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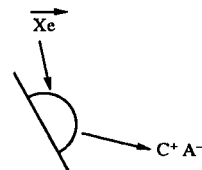
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Significant information on the structure of various bisazolium salts of the type CA_2 ($C^{++} 2A^-$) were revealed by the study of the FAB spectra of their positive and negative ions. Thus only one spectrum, whatever it consists of the positive or of the negative ions spectrum, enables the identification of the cation C^{++} and of the anion A^- . Moreover, the same information are collected from the CAD spectrum of the adduct ion CA^+ allowing the identification of such a compound in a mixture.

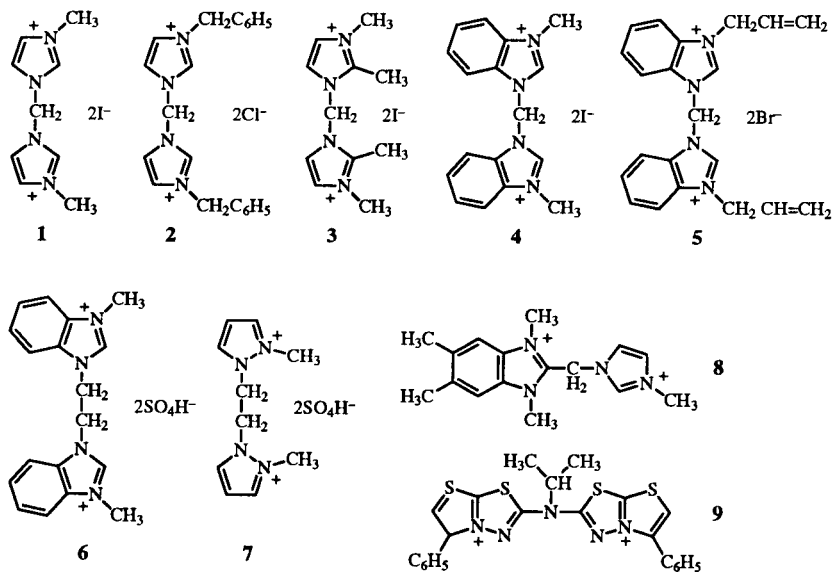
J. Heterocyclic Chem., 34, 367 (1997).

For the characterization of a solid organic compound by mass spectrometry involving an ionization method such as electron bombardment, the compound studied must be in the gaseous state during that ionization, therefore necessitating a preliminary heating. For a long time such a constraint has reduced the scope of mass spectrometry towards the identification of organic salts because thermal degradation was often encountered during that process. This constraint does not exist any more if desorption ionization technics are used and in particular with the FAB (Fast Atom Bombardment) method [1]. With the latter the ionization is achieved without any heating by the action of the energized beam on the solution of the compound studied in a solvent named matrix (Scheme 1).

Scheme 1



Fast Atom Bombardment (FAB) mass spectrometry is therefore a very suitable technic for the identification of organic salts of the type $[C^+A^-]$ (where C^+ and A^- respectively represent the cation and the anion) since the observed ions are very abundant and since the spectra, which are easy to analyze, give significant analytical



information. The energized beam enables the desorption of positive and negative ions in the gaseous phase. Such a process cannot be called a true ionization as the ions already exist in the condensed phase.

In the case of a compound of the type $[C^+A^-]$, the FAB spectrum of the positive ions contains the cation C^+ with a large abundance as well as various adducts of higher masses such as $[C_2A]^+$, allowing the identification of A^- , $[C+M]^+$ (where M represents the matrix), ... Similarly, the FAB spectrum of the negative ions shows the anion A^- with a strong abundance and miscellaneous adducts which have higher masses, viz. $[CA_2]^-$ allowing the identification of C^+ , $[A+M]^-$, ... [2-9].

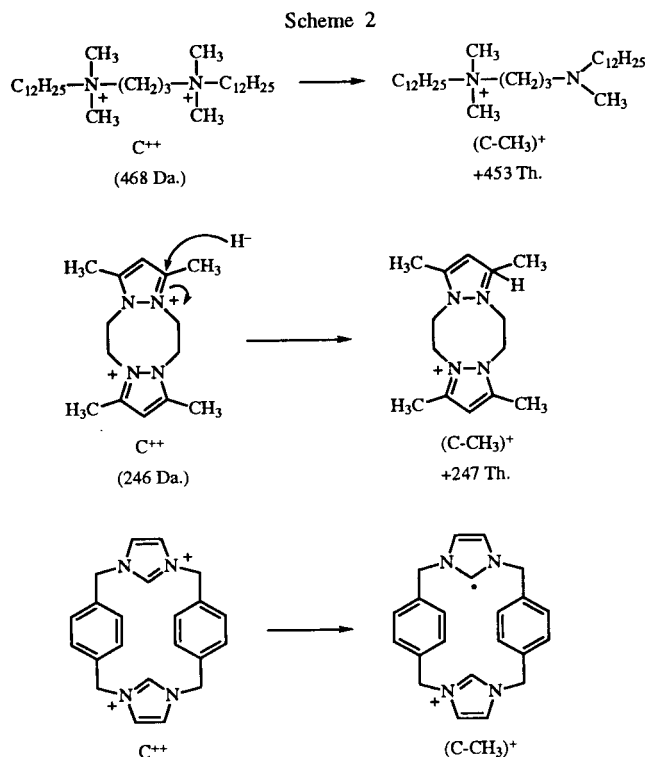
FAB mass spectrometry also permits us to characterize doubly charged organic cations C^{++} (Compound: CA_2 , C^{++} : cation, A^- : anion), but such spectra are more complex [6,10-18]. Three ions are often present in the spectrum of the positive ions:

- The adduct ion: $[CA]^+$,
- The ion formed by loss of a proton: $[C-H]^+$,
- The doubly charged ion at $C/2$.

