Heteroaromatic Tripoles. 2,6-Bis(hetarenio)pyrimidin-4-olates: Hybrids between Hetarenium Salts and Cross-Conjugated Mesomeric Betaines

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A novel tandem nucleophilic displacement reaction on tetrachloropyrimidine **7** leads to molecules with two delocalized positive and one delocalized negative charge, which comprise a common π-electron system, plus one external anion. Thus, treatment of **7** with an excess of heteroaromatic nucleophiles such as 4-(dimethylamino)pyridine, 4-(pyrrolidin-1-yl)pyridine, and 1-methylimidazole, respectively, followed by the addition of water formed the tripolar bis(hetarenio)pyrimidin-4-olates **8**, **9**, and **10**. Addition of anhydrous alcohols furnished the O-alkylated dicationic species **11**−**16**. We contrast the spectroscopic features of the monocationic **8**−**10** and the dicationic **11**−**16** and performed a conformational study (PM3). The HOMO/LUMO profile was calculated to evaluate our classification of **8**−**10** as CCMB derivatives.

Introduction

Since the first synthesis of the type B mesoionic heterocycle dehydrodithizone in 1882,[1] a large number of heterocyclic mesomeric betaines have been described,[2] some of which were identified as modified nucleobases[3] or alkaloids[4] from natural sources or prepared as pharmaceutical agents.[5] In 1985, Ollis, Stanforth, and Ramsden proposed a comprehensive classification, which is based upon the definition of heterocyclic mesomeric betaines (MB), and contrasted the characteristic features of conjugated (CMB), cross-conjugated (CCMB), and pseudo-cross-conjugated (PCCMB) mesomeric betaines.[2] According to the definition, mesomeric betaines are neutral conjugated molecules that can be represented only by dipolar structures in which both the positive and negative charges are delocalized within the π-electron system. In sharp contrast, very few examples are known to date of conjugated molecules with more than one positive and one negative charge,[6] although—on the other hand—charge-cumulated systems such as poly*cationic* molecules have attracted considerable attention as novel organic oxidizing agents,[7] precursors of organic radicals,[8] and potential semiconductors.[9] Moreover, there has been renewed interest in the synthesis of betaines with antileishmanial,[10] antiprotozoal,[11] and antitrichomonal activities.[12]

We were interested in new systems that combine charge-cumulated and betainic properties and sought methodologies that would permit the construction of conjugated molecules that can only be represented by an *odd* number of positive and negative charges that comprise a common π-electron system. Due to their overall charge, those molecules are no mesomeric betaines. Thus, the resulting oligopolar systems must form a new class of compounds anticipated to have interesting chemical, spectroscopic, and biological properties. We want to present here our results concerning the synthesis of tripolar bis(hetarenio)pyrimidin-4-olates and some of their alkylated dicationic derivatives by a tandem S_N reaction via a highly electrophilic intermediate. The pyrimidin-4-olates were classified as hybrids between cross-conjugated mesomeric betaines and hetarenium salts, which apparently form a new class of compounds. To evaluate our classification, we performed computations on a representative compound.

Results and Discussion

In continuation of our work on charge-cumulated and charge-separated pyrimidines,[13] we chose the pyrimidin-4-olate moiety **I**, the anion of 4(*3H*)-pyrimidone,[14] as the

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(5) E.g., well-known examples are the heterocyclic *N*-oxide Librium (Multum) and the sydnonimine molsidomin (Corvaton), which are currently used as a tranquillizer and a NO donor in coronary therapy, respectively.
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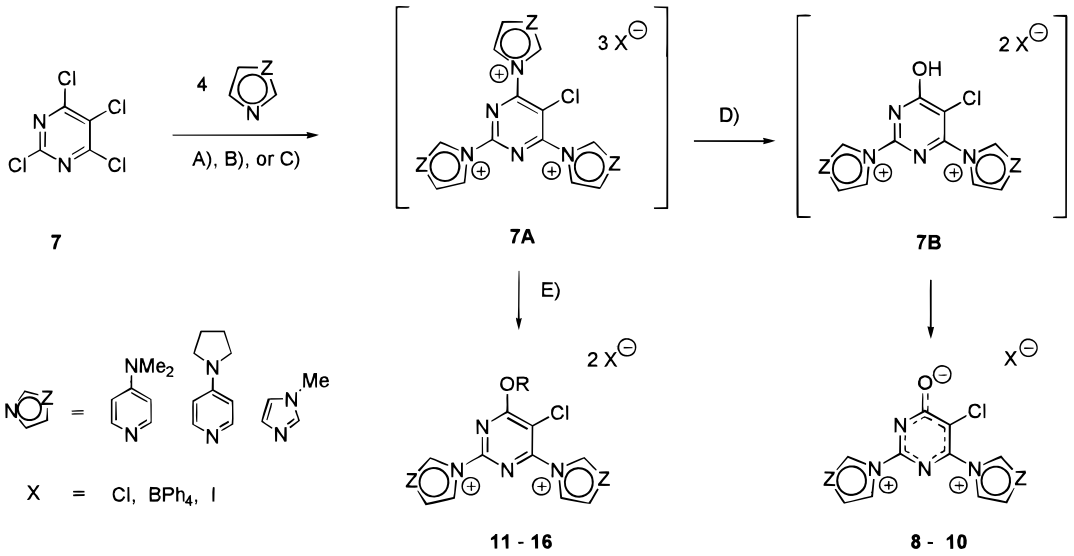
Scheme 1[a]



[a] Reagents and conditions: method A for the preparation of the chlorides **8a**, **9a**, and **10a**: anhydrous ethyl acetate, rt, 2 h. Method B for the preparation of the tetraphenylborates **8b**, **9b**, **10b**, and **11**−**16**: anhydrous ethyl acetate, 3 equiv of sodium tetraphenylborate, rt, 2 h. Method C for the preparation of the iodides **8c**, **9c**, and **10c**: anhydrous acetone, sodium iodide, 56 °C, 1 h. Method D: ethanol, acetone, water, reflux. Method E: anhydrous alkohols ROH [for **11**, **14**: ethanol; for **12**, **15**: methanol; for **13**, **16**: 2-propanol], reflux.

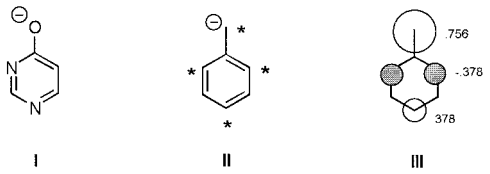


Figure 1. Pyrimidin-4-olate fragment of mesomeric betaines (I). Starred (*) and unstarred positions (II) as well as HOMO profile (III) of the isoconjugate benzyl anion.

target fragment of the desired heterocyclic tripoles. The delocalized negative charge is associated with a fragment that is isoconjugate[15] with the benzyl anion **II**. The starred and unstarred positions of **II** and the HOMO ψ_4 **III** of this odd alternant hydrocarbon anion are shown in Figure 1. As depicted in Figure 2, conjugated (CMB, **1**) and cross-conjugated mesomeric betaines (CCMB, **2** and **3**) are obtained by connection of positive fragments such as hetarenium substituents through one of the starred and unstarred positions, respectively. Note that cross-conjugation is a result of an union[16] of the positive segment of the molecule to the negative portion at atoms that are nodal positions of the HOMO **II** of the benzyl anion. As depicted in Figure 2, two unstarred positions (C-2, C-6) in the pyrimidin-4-olate moiety, however, give rise to three additional possibilities. Due to their charge, the resulting molecules **4**−**6** are hybrids of mesomeric betaines and hetarenium salts that comprise a single π-electron system. The compounds **4** and **5** combine CMB and CCMB substructures, whereas **6** contain two overlapped partial structures of cross-conjugated mesomeric betaines.

