

Molecular and Crystal Structure of 1-Amino-X-pyrazinium Mesitylenesulfonates*

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Received June 5, 2007

Abstract—X-Ray diffraction analysis was performed of 1-amino-X-pyrazinium mesitylenesulfonates (X = H, 2-NH₂, 3-NHCOMe, 3-OMe, 3-Cl). In all events save 1,2-diaminopyrazinium cation the bond length of N–NH₂ was shorter than that of N–N bond but considerably longer than the length of the double bond N=N. In the 1,2-diaminopyrazinium cation the bond distance C²–NH₂ was close to the length of a common double bond C=N indicating the iminium character of the cation. Quantum-chemical calculations [AM1, PM3, DFT/(PBE/3z), B3LYP/6-31G++(2d,p)] provided the geometry of cations similar to the experimental one. In the crystals under investigation motifs were observed of 0D, 1D, and 2D type mainly due to hydrogen bonds N–H···O and π -stacking interactions of the aromatic rings.

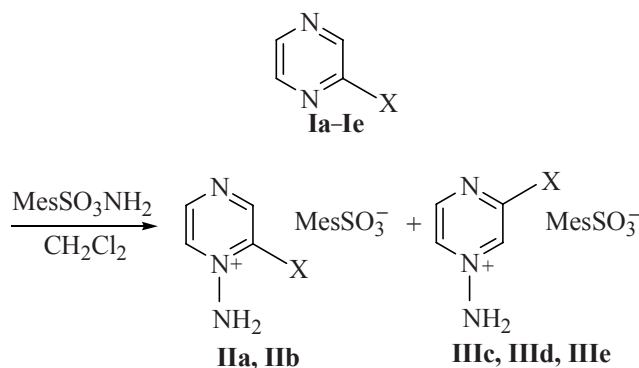
DOI: 10.1134/S1070428008020188

N-Amine salts of azines are widely used as reagents for arenes amination [2], preparation of imines [3], versatile heterocyclic and biologically active compounds [3–10]. Up till now the X-ray studies of N-amine salts of heteroaromatic compounds were limited to derivatives of pyridine [11–14], isoquinoline [15], 1,10-phenanthroline [16], and azoles [17–20], but were lacking for diazines.

The target of the present study was the investigation by X-ray diffraction analysis of the molecular structure of 1-amino-X-pyrazinium mesitylenesulfonates, the estimation of effect of substituents in the pyrazinium ring on the cation geometry, and also revealing the role of hydrogen bonds and stacking interactions in the formation of the crystalline structure of the salts.

The amination of X-pyrazines **Ia–Ie** with O-mesitylsulfonylhydroxylamine occurred virtually regioselectively with the formation of 1-amino-X-pyrazinium mesitylenesulfonates **IIa, IIb, IIIc–IIIe** [1, 4], that made it possible to obtain crystals of individual isomers fit for X-ray diffraction study.

* For preliminary communication see [1].



X = H (**a**), NH₂ (**b**), NHAc (**c**), MeO (**d**), Cl (**e**).

At X = H, Cl the cell contains two crystallographically independent types of ions with slightly different geometric parameters (Tables 1–6). The crystals of mesitylenesulfonate **IIa** contain additionally water molecules.

As seen from Tables 2–6 and Fig. 1 the skeleton of cations of salts **IIa, IIb, IIIc–IIIe** is virtually planar and atoms C and N according to the bond angles have the hybridization close to *sp*². The nitrogen of the amino group insignificantly deviates from the plane of the

Table 1. Data of X-ray diffraction analysis of 1-amino-X-pyrazinium mesitylenesulfonates **IIa**, **IIb**, **IIIc–IIIe**, parameters of experiment and refinement

Parameter	IIa	IIb	IIIc	IIId	IIIe
Molecular formula	$[\text{C}_4\text{H}_6\text{N}_3]^+$, $\text{C}_9\text{H}_{11}\text{O}_3\text{S}]^-$, $0.5\text{H}_2\text{O}$	$[\text{C}_4\text{H}_7\text{N}_4]^+$, $[\text{C}_9\text{H}_{11}\text{O}_3\text{S}]^-$	$\text{C}_6\text{H}_9\text{N}_4\text{O}]^+$, $[\text{C}_9\text{H}_{11}\text{O}_3\text{S}]^-$	$[\text{C}_5\text{H}_8\text{N}_3\text{O}]^+$, $[\text{C}_9\text{H}_{11}\text{O}_3\text{S}]^-$	$[\text{C}_4\text{H}_5\text{ClN}_3]^+$, $[\text{C}_9\text{H}_{11}\text{O}_3\text{S}]^-$
Molecular weight	304.36	310.37	352.41	325.38	329.80
Crystal system	monoclinic	rhombic	rhombic	triclinic	triclinic
Space group	$P2_1/n$	$Pbca$	$Pbcn$	$P-1$	$P-1$
a , Å	16.218(2)	12.372(2)	13.884(3)	5.753(1)	7.071(1)
b , Å	10.479(1)	7.5319(9)	7.202(3)	9.030(2)	14.599(4)
c , Å	17.972(1)	31.249(4)	34.202(6)	15.305(4)	14.810(3)
α , deg	90	90	90	96.80(2)	84.57(1)
β , deg	103.292(6)	90	90	95.16(2)	89.85(1)
γ , deg	90	90	90	91.83(2)	79.47(1)
V , Å ³	2972.7(4)	2911.9(6)	3420(2)	785.6(3)	1496.2(6)
Z	8	8	8	2	4
d_{calc} , g/cm ³	1.360	1.413	1.369	1.376	1.464
θ_{max} , deg	26.0	26.0	26.0	70.0	25.0
Accounting for extinction	empiric	by faceting	no	empiric	empiric
Transmission min./max	0.949/0.998	0.969/0.985	—	0.601/0.930	0.873/0.914
Reflections measured./independent.	6041/5830	2857/2857	3265/3251	3268/2951	5501/5271
wR_2 (all I)	0.1820	0.1301	0.1394	0.1309	0.2012
$GOOF$	1.017	1.013	1.004	1.031	1.057
$R_1 [I > 2\sigma(I)]$	0.0589	0.0479	0.0588	0.0468	0.0599