Furthermore, the spectra frequently exhibit the characteristic ions of the matrix which is not the case for the FAB spectra of the compounds $[CA]$.

In addition to the easy identification of the ions C^{++} and A^- , the study of the FAB spectra of positive ions from compounds $[CA_2]$ has another aspect. In this respect, the presence of the second charge allows one to investigate the reactivity encountered in the matrix (for example, reduction following the attachment of an electron in the initial step) as well as in the gaseous phase (study of the CAD spectra of the adduct ion) [15-18]. Indeed, the second

charge makes it possible to observe the singly charged ion resulting from the chemical reaction of a negative entity with the doubly charged cation. Three examples of such an observed reaction are depicted in the Scheme 2:



- Nucleophilic substitution [15,16],
- Hydride addition [17],
- Reduction by fixing one electron [18].

Table 1

Positive Ion FAB Mass Spectra of Compounds 1-7, Matrix, *m*-Nitrobenzyl Alcohol
(For each ion the numerical value of the abundance is indicated in parentheses)

Compound	C^{++}	CA_2	$(CA)^+ + nCA_2$ ($n=0, 1, \dots$)	$(C-H)^+ + nCA_2$ ($n=0, 1, \dots$)	$(C-H+16)^+$	$(C-R)^+$	Others ions				
1	178	432	305/737/1169 (39)/(8.5)/(2)	177/609 (100)/(4-4)	193 (4)	163 (11)	95 (24.5)	96 (14)			
2	330	400	365 (10.7)	329 (100)	345 (4.5)	239 (25.8)	171 (12)	172 (16)	173	159	
3	206	460	333/793 (91)/(5.6)	205/665 (100)/(2-6)	221 (3.5)	191 (17.5)	109 (77)	110 (26.5)			
4	278	532	405/937 (43)/(3)	277/809 (100)/(<1)	293 (4.4)	263 (13-7)	145 (34.5)	146 (31)	147	133	
5	330	488	409/897 (22.7)/(1)	329/817 (100)/(<1)	345 (3.5)	289 [a]	171 (20)	172 (25.8)	173 (6.5)	159 (16-5)	131 (21)
6	292	486	389 (48)	291 (51)	307 [a]	277 (100)	159 (54)	160 (7)			
7	192	386	289 [a]	191/192 (17)/(10)	207 (2.5)	177 (100)	109 (64)	110 (13)	107 (49)		

[a] Same value as the matrix ion. [b] R = Me: 1, 3, 4, 6, 7; R = $C_6H_5CH_2$: 2; R = $CH_2=CHCH_2$: 5.

Table 2
Negative Ion FAB Mass Spectra of Compounds 1-7, Matrix, Nitrobenzyl Alcohol
(For each ion, numerical value of the abundance is indicated in parentheses)

Compound	CA ₂	A ⁻	(CA ₂ -H) ⁻	(A + nCA ₂) ⁻ (n=1, 2, ...)	(A+M) ⁻ (n = 0, 1..)	(NBA+nCA ₂) ^{-*} (n=1,2, ..)
1	432	127	431 (18.5)	559/991/1423/1855 (55.5)/(9)	127/280 (41)/(100)	585/1017/1449 (12)
2	400	35	399 (15.5)	435/835/1235 (24.5)	35/188 (15)/(100)	553/953/1353 (8.5)
3	460	127	459 (29.5)	587/1047/1507/1967 (100)/(24)	127/280 (74)/(84.5)	
4	532	127	531 (5)	659/1191/1723 (79)/(9)	127/280 (63)/(100)	
5	488	79	487 (13)	567/1055 (28)/(100)	79/232	
6	486	97	485 (1)		97/250/403 (100)/(81)/(16)	
7	386	97	385 (1.5)		97/250/403 (100)/(94)/(21)	

M = Matrix.

In this work we report the FAB mass spectrometry of the positive and negative ions of methane-bisazoliums 1-5, of ethane-bisazoliums 6, 7 and of similar compounds 8, 9 (See structures above). The analytical interest of such studies is discussed. The relevant intensity data corresponding to the spectra obtained with *m*-nitrobenzyl alcohol as the matrix [19-21] are gathered in Table 1 for the positive ions and in Table 2 for the negative ions. As a matter of fact, this matrix was found to give the most abundant ions as it has

already been observed during the study of the FAB spectra of organometallic compounds [22].

Furthermore, similar to previous work on FAB mass spectrometry of bisammonium ions [16], structural information has been obtained during the study of the CAD spectrum of the adduct ion [CA]⁺.

By way of illustration, the ions formed from compound 1 are given in Figures 1 and 2 (Cation: 178 Da. - Anion: 127 Da. - Molecule: 432 Da).

