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MESOMERIC BETAINIUM SALTS. SYNTHESIS, X-RAY ANALYSIS, AND ESIMS STUDIES OF TRIPOLAR PYRIMIDIN-4-OLATES AND PYRIMIDIN-4-AMINIDES

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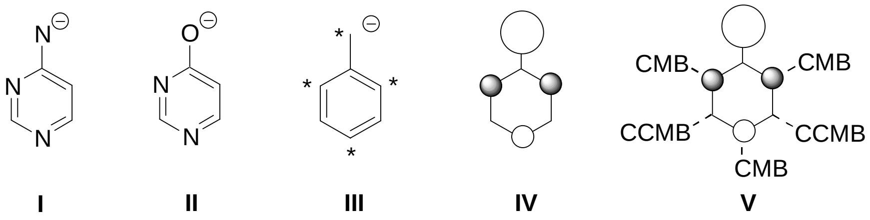
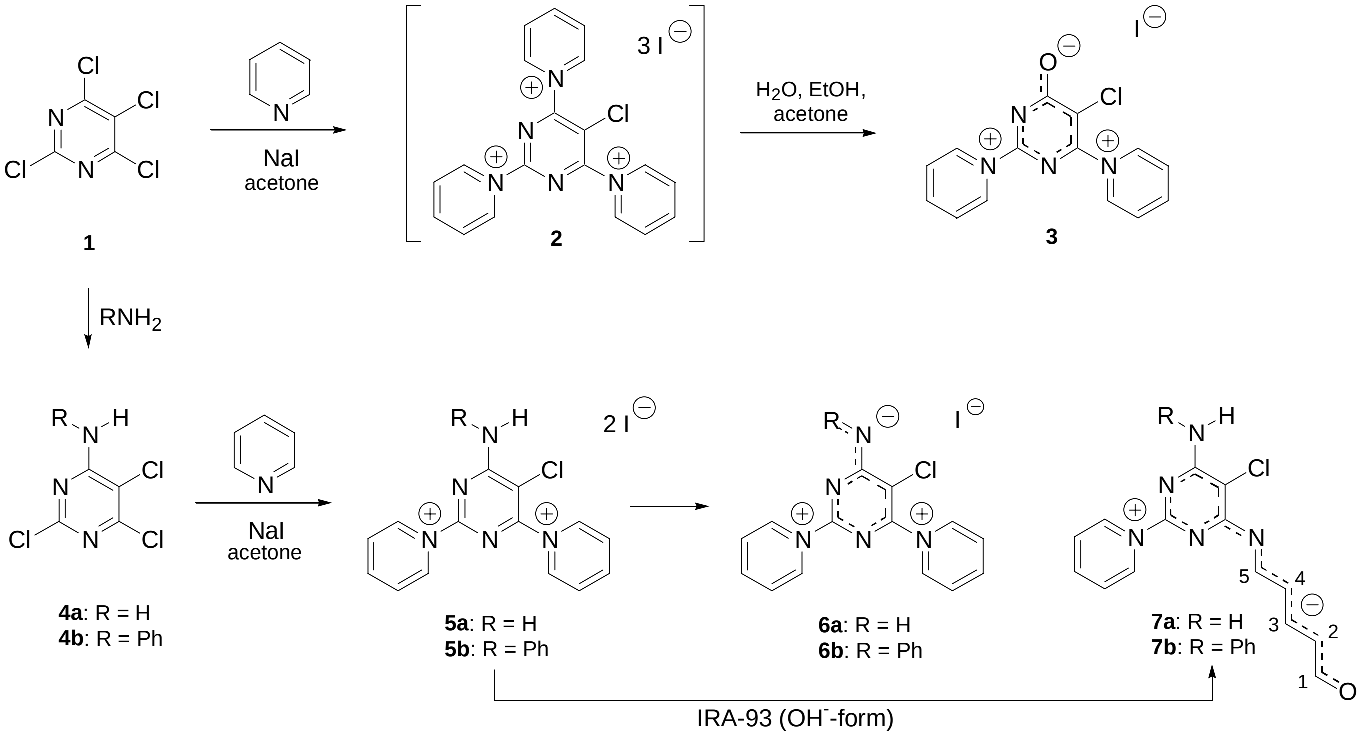
Abstract - Reaction of tetrachloropyrimidine (**1**) with pyridine in acetone in the presence of sodium iodide yielded the pyrimidin-4-olate (**3**). Applying analogous reaction conditions to 4-amino substituted 2,5,6-trichloropyrimidine (**4a,b**) resulted in the formation of bispyridinium salts (**5a,b**) which yield aminides (**6a,b**) on deprotonation. As evidenced by means of UV spectroscopy and electron spray MS spectrometry, the title compounds (**3**) and (**6a,b**) form π-sandwich complexes in solution.