Table 2. Some bond lengths (Å), bond and dihedral angles (deg) of cation of salt **IIa** obtained by X-ray diffraction analysis and quantum-chemical calculations

Parameter	X-ray study		AM1	PM3	DFT	
					PBE/3z	B3LYP/ 6-31G++(2d,p)
N ¹ –N ⁷	1.380(3)	1.376(3)	1.370	1.437	1.382	1.382
N ¹ –C ²	1.342(4)	1.345(4)	1.383	1.379	1.360	1.355
N ¹ –C ⁶	1.342(4)	1.338(4)	1.383	1.378	1.360	1.355
C ² –C ³	1.363(4)	1.360(4)	1.417	1.402	1.391	1.391
C ³ –N ⁴	1.332(4)	1.326(5)	1.346	1.352	1.339	1.335
N ⁴ –C ⁵	1.329(4)	1.328(5)	1.346	1.352	1.339	1.335
C ⁵ –C ⁶	1.361(4)	1.372(5)	1.417	1.402	1.360	1.391
C ² N ¹ N ⁷	120.5(3)	120.3(3)	120.9	119.9	119.9	119.7
C ⁶ N ¹ N ⁷	119.6(3)	119.8(3)	121.0	119.9	119.9	119.7
N ¹ C ² C ³	118.7(3)	118.7(3)	119.6	119.2	118.5	118.5
C ² C ³ N ⁴	123.4(3)	123.8(3)	123.2	120.9	123.2	123.2
C ² N ¹ C ⁶	119.8(3)	119.8(3)	117.7	119.7	119.9	119.9
C ³ N ⁴ C ⁵	115.8(3)	115.6(3)	116.6	119.9	116.6	116.7
N ⁴ C ⁵ C ⁶	123.7(3)	123.8(3)	123.2	120.9	123.2	123.2
C ⁵ C ⁶ N ¹	118.6(3)	118.3(3)	119.6	119.2	118.5	118.5
H ⁷ N ⁷ H ^{7'}	112(3)	113(3)	110.8	112.8	112.0	111.8
N ¹ N ⁷ H ⁷	110(3)	108(3)	111.0	110.8	111.6	111.5
N ¹ N ⁷ H ^{7'}	112(3)	112(3)	111.0	110.8	111.6	111.5
N ⁷ N ¹ C ² C ³	–174.9(3)	–178.5(3)	172.0	173.1	0.0	175.0
N ¹ C ² C ³ N ⁴	–0.5(5)	0.4(5)	0.0	–0.3	–0.1	–0.2
H ⁷ N ⁷ N ¹ C ²	–28(2)	–28(2)	33.1	30.3	29.2	29.9
H ^{7'} N ⁷ N ¹ C ²	–153(2)	–152(2)	155.3	156.4	155.6	155.7

Table 3. Some bond lengths (E), bond and dihedral angles (deg) of cation of salt **IIb** obtained by X-ray diffraction analysis and quantum-chemical calculations

Parameter	X-ray study	AM1	PM3	DFT	
				PBE/3z	B3LYP/ 6-31G++(2d,p)
N ¹ –N ⁷	1.418(4)	1.376	1.456	1.420	1.412
N ¹ –C ²	1.351(4)	1.404	1.397	1.371	1.360
N ¹ –C ⁶	1.368(4)	1.405	1.412	1.374	1.373
C ² –C ³	1.421(4)	1.486	1.455	1.435	1.434
C ³ –N ⁴	1.306(4)	1.308	1.313	1.311	1.304
N ⁴ –C ⁵	1.353(5)	1.375	1.388	1.361	1.358
C ⁵ –C ⁶	1.340(5)	1.382	1.367	1.371	1.366
C ² –NH ₂	1.312(4)	1.348	1.358	1.332	1.329
C ² N ¹ N ⁷	116.2(3)	118.9	118.4	116.2	116.4
C ⁶ N ¹ N ⁷	123.3(3)	122.9	121.8	122.7	122.7
N ¹ C ² C ³	116.4(3)	116.4	117.2	116.0	116.0
C ² C ³ N ⁴	123.6(3)	123.9	121.4	123.2	123.2
C ² N ¹ C ⁶	120.5(3)	118.0	119.7	120.9	120.2
C ³ N ⁴ C ⁵	117.2(3)	117.8	120.9	118.7	118.7
N ⁴ C ⁵ C ⁶	122.9(3)	121.2	119.9	119.4	119.5
C ⁵ C ⁶ N ¹	119.4(3)	121.1	119.9	120.0	119.8
N ¹ C ² NH ₂	120.7(3)	123.6	122.1	119.7	119.7
C ³ C ² NH ₂	123.0(3)	119.8	120.6	124.1	124.1
H ⁸ N ⁸ H ^{8'}	118(4)	118.2	118.9	120.3	120.3
H ⁷ N ⁷ H ^{7'}	110(4)	109.4	108.4	108.7	109.3
N ¹ N ⁷ H ⁷	106(2)	109.4	108.3	108.7	109.4
N ¹ N ⁷ H ^{7'}	107(2)	109.2	111.1	109.0	110.0
N ⁷ N ¹ C ² NH ₂	0.5(4)	0.0	0.8	0.0	0.0
N ⁷ N ¹ C ² C ³	–178.5(3)	180.0	–179.5	179.9	179.9
NH ₂ C ² N ¹ C ⁶	179.3(3)	180.0	–179.0	–179.9	–179.9
H ⁷ N ⁷ N ¹ C ²	–85(2)	–120.0	–119.4	–119.9	–119.8
H ^{7'} N ⁷ N ¹ C ²	157(3)	120.4	121.3	120.7	120.2
H ⁸ N ⁸ C ² N ¹	1(3)	0.0	–3.1	0.0	0.0