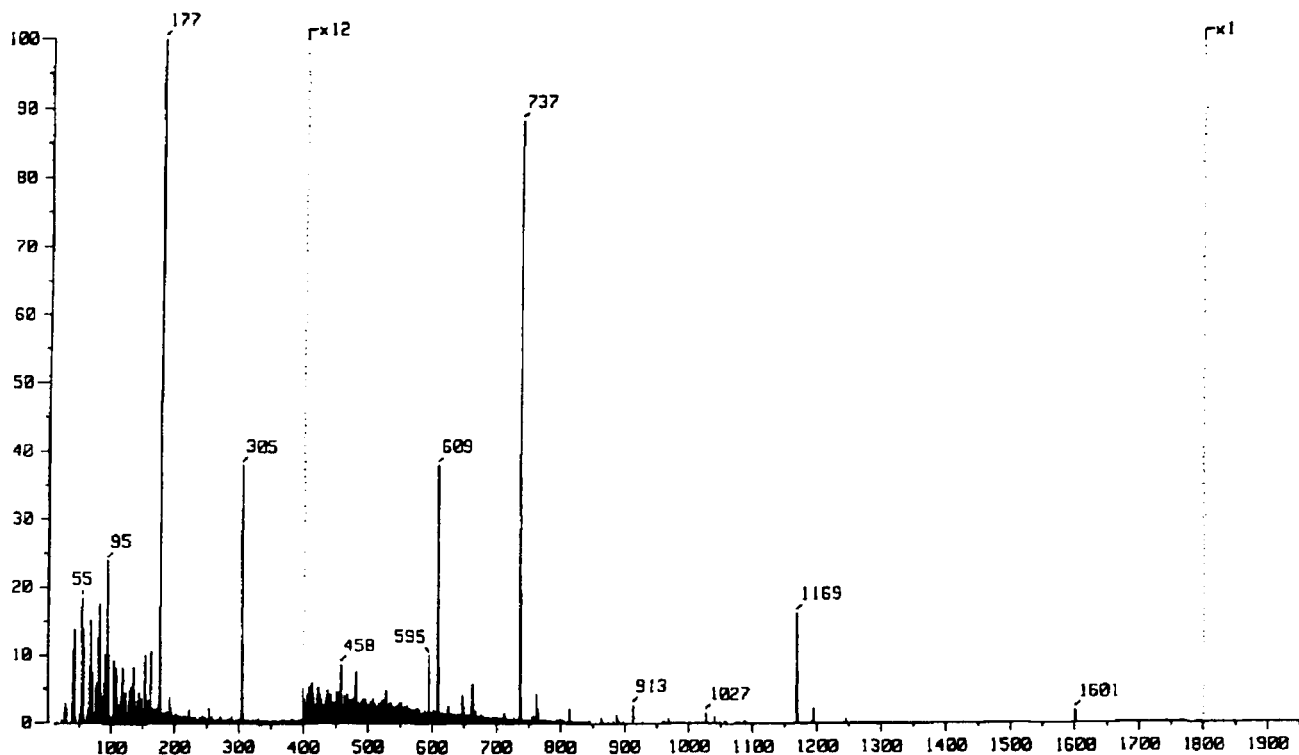


Figure 1. Positive ion FAB mass spectrum of compound 1, (matrix, *m*-nitrobenzyl alcohol).

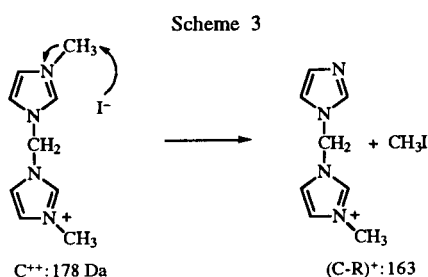
In the spectrum of the positive ions (Figure 1), two series of ions which are given below predominate:

	$[C-H]^{+} + n[CA_2]$	$[CA]^{+} + n[CA_2]$
n = 0	177	305
n = 1	609	737
n = 2	---	1169
n = 3	---	1601

Three other ions are also present:

- The $[C-H+16]^+$ ion at +193 Th. whose formation is due to the oxidizing properties of the *m*-nitrobenzyl alcohol matrix [23-25],

- The $[C-CH_3]^+$ ion at +163 Th. formed from the nucleophilic substitution depicted in Scheme 3,



- The ion at + 95 Th. which is a *N*-methylated biazole aromatic ion (See below) and which allows the identification of the heterocycle.

In the spectrum of the negative ions (Figure 2), similar ions, given below, are present:

	$A^{-} + nNBA$	$[CA_2-H]^{-} + n[CA_2]$	$A^{-} + n[CA_2]$	$NBA^{-} + n[CA_2]$	$NO_2^{-} + n[CA_2]$
n = 0	127	431	559	153	46
n = 1	280	863	991	585	478
n = 2	---	---	1423	---	---
n = 3	---	---	1855	---	---

The ion A_2^{-} is also present in weak abundance.

In a general manner, for all the compounds 1-5, the following ions are seen in the positive FAB spectra:

- The $[C-H]^+$ and $[CA]^+$ ions enabling the identification of both the cation and the anion,

- An ion similar to the ion A shown below (identification of the heterocycle) (Table 3),

- The $[C-R]^+$ ion resulting from the nucleophilic substitution of the anion and indicating the nature of the substituent on the positively charged nitrogen (Table 4).

By comparison with the FAB mass spectra of bisazolonium cations previously described [15,16], the spectra of bisazolonium cations studied in this work are featured by the absence of the doubly charged cation (which would be seen at $C/2$), although the spectra have been recorded in the *m*-nitrobenzyl alcohol matrix. As a matter of fact, this matrix inhibits the reduction thanks to its oxidizing properties and thus should facilitate the presence of such a doubly charged ion.