In contrast to the pyrimidin-4-aminide (**I**), the corresponding 4-olate moiety (**II**) is a well-known structure element of mesomeric betaines (MB).[1] Depending on the *union*[2] of positive partial structures to the isoconjugated benzyl anion (**III**), the design of distinct types of betaines is possible. Union to an electronically inactive atom, *i.e.* an unstarred atom in **III** and a nodal position of the HOMO **IV** results in cross-conjugated mesomeric betaines (CCMB), whereas union to an active position forms conjugated systems (CMB).[3] Molecules with an odd number of positive and negative structure elements are hybrids between MB and heteroaromatic salts. In continuation of our interest in betaines[4] we report here the synthesis, X-Ray analysis, and ESIMS studies of cationic tripolar representatives of these systems, *i.e.* mesomeric betainium salts.



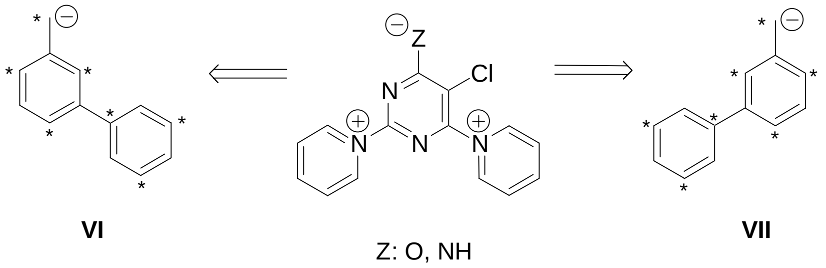
Scheme 1

Treatment of tetrachloropyrimidine (**1**) with sodium iodide in anhydrous acetone resulted in the formation of a brown solution which is due to the partial or complete nucleophilic exchange of the 2,4,6-chlorine atoms to iodine.[5] Addition of pyridine to the solution formed a yellow-orange precipitate which presumably consisted of the highly electrophilic tricationic species (**2**) which is not isolable.[6] Heating at reflux temperature for 1 h and subsequent quenching of the suspension with aqueous ethanol/acetone resulted in the formation of the heteroaromatic tripole 2,6-dipyridiniopyrimidin-4-olate iodide (**3**) (79%) in one single step.[7] In contrast to that, applying analogous reaction conditions to the 4-amino substituted 2,5,6-trichloro-pyrimidines (**4a,b**) - readily available from **1** on treatment with ammonia and aniline, respectively[8] - yielded 1,1´-(4-amino-5-chloropyrimidine-2,6-diyl)dipyridinium diiodides (**5a**) and 1,1´-(4-anilino-5-chloropyrimidin-2,6-diyl)dipyridinium diiodide (**5b**) in 74 and 62% yields, respectively. Attempts to deprotonate **5a,b** in aqueous ethanol to the tripoles (**6a,b**) using Amberlite® IRA-93 in its hydroxy form resulted in the pericyclic ring-cleavage to the purple colored *N*-(6-anilino-5-chloro-2-pyridiniopyrimidin-4-yl)-5-iminopenta-1,3-dienolate (**7b**) in 44% yield, whereas **7a** proved to be unstable and decomposed rapidely on the anion exchange resin.[9] As evidenced by the coupling constants $J_{2,3}$ = 15.0 and $J_{4,5}$ = 13.2 Hz, **7b** adopts the *all-E* configuration in the pentadienolate side chain.[10] Whereas **5a** could not be transformed to the tripole (**6a**), deprotonation of the phenylamino derivative (**5b**) to 2,6-dipyridiniopyrimidin-4-phenylaminide iodide (**6b**) was accomplished by potassium carbonate in anhydrous DMSO at room temperature in 82% yield. This observation is in accord to *Kröhnke*´s rule which predicts increasing stability of ylides with increasing number of atoms involved in the delocalisation of the negative charge.[11] However, tripole (**6a**) unambiguously forms during ESIMS spectrometry. The novel heteroaromatic tripoles (**3**) and (**6a,b**) form π-sandwich complexes with iodide in solution (*vide infra*).