Table 4. Some bond lengths (E), bond and dihedral angles (deg) of cation of salt **IIIc** obtained by X-ray diffraction analysis and quantum-chemical calculations

Parameter	X-ray study	AM1	PM3	DFT	
				PBE/3z	B3LYP/6-31G++(2d,p)
N ¹ –N ⁷	1.385(5)	1.372	1.431	1.385	1.387
N ¹ –C ²	1.340(5)	1.376	1.368	1.351	1.343
N ¹ –C ⁶	1.351(5)	1.377	1.372	1.361	1.352
C ² –C ³	1.403(6)	1.444	1.417	1.412	1.409
C ³ –NH	1.369(5)	1.384	1.391	1.372	1.372
C ³ –N ⁴	1.333(5)	1.385	1.379	1.334	1.341
N ⁴ –C ⁵	1.338(5)	1.331	1.339	1.332	1.327
C ⁵ –C ⁶	1.374(6)	1.420	1.410	1.391	1.389
C ² N ¹ N ⁷	118.3(4)	120.7	119.5	119.2	119.8
C ⁶ N ¹ N ⁷	120.3(4)	120.0	119.7	119.0	119.0
N ¹ C ² C ³	117.9(4)	120.2	118.9	117.8	118.0
C ² C ³ N ⁴	123.0(4)	120.2	120.7	121.9	121.5
C ² N ¹ C ⁶	121.3(4)	118.8	120.4	121.6	121.8

Table 4. (Contd.)

Parameter	X-ray study	AM1	PM3	DFT	
				PBE/3z	B3LYP/6-31G++(2d,p)
C ³ N ⁴ C ⁵	115.8(4)	117.3	119.0	117.6	117.9
N ⁴ C ⁵ C ⁶	124.6(4)	124.4	121.7	124.1	124.1
C ⁵ C ⁶ N ¹	117.4(4)	118.8	119.2	117.5	117.3
C ² C ³ NH	121.8(4)	121.8	123.0	122.4	122.4
NHC ³ N ⁴	115.0(4)	117.8	116.1	115.6	115.6
H ⁷ N ⁷ H ^{7'}	120(4)	110.8	112.9	111.9	111.2
N ¹ N ⁷ H ⁷	108(3)	111.2	111.2	111.0	110.8
N ¹ N ⁷ H ^{7'}	106(2)	110.6	110.9	110.9	110.5
N ⁷ N ¹ C ² C ³	−178.5(4)	172.5	173.6	174.8	174.8
NHC ³ N ⁴ C ⁵	177.1(4)	180.0	179.6	179.9	179.5
H ⁷ N ⁷ N ¹ C ²	−34(3)	−20.5	−22.6	22.7	20.7

Table 5. Some bond lengths (E), bond and dihedral angles (deg) of cation of salt **IIIId** obtained by X-ray diffraction analysis and quantum-chemical calculations

Parameter	X-ray study	AM1	PM3	DFT	
				PBE/3z	B3LYP/6-31G++(2d,p)
N ¹ –N ⁷	1.354(3)	1.370	1.432	1.386	1.412
N ¹ –C ²	1.334(3)	1.373	1.373	1.346	1.373
N ¹ –C ⁶	1.363(3)	1.383	1.373	1.366	1.360
C ² –C ³	1.386(3)	1.438	1.419	1.415	1.434
C ³ –O	1.331(3)	1.356	1.341	1.322	1.304
C ³ –N ⁴	1.323(3)	1.365	1.373	1.338	1.358
N ⁴ –C ⁵	1.350(3)	1.339	1.342	1.338	1.366
C ⁵ –C ⁶	1.355(3)	1.418	1.408	1.387	1.329
C ² N ¹ N ⁷	119.4(2)	120.6	119.5	119.9	116.4
C ⁶ N ¹ N ⁷	120.0(2)	120.5	119.7	118.9	122.7
N ¹ C ² C ³	117.9(2)	119.2	118.3	118.1	119.7
C ² C ³ N ⁴	124.0(2)	122.8	121.4	122.4	123.2
C ² N ¹ C ⁶	120.6(2)	118.3	120.3	121.0	120.2
C ³ N ⁴ C ⁵	115.5(2)	116.0	118.9	117.1	117.2
N ⁴ C ⁵ C ⁶	124.0(2)	124.0	121.5	123.7	120.3
C ⁵ C ⁶ N ¹	118.1(2)	119.5	119.5	117.7	117.6
C ² C ³ O	115.3(2)	113.5	116.8	115.6	124.1
OC ³ N ⁴	120.7(2)	123.6	121.7	122.0	116.0
C ² C ³ N ⁴	124.0(2)	122.8	121.4	122.4	123.2
H ⁷ N ⁷ H ^{7'}	120(3)	111.0	112.9	111.6	110.0
N ¹ N ⁷ H ⁷	114(2)	111.2	111.2	111.1	110.7
N ¹ N ⁷ H ^{7'}	113(2)	110.9	111.1	110.8	110.5
N ⁷ N ¹ C ² C ³	176.2(2)	172.3	173.5	174.8	175.2
OC ³ C ² N ¹	−179.3(2)	180.0	180.0	−179.7	179.9
H ⁷ N ⁷ N ¹ C ²	36(2)	−28.9	−28.8	25.8	−179.9

