18} - 5113498\,\varepsilon^{16} + 5376853\,\varepsilon^{14} - 4105036\,\varepsilon^{12} + 2204404\,\varepsilon^{10} - 787968\,\varepsilon^{8} + 169088\,\varepsilon^{6} - 17152\,\varepsilon^{4} + 256\varepsilon^{2} = (\varepsilon^{11} - \varepsilon^{10} - 15\varepsilon^{9} + 13\varepsilon^{8} + 81\varepsilon^{7} - 57\varepsilon^{6} - 191\,\varepsilon^{5} + 97\,\varepsilon^{4} + 188\,\varepsilon^{3} - 56\,\varepsilon^{2} - 56\,\varepsilon + 8)\,\varepsilon^{2}(\varepsilon^{11} + \varepsilon^{10} - 15\,\varepsilon^{9} - 13\,\varepsilon^{8} + 81\varepsilon^{7} + 57\,\varepsilon^{6} - 191\,\varepsilon^{5} - 97\,\varepsilon^{4} + 188\,\varepsilon^{3} + 56\,\varepsilon^{2} - 56\,\varepsilon - 8)(\varepsilon^{2} - 2)^{2}(\varepsilon - 1)^{3}(\varepsilon + 1)^{3}$

and P(ε)(10) = $\varepsilon^{34} - 38\,\varepsilon^{32} + 649\,\varepsilon^{30} - 6600\,\varepsilon^{28} + 44646\,\varepsilon^{26} - 212608\,\varepsilon^{24} + 735810\,\varepsilon^{22} - 1883612\,\varepsilon^{20} + 3594549\,\varepsilon^{18} - 5111594\,\varepsilon^{16} + 5369621\,\varepsilon^{14} - 4088572\,\varepsilon^{12} + 2181124\,\varepsilon^{10} - 767632\,\varepsilon^{8} + 158656\,\varepsilon^{6} - 14400\,\varepsilon^{4}$
$= \varepsilon^{4}(\varepsilon^{10} + \varepsilon^{9} - 15\,\varepsilon^{8} - 13\,\varepsilon^{7} + 81\,\varepsilon^{6} + 57\,\varepsilon^{5} - 191\varepsilon^{4} - 97\,\varepsilon^{3} + 188\,\varepsilon^{2} + 56\,\varepsilon - 60)\,(\varepsilon^{10} - \varepsilon^{9} - 15\,\varepsilon^{8} + 13\,\varepsilon^{7} + 81\,\varepsilon^{6} - 57\,\varepsilon^{5} - 191\varepsilon^{4} + 97\,\varepsilon^{3} + 188\,\varepsilon^{2} - 52\,\varepsilon - 60) * (\varepsilon^{2} - 2)^{2}(\varepsilon - 1)^{3}(\varepsilon + 1)^{3}$.

There seem to be no *analytical* solutions for **P(ε)(8)** and **P(ε)(10)**.

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