Scheme 2

The compounds (**7a,b**) – possessing an even number of positive and negative charges - are cross-conjugated mesomeric betaines CCMB. However, two positive and one negative charges are delocalized in separated parts of the common π-electron system in **3** and **6**, forming monocationic systems plus one external anion, respectively. The tripoles (**3**) and (**6**), mesomeric betainium salts, contain two *overlapped* partial structures of CCMB that are isoconjugated to the odd alternant hydrocarbon anions (**VI**) and (**VII**). Per definition,[1] they do not belong to the class of mesomeric betaines as they are charged.



Scheme 3

We performed a X-Ray single crystal structure analysis to unambigously elucidate the structure of the mesomeric betainium salt **3**.[12] The ORTEP-plots and the elemental cell are presented in Figures 1, 2 and 3, respectively. Monoclinic single crystals were obtained by slow evaporation of a concentrated solution of **3** in water.

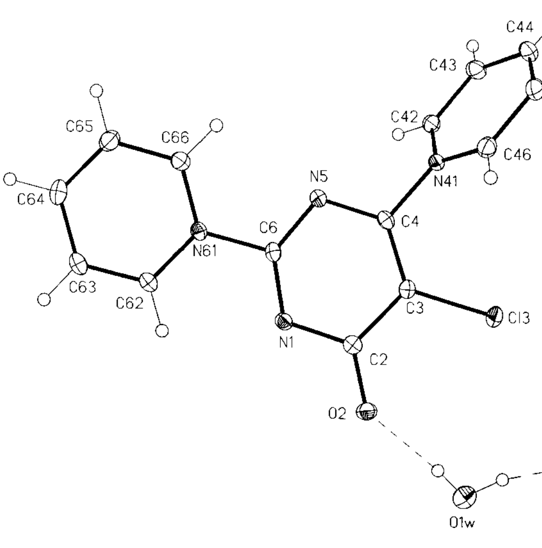


Figure 1

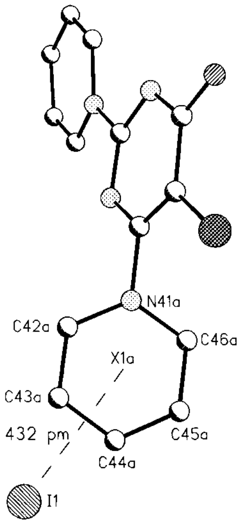


Figure 2

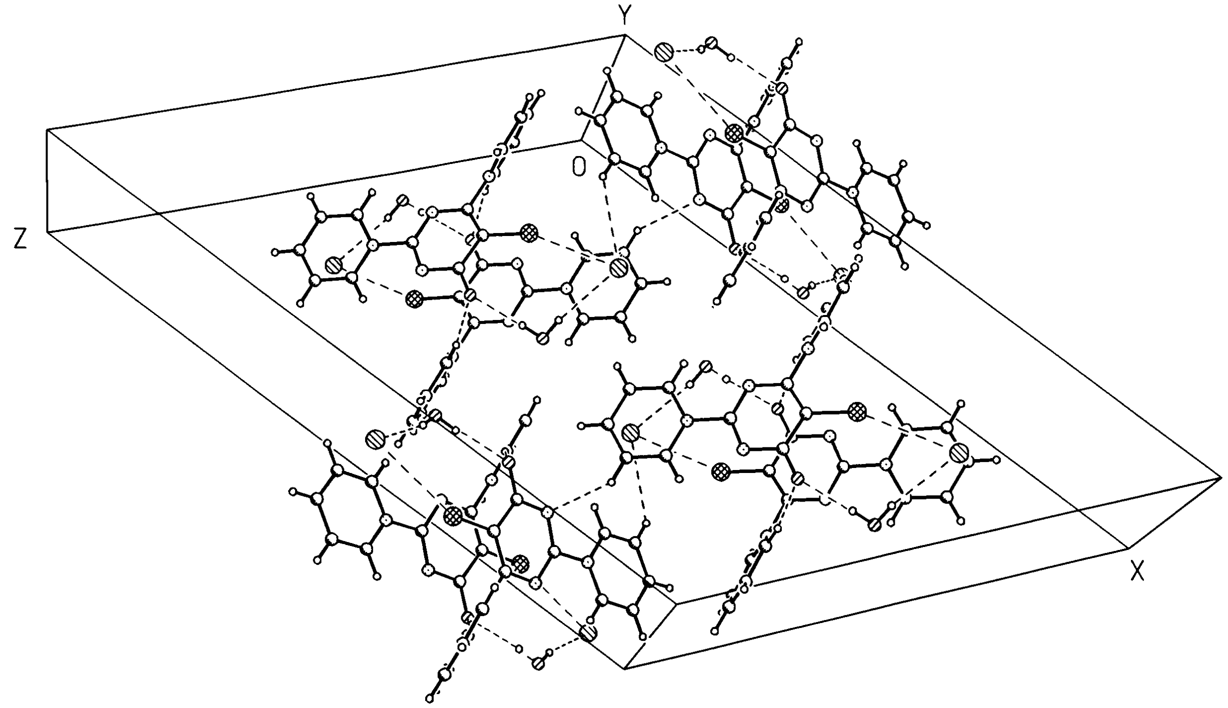


Figure 3

In the elemental cell, the tripole adopts a nonplanar conformation with the pyridinium substituents twisted by 9.96° and –57.0(2)° from the pyrimidin-4-olate plane. One molecule of water of crystallization is found per molecule of **3**. The larger torsion angle of the C(6)-bound pyridinium ring (crystallographic numbering