Table 6. Some bond lengths (E), bond and dihedral angles (deg) of cation of salt **IIIe** obtained by X-ray diffraction analysis and quantum-chemical calculations

Parameter	X-ray study		AM1	PM3	DFT	
					PBE/3z	B3LYP/6-31G++(2d,p)
N ^I –N ⁷	1.338(6)	1.345(6)	1.370	1.435	1.381	1.383
N ^I –C ²	1.354(6)	1.335(6)	1.381	1.378	1.356	1.348
N ^I –C ⁶	1.330(6)	1.343(6)	1.381	1.373	1.363	1.353
C ² –C ³	1.352(7)	1.374(7)	1.426	1.407	1.401	1.399
C ³ –Cl	1.717(5)	1.720(5)	1.684	1.646	1.718	1.715
C ³ –N ⁴	1.318(7)	1.309(7)	1.359	1.369	1.329	1.323
N ⁴ –C ⁵	1.338(7)	1.337(6)	1.341	1.342	1.339	1.332
C ⁵ –C ⁶	1.351(7)	1.351(7)	1.419	1.408	1.390	1.388
C ² N ^I N ⁷	120.1(4)	119.9(4)	120.6	119.6	119.8	119.4
C ⁶ N ^I N ⁷	120.3(4)	119.8(4)	121.0	120.0	119.6	119.6
N ^I C ² C ³	118.2(5)	117.2(5)	119.9	119.3	117.9	117.9
C ² C ³ N ⁴	124.9(5)	125.3(5)	122.4	120.3	123.3	122.9
C ² N ^I C ⁶	119.6(4)	120.3(4)	118.0	120.0	120.5	120.6
C ³ N ⁴ C ⁵	114.2(5)	114.5(5)	116.6	120.0	116.9	117.5
N ⁴ C ⁵ C ⁶	124.7(5)	124.2(5)	123.7	121.1	123.3	122.8
C ⁵ C ⁶ N ^I	118.4(5)	118.4(5)	119.4	119.2	118.1	118.2
C ² C ³ Cl	117.9(4)	117.3(4)	117.4	121.0	117.7	118.7
H ⁷ N ⁷ H ^{7'}	121(5)	127(6)	110.9	112.8	112.3	111.3
N ^I N ⁷ H ⁷	115(3)	120(4)	111.0	111.0	111.5	111.0
N ^I N ⁷ H ^{7'}	117(4)	114(5)	111.2	111.0	111.7	111.3
N ⁷ N ^I C ² C ³	179.0(3)	179.7(3)	172.2	173.3	175.0	175.1
ClC ³ C ² N ^I	177.0(4)	176.9(4)	179.0	–179.0	180.0	180.0
H ⁷ N ⁷ N ^I C ²	20(4)	6(5)	–32.8	30.0	–27.4	30.5
H ⁷ N ⁷ N ^I C ²	170(4)	–171(5)	154.3	156.4	–153.8	–155.2

pyrazine ring. The experimentally measured angles C³N⁴C⁵ are significantly smaller than angles C²C³N⁴ and N⁴C⁵C⁶ characteristically for the compounds with a pyrazine ring [21–23]. In all cations the angles C²N^IC⁶ are larger than angles C³N⁴C⁵ in conformity to the theory of electron pairs repulsion [24]. As show the bond angles N^IN⁷H⁷, N^IN⁷H^{7'}, and H⁷N⁷H^{7'} in cations of salts **IIa**, **IIb**, **IIIc**, and **IIId** the amino group possesses a pyramidal configuration, and in cation of salt **IIIe** its configuration is close to planar. According to quantum-chemical calculations in all cations the hybridization of the nitrogen of amino group should be close to *sp*³ (Tables 2–6). In all cases but in cation of salt **IIb** the bond length N^I–NH₂ is less than ordinary bond N_{planar}–N_{planar} (1.401 E) or N_{planar}–N_{pyramidal} (1.420 E) [25], but significantly longer than the double bond N=N (1.25 E) [26] indicating weak involvement of the unshared electron pair of the amino group nitrogen into the conjugation with the pyrazine fragment. In cations of salts **IIa**, **IIIc–IIIe** the bond distance N^I–NH₂ is considerably shorter than in pyridine derivatives: N-amino-2,4,6-triphenylperidinium