Synthesis. Tetrachloropyrimidine **7** appeared as an ideal starting material for chlorine displacement reactions by nucleophilic heteroaromatics since it possesses three potential leaving groups at C-2, C-4, and C-6, permitting the formation of tricationic systems such as **7A** (Scheme 1). The nucleofugical properties of the chlorine atom at C-5 of those systems could not be estimated a priori, but pyrimidines substituted with electron-releasing groups are known to be not very susceptible to halogen displacement reactions at this position.[17] However, the electron deficiency brought about by three hetarenium substituents plus an additional chlorine atom at C-5 should provide the impetus for subsequent nucleophilic attacks on the pyrimidine moiety. Our intention was furthermore to take advantage of the well-documented nucleophilicity of 4-(dimethylamino)pyridine, 4-(pyrrolidin-1-yl)pyridine, and 1-methylimidazole, which form hetarenium salts known to be stable toward ring-cleavage reactions and nucleophilic ring transformations.[18] Due to the dialkylamino [$\sigma_p = -0.83$][19] and methyl substituents [$\sigma_p = -0.17$],[19] respectively, the ylidic C−N$^+$ bonds are stabilized, and this causes moderate nucleofugical properties of the hetarenium rings, thus allowing selective subsequent nucleophilic substitutions on the product obtained.

Indeed, tetrachloropyrimidine **7** reacted smoothly with heteroaromatic nucleophiles. Thus, treatment of **7** with the heteroaromatics mentioned above resulted in the formation of the highly reactive (5-chloropyrimidin-2,4,6-triyl)trishetarenium salts **7A**. Without exception, these compounds proved to be extremly sensitive toward minute traces of water and decomposed rapidly even if the tetraphenylborates—sterically bulky and nonnucleophilic—were generated under argon in anhydrous dichloromethane. The ^{1}H NMR spectrum of the crude product formed upon addition of the pyridines to a DMSO-d_6

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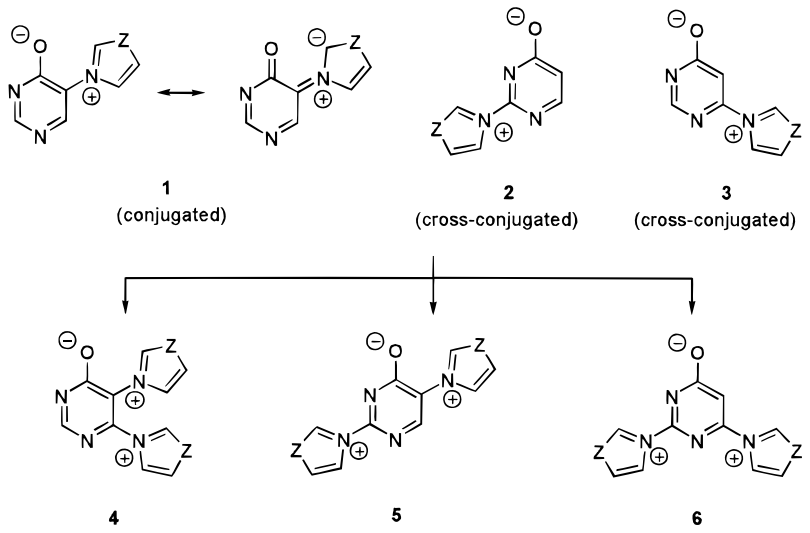
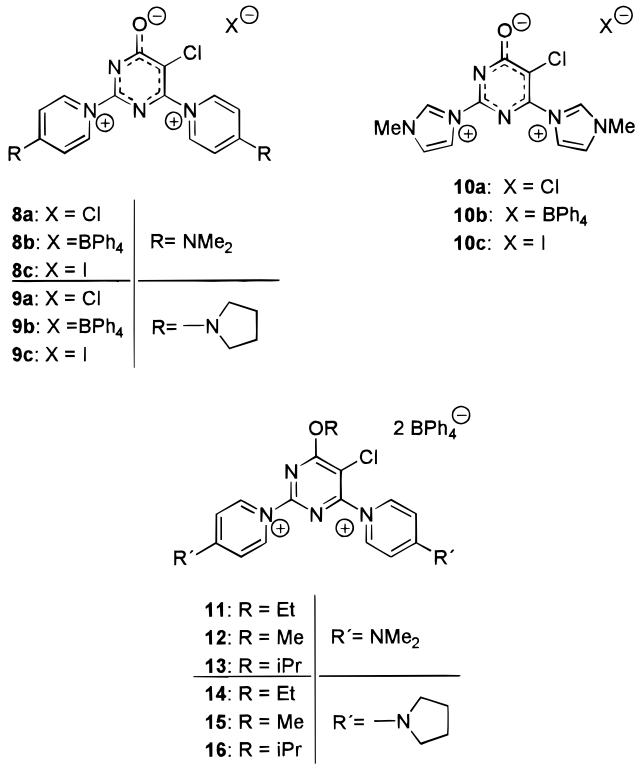


Figure 2. Top: conjugated (CMB) and cross-conjugated mesomeric betaines (CCMB). Bottom: possible combinations of the pyrimidin-4-olate moiety (**I**) and hetarenium substituents leading to tripolar mesomeric betainium salts with CMB and CCMB substructures. Possible partial structures Z are NMe; CH═CH; CR═CH; CH═N; *etc.*

Scheme 2



solution of **7** shows two dublets of the pyridinium α-protons at 9.25/9.35 ppm and 8.98/9.22 ppm in a 1:2 ratio, and as expected, these chemical shifts are extremly shifted downfield in relation to known 4-(dimethylamino)pyridinium and 4-(pyrrolidin-1-yl)pyridinium salts, respectively.

Interception of the highly reactive intermediates **7A** with water in ethanol/acetone resulted in the formation of the desired cationic mesomeric betaine derivatives. Thus, reaction of tetrachloropyrimidine (**7**) with a 4-fold excess of the heteroaromatics in anhydrous ethyl acetate, subsequent evaporation of the solvent at room temperature, and treatment of the pale yellow to orange residues with a mixture of aqueous ethanol and acetone yielded

Table 1. Substitution Pattern, Required Anions, and Synthetic Methods of the 5-Chloro-2,6-bis-(Hetarenio)pyrimidin-4-olates 8−10 and of the 1,1′-(5-Chloro-6-alkoxypyrimidin-2,4-diyl)bishetarenium Salts 11−16

Compd		X	R	method
8a	DMAP[a]	Cl		A
8b	DMAP	BPh_4		B
8c	DMAP	I		C
9a	PPY[b]	Cl		A
9b	PPY	BPh_4		B
9c	PPY	I		C
10a	NMI[c]	Cl		A
10b	NMI	BPh_4		B
10c	NMI	I		C
11	DMAP	BPh_4	ethyl	B, E
12	DMAP	BPh_4	methyl	B, E
13	DMAP	BPh_4	i-propyl	B, E
14	PPY	BPh_4	ethyl	B, E
15	PPY	BPh_4	methyl	B, E
16	PPY	BPh_4	i-propyl	B, E

[a] DMAP = 4-(dimethylamino)pyridine. [b] PPY = 4-(pyrrolidin-1-yl)pyridine. [c] NMI = 1-methylimidazole.

the first representatives of positively charged mesomeric betaines, the 5-chloro-2,6-bis(hetarenio)pyrimidin-4-olate chlorides **8a**, **9a**, and **10a**, which were finally isolated as light gray to cream-colored solids (Scheme 2, Table 1). As outlined in the spectroscopic section, no traces of the protonated intermediates **7B** and of their possible tautomeric forms were found. To verify the cation-to-anion ratio NMR-spectroscopically, we intercepted the leaving group, which is a hard anion according to the HSAB classification, by the soft tetraphenylborate in anhydrous ethyl acetate. Thus, nucleophilic substitution of tetrachloropyrimidine **7** with DMAP, 4-(pyrrolidin-1-yl)pyridine, and 1-methylimidazole, respectively, in the presence

of stoichiometric amounts of sodium tetraphenylborate in anhydrous ethyl acetate, subsequent isolation of the resulting precipitates under inert atmospheres, and addition of aqueous ethanol afforded the gray tetraphenylborates **8b** and **9b**. The 2,6-bis(imidazolio)pyrimidin-4-olate **10b**, however, crystallized on cooling as a beige solid after a short period of time at 77 °C in a mixture of ethyl acetate and chloroform.

