The Structure of $[C_3H_4N_2]^{+\cdot}$ and $[C_5H_5N_2]^+$ Ions Formed from Vinylimidazoles, Studied by Collisionally Activated Dissociation Mass Spectrometry

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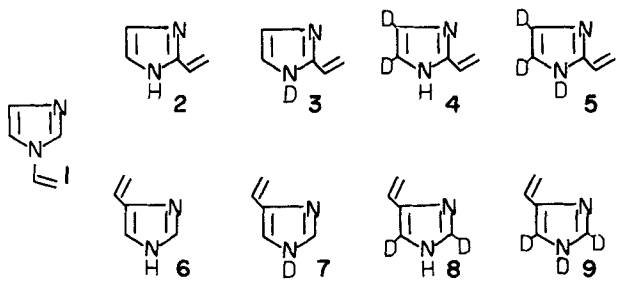
Mass spectra of the three isomeric vinylimidazoles have been compared and the structures of the fragment ions $[C_3H_4N_2]^{+\cdot}$ and $[C_5H_5N_2]^+$ have been investigated by collisionally activated dissociation mass spectrometry. The greater part of the non-decomposing ions *m/z* 68 from 2-vinylimidazole and from 2-imidazolecarboxylic acid methyl ester, and a minor part of this ion formed from the free acid, all have the same structure: the imidazole ring system, with hydrogens at both nitrogen atoms but none at C(2). An analogous structure, with an ethynyl group at C(2), is proposed for the *m/z* 93 ion from 2-vinylimidazole.

INTRODUCTION

In a recent publication[1] we described a simple standard procedure to obtain a so-called corrected collisionally activated dissociation (CCAD) mass spectrum representing only fragmentations due to collisions, and applied the method in such a way that in combination with deuterium labelling it was possible to arrive at the CCAD spectrum of one ion species in a multiplet peak. In the present article this procedure is used to obtain the CCAD spectrum of the $[M-H]^+$ fragment from an incompletely labelled sample.

In spite of their importance in polymer chemistry, mass spectra of the vinylimidazoles **1**, **2** and **6** have not been previously studied. Comparison of the EI spectra of the three isomers (Fig. 1) at once shows a striking difference in the intensity of the $[M-H]^+$ ion at *m/z* 93. A second difference between the mass spectra of these compounds is the occurrence of the radical cation $[C_3H_4N_2]^{+\cdot}$, *m/z* 68, in **2**. In this paper these two fragmentation processes and the structures of the resulting ions have been studied by CAD mass spectrometry and by taking into account the behaviour of the labelled analogues **3–5** and **7–9**.



EXPERIMENTAL

Mass spectral data were obtained with a Kratos MS9/50 double focusing mass spectrometer under the following conditions: ion source temperature, 400 K; trap current, 300 μA; accelerating voltage, 8 kV; electron energy, 70 eV. Elemental compositions of ions were determined at resolving powers above 15 000. The collision cell was situated near the focal point of the first field free region. Air was used as collision gas; the main beam was attenuated to approximately 10% and its intensity was determined accurately in each experiment. The pressure in the pump line of the differentially pumped collision chamber was about 6×10^{-5} Torr. MI and CAD spectra were recorded using the *B/E* linked scan technique; CCAD spectra were obtained by a procedure described elsewhere.[1] In case of the compounds **3**, **5**, **7** and **9**, labelled at the nitrogen atom, the CCAD spectrum of the molecular ions of the corresponding N—H compounds was established, after which D_2O was introduced into the ion source. When an equilibrium had been attained, the label content was determined and again the CCAD spectrum at the same mass, now a mixture of unlabelled $[M]^{+\cdot}$ and labelled $[M-H]^+$ ions, was obtained. Subtraction of the first spectrum, proportional to the unlabelled molecule content, from the last, followed by normalization, gave the CCAD spectrum of the $[M-H]^+$ ion under investigation.

The 2-imidazolecarboxylic acid **13** and its methyl ester **14** were admitted by a direct insertion (DI) probe kept at ambient temperature, at a source temperature below 365 K, and all other samples were admitted through an all-glass heated inlet system (AGHIS) at a temperature of about 400 K.