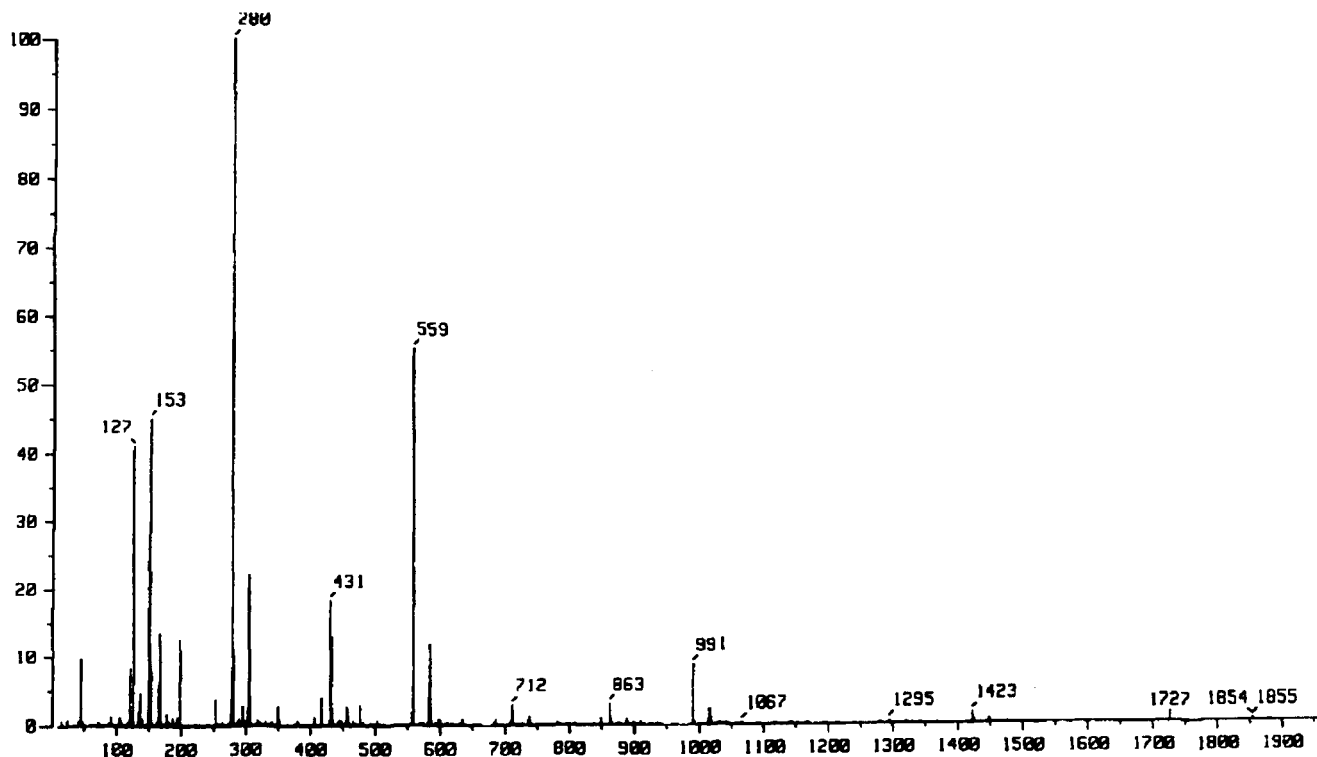


Figure 2. Negative ion FAB mass spectrum compound 1, (matrix, *m*-nitrobenzyl alcohol).

Table 3

Identification of the Heterocycle (Het⁺) for Compounds
C⁺⁺ of the Type (Het-CH₂-Het)⁺⁺ (1-5)

Compound	C ⁺⁺	(Het-CH ₂)	Ion observed
1	178	96 Da.	+95 Th.
2	330	172 Da.	+172 Th.
3	206	110 Da.	+109 Th.
4	278	146 Da.	+145 Th.
5	330	172 Da.	+172 Th.

The cleavage of the bond between the sp³ carbon and the heterocycle occurs with hydrogen transfers for compounds 1, 3 and 4 and without hydrogen transfers for compounds 2 and 5.

Table 4

Ion resulting from the nucleophilic substitution of the anion on the cation

Compound	R	C ⁺⁺	(C-R) ⁺
1	CH ₃	178 Da.	+163 Th.
2	C ₆ H ₅ CH ₂	330 Da.	+239 Th.
3	CH ₃	206 Da.	+191 Th.
4	CH ₃	278 Da.	+263 Th.
5	C ₃ H ₅	330 Da.	+289 Th.
6 [a]	CH ₃	292 Da.	+277 Th.

[a] Compound 6 belongs to bisazoliumethene structures.

As previously mentioned for the positive ions, the anion and the cation can also be identified in the same manner by the FAB mass spectra of the negative ions (Table 2). By way of illustration, the compositions of the various series of ions obtained from compound 1 (Anion A: I⁻: 127 Da. -Mass: 432 Da) are given above. It is easy to identify A⁻ and C⁺⁺ from the A⁻, [CA₃]⁻ and [CA₂-H]⁻ ions.

The CAD spectra of the [CA]⁺ and [CA₃]⁻ adduct ions have been recorded when these ions were sufficiently abundant in the FAB mass spectra. They have been studied for the following reasons.

- First, it is often necessary in FAB mass spectrometry to use tandem mass spectrometry [23] because the matrix ions, which are always very abundant in FAB mass spectrometry, are not observed any longer with this two-dimensional method. Very significant results have been obtained with regard to the structural identification of the compound studied: for instance, the CAD spectrum of a peptide molecular ion exhibits the characteristic ions of the entire sequence [24].

- Second, since the [CA]⁺ and [CA₃]⁻ adduct ions are composed of the cation C⁺⁺ and of the anion A⁻, the CAD spectra feature these two ions.