Upon addition of dry sodium iodide, the color of a solution of **7** in anhydrous acetone turned to intense brown immediately. Carefull treatment with a 4-fold excess of the heteroaromatics led to orange-yellow precipitates, which were filtered off in vacuo and dissolved in hot aqueous ethanol. After cooling, the iodides **8c**, **9c**, and **10c** separated as intense yellow-orange crystals. Despite the well-documented nucleophilicity of the iodide, no displacement of the chlorine atom at C-5 of **8c**, **9c**, and **10c** by iodine occurred as evidenced by FAB mass spectrometry. In any case, 2-fold stoichiometric amounts of hetarenium salts, isolated from the mother liquor, lend strong support to the proposed mechanism via the intermediates **7A** and **7B**. Despite intense efforts, alkylation of the betaines **8**−**10** by alkyl halides could not be accomplished.

However, the O-alkylated derivatives were obtained by nucleophilic attack on the in-situ generated chloropyrimidin-2,4,6-triyltrispyridinium tetraphenylborates **7A** by anhydrous alcohols, resulting in the formation of the (6-alkoxy-5-chloro-pyrimidin-2,4-diyl)bispyridinium salts **11**−**16**. Thus, reaction with DMAP and workup involving ethanol furnished the 6-ethoxy derivative **11** as yellow crystals, whereas treatment with methanol and 2-propanol, respectively, resulted in **12** and **13**, which are brownish and light yellow in color. As expected for the intermediacy of **7A**, stoichiometric amounts of 4-(dimethylamino)pyridinium tetraphenylborate ($DMAPH^+$ TPB^-) were isolated from the mother liquor. Under the same conditions, the syntheses of the (6-alkoxy-5-chloropyrimidin-2,4-diyl)bis[4-(pyrrolidin-1-yl)pyridinium] bis(tetraphenylborates) **14**−**16** were achieved on heating tetrachloropyrimidine **7** subsequently with 4-(pyrrolidin-1-yl)pyridine (PPY) and anhydrous alcohols. The formation of the corresponding bis-3-methylimidazolium derivatives with 1-methylimidazole as the nucleophile could not be accomplished. Instead, mixtures of the betaine **10b** and decomposition products were obtained.

Spectroscopic Features. In NMR spectroscopy, the betaines **8**−**10** and the salts **11**−**16** display the α- and *β*-protons of the pyridinium units splitting to two dublets in a 1:1 ratio, respectively. In accordance with the two positive charges of the molecules, the chemical shifts of the pyridinium rings were found between the resonance frequencies of the hetarenium salts [e.g., $DMAPH^+$ X^-: $\delta(\beta\text{-H}) = 7.00$ ppm, $\delta(\alpha\text{-H}) = 8.22$ ppm] and the tricationic (5-chloro-pyrimidin-2,4,6-triyl)trishetarenium salts **7A**. The resonances of the betaines are relatively unaffected by the negative charge of the central pyrimidine ring, although—as expected—the signals are slightly shifted upfield in relation to the dicationic species **11**−**16** [e.g., $\Delta\delta(\alpha\text{-H}_{DMAP}) = -0.10$ to -0.05 ppm]. The integration of the ^{1}H NMR signals of the tetraphenylborates **8b**, **9b**, and **10b** confirms unambiguously the 1:1 ratio of cation and anion, thus proving the existence of a *mono*cationic system despite the presence of two hetarenium rings. Likewise, the 1:2 ratio of the cation and anions of the salts **11**−**16** was determined. According to the nonsymmetric substitution pattern of the central pyrimidine, the ^{13}C NMR spectra of all compounds showed four quaternary carbon atoms of the pyrimidine moiety. In general, the C-5 resonances of 4(3*H*)-pyrimidones are not significantly influenced in passing from the neutral to the anionic species.[14] Likewise, the chemical shifts of the C-5 positions of the dications and the betaines are similar, whereas the resonances of the C-2 and C-6 atoms differ significantly [e.g., **11**: $\delta = 152.21$, 152.77 ppm; **8a**: $\delta = 150.82$, 155.49 ppm]. The absence of any NH or OH resonance frequencies in the ^{1}H NMR spectra conducted at 300 MHz in DMSO-d_6, DMF-d_7, CD_3CN, acetone-d_6, and $CDCl_3$, respectively, proves the existence of a nonprotonated species. The NMR spectra do not point at any tautomeric equilibrium. In addition, neither ν_{NH} absorption bands of the pyrimidone forms nor ν_{OH} absorptions of its tautomeric pyrimidol **7B**, which should appear at approximately 3440 and 3590 cm^{-1}, respectively,[20] were detectable. We compared ^{1}H NMR spectra of the betaine **8a** and the O-alkylated species **11** measured in 10% (v/v) D_2SO_4 in DMSO-d_6 to determine the possible protonation site of **8a**. In relation to the resonance frequencies obtained in pure DMSO-d_6, all signals were shifted upfield [e.g., **8a**: $\Delta\delta(\alpha\text{-H}) = -0.67$, $(\alpha'\text{-H}) = -0.60$, $(NMe_2) = -0.27$ ppm; **11**: $\Delta\delta(\alpha\text{-H}) = -0.47$ ppm, $(\alpha'\text{-H}) = -0.40$; $(NMe_2) = -0.31$ ppm]. However, as no standard is known for D_2SO_4,[9] and the protonation is not accompanied by a change of the symmetry of the molecule, the protonation site could not unambiguously be elucidated. Protonation at the exocyclic oxygen atom should cause considerably decreased electron donating properties [$\sigma_p(O^-) = -0.519$; $\sigma_p(OH) = -0.357$],[18] resulting in large changes of the α-protons in comparison with the dimethylamino group.

FAB mass spectrometry proved to be an important tool in the structure determination of organic salts.[21] We recorded FAB mass spectra in the positive-ion detection mode in 3-nitrobenzyl alcohol (*m*-NBA), known to inhibit reduction processes that are due to the presence of electrons in the matrix. Thus, *m*-NBA acts as an electron scavenger, forming again the starting compound from the radical ion.[22] In accordance with the assigned structure, the ions of the doubly charged system **11** ($M^{2+} = 400.2$ u), which appear at $M^{2+}/2$ ($m/z = 200.1$ u), as well as of the reduced species $[M^{2+} + e^-]^+$ at $m/z = 400.2$ u and their hydrogen adducts $[M + nH]^+$ ($m/z = 401.2$ u, 402.2 u, 403.2 u], were registered. Furthermore, addition of M^{2+} to the nitrite anion, formed from matrix degradation during the FABMS study, is responsible for the formation of the characteristic $[M^{2+}NO_2^-]^+$ ion monitored at $m/z = 446.1$ u, which is—in the case of FABMS of uncharged compounds—detectable in the negative-ion mass spectra. Consistent with the expected fragmentation pattern of **11**, the spectra exhibit intense peaks at $m/z = 371.1$ and 278.1, originated by loss of ethene and DMAP from the molecular ion, respectively.

In accordance with the assigned structure of a monocationic mesomeric betaine derivative **8**, neither the ions

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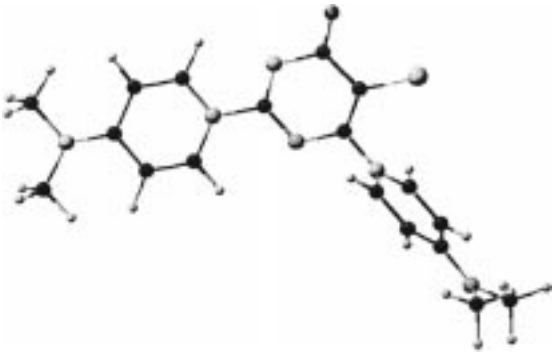


Figure 3. Most stable conformation (PM3) of the CCMB derivative **8**.

of the dicationic **7B** (M^{2+} = 371.8 u), which should be observable at $M^{2+}/2$ (m/z = 185.9 u), nor the characteristic formations of substitution products (e.g., $[M^{2+}Cl^-]^+$; $[M^{2+}I^-]^+$; $[M^{2+}NO_2^-]^+$)[21] were registered in the FAB mass spectra. Instead, the molecular ion of $[MH]^+$ of **8** was monitored in the positive-ion mode. Further details are given in the Experimental Section.