in Figure 1: C4) is obviously due to steric hindrance to the C(5)-Cl atom (crystallographic numbering: Cl3). Thus, the charge-separation within the π-electron system is due to cross-conjugation as well as reduced *p*-overlap between the positively and negatively charged partial structures. As presented in Figure 2, the iodine anion is located in a distance of 432 pm from the center of the C(6)-bound pyridinium, so that in the solid state no π-interactions between anion and heteroaromatic π-electron sextet can be observed. Some selected bond lengths, bond angles, and torsion angles are given in Tables 1 and 2.

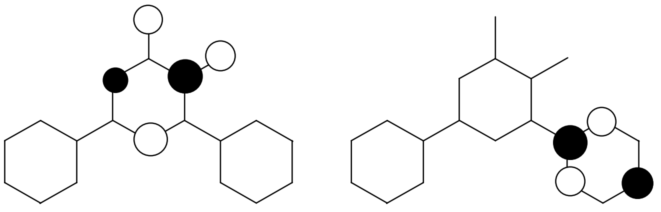
Table 1. Atom Nos. / Selected bond lengths [pm], bond angles [°], and torsion angles [°] of (**3**).

N(1)-C(6)	131.2(2)	C(4)-C(3)-C(2)	117.97(14)	C(6)-N(1)-C(2)-O(2)	-179.51(15)
N(1)-C(2)	137.1(2)	C(4)-C(3)-Cl(3)	124.41(12)	C(6)-N(1)-C(2)-C(3)	-0.4(2)
C(2)-O(2)	124.75(19)	N(5)-C(4)-C(3)	124.94(14)	O(2)-C(2)-C(3)-Cl(3)	0.5(2)
C(2)-C(3)	145.3(2)	N(5)-C(4)-N(41)	113.77(13)	N(1)-C(2)-C(3)-Cl(3)	-178.63(11)
C(3)-C(4)	136.1(2)	C(3)-C(4)-N(41)	121.30(14)	N(5)-C(4)-N(41)-C(42)	-56.99(18)
C(4)-N(5)	134.5(2)	N(1)-C(6)-N(61)	114.65(13)	C(3)-C(4)-N(41)-C(42)	122.99(17)
C(4)-N(41)	145.4(2)	N(5)-C(6)-N(61)	114.57(13)	N(1)-C(6)-N(61)-C(66)	167.36(14)
C(6)-N(61)	146.1(2)	C(42)-N(41)-C(4)	118.60(13)	N(5)-C(6)-N(61)-C(62)	70.04(14)
C(3)-Cl(3)	172.02(16)	C(66)-N(61)-C(6)	119.70(13)	N(1)-C(6)-N(61)-C(62)	-10.0(2)