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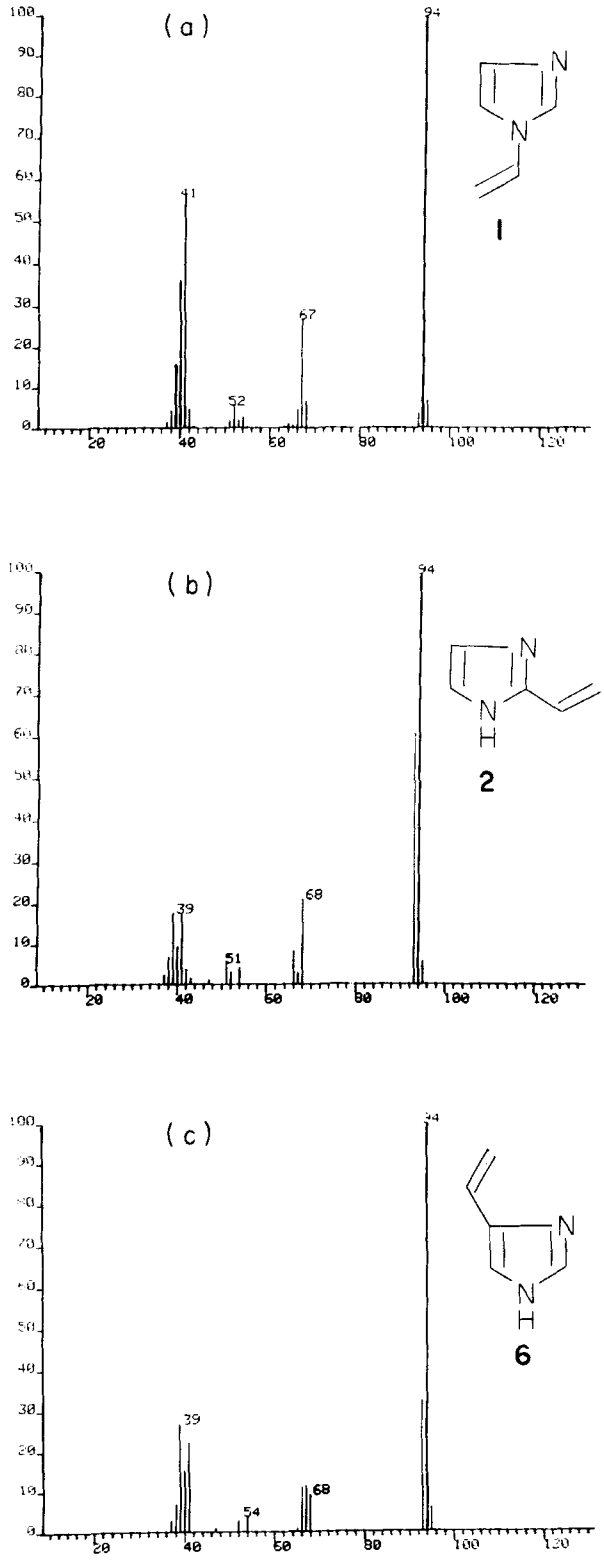


Figure 1. Mass spectra (70 eV) of the vinylimidazoles: (a) 1-vinyl-(**1**), (b) 2-vinyl-(**2**) and (c) 4(5)-vinyl-(**6**).

1-Vinylimidazole was commercially available. The 2-isomer was obtained from 2-β-bromoethylimidazole,[2] synthesized following a literature procedure.[3] 4(5)-vinylimidazole (**6**) was prepared by decarboxylation[4] of the commercially available urocanic acid. 4,5-d_2-2-Vinylimidazole (**4**) and 2,4(5)-d_2-5(4)-vinylimidazole (**8**) were prepared by refluxing the appropriate imidazole in a NaOD solution in D_2O for 5–19 h,[5] followed by extraction with ether. Label positions and approximate deuterium contents were checked by NMR. 2-Imidazolecarboxylic acid **13** was prepared as described in the literature,[6] and its methyl ester **14** by treatment of the acid with diazomethane.

RESULTS AND DISCUSSION

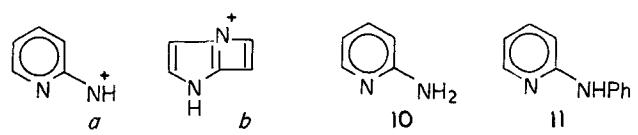
The mass spectra of the three unlabelled isomers are given in Fig. 1.