Conformational Study. As depicted in Figure 3, a PM3 calculation[23,25] leads to a most stable conformation of the 5-chloro-2,6-bis[4-(dimethylamino)pyridinio]pyrimidin-4-olate cation **8** [ΔH_f = 852.92 kJ mol^{-1}] with the two pyridinium rings twisted by 146.71° [N(3)−C(2)−N(7)−C(8)] and 128.19° [N(1)−C(6)−N(13)−C(18)] from the pyrimidin-4-olate plane. The number and energy of the minima depends essentially on the rotation of the pyridinium rings, which must be discussed independently due to the central nonsymmetric pyrimidin-4-olate moiety. As expected, upon rotation about the C(2)−N(7) bond, the maximum of the heat of formation ΔH_f is found at perpendicular dihedral angles Φ [N(3)−C(2)−N(7)−C(8)] = 85.2° (ΔH_f = 856.81 kJ mol^{-1}) and 269.2° (ΔH_f = 857.47 kJ mol^{-1}) that prevent stabilizing π interactions between the cationic and the anionic segment of the molecule [$\Delta\Delta H_f$(PM3) = 3.89 and 4.55 kJ mol^{-1}, respectively]. As shown in Figure 4, four minima were found, the differences in energy of which depend on the orientation of the lone pair of the slightly pyramidal dimethylamino group relative to the central pyrimidin-4-olate ring. The corresponding dihedral angles are widened to 29.1°, 146.7°, 203.3°, and 331.2°. This finding is somewhat surprising at first sight, because on one hand it indicates a reduced p overlap between the p_z component of the molecular orbital at N(7) of the pyridinium ring and the C(2) p_z orbital of the pyrimidin-4-olate segment. On the other hand, the interaction between the lone pairs of nitrogen atoms such as N(1) and N(3) and aromatic hydrogen atoms is known to be an attractive one.[26] However, this finding is, as anticipated, consistent with the characteristic union bonds between cationic and

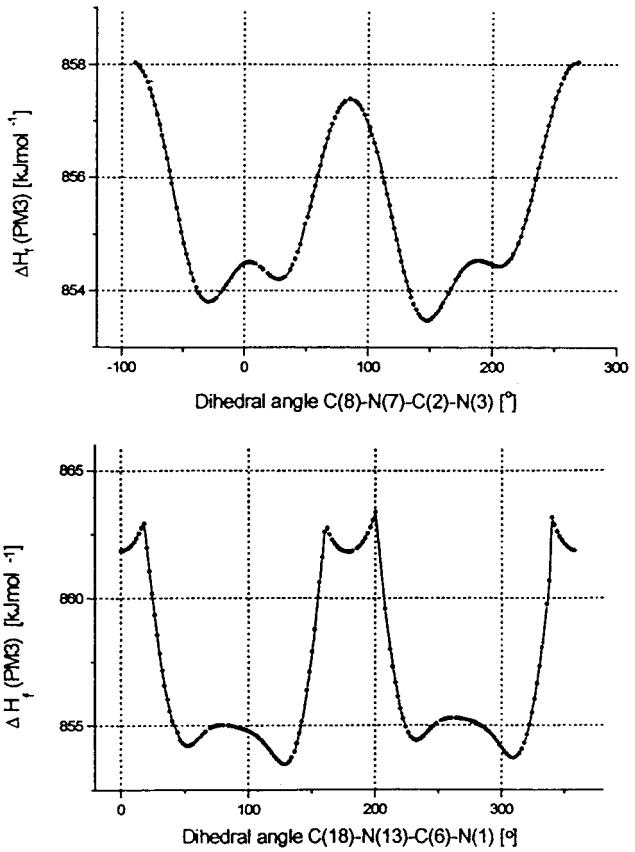


Figure 4. Conformational study (PM3) on **8**. Heat of formation ΔH_f vs dihedral angles Φ. Top: pyridinium ring at C-2. Bottom: pyridinium ring at C-6.

anionic segments of cross-conjugated mesomeric betaines.[15] The noncoplanarity of the C(6)-bound pyridinium understandably arises from steric repulsion between the α-hydrogen atoms and the chlorine at C(5), the interatomic distance of which, calculated to be 270.14 pm in the ground state, is smaller than the sum of the van der Waals radii $r_H^{vdW} + r_{Cl}^{vdW}$ = 300 pm. However, stabilizing p overlap between the pyridinium and the pyrimidin-4-olate segment causes a small local minimum at Φ = 0.0 and 178.1° with ΔH_f = 205.99 and 205.97 kJ mol^{-1}, respectively. Notably, the perpendicular conformation about the C(6)−N(13) bond is less stable than a twisted conformation with dihedral angles of approximately 51.8°.[27] A possible explanation for this torsional angle may be due to repulsive interactions between the lone pairs of the chlorine atom and the p_z component of the MO at N(13). The calculated small energy barrier of maximal 1.5 kJ mol^{-1} between the ground state and the transition state at Φ = 80° indicate a rapid conversion of the conformers with Φ = 51.7°/128.2°, and 232.7°/308.9° at room temperature, whereas any rotation via the planar conformation seems to be unfavorable [$\Delta\Delta H_f$(PM3) = 9.6 kJ mol^{-1}].

The bond lengths C(2)−N(7) and C(6)−N(13) were found to be 147.10 and 146.17 pm, respectively, and deviate only a little from normal C−N single bonds (147 pm).[28] The calculated bond orders are 0.94 and 0.96,

(23) Calculations were carried out using MOPAC 6.0[24] on a CONVEX 3440. The structures were first optimized with the default gradient requirements and subsequently refined with the options EF DMAX = 0.1, GNORM = 0.1, SCFCRT = 1 × 10^{-6}; the cationic mesomeric betaine **8** was calculated with the option CHARGE = +1. The absolute minima were proved with a force calculation.

(24) Stewart, J. J. P. *QCPE*, No 455, Department of Chemistry, Bloomington, IN, 1989.

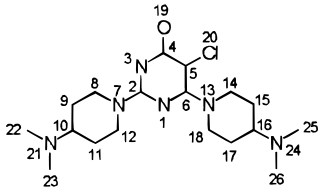
(25) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(26) (a) Alcalde, E.; Dinarés, I.; Frigola, J.; Jaime, C.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Rius, J. *J. Org. Chem.* **1991**, *56*, 4223. (b) Castellanos, M. L.; Olivella, S.; Roca, N.; De Mendoza, J.; Elguero, J. *Can. J. Chem.* **1984**, *62*, 687.

(27) Φ = 51.7° (ΔH_f = 854.2 kJ mol^{-1}); Φ = 128.2° (ΔH_f = 852.9 kJ mol^{-1}); Φ = 232.4° (ΔH_f = 854.4 kJ mol^{-1}); Φ = 308.9° (ΔH_f = 853.7 kJ mol^{-1}).

(28) Higginbotham, H. K.; Bartell, L. S. *J. Chem. Phys.* **1965**, *42*, 1131.

Table 2. PM3 Calculated Charge Densities of the Bis(pyridinio)pyrimidinolate 8. Numbering

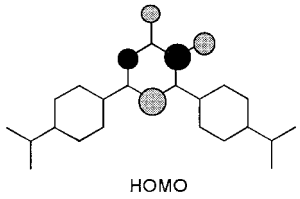


atom no.	charge	atom electron density
N(1)	−0.3312	5.3312
N(3)	−0.2534	5.2534
C(5)	−0.3422	4.3422
N(7)	+0.4693	4.5307
C(8)	−0.0972	4.0972
C(10)	+0.0587	3.9413
C(12)	−0.0874	4.0874
N(13)	+0.4904	4.5096
N(21)	+0.1324	4.8676
N(24)	+0.1378	4.8622
O(19)	−0.3080	6.3080
Cl(20)	+0.1428	6.8572

respectively. In agreement with known carbon-to-oxygen bond lengths of cross-conjugated mesomeric betaines,[15] the C(4)−O(19) distance (121.43 pm) with a calculated bond order of 1.84 corresponds to a normal carbonyl group.