Table 2. Hydrogen bonds of (**3**): Distances [pm] and angles [°].

D-H····A	d(D-H)	d(H····A)	d(D····A)	<(DHA)
O(1W)-H(1W1)····O(2)	83.2(17)	206.2(17)	289.06(17)	174(3)
O(1W)-H(1W2)····I(1)	82.6(17)	279.6(18)	360.58(14)	167(2)

However, in UV spectroscopy, with increasing solvent polarity the absorption maxima of **3** shift to shorter wavelengths ($\Delta\lambda_{max}(CH_2Cl_2/MeOH) = 30.2$ nm). This effect of negative solvatochromism is indicative of a charge-separation in the ground-state of a molecule.[15] In **3**, two effects can be differentiated. First, on electronic excitation electrons are shifted from the HOMO which is located in the pyrimidin-4-olate moiety, to the LUMO which is essentially located in the pyridinium substituent bound at C-6 of the central pyrimidine ring[16] (Figure 4). As a consequence, the permanent dipole moment of the molecule decreases on electronic excitation. Second, it is known that iodide forms *charge-transfer* complexes with pyridinium rings.[18] On electronic excitation, electron density is shifted from the iodide to the pyridinium rings. To investigate these two possibilities, we performed *electron spray ionization* MS spectrometry (ESIMS) in the positive mode on **3** as well as on **5a,b** in anhydrous acetonitrile at fragmentor voltages between 0 and 150 V. As a matter of fact, the monocationic associate (**8**) between two molecules of **3** and one iodide anion was unambigously identified between fragmentor voltages of 0 and 90 V as a peak at *m/z* = 697.0. The base peak was found at 285.0 which corresponds to the tripole (**3**) without anion (Figure 5). As the ESI method exclusively allows the measurement of charged systems,[19] we added 0.1 parts of 1% formic acid to the acetonitrile. However, **3** remained unprotonated, so that 1:1-π-interactions of the cation and the anion in **3** – which result in a neutral species - could not be detected. At higher fragmentor voltages, **3** decomposes under loss of the pyridinium rings as presented in the Scheme 4. The ESIMS spectra performed at fragmentor voltages of 0 and 120 V, respectively, are given in Figures 5 and 6.



3, HOMO(PM3) **3**, LUMO (PM3)