- Lastly, we have established in similar work dealing with bisammonium cations [15,16] that the ions observed in the CAD spectrum of the adduct ion are also present in the FAB mass spectrum. Fragmentations occurring in the gaseous phase following the collision are thus the same as the ones encountered in the source during the FAB ionization. Consequently, the CAD spectra of the adduct ion provide analytical information as significant as the ones given by the FAB mass spectra.

The relevant intensity data of the CAD spectra of the adduct ion [CA]⁺ for compounds 1-5 are tabulated below (Table 5). All the spectra consist of the three ions whose generations have already been discussed in the presentation of the FAB mass spectra:

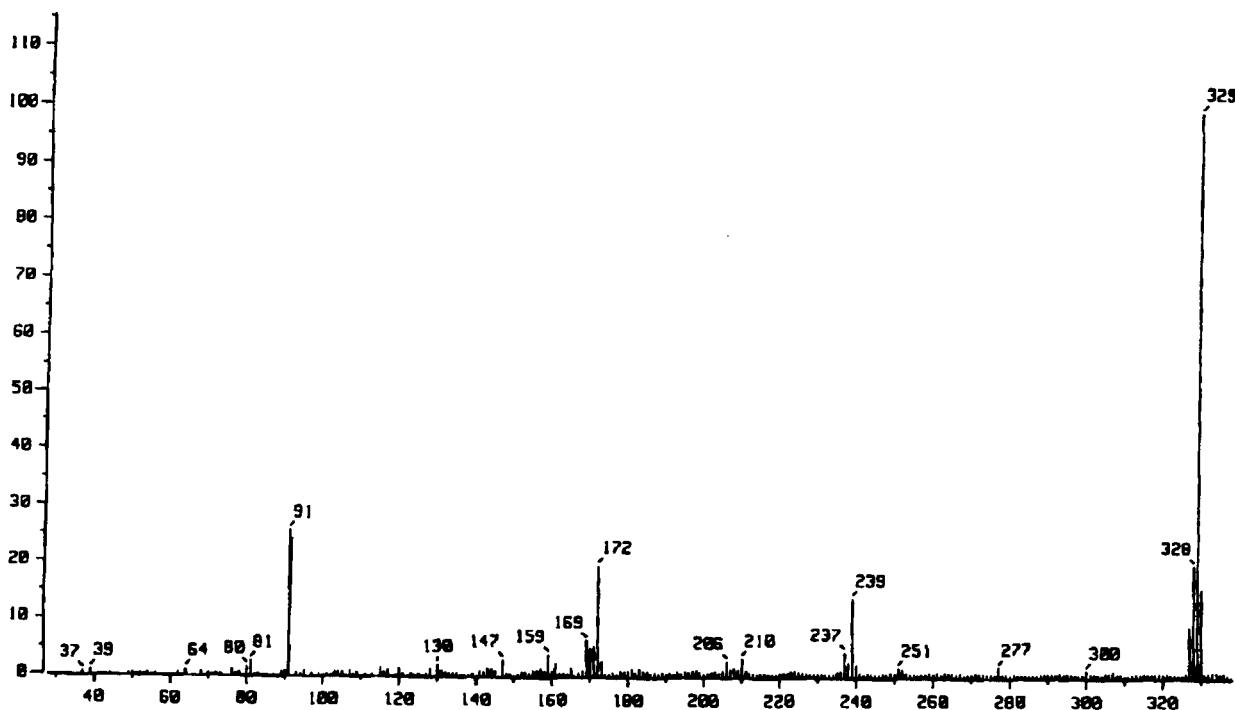


Figure 3. CAD spectra of ion m/z: 365, (CA⁺ of compound 2).

- The [C-H]⁺ ion which is the most abundant,
- The [C-R]⁺ ion which enables the identification of the substituent fixed on the positively charged nitrogen,

- The heterocyclic (Het⁺) ion (see below and Table 3) featuring the heterocycle. By way of illustration, Figure 3 represents the CAD spectrum of the [CA]⁺ ion at *m/z* 365 for compound 2. In this case, the benzyl cation is not only identified by the fragmentation *m/z* 365 → *m/z* 239 (365-239 = 126 which is the mass of benzyl chloride) but also by the presence of the tropylium ion.

The observed fragmentations in the two types of spectra (FAB mass spectrum and CAD spectrum of the ion [CA]⁺) are hence identical but the CAD spectra are easier to interpret because the matrix ions are not any longer present.

The spectra of the ions [CA₃]⁻ present in the FAB mass spectra of compounds 1-4 are summarized in Table 6. By way of illustration, the CAD spectrum of the [CA₃]⁻ ion at *m/z* 659, which is present in the FAB mass spectrum of compound 4, is given in Figure 4.

Ions present in the CAD spectra can be classified in two categories. First, the A⁻ and A₂⁻ ions (at *m/z* 127 and 254 for the compounds 1, 3 and 4; and at *m/z* 35 and 70 for compound 2) and then three other ions, which give information on the cation, can be distinguished. The latter three ions are formed by the same fragmentations than the ones leading to the ions [C-H]⁺, [C-R]⁺ and [CH₂-Het]⁺ in the CAD spectra of the ions [CA]⁺ (Table 5). These are:

Table 5

CAD spectra of ions CA⁺ (For each ion the numerical value of the relative abundance is indicated in parentheses)

Compound	Ion studied	C ⁺⁺	A ⁻	(C-H) ⁺	(CA-RA) ⁺	other ions			Het
1	305	178	127 (100)	177 (4.5)	163	222	149	134	95 (17)
2	365	330	35 (100)	329 (14)	239 (26)	91			172 (20)
3	333	206	127 (100)	205 (8)	191	237 (14.5)	176	95 (11)	109 (73)
4	405	278	127 (100)	277 (4.5)	263 (20.5)	146			145 (23.5)
5	409	330	79 (100)	329 (4)	289 (8)	131			172 (10)