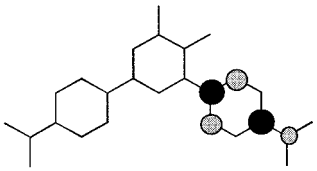
Classification. As already mentioned, under the definition mentioned above, the compounds **8**−**10** are no members of the class of mesomeric betaines because they are charged. Nevertheless, following the approaches developed by Ollis, Stanforth, and Ramsden to classify a mesomeric betaine,[2] (i) the recognition of characteristic dipole types, (ii) the valence bond theory, and (iii) the perturbation theory, **8**−**10** match all criteria of cross-conjugated mesomeric betaines (CCMB) and may thus be regarded as hetarenium-substituted mesomeric betaines with a common π-electron system, i.e., mesomeric betainium salts. This classification is confirmed by spectroscopic as well as by theoretical methods. The characteristic dipole-types and their vinylogues of the class of CCMB can be dissected from the canonical formulas. Furthermore, application of the valence bond approach demonstrates that **8**−**10** contain isolated anionic and cationic segments because the positive and negative charges are exclusively restricted to separate parts of the conjugated system. In accordance with CCMB, the anionic segment is isoconjugate with the benzyl anion, which is an odd alternant hydrocarbon anion.[2] To evaluate theoretically our classification, we determined charge densities (Table 2) and HOMO/LUMO coefficients of **8** (Table 3). As expected, a high degree of negative charge is predicted on the exocylic O(19), on N(1), N(3) and on C(5), which is confirmed by the high deshielding of this position observed in ^{13}C NMR spectroscopy [δ(C-5) = 109.04−110.91 ppm]. A high degree of positive charge is developed on the pyridinium nitrogen atoms N(7) and N(13). The HOMO [IP(PM3) = 10.72 eV] is essentially associated with the pyrimidin-4-olate segment of the molecule, and characteristically, the hetarenium rings are joined by union bonds at C-2 and C-4 in the anionic fragment, which are nodal positions in the HOMO ψ_4 of the benzyl anion. Upon excitation, an electron is shifted from the HOMO to one of the LUMOs, which have their largest coefficients in one of the pyridinium rings. The LUMO [IP(PM3) = 4.33 eV] is essentially located in the pyridinium ring at C(6), as shown in Table 3, whereas the LUMO+1 [IP(PM3) = 4.19 eV] is essentially associated with the pyridinium ring at C(2). As the energetic differences are very small, excitation of one electron seems to be possible to the LUMO as well as to the LUMO + 1, whereas the calculated ionization potential of the LUMO + 2 (IP(PM3) = −3.74 eV) seems to prevent a HOMO − LUMO + 2 excitation. As a consequence of the HOMO/LUMO profile of the molecule, the dipole moments of the most stable ground state (13.356 D)[29] and the first excited state (7.744 D)[29] differ significantly.

Table 3. HOMO and LUMO Profiles (PM3) for the Bis(pyridinio)pyrimidinolate 8



HOMO

Atom No. / HOMO coefficients			
N(1)	0.5257	C(2)	0.0520
N(3)	0.3972	C(4)	0.0522
C(5)	0.4797	C(6)	0.1719
O(19)	0.3662	Cl(20)	0.3963



LUMO

Atom No. / LUMO coefficients			
C(5)	0.1682	N(13)	0.4463
C(14)	0.3758	C(15)	0.0978
C(16)	0.4463	C(17)	0.0655
C(18)	0.3942	N(24)	0.3190

The charge transfer upon excitation is confirmed experimentally by the effect of negative solvatochromism, a specific example of a linear free energy relationship, which is considered to be an important indicator of charge separation in the ground state of a molecule.[30] The π−π* absorption, which is associated with an intramolecular charge transfer, shifts to shorter wavelengths with increasing solvent polarity because the ground state is better stabilized by polar rather than by nonpolar

(29) Given is the total moment (Σ), the vectorial sum of the dipole moments on the *x*, *y*, and *z* axes: [*x*-axis, C(4)−N(3); *xy*-plane, C(4)−N(3)−C(2); *z*-axis, rectangular to the *xy*-plane]; ground state: 6.939, 11.410, −0.192; first excited state: 5.412, 5.538, −0.040, respectively.

(30) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH Verlagsgesellschaft mbH: Weinheim, 1990; pp 359−363.

solvents. However, the halide gegenions of multiply charged systems are known to be heavily solvated,[13,31] and moreover, the formation of clathrates by dicationic onium compounds is well-documented.[32] In accordance with these findings, the elemental analyses of **8**−**10** indicate the presence of nonstoichiometric amounts of water of hydration. This must be taken into account when solvatochromism is discussed because the measurements vary in accuracy due to changes of the solvent polarity. Nevertheless, in accordance with the assigned dicationic and betainic structures and the calculated HOMO/LUMO profiles, all but two of these compounds exhibit an effect of negative solvatochromism. A solvent change from dichloromethane ($E_T^N = 0.309$) to acetonitril ($E_T^N = 0.460$) causes a hypsochromic shift of the UV maxima up to 28 nm. As expected, stabilization by hydrogen bonding results in deviation of the absorption maxima determined in protic solvents such as methanol ($E_T^N = 0.762$).[30]

Conclusions

Despite their odd number of positive and negative charges, which comprise a common π electron system, the compounds **8**−**10** exhibit characteristic properties of cross-conjugated mesomeric betaines (CCMB). As a result of the restriction of the charges to separate parts of the molecules, the typical resonance frequencies are observed in NMR spectroscopy. The ^{1}H NMR spectroscopically determined cation-to-anion ratio as well as the FAB mass spectra confirm the existence of a monocationic system despite the presence of two hetarenium substituents. Indicative of a high degree of charge separation in the ground state, the effect of negative solvatochromism is observed. This is readily explained by the calculated HOMO/LUMO profile and the distinct dipole moments in the ground state and first excited state. Furthermore, characteristic for the class of CCMB, the hetarenium rings are joined to the anionic pyrimidin-4-olate moiety at atoms, which are nodal positions of the HOMO of the isoconjugate odd alternant hydrocarbon anion, i.e., the benzyl anion. Thus, the cationic compounds **8**−**10** are members of a new class of compounds—hybrids between hetarenium salts and mesomeric betaines—and can thus be referred to as cross-conjugated mesomeric betainium salts.

Experimental Section

General Methods. For spectrometers used, see ref 13. Chemicals were purchased from Aldrich Chemical Co., except for nondeuterated solvents. All NMR samples were prepared in DMSO-d_6. IR spectra were determined on KBr disks. Prior to submission for analyses, all samples were dried for at least 24 h at 80 °C. However, in accordance with known hetarenium derivatives,[13,31] most of the compounds crystallize with nonstoichiometric amounts of water. The water of hydration indicated in the formulas give the best fit to the values obtained. Therefore the UV−visible spectra were determined qualitatively. All melting points were determined on a Boëtius melting apparatus; the values reported are uncorrected.

General Procedure for the Preparation of the 5-Chloro-2,6-bis(hetarenio)pyrimidin-4-olate Chlorides 8a, 9a, and 10a. Tetrachloropyrimidine (**7**) (0.27 g, 1.25 mmol) was suspended in 70 mL of anhydrous ethyl acetate, and the hetarene was added [**8a**: 0.61 g (5.00 mmol) of 4-(dimethylamino)pyridine; **9a**: 0.74 g (5.00 mmol) of 4-(pyrrolidin-1-yl)pyridine; **10a**: 0.41 g (5.00 mmol) of 1-methylimidazole]. After the mixture was stirred for 2 h, the precipitate was collected by filtration, washed subsequently with ethyl acetate, and recrystallized from ethanol/acetone/water (30:10:1) to yield cream-colored solids.