cation (1.418 E) [12], complex of 1-aminopyridinium tetrafluoroborate with dibenzo-18-crown-6 (1.414 E) [14], 1-amino-1,10-phenanthroline cation (1.403 E) [16]. This is apparently caused by the acceptor effect of the additional nitrogen in the ring of cations of salts **IIa**, **IIIc–IIIe**. According to the resonance theory the increase in the bond order between atom N^I and NH₂ group should increase the contribution into the resonance hybrid of the saturated structures **A–A''** and should result in appearance of negative charge on atoms C², C⁶, and N⁴; therewith the high electronegativity of the nitrogen leads to larger contribution of structure **A''** compared to analogous amino cations of the pyridine series. Taking into consideration that the saturated structures **A–A''** include two adjacent positively charged nitrogen atoms their contribution into the resonance hybrid should not be significant. The acceptor substituents should favor the growth of this contribution and of the bond order N–NH₂. Actually, in the series of cations of salts **IIa**, **IIId**, and **IIIe** a trend is observed to shortening of N^I–NH₂ bond that may be attributed to the growing conjugation

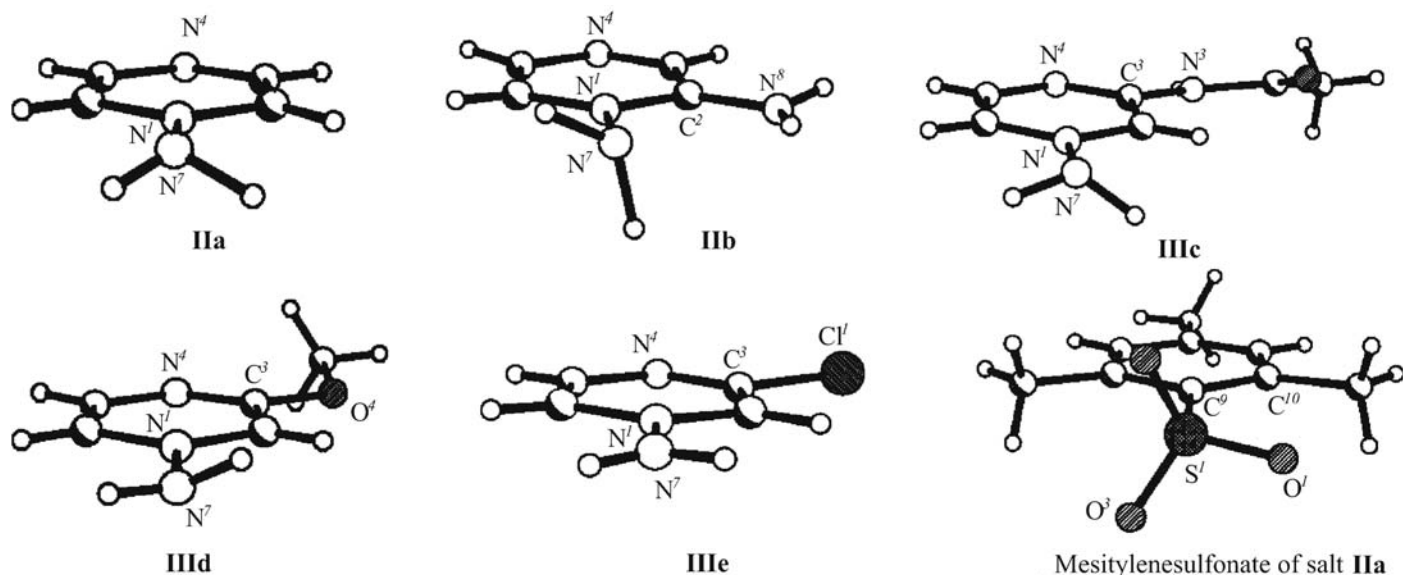
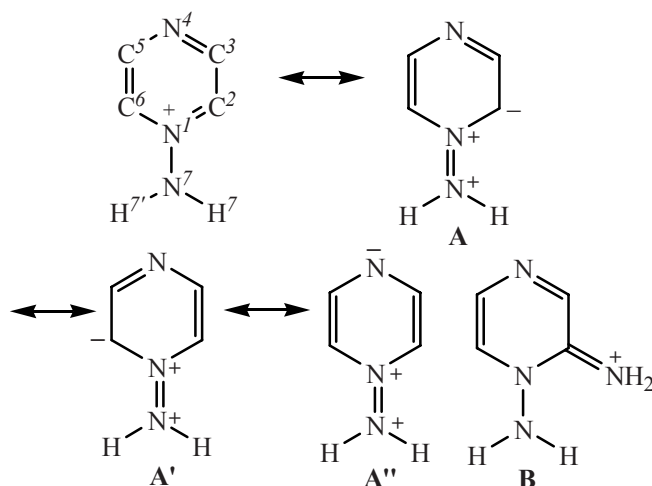


Fig. 1. Structure of cations of salts **IIa**, **IIb**, **IIc–IIe** and of anion of salt **IIa**.

between the NH_2 group and atom N^1 in keeping with the increasing acceptor character of the substituent X.