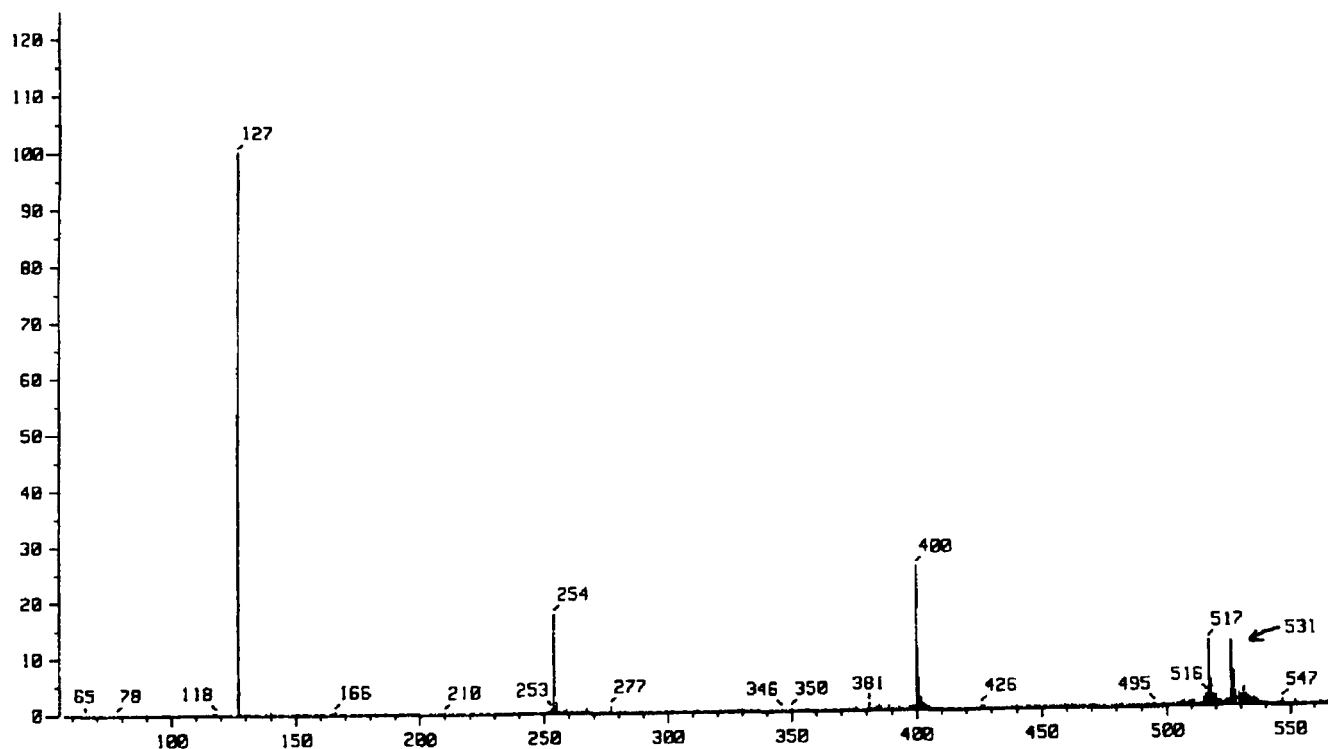


Figure 4. CAD spectra of ion *m/z*: 659, (CA₃⁻ of compound 4).

Compound	[C-H] ⁺ + A ₂ ⁻	[C-R] ⁺ + A ₂ ⁻	[CH ₂ Het] ⁺ + A ₂ ⁻
1	431 (177+254)	417	350 (96 + 254)
2	399 (329+70)	309	242 (172 + 70)
3	459 (205+254)	445	364 (110 + 254)
4	531 (277+254)	517	400 (146 + 254)

borate. This study was carried out in order to check if the shift of the anion previously observed in the FAB mass spectra of bisammonium salts during the addition of an alkaline halogen is also seen when the initial anion present in the compound is the tetrafluoroborate. Indeed, in that

Table 6

CAD Spectra of Ion CA₃⁻ (For each ion the numerical value of the relative abundance is indicated in parentheses)

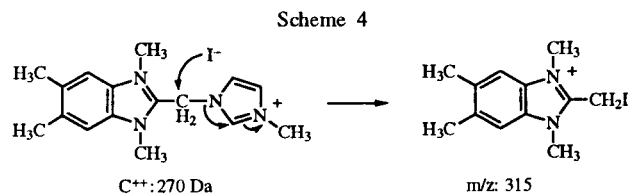
Compound CA	C ⁺⁺	A ⁻	Studied ion CA ₃ ⁻	Observed Ions									
				A ⁻	A ₂ ^{-*}	(CA ₃ -HA) ⁻	(CA ₃ -RA) ⁻	Others ions					
1	432	178	127	559	127 (100)	254 (26)	431 (30)	417 (44)	350 (28)	476 (18)			
2	400	330	35	435	35 (5)	70 (1)	399 (100)	309 (10)	242 (8)	343 (3)	322 (2.5)	273 (3)	206 (2)
3	460	206	127	587	127 (92)	254 (14.5)	459 (25)	445 (100)	364 (125)	491 (125)	433 (6)	280 (4.4)	223 (4)
4	532	278	127	659	127 (100)	254 (10)		517 (12)	400 (26)	526 (11)			

Compared to the other bisazolium salts 1-7, compound 8 is disymmetrical. Moreover, the group CH₂ is bound to an sp² carbon atom and to a nitrogen atom.