5-Chloro-2,6-bis[4-(dimethylamino)pyridinio]pyrimidin-4-olate chloride (8a): yield 0.38 g (75%); dec > 214 °C; ^{1}H NMR δ 3.31 (s, 12H), 7.15 (d, J = 8.2 Hz), 7.18 (d, J = 7.9 Hz), 8.59 (d, J = 7.9 Hz), 9.07 (d, J = 8.2 Hz); IR 3054.9, 3036.5, 1652.4, 1580.0, 1374.4, 1163.4, 735.0, 706.3; ^{13}C NMR δ 40.2, 107.0, 107.1, 110.9, 136.6, 140.7, 152.2, 152.7, 156.4, 157.2, 167.4; FABMS m/z 372.2 (9; MH^+), 327.8 (1; $M^+ - NMe_2$), 285.7 (13; $M^+ - DMAP + Cl^-$), 249.6 (5; $M^+ - DMAP$), 123.3 (100; $DMAPH^+$); UV λ_{max} (CH_2Cl_2) 314.70 nm; λ_{max}(MeCN) 315.90 nm; λ_{max}(MeOH) 317.40 nm. Anal. Calcd for $C_{18}H_{20}Cl_2N_6O\cdot 4H_2O$: C, 45.10; H, 5.89; N, 17.53. Found: C, 44.90; H, 5.39; N, 17.15.

5-Chloro-2,6-bis[4-(pyrrolidin-1-yl)pyridinio]pyrimidin-4-olate chloride (9a): yield 0.29 g (50%); slow dec > 215 °C; ^{1}H NMR δ 2.05 (m, 8H), 3.63 (m, 8H), 7.01 (m, 4H), 8.57 (d, J = 7.5 Hz, 2H), 9.08 (d, J = 7.5 Hz, 2H); ^{13}C NMR δ 24.5, 48.7, 48.8, 107.7, 107.8, 110.7, 136.6, 140.7, 152.2, 152.8, 153.5, 154.3, 167.4; IR 1647.9, 1590.1, 1559.4, 1419.4, 1356.0, 1326.7, 1191.7, 1152.1, 839.3; FABMS m/z 424.2 (5; M^+), 275.6 (3), 149.4 (100); UV λ_{max} (CH_2Cl_2) 285.50 nm; λ_{max} (MeCN) 288.40 nm; λ_{max} (MeOH) 290.60 nm. Anal. Calcd for $C_{22}H_{24}Cl_2N_6O\cdot 2H_2O$: C, 53.34; H, 5.69; N, 16.96. Found: C, 53.09; H, 6.32; N, 16.19.

5-Chloro-2,6-bis(3-methylimidazolio)pyrimidin-4-olate chloride (10a): yield 0.22 g (55%); mp 258−262 °C; ^{1}H NMR δ 3.95 (s, 3H), 4.02 (s, 3H), 7.88 (s, 1H), 7.98 (s, 1H), 8.33 (s, 1H), 8.41 (s, 1H), 10.06 (s, 1H), 10.08 (s, 1H); ^{13}C NMR δ 36.2, 36.3, 109.1, 118.7, 121.6, 123.5, 124.3, 136.0, 137.4, 146.7, 149.8, 167.6; IR 3086.0, 1607.9, 1577.1, 1435.0, 1151.2, 1040.5, 780.2, 620.0; FABMS m/z 291.5 (79; $M^+ + 1$), 209.3 (37), 83.2 (100); UV λ_{max} (CH_2Cl_2) 314.00 nm; λ_{max} (MeCN) 310.50 nm; λ_{max} (MeOH) 301.50 nm. Anal. Calcd for $C_{12}H_{12}Cl_2N_6O\cdot 3H_2O$: C, 37.81; H, 4.76; N, 22.04. Found: C, 38.04; H, 4.99; N, 22.06.

General Procedure for the Preparation of the 5-Chloro-2,6-bis(hetarenio)pyrimidin-4-olate Tetraphenylborates 8b, 9b, and 10b. A vigorously stirred solution of the nucleophile [**8b**: 0.61 g (5.00 mmol) of 4-(dimethylamino)pyridine; **9b**: 0.74 g (5.00 mmol) of 4-(pyrrolidin-1-yl)pyridine; **10b**: 0.41 g (5.00 mmol) of 1-methylimidazole] and 1.71 g (5.00 mmol) of sodium tetraphenylborate in 200 mL of anhydrous ethyl acetate was treated with 0.27 g (1.25 mmol) of tetrachloropyridine (**7**), dissolved in 70 mL of the same solvent. Except for the synthesis of **10b**, after stirring for 2 h at rt, the precipitates were filtered off and recrystallized twice from ethanol/acetone/water (30:10:1).

5-Chloro-2,6-bis[4-(dimethylamino)pyridinio]pyrimidin-4-olate tetraphenylborate (8b): yield 0.38 g (50%); colorless needles after slow crystallization at rt and drying at 80 °C; mp 227−235 °C; ^{1}H NMR δ 3.43 (s, 6H), 3.45 (s, 6H), 6.78 (t, J = 7.3 Hz, 4H), 6.91 (t, J = 7.3 Hz, 8H), 7.17 (m, 10H), 7.29 (d, J = 8.1 Hz, 2H), 8.57 (d, J = 8.2 Hz, 2H), 9.08 (d, J = 8.1 Hz, 2H); ^{13}C NMR not measured due to insufficient solubility; IR 3054.5, 1650.9, 1567.7, 1398.0, 1380.1, 1159.2, 734.0, 706.8; FABMS m/z 371.9 (51; MH^+), 327.7 (3; $M^+ - NMe_2$), 249.5 (27; $M^+ - DMAP$), 123.2 (49; $DMAPH^+$), 39.1 (100); UV λ_{max} (CH_2Cl_2) 344.17 nm; λ_{max} (MeCN) 338.28 nm; λ_{max} (MeOH) 323.56 nm. Anal. Calcd for $C_{42}H_{40}BClN_6O$: C, 72.99; H, 5.83; N, 12.16. Found: C, 72.97; H, 6.15; N, 12.03.

5-Chloro-2,6-bis[(4-pyrrolidin-1-yl)pyridinio]pyrimidin-4-olate tetraphenylborate (9b): yield 0.41 g (40%) after slow crystallization at rt; slow dec > 267 °C; ^{1}H NMR δ 2.03 (m, 8H), 3.61 (m, 8H), 6.77 (t, J = 7.2 Hz, 4H), 6.92 (t, J = 7.2 Hz, 8H), 7.17 (m, 10H), 8.56 (d, J = 7.7 Hz, 2H), 9.08 (d, J = 7.9 Hz, 2H); ^{13}C NMR δ 24.0, 24.1, 48.3, 48.4, 107.3, 108.4, 110.2, 121.0, 124.7 (q, J_{CB} = 2.2 Hz), 127.7, 135.0, 136.1, 140.2,

(31) Koch, A. S.; Waterman, K. C.; Banks, K.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6166.

(32) (a) Vögtle, F.; Löhr, H. G.; Puff, H.; Schuh, W. *Angew. Chem.* **1983**, *95*, 425. (b) Vögtle, F.; Löhr, H. G.; Franke, J.; Worsch, D. *Angew. Chem.* **1985**, *97*, 721.

152.5, 153.0, 153.5, 153.8, 162.8 (q, J_{CB} = 49.8 Hz), 167.2; IR 3055.1, 1650.8, 1577.3, 1567.2, 734.5, 706.5, 612.4; FABMS *m/z* 423.9 (1; M^+), 154.3 (100); UV λ_{max} (CH_2Cl_2) 349.21 nm; λ_{max} (MeCN) 321.00 nm; λ_{max} (MeOH) 327.73 nm. Anal. Calcd for $C_{46}H_{45}BClN_6O\cdot1.5H_2O$: C, 71.62; H, 5.88; N, 10.90. Found: C, 71.63; H, 6.05; N, 7.67.