The presence of donor substituents in position 2 should decrease the contribution of structures **A**, **A'** and decrease the order of this bond. Actually in the cation of salt **IIb** the bond length $\text{N}^1\text{--NH}_2$ is close to the length of an ordinary N--N bond, whereas the bond $\text{C}^2\text{--NH}_2$ is shortened and close in the length to a common double bond $\text{C}_{\text{sp}^2}\text{=N}$ (1.3 Å) [25]. This indicates a significant contribution of iminium structure **B** into the corresponding resonance hybrid. The carbon-carbon distances in the pyrazine ring of the cations of salts **IIa**, **IIb**, **IIc–IIe** are close to the corresponding values in pyrazine [21]; therewith introducing donor substituents into positions 2 and 3 results in elongation of the bond between atoms C^2 and C^3 .

The structure of anions of salts **IIa**, **IIb**, **IIc–IIe** is analogous (Fig 1) and similar to the structure of ammonium mesitylenesulfonate [27].

The data on geometry of cations obtained by X-ray diffraction analysis are compared to results of quantum-chemical calculations. Both semiempirical and ab initio calculations give cations geometry close to experimentally found, but as a rule the calculated bond lengths are somewhat overestimated (Tables 2–6). The closest to the experimental values of bond lengths were obtained by method DFT [(PBE/3z) and B3LYP/6-31G++(2d,p)], average deviation of bond distances CC, CN, CO, NN, and CCl from the experimental values was 0.014 and 0.016 Å respectively. The calculations by AM1 and PM3 procedures give larger average deviations (0.033 and 0.038 Å respectively).

The analysis of the crystal structure of salts **IIa**, **IIb**, **IIc–IIe** shows that the main building blocks governing it are fragments $\text{N--H}\cdots\text{O}$ leading to supermolecules (0D architecture) or chains/bands (1D architecture) (cf. [28]). Parameters of hydrogen bonds of salts **IIa**, **IIb**, **IIc–IIe** are presented in Table 7. In the crystals of salts **IIId** and **IIe** the amino group plays the part of hydrogen donor in the hydrogen bond forming as a result supermolecules possessing a symmetry center (Fig. 2). The form of the eight-membered ring $(\cdots\text{OSO}\cdots\text{N}\cdots)_2$ of supermolecule **IIId** resembles a chair with equatorial aromatic rings. Owing to π -stacking interactions in pairs pyrazinium–pyrazinium (distances between the centers and the planes are 3.48 and 3.31 Å respectively) and interactions $\text{S--O}\cdots\pi(\text{pyrazinium})$ (cf. [29]) [O^1 -

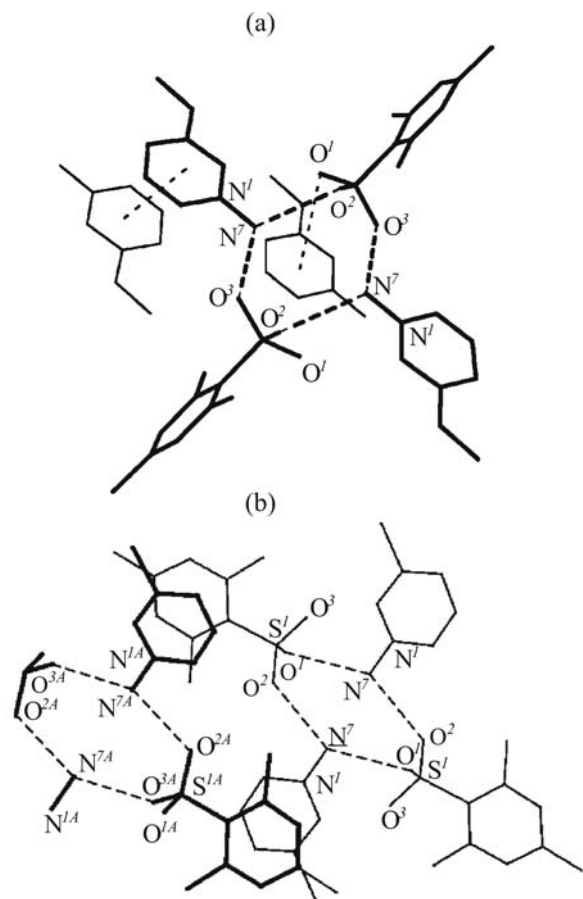


Fig. 2. Fragments of packing of supermolecules in crystals of salts **IIIc** (a) and **IIIe** (e) (hydrogen atoms not shown). The second crystallographically independent ions are marked with A character in the numbers of atoms.

centroid(Cg), 3.317 E, S–O^l...Cg 100.2°] the supermolecules form layers parallel to the *ab* plane (Fig. 2a). Similar supermolecules having a symmetry center formed in the crystal of **IIIe** salt (Fig. 2b), and therewith two of them are crystallographically independent. Unlike mesitylenesulfonate **IIIc** the supermolecules are stacked due to the π -stacking interaction between pyrazinium and mesitylene rings of the contiguous supermolecules resulting in layers formation parallel to the *ac* plane. The distances between the centers and the planes are in the range 3.48–3.62 and 3.45–3.51 E respectively.