The mass spectrum of the positive ions includes six ions already present in the spectra of the compounds 1-7:

- [C-H] + at m/z 269, with a large abundance,
- [CI]⁺ at m/z 397,
- [CI+CI₂] at m/z 921,
- [C-CH₃]⁺ at m/z 255,
- [Het-CH₂]⁺ at m/z 188,

and the ion at m/z 315 formed from the nucleophilic substitution depicted in Scheme 4. The same ions at m/z 315, 269, 255 and 188 have been observed in the CAD spectrum of the [CI]⁺ ion at m/z 397.



A similar FAB mass spectrum is observed for the negative ions with the following ions (CI₂: 524 Da):

- I⁻ + nNBA: 127, 280, 433 (n = 0, 1, 2),
- Cl₂-H + nNBA: 523, 1047 (n = 0, 1),
- I⁻ + nCl₂: 127, 651, 1175, 1699 (n = 0, 1, 2, 3).

Lastly, we have investigated the FAB mass spectra of the positive and of the negative ions obtained from compound 9 for which the anion is not the iodide but the tetrafluoro-

work [15], addition of potassium iodide on compound [C⁺⁺ 2Cl⁻] led to the presence of the ion [CI]⁺ in the spectrum.

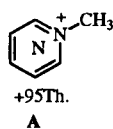
The study of the FAB mass spectra shows that a similar phenomenon occurs for compound 9. The major ions present in the spectra are gathered below:

C⁺⁺: (493 Da) - BF₄⁻: (87 Da); I⁻: (127 Da) - K⁺: (39 Da)

	Positive ions	Negative ions
Before addition of KI	[C-C ₃ H ₇] ⁺ : 450 [CBF ₄] ⁺ : 580	BF ₄ ⁻ : 87 NBA + BF ₄ ⁻ : 240 [C(BF ₄) ₂] + BF ₄ ⁻ : 754
After addition of KI	K ⁺ : 39 NBA + K ⁺ : 192 [C-C ₃ H ₇] ⁺ : 450 [CI] ⁺ : 620 [Cl ₂] + K ⁺ : 786	I ⁻ : 127 NBA + I ⁻ : 280 2 NBA + I ⁻ : 433 [Cl ₂] + I ⁻ : 874

Noteworthy is the presence of the ions at m/z 620, 786 (positive ions) and 874 (negative ions) after the addition of KI.

Thus, this study has established that it is easy to characterize various bisazolium salts of the type [C⁺⁺2A⁻] by FAB mass spectrometry and by tandem spectrometry. Similarities have been noticed with already published results dealing with similar studies on other doubly charged cations since the [CA]⁺, [C-H]⁺ and [C-R]⁺ ions (and the corresponding negative ions generated from by addition of A₂⁻) are observed. However, in contrast to these similar studies on other doubly charged cations, the cation C⁺⁺ has never been seen at C/2. Lastly, the fact that the [C-H]⁺ and [C-R]⁺ ions (and similar negative ions) are also present in the CAD spectrum of the ion [CA]⁺ (or of ion [CA₃]⁻) has an obvious analytical interest as it is possible to identify the compound [C⁺⁺2A⁻] present in a mixture. This is an essential feature of tandem mass spectrometry [26].



In conclusion, all results are presented in Table 7 which contains the positive and negative ions of the following compounds: [CA], [C+A⁻] [2-9], [CA₂] [C⁺⁺2A⁻] [13,15-17 and this work] and [C₂A] [2C⁺⁺A⁻] [27-29].

Table 7

Summary of the Structure of the Possible Ions in Salts
C⁺⁺A⁻, C⁺⁺2A⁻ and 2C⁺⁺A⁻

Salt	Positive ions	Negative ions
CA (C+A ⁻)	C ⁺ , C ₂ A ⁺ (C+M) ⁺	A ⁻ , CA ₂ ⁻ , (A+M) ⁻
CA ₂ (C ⁺⁺ 2A ⁻)	CA ⁺ , (C-H) ⁺ , (C/2) ⁺⁺ , (C-R) ⁺	A ⁻ , CA ₃ ⁻ , (CA ₂ -H) ⁻
C ₂ A (2C ⁺⁺ A ⁻)	C ⁺⁺ ...	CA ⁻

M = Matrx.

EXPERIMENTAL

The mass spectra were recorded on a SX102 type spectrometer, Jeol Ltd, Tokyo, Japan. Xenon was used in the FAB experiments. The energy of the neutral atom beam was 3 keV (emission current: 20 mA). Calibration was accomplished using Ultramark 1621, Heraeus, Kalsruhe, Germany, as a reference. The FAB mass spectra were measured at a resolution of 1000. CAD spectra were taken using xenon as the collision gas at a pressure to reduce the beam of the parent ions by 30%. The collision cell is located in the region before the magnetic sector. The collision energy was 6 keV. The resulting fragments ions were analysed by a B/E linked scan method. The data were acquired and processed with an HP Apollo series 400 using the JEOL complement software.

Samples were placed on a target by dissolving them directly in the matrix, *m*-nitrobenzyl alcohol obtained from commercial suppliers, Aldrich, Milwaukee, WI, USA.

The syntheses of compounds 1, 2, 4, 5, 6 and 7 have been previously described: 1 [30]; 2, 4, 5 [31]; 6, 7 [32]. Compound 3, mp 261-264°, was prepared from 2,2'-dimethylbisimidazol-1,1'-ylmethane [33] and methyl iodide following the procedure used for compound 1 [30].