5-Chloro-2,6-bis(3-methylimidazolio)pyrimidin-4-olate Tetraphenylborate (10b). The suspension was stirred for 1 h at reflux and then evaporated in vacuo to dryness. The resulting crude solid was taken up with 30 mL of ethyl acetate/chloroform (10:1), heated under reflux for 10 min, and cooled. The precipitate was collected by filtration, recrystallized from ethanol/acetone/water (30:10:1), and dried in vacuo: yield 0.23 g (30%) after slow crystallization at rt; mp 270−273 °C; ^{1}H NMR δ 3.92 (s, 3H), 3.97 (s, 3H), 6.78 (t, J = 7.2 Hz, 4H), 6.92 (t, J = 7.2 Hz, 8H), 7.17 (m, 8H), 7.83 (m, 1H), 7.94 (m, 1H), 8.28 (m, 1H), 8.34 (m, 1H), 9.87 (s, 1H), 9.91 (s, 1H); ^{13}C NMR δ 36.2, 36.3, 109.5, 118.7, 121.4, 121.7, 123.5, 124.3, 125.1 (q, J_{CB} = 2.2 Hz), 135.4, 135.8, 137.2, 146.7, 149.9, 163.2 (q, J_{CB} = 49.8 Hz), 167.4; IR 3054.8, 1623.3, 1602.7, 1437.7, 1426.7, 1147.4, 1038.2, 734.8, 708.0, 614.1; FABMS *m/z* 291.5 (49; M^+), 154.3 (100); UV λ_{max} (CH_2Cl_2) 314.40 nm; λ_{max} (MeCN) 310.10 nm; λ_{max} (MeOH) 299.10 nm. Anal. Calcd for $C_{36}H_{32}BClN_6O$: C, 70.77; H, 5.28; N, 13.76. Found: C, 70.97; H, 5.69; N, 13.56.

General Procedure for the Preparation of the 5-Chloro-2,6-bis(hetarenio)pyrimidin-4-olate Iodides 8c, 9c, and 10c. Tetrachloropyrimidine (**7**) (0.27 g, 1.25 mmol) was dissolved in 50 mL of anhydrous acetone. Sodium iodide (0.83 g, 5.50 mmol) was added, whereupon the orange color of the solution changed to brown. Then, on careful addition of 5.50 mmol of the hetarenes [**8c**: 0.67 g of 4-(dimethylamino)pyridine; **9c**: 0.81 g (5.5 mmol) of 4-(pyrrolidin-1-yl)pyridine; **10c**: 0.41 g (5.5 mmol) of 1-methylimidazole], yellow precipitates separated. The resulting suspension was heated at reflux for 1 h and allowed to cool to rt. The solid was finally collected by filtration, washed several times with acetone, aqueous acetone, and ethanol, and recrystallized from ethanol/acetone. Slow crystallization gave yellow to orange solids.

5-Chloro-2,6-bis[4-(dimethylamino)pyridinio]pyrimidin-4-olate iodide (8c): yield 0.22 g (35%); dec >170 °C; ^{1}H NMR δ 3.31 (s, 6H), 3.32 (s, 6H), 7.15 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 8.58 (d, J = 8.1 Hz, 2H), 9.07 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 40.1, 40.2, 107.0, 107.1, 110.8, 136.6, 140.7, 152.1, 152.7, 156.4, 157.2, 167.4; IR 1648.0, 1596.2, 1575.8, 1422.4, 1394.0, 1312.9, 1143.2, 1029.5, 828.7; FABMS *m/z* 372.2 (22; M^+), 327.9 (1; $M^+ - NMe_2$), 249.6 (11; M^+ − DMAP), 123.3 (100; $DMAPH^+$); UV: not soluble in CH_2Cl_2; λ_{max} (MeCN) 315.60 nm; λ_{max} (MeOH) 319.30 nm. Anal. Calcd for $C_{18}H_{20}ClN_6IO\cdot HI\cdot5H_2O$: C, 30.16; H, 4.36; N, 11.73. Found: C, 30.11; H, 3.89; N, 11.43.

5-Chloro-2,6-bis[(4-pyrrolidin-1-yl)pyridinio]pyrimidin-4-olate iodide (9c): yield 0.28 g (35%); slow dec > 190 °C; ^{1}H NMR δ 2.01 (m, 8H), 3.47 (m, 8H), 6.98 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 8.58 (d, J = 7.8 Hz, 2H), 9.07 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 24.5, 24.56, 48.85, 48.96, 107.78, 107.95, 110.68, 136.58, 140.70, 152.23, 153.51, 153.80, 154.30, 167.56; IR 3030.1, 1648.0, 1569.6, 1406.7, 1384.5, 1332.0, 1220.0, 1160.8, 1150.2, 838.4; FABMS *m/z* 424.0 (100; M^+), 149.4 (20; PPY); UV λ_{max} (CH_2Cl_2) 336.87 nm; λ_{max} (MeCN) 317.70 nm; λ_{max} (MeOH) 326.96 nm. Anal. Calcd for $C_{22}H_{24}ClIN_6O\cdot HI\cdot10H_2O$: C, 30.76; H, 5.28; N, 9.78. Found: C, 30.77; H, 3.80; N, 9.32.

5-Chloro-2,6-bis(3-methylimidazolio)pyrimidin-4-olate iodide (10c): yield 0.26 g (55%); mp >300 °C; ^{1}H NMR δ 3.94 (s, 3H), 4.00 (s, 3H), 7.86 (s, 1H), 7.97 (s, 1H), 8.30 (s, 1H), 8.37 (s, 1H), 9.91 (s, 1H), 9.94 (s, 1H); ^{13}C NMR δ 36.3, 36.4, 109.0, 118.8, 121.7, 123.7, 124.4, 135.6, 136.1, 146.7, 149.9, 167.7; IR 3087.1, 1599.5, 1591.7, 1537.3, 1510.9, 1433.1, 1253.4, 1237.9, 1142.3, 1035.4, 618.0; FABMS *m/z* 291.6 (10; M^+), 209.6 (5; M^+ − *imidazole*); UV λ_{max} (CH_2Cl_2) 362.67, 294.14 nm; λ_{max} (MeCN) 361.60, 291.80, 242.9 nm; λ_{max} (MeOH) 358.10, 291.55 nm. Anal. Calcd for $C_{12}H_{12}ClIN_6O\cdot HI\cdot3.5H_2O$: C, 23.64; H, 2.72; N, 13.78. Found: C, 23.68; H, 2.72; N, 13.60.

General Procedure for the Preparation of the 1,1′-(6-Alkoxy-5-chloropyrimidine-2,4-diyl)bispyridinium Bis(tetraphenylborates) 11−16. A solution of 15.20 mmol of the hetarene [1.85 g of 4-(dimethylamino)pyridine; 2.25 g of 4-pyrrolidin-1-yl)pyridine; 1.30 g of 1-methylimidazole] and 15.20 mmol of sodium tetraphenylborate (5.20 g) in 200 mL of anhydrous ethyl acetate was treated with a solution of tetrachloropyrimidine (**7**) (0.95 g, 4.34 mmol) in 100 mL of the same solvent, whereupon an immediate formation of a precipitate occurred. After the suspension was stirred for 30 min at rt, the precipitate was filtered off and recrystallized as described below.

1,1′-(5-Chloro-6-ethoxypyrimidine-2,4-diyl)bis[4-(dimethylamino)pyridinium] Bis(tetraphenylborate) (11). Recrystallization from ethanol/acetone (1:1) gave a light yellow solid: yield 3.6 g (80%); dec > 157 °C; ^{1}H NMR δ 1.48 (t, J = 6.9 Hz, 3H), 3.43 (s, 6H), 3.45 (s, 6H), 4.81 (q, J = 6.9 Hz, 2H), 6.78 (t, J = 7.3 Hz, 8H), 6.91 (t, J = 7.3 Hz, 16H), 7.16 (m, 18H), 7.29 (d, J = 8.2 Hz, 2H), 8.57 (d, J = 8.2 Hz, 2H), 9.17 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 13.8, 40.4, 40.6, 66.8, 107.4, 107.9, 108.7, 121.4, 125.1 (q, J_{BC} = 2.2 Hz), 135.4, 140.0, 150.8, 155.4, 156.6, 157.3, 163.2 (q, J_{BC} = 49.8 Hz), 167.5; IR 3054.5, 1652.4, 1580.0, 1374.4, 1225.0, 1163.4, 735.0, 706.3; FABMS *m/z* 446.1 ($[M^{2+}NO_2^-]^+$), 403.2 ($M^{2+} + e^- + 3H$), 402.2 ($M^{2+} + e^- + 2H$), 401.2 ($M^{2+} + e^- + H$), 400.2 ($M^{2+} + e^-$), 200.1 (M^{2+}), 371.5 ($M^{2+} - C_2H_4$), 329.1 ($M^{2+} - 77$), 278.1 (M^{2+} − DMAP); UV λ_{max} (CH_2Cl_2) 331.40 nm; λ_{max} (MeCN) 327.70 nm; λ_{max} (MeOH) 318.90 nm. Anal. Calcd for $C_{68}H_{65}B_2ClN_6O\cdot0.5H_2O$: C, 77.90; H, 6.35; N, 8.01. Found: C, 77.75; H, 6.74; N, 8.01.