The formation of molecular ensembles like supermolecules of salts **IIIc** and **IIIe** with a ring ($\cdots$ OSO $\cdots$ N $\cdots$)₂ in the boat form is also observed in the crystals of salts **IIa** and **IIIc**. However these ensembles cannot be regarded as supermolecules [30] for in salt **IIa** solvate water molecules combine them in wide bands oriented along *b* axis (Fig. 3a), and in salt **IIIc** the uniting role plays the aminoacetyl group leading to the formation

Table 7. Parameters of hydrogen bonds (D–H $\cdots$ A) in crystals of salts **IIa**, **IIb**, **IIIc–IIIe**

D–H $\cdots$ A IIa	D–H, Å	H $\cdots$ O, Å	D–H $\cdots$ A, deg	D $\cdots$ A, Å
N ⁷ –H ⁷ ...O ²	0.99(4)	1.89(4)	171(3)	2.878(4)
N ⁷ –H ⁷ ...O ^{2A}	0.79(3)	2.08(3)	164(3)	2.843(3)
N ^{7A} –H ^{7A} ...O ^l	0.95(4)	1.88(4)	168(4)	2.816(4)
N ^{7A} –H ^{7A} ...O ^{lA}	0.85(4)	1.96(4)	172(3)	2.805(4)
O ^{lW} –H...O ³	-	-	-	2.918(5)
O ^{lW} –H...O ^{3A}	-	-	-	2.740(5)
O ^{lW} –H...N ⁴	-	-	-	2.953(5)
IIb				
N ⁷ –H ⁷ ...O ²	0.88(4)	2.19(4)	160(4)	3.035(4)
N ⁷ –H ⁷ ...O ³	0.95(4)	2.05(4)	159(3)	2.958(4)
N ⁸ –H ⁸ ...O ^l	0.87(4)	1.95(4)	172(3)	2.813(4)
N ⁸ –H ⁸ ...N ⁴	0.91(4)	2.21(4)	147(4)	3.018(4)
IIIc				
N ⁷ –H ⁷ ...O ³	0.99(5)	2.02(5)	161(4)	2.969(5)
N ⁷ –H ⁷ ...O ²	0.93(4)	2.01(4)	167(4)	2.923(5)
N ³ –H ³ ...O ³	0.86	1.97	173	2.823(5)
IIId				
N ⁷ –H ⁷ ...O ²	0.95(3)	1.91(3)	170(3)	2.855(3)
N ⁷ –H ⁷ ...O ³	0.85(3)	2.01(3)	177(3)	2.859(3)
IIIe				
N ⁷ –H ⁷ ...O ^l	0.85(6)	2.01(6)	167(5)	2.852(7)
N ⁷ –H ⁷ ...O ²	0.75(6)	2.08(6)	166(6)	2.813(7)
N ^{7A} –H ^{7A} ...O ^{2A}	0.87(5)	1.99(5)	158(4)	2.815(6)
N ^{7A} –H ^{7A} ...O ^{3A}	0.87(6)	2.01(6)	168(5)	2.870(6)

of bands along *b* axis (Fig. 3, b). Note the interactions within the band C^{17A}–H $\cdots$ π (C⁹–C¹⁴) for the salt **IIa** with parameters H $\cdots$ Cg 2.74 E, C–H $\cdots$ Cg 164°, and also shortened contacts C–H $\cdots$ O: C⁵H⁵...O³ 2.32, C^{5A}H^{5A}...O^{3A} 2.32, C⁶H⁶...O^{lW} 2.43 E (cf. [31]). In the crystal of salt **IIIc** also shortened contacts were observed: inside the band C⁶H⁶...O^l (2.29 E) and between the bands C⁸H^{8A}...O^l (2.44 E).

In the crystal of salt **IIb** form bands oriented along *b* axis of another type, involving both amino groups (Fig. 4). The amino group at the atom N^l is of *sp*³ hybridization and is turned from the plane of the pyrazinium ring [torsion angle C²N⁷N⁷H^{7A}–85(3) deg], whereas the second amino group is planar and located in the plane of the ring. This geometry of amino groups evidently originates from the hydrogen bonds N–H $\cdots$ O. Mark the interaction within the band S^l–O^l... π (pyrazinium), O $\cdots$ Cg (3.15 E), S–O $\cdots$ Cg [129.8(2) deg]. Owing

to the hydrogen bonds $N^8-H^8 \cdots N^4$ the bands are joined into layers parallel to the *ab* plane.

Thus the substituent *X* in 1-amino-*X*-pyrazinium mesitylenesulfonates significantly affects the cation geometry, and the main building blocks governing the crystal structure are the $N-H \cdots O$ fragments leading to the formation of supermolecules or chains/bands.

EXPERIMENTAL

X-Ray analysis was performed on diffractometers Bruker P4 (MoK_{α} -radiation) and Syntex P21 (CuK_{α} -radiation), graphite monochromators, $\theta/2\theta$ -scanning and ω -scanning (salts **IIa**, **IIIc**, **IIe** and **IIf**, **IIc** respectively). Crystallographic data of the salts are compiled in Table 1. The structures were solved using SHELXS-97 software and refined by the least-squares method in the anisotropic approximation applying the program SHELXL-97 [32]. The hydrogens of amino groups were refined in isotropic approximation, the other hydrogen atoms, in isotropic approximation and using *rider* model (salts **IIf**, **IIIc** and **IIc**, **IIId** respectively), and also by a mixed procedure (for **IIa**). We failed to localize the hydrogen atoms of water in salt **IIa**. The atomic coordinates are deposited into the Cambridge Structural Database (nos. CCDC 647105–647109).

The quantum-chemical calculations by AM1 and PM3 procedures were carried out using software package MOPAC [33]. The calculations by DFT method in approximations PBE [34] and B3LYP [35, 36] were performed employing programs PRIRODA [37, 38] {basis 3z, (11s6p2d)/[6s3p2d] for C and O, (5s1p)/[3s1p] for H} and GAMESS [39]. The evaluation of the type of the critical points on the potential energy surface was performed by calculation of Hesse matrix [40].