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REFERENCES AND NOTES

- [1] M. Barber, R. S. Bordoli, R. D. Sedgwick and A. N. Tyler, *Nature*, **293**, 270 (1981).
- [2] C. Javanaud and J. Eagles, *Org. Mass Spectrom.*, **18**, 93 (1983).
- [3] H. J. Veith, *Org. Mass Spectrom.*, **18**, 154 (1983).
- [4] D. A. McCreery, D. A. Peake and M.L. Gross, *Anal. Chem.*, **57**, 1181 (1985).
- [5] F. De Angelis, G. Doddi and G. Ercolani, *J. Chem. Soc., Perkin Trans 2*, 633 (1987).
- [6] R. E. Carlson and K. L. Busch, *Org. Mass Spectrom.*, **29**, 632 (1994).
- [7] M. Bambagiotti-Alberti, S. A. Coran, F. Benvenuti, P. Lonostro, S. Catinella, D. Favretto and P. Traldi, *J. Mass Spectrom.*, **30**, 1742 (1995).
- [8] J. M. Miller and J. Ni, *J. Mass Spectrometry*, **31**, 16 (1996).
- [9] G. J. C. Paul, I. Marcotte, J. Anastassopoulou, T. Theophanides, M. Arkas, C. M. Paleos and M. J. Bertrand, *J. Mass Spectrom.*, **31**, 95 (1996).
- [10] T. M. Ryan, R. J. Day and R. G. Cooks, *Anal. Chem.*, **52**, 2054 (1980).
- [11] D. N. Heller, J. Yergey and R. J. Cotter, *Anal. Chem.*, **55**, 1310 (1983).
- [12] D. H. Williams, A. F. Findeis, S. Naylor and B. W. Gibson, *J. Am. Chem. Soc.*, **109**, 1980 (1987).
- [13] J.-L. Aubagnac, R. M. Claramunt, J.-L. Lavandera and J. Elguero, *Bull. Soc. Chim. Belg.*, **100**, 459 (1991).
- [14] G. J. Kunkel, K. L. Bush, R. Dunphy, D. J. Burinsly, R. Barak, P. Bel, G. Amitai and A. Vincze, *J. Mass Spectrom.*, **30**, 282 (1995).
- [15] J.-L. Aubagnac, I. Gilles, M. Calas, G. Cordina, G. Piquet, P. Portefaix and L. Giral, *J. Mass Spectrom.*, **30**, 985 (1995).
- [16] M. Calas, G. Cordina, I. Gilles and J.-L. Aubagnac, *J. Mass Spectrom.*, accepted for publication.
- [17] P. Cabildo, R. Claramunt, P. Cornago, J.-L. Lavandera, D. Sanz, C. Jagerovic, M. L. Jimeno, J. Elguero, I. Gilles and J.-L. Aubagnac, *J. Chem. Soc., Perkin Trans. 2*, 701 (1996).
- [18] P. Cabildo, R. Claramunt, D. Sanz, J. Elguero, C. Enjalbal and J.-L. Aubagnac, *Rapid Commun. Mass Spectrom.*, **10**, 1071 (1996).
- [19] J. Meili and J. Seibl, *Org. Mass Spectrom.*, **19**, 581 (1984).
- [20] J. Sweetman and I. A. Blair, *Biomed. Environm. Mass Spectrom.*, **17**, 337 (1988).
- [21] J.-L. Aubagnac, *Rapid Commun. Mass Spectrom.*, **4**, 114 (1990).
- [22] J. M. Miller, K. Balasanmugam, J. Nye, G. B. Deacon and N. C. Thomas, *Inorg. Chem.*, **26**, 560 (1987).
- [23] M. H. Kowalski, T. R. Sharp and P. J. Stang, *Org. Mass Spectrom.*, **22**, 642 (1987).
- [24] G. Fachin, L. Zanotto, R. Sertaglia and P. Traldi, *Org. Mass Spectrom.*, **27**, 1181 (1992).
- [25] J. M. Miller and L. Z. Chen, *Rapid Commun. Mass Spectrom.*, **6**, 6184 (1992).
- [26] F. W. McLafferty ed, *Tandem Mass Spectrometry*, John Wiley and Sons, New York, NY 1983.
- [27] G. Cerveau, C. Chuit, R. J. P. Corriu, L. Gerbier, C. Reye, J.-L. Aubagnac and B. El Amrani, *Int. J. Mass Spectrom. In. Proc.*, **87**, 259 (1988).
- [28] G. Cerveau, C. Chuit, R. J. P. Corriu, C. Reye and J.-L. Aubagnac, *Int. J. Mass Spectrom. In. Proc.*, **91**, 145 (1989).
- [29] G. Cerveau, C. Chuit, C. Reye and J.-L. Aubagnac, *Org. Mass Spectrom.*, **27**, 822 (1992).
- [30] R. M. Claramunt, H. Hernandez, J. Elguero and S. Julia, *Bull. Soc. Chim. France*, II, 5 (1983).
- [31] R. M. Claramunt, J. Elguero and T. Meco, *J. Heterocyclic Chem.*, **20**, 1245 (1983).
- [32] J. Torres, J. L. Lavandera, P. Cabildo, R. M. Claramunt and J. Elguero, *Bull. Soc. Chim. Belg.*, **101**, 29 (1992).
- [33] C. Acerete, M. L. Banon, P. Cabildo, R. M. Claramunt, J. Elguero and J. L. Lavandera, *Rev. Roum. Chim.*, **36**, 629 (1991).