Figure 4

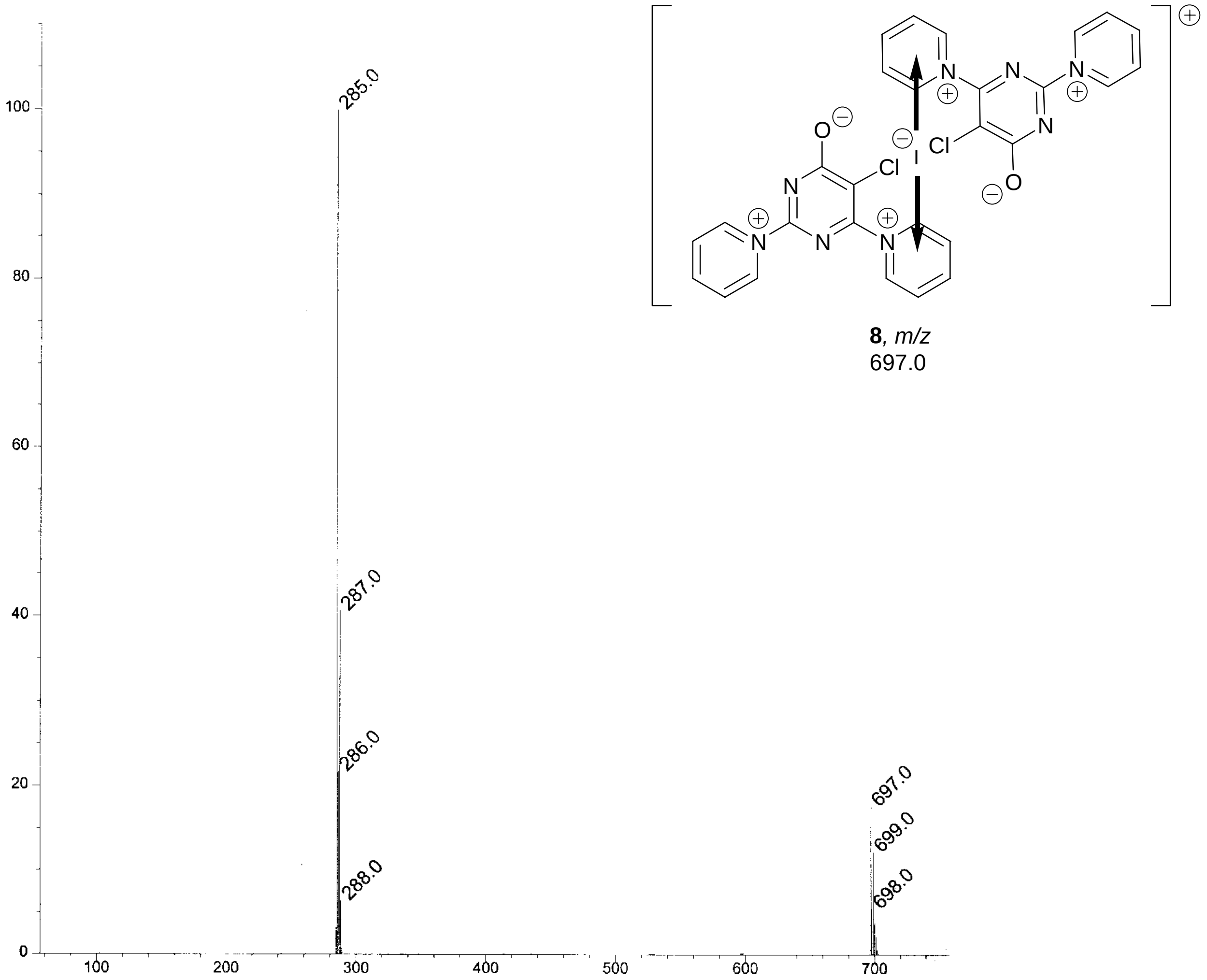
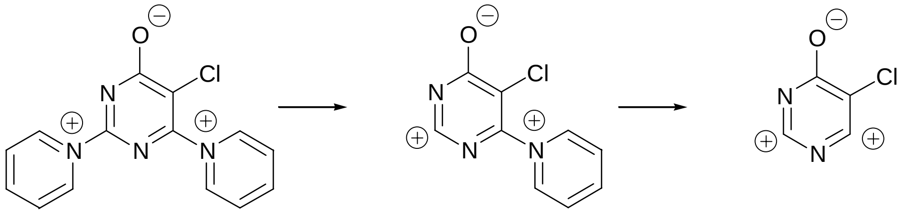