1,1′-(5-Chloro-6-methoxypyrimidine-2,4-diyl)bis[4-(dimethylamino)pyridinium] Bis(tetraphenylborate) (12). Recrystallization from methanol/acetone (1:1) furnished cream-colored stars: yield 2.9 g (65%); dec 165−170 °C; ^{1}H NMR δ 3.32 (s, 12H), 4.32 (s, 3H), 6.78 (t, J = 7.3 Hz, 8H), 6.92 (t, J = 7.3 Hz, 16H), 7.17 (m, 18H), 7.24 (d, J = 7.4 Hz, 2H), 8.57 (d, J = 7.3 Hz, 2H), 9.17 (d, J = 7.4 Hz, 2H); ^{13}C NMR δ 40.5, 40.7, 57.5, 107.5, 108.0, 108.9, 121.4, 125.2 (q, J_{BC} = 2.2 Hz), 135.5, 136.8, 140.1, 150.9, 155.5, 156.7, 157.4, 163.3 (q, J_{BC} = 49.8 Hz), 168.1; IR 3054.3, 3036.3, 1652.0, 1580.1, 1393.1, 1373.9, 1163.3, 734.7, 706.6; FABMS *m/z* 386.9 (41; $M^{2+} + e^-$), 371.9 ($M^{2+} + e^- - CH_4$); UV λ_{max} (CH_2Cl_2) 331.60 nm; λ_{max} (MeCN) 327.70 nm; λ_{max} (MeOH) 326.50 nm. Anal. Calcd for $C_{67}H_{63}B_2ClN_6O\cdot0.75\ H_2O$: C, 77.46; H, 6.26; N, 8.08. Found: C, 77.45; H, 6.49; N, 7.87.

1,1′-[5-Chloro-6-(2-propoxy)pyrimidine-2,4-diyl]bis-[4-(dimethylamino)pyridinium] Bis(tetraphenylborate) (13). Recrystallization of the crude reaction product from 2-propanol/acetone (1:1) gave a yellow solid: yield 2.0 g (45%); slow dec > 108 °C; ^{1}H NMR δ 1.47 (d, J = 6.3 Hz, 6H), 3.32 (s, 12H), 4.02 (q, J = 6.3 Hz, 1H), 6.77 (t, J = 7.3 Hz, 8H), 6.92 (t, J = 7.3 Hz, 16H), 7.17 (m, 18H), 7.24 (d, J = 8.1 Hz, 2H), 8.57 (d, J = 8.1 Hz, 2H), 9.13 (d, J = 8.2 Hz, 2H); ^{13}C NMR not measured due to insufficient solubility; IR 3054.3, 1651.8, 1578.8, 1568.2, 1398.0, 1378.5, 1160.3, 734.2, 706.3, 612.7; FABMS *m/z* 415.9 (4; $M^{2+} + e^-$), 371.8 (28; $M^{2+} + e^-$ − $MeCH{=}CH_2$), 123.2 (100; $DMAPH^+$); UV λ_{max} (CH_2Cl_2) 322.70 nm; λ_{max} (MeCN) 322.00 nm; λ_{max} (MeOH) 317.70 nm. Anal. Calcd for $C_{69}H_{67}B_2ClN_6O$: C, 76.50; H, 6.41; N, 7.98. Found: C, 76.64; H, 6.64; N, 8.74.

1,1′-(5-Chloro-6-ethoxypyrimidine-2,4-diyl)bis[4-(pyrrolidin-1-yl)pyridinium] Bis(tetraphenylborate) (14). Recrystallization from ethanol/acetone (1:1) furnished beige needles: yield 4.0 g (85%); slow dec > 132 °C; ^{1}H NMR δ 1.47 (t, J = 7.2 Hz, 3H), 2.02 (m, 8H), 3.64 (m, 8H), 4.79 (q, J = 7.2 Hz, 2H), 6.77 (t, J = 7.2 Hz, 8H), 6.91 (t, J = 7.2 Hz, 16H), 7.17 (m, 20H), 8.55 (d, J = 7.7 Hz, 2H), 9.14 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 13.9, 24.4, 24.5, 49.2, 49.4, 66.7, 107.4, 108.1, 108.6, 121.3, 125.1 (q, J_{CB} = 2.2 Hz), 135.4, 136.6, 140.0, 150.9, 153.6, 154.3, 155.5, 153.8, 163.2 (q, J_{CB} = 49.8 Hz), 167.5; IR 3034.7, 2998.1, 2923.8, 1653.3, 1578.7, 1376.9, 1167.7, 734.3, 706.0, 612.8; UV λ_{max} (CH_2Cl_2) 334.20 nm; λ_{max} (MeCN) 330.80

nm; λ_{max} (MeOH) 328.90 nm; FABMS m/z = 451.6 (3; $M^+ - H$), 397.9. Anal. Calcd for $C_{72}H_{65}B_2ClN_6O \cdot 0.5H_2O$: C, 78.87; H, 6.06; N, 7.66. Found: C, 78.74; H, 6.73; N, 7.64.

1,1′-(5-Chloro-6-methoxypyrimidine-2,4-diyl)bis[4-(pyrrolidin-1-yl)pyridinium] bis(tetraphenylborate) (15): yield 0.83 g (24%); mp 172 °C; ^{1}H NMR δ 2.02 (m, 8H), 3.64 (m, 8H), 4.31 (s, 3H), 6.78 (t, J = 7.2 Hz, 8H), 6.92 (t, J = 7.2 Hz, 16H), 7.17 (m, 20H), 8.57 (d, J = 7.7 Hz, 2H), 9.17 (d, J = 8.1 Hz, 2H); ^{13}C NMR not measured due to insufficient solubility; IR 3054.7, 1652.9, 1578.8, 1376.0, 1167.9, 734.5, 706.3; UV λ_{max} (CH_2Cl_2) 291.20 nm; λ_{max} (MeCN) 318.50 nm; λ_{max} (MeOH) 319.80 nm; FABMS m/z = 439.1 (2; $M^+ - 1$), 424.1 (14; $M^+ - 15$), 149.3 (76; $PPYH^+$), 63.2 (100). Anal. Calcd for $C_{47}H_{47}BClN_6O \cdot 1.5H_2O$: C, 71.89; H, 6.42; N, 10.70. Found: C, 72.01; H, 6.21; N, 6.71.

1,1′-[5-Chloro-6-(2-propoxy)pyrimidine-2,4-diyl]bis[4-(pyrrolidin-1-yl)bispyridinium] Bis(tetraphenylborate) (16). Recrystallization from 2-propanol/acetone (1:1) gave beige crystals: yield 0.86 g (18%); slow dec > 142 °C; ^{1}H NMR δ 1.46 (d, J = 6.2 Hz, 6H), 2.06 (m, 8H), 3.64 (m, 9H), 6.77 (t, J = 7.2 Hz, 8H), 6.91 (t, J = 7.2 Hz, 16H), 7.17 (m, 20H), 8.53 (d, J = 7.7 Hz, 2H), 9.12 (d, J = 7.9 Hz, 2H); ^{13}C NMR not measured due to insufficient solubility; IR 3054.8, 1652.4, 1578.5, 1426.6, 1406.7, 1377.1, 1167.4, 734.2, 705.9, 612.8; FABMS m/z 467.2 (3; M^+), 423.9 (17; $M^+ - CH_3CH{=}CH_2$), 149.3 (79; $PPYH^+$), 77.2 (100); UV λ_{max} (CH_2Cl_2) 334.10 nm; λ_{max} (MeCN) 330.10 nm; λ_{max} (MeOH) 327.30 nm. Anal. Calcd for $C_{73}H_{71}B_2ClN_6O$: C, 79.31; H, 6.47; N, 7.60. Found: C, 79.18; H, 6.80; N, 7.61.

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