We used in the study pyrazine (99+%), 2-amino-pyrazine (98%), 2-chloropyrazine (98%), 2-methoxy-pyrazine (98%) purchased from Lancaster. O-Mesitylsulfonylhydroxylamine ($MesSO_3NH_2$) and 2 acylamino-pyrazine were prepared by procedures [4] and [41, 42] respectively. Dichloromethane was purified by washing with saturated solution of Na_2CO_3 followed by boiling with activated carbon, drying, and distillation over anhydrous $CaCl_2$ [26].

General procedure of salts preparation. A solution of 2-*X*-pyrazine (~0.5 mmol) in 1 ml of dichloromethane was cooled to 0°C and at vigorous stirring it was added dropwise into a solution of $MesSO_3NH_2$ (~0.75 mmol) in 1.5 ml of CH_2Cl_2 preliminary dried over Na_2SO_4 (in

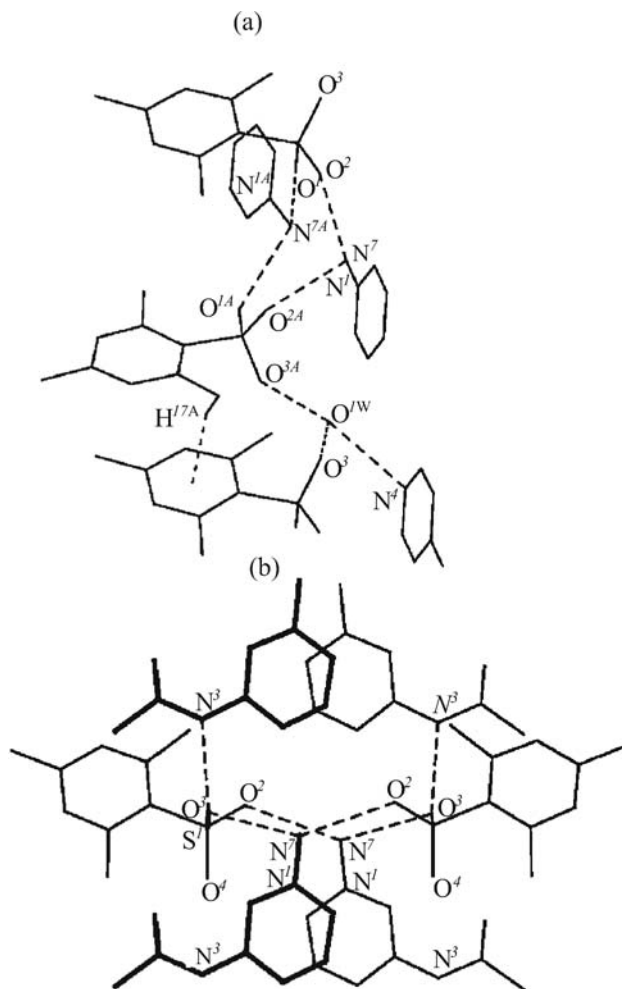
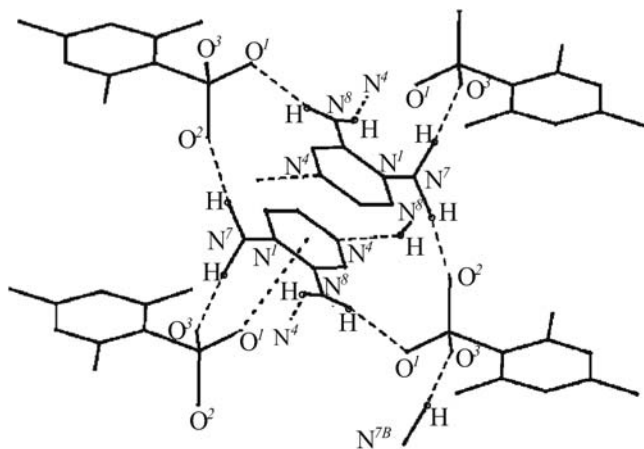


Fig. 3. 1D motifs in crystals of salts **IIa** (a) and **IIIc** (b) (hydrogen atoms not shown save H^{17A} in cation **IIa**). The second crystallographically independent ions are marked with A character in the numbers of atoms.



the case of mesitylenesulfonate **III**d CHCl_3 was used for solvent and the salt was recrystallized from *i*-PrOH]. The mixture was stirred at 0°C for 30 min, then warmed to room temperature and additionally stirred for 3 h. Into the solution 10 ml of Et_2O was added, the formed precipitate was separated, washed with ether, and dried in a vacuum. Yields of the salts **II**a, **II**b, **III**c–**III**e were 65, 75, 60, 82, and 40% respectively. Crystals of salts **II**a, **III**c, and **III**e for the X-ray diffraction study were obtained by recrystallization from a mixture *i*-PrOH–MeOH, 10:1. 1-Amino-pyrazinium mesitylenesulfonate was precipitated by adding petroleum ether to the salt solution in CH_2Cl_2 containing equimolar to the salt amount of dibenzo-18-crown-6.

The study was carried out under a financial support of the Russian Foundation for Basic Research (grants nos. 06-03-32406 and 06-03-32229) and of Department of Chemistry and Material Science of the Russian Academy of Sciences (Program 5.1.9).

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