Figure 5



3, *m/z* 285.0

m/z 205.9

m/z 126.9

Scheme 4

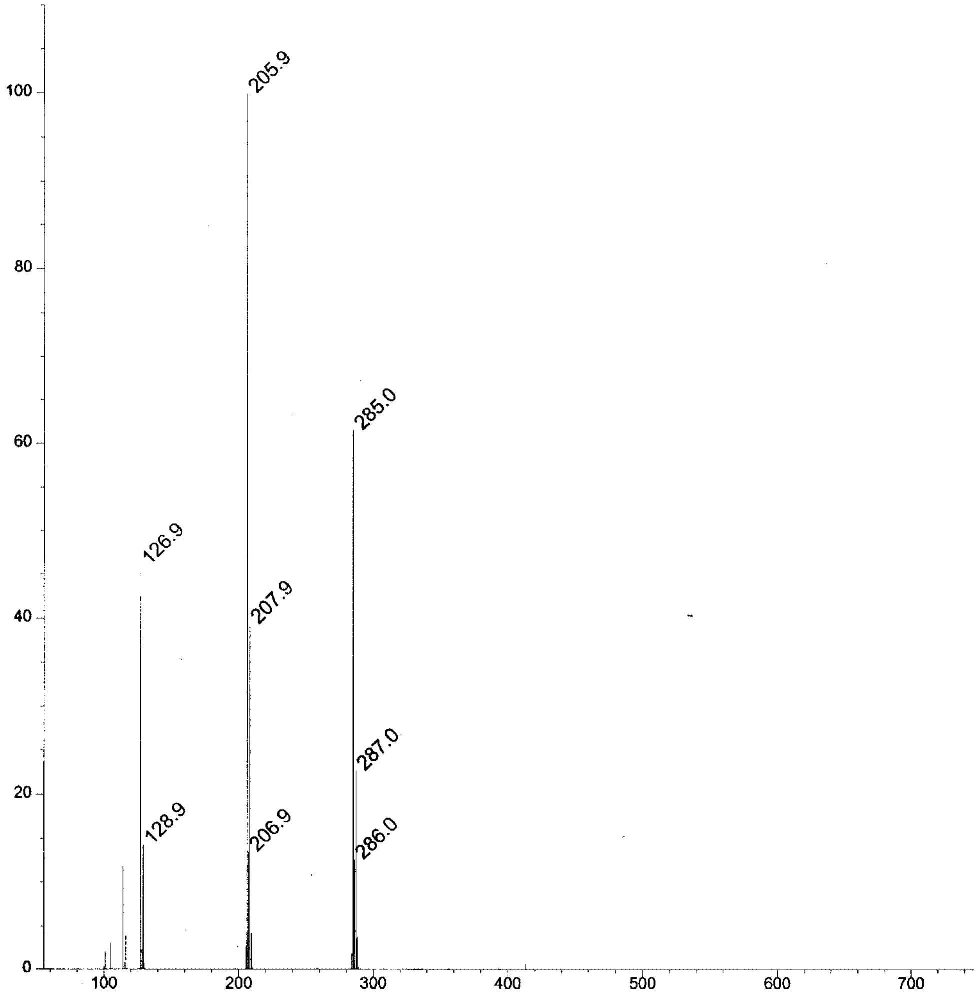
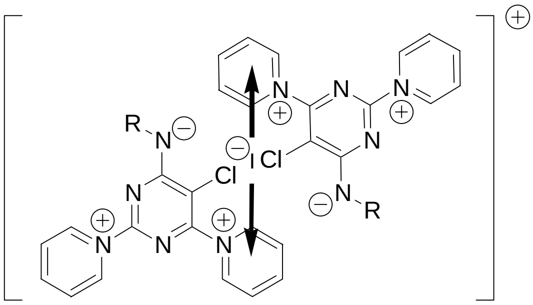


Figure 6

The dicationic 4-amino derivatives (**5a,b**), however, display a distinct behavior. At fragmentor voltages between 10 V and 40 V, the dicationic species (**5a,b**) are detectable at $M^{2+}/2$ = 142.6 and 180.6, respectively. At voltages between 80 and 200 V, the molecular peak of the tripoles (**6a,b**) increase gradually and reach a maximum at 150 V, whereas the peak of **5a,b** disappears. Parallely, the peak of the π-complexes (**9a,b**) at *m/z* = 695.2 and 847.2 develop. Obviously, the formation of π-complexes is dependend on the tripole concentration and on the fragmentor voltage. These results gain insights into the interesting supramolecular properties of the novel class of mesomeric betainium salts.



9a: R = H, *m/z* 695.2
9b: R = Ph, *m/z* 847.2

Scheme 5

ACKNOWLEDGEMENTS

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