1-Vinylimidazole (1)

In the fragmentation of this compound the two processes mentioned above are almost absent. Abundant fragment ions are *m/z* 40, 41 and 67. The last ion $[C_4H_5N]^{+\cdot}$, is generated from the molecular ion by loss of HCN. This process will be discussed in a forthcoming paper on $[C_4H_5N]^{+\cdot}$ ions, formed from precursors $C_5H_6N_2$. The ion *m/z* 41, $[C_2H_3N]^{+\cdot}$, is formed from *m/z* 67 by loss of C_2H_2. The third abundant fragment, *m/z* 40, is a doublet with an approximately equal intensity: $[C_2H_2N]^+$, formed by loss of H$^\cdot$ from *m/z* 41; and $[C_3H_4]^{+\cdot}$, formed by expulsion of HCN from *m/z* 67.

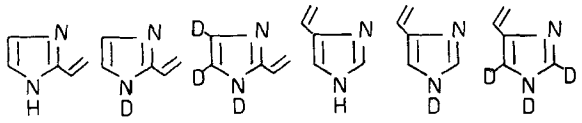
2-Vinylimidazole (2)

In order to investigate the structure of the abundant $[M-H]^+$ ion, we studied the labelled compounds **3–5** in detail. *B/E* linked scans of molecular ions, decomposing in the first field-free region, showed a D$^\cdot$ loss of less than 3% as compared with loss of H$^\cdot$, indicating that in the process $[M]^{+\cdot} \rightarrow [M-H]^+$ a vinylic proton is involved. In view of the apparent stability of the product ion a ring expanded structure like *a* appears reasonable,[7] but this idea had to be abandoned after comparison of the CCAD spectra of $[C_5H_5N_2]^+$, *m/z* 93, formed from 2-aminopyridine (**10**) and phenyl-2-pyridylamine (**11**) with the $[M-H]^+$ ion from 2-vinylimidazole (**2**). Another explanation could be the formation of ion *b*, isoelectronic systems of which have been reported before.[8–10] An analysis of the CCAD



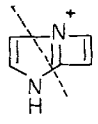
spectra of this $[M-H]^+$ ion (Table 1) shows that structure *b* is quite unlikely. The two most abundant ions in this spectrum of the unlabelled ion appear at *m/z* 52 and 65. The first represents a loss of 41 mass units, which could either be $C_3H_5^\cdot$ or C_2H_3N. The first is rather improbable, but loss of C_2H_3N can be ac-

Table 1. Corrected collisionally activated dissociation (CCAD) spectra of $[M-H]^+$ ions formed from compounds 2, 3 and 5 (2-vinylimidazole) and 6, 7 and 9 (4(5)-vinylimidazole). Peaks in the higher mass area (above *m/z* 71) have been omitted due to interference by artefact peaks. Intensities of the remaining peaks were normalized to a total fragment abundance = 100

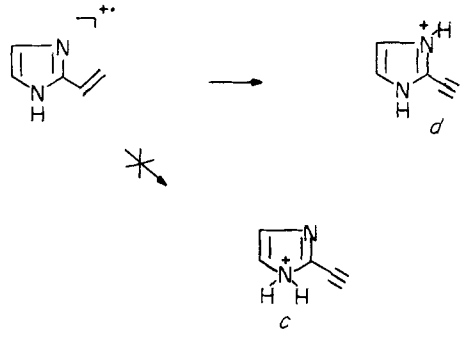


	2	3	5	6	7	9
m/z						
71	—	—	2	—	—	3
70	—	—	—	—	—	3
69	—	2	6	—	2	6
68	2	1	6	2	5	9
67	1	4	6	4	11	7
66	8	7	5	15	10	4
65	11	7	3	11	4	2
64	6	4	1	4	2	1
63	1	1	1	1	1	—
62	1	1	1	—	—	—
55	—	1	2	—	2	1
54	1	1	1	1	1	2
53	2	10	11	1	3	4
52	20	11	7	6	4	4
51	7	5	3	4	3	4
50	1	1	1	4	3	2
49	—	—	—	1	1	—
45	—	—	3	—	—	—
44	—	—	3	—	—	—
43	—	5	4	—	—	2
42	4	4	4	1	2	6
41	4	4	3	3	4	5
40	6	5	4	4	6	5
39	6	5	4	13	12	8
38	7	6	5	9	8	6
37	5	4	3	5	5	3
36	1	1	1	1	1	1
30	—	—	2	—	—	5
29	—	3	3	—	4	3
28	3	2	2	6	3	2
27	1	1	1	2	1	1
26	1	2	1	1	1	1
25	1	1	1	1	1	—
24	—	1	—	—	—	—

counted for by cleavage of the imidazole ring:

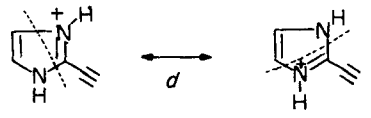


This would mean that in the labelled compounds the peak at *m/z* 52 is not shifted to higher mass values, since in this structure all labels should be lost with this fragmentation. Table 1 reveals that this is not the case: *m/z* 52 and 53 appear in approximately equal abundance. From the MI spectra of the compounds **2–5** there is no evidence for hydrogen randomization. As a consequence, the structure of the $[M-H]^+$ ion must be symmetric with respect to loss of C_2H_3N, implying the involvement of both nitrogens rather than one. On the basis of this and on further interpretation of the CCAD spectra, a scheme for the formation of the $[M-H]^+$ ion *m/z* 93 is proposed (Scheme 1). Apart



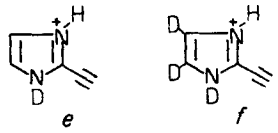
Scheme 1

from the evidence present in the MI spectra, structure *c* can be excluded on the ground that loss of C_2H_3N cannot be explained in a proper manner. Moreover, the data are in very good agreement with structure *d*.



Loss of C_2H_3N from the $[M-H]^+$ ion can well be visualized from the highly symmetrical structure *d*. Thus, analogue **3** will expel C_2H_2DN and C_2H_3N in equal abundance, yielding *m/z* 52 and 53, as will **5**, by respective losses of C_2D_3N and C_2HD_2N.

The other abundant ion, *m/z* 65, in the CCAD spectrum of the unlabelled $[M-H]^+$ ion could arise by loss of C_2H_4 or HCNH$^\cdot$. The first is rather unlikely and it is impossible to interpret the data on the basis of this expulsion. As to the second, the picture is obscured by the fact that *m/z* 65 is part of a cluster of ions. Thus, according to Scheme 1, the labelled compounds **3** and **4** would give the respective ions *e* (*m/z* 94) and *f* (*m/z* 96). For ion *e*, one would expect equal



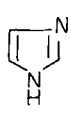
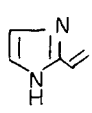
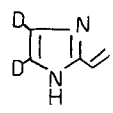
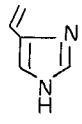
loss of HCND$^\cdot$ and HCNH$^\cdot$, yielding *m/z* 65 and 66, for ion *f* equal loss of DCND$^\cdot$ and DCNH$^\cdot$, leading to *m/z* 66 and 67. This was confirmed by the results for both compounds:†

† Compounds **4** and **8** contain isobaric impurities due to the fact that labelling was not entirely complete and, therefore, their CCAD spectra are not given in Table 1. In some instances, like here, the data were helpful in the interpretation of the results.

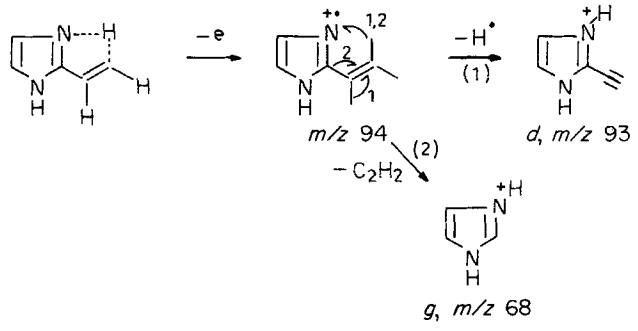
It has been stated that in the case of high energy collisions the number of fragmentation pathways and the percentage of fragment ions formed by simple cleavage as compared with the percentage formed by rearrangement reactions is great.[11] In the CCAD spectra of the $[M-H]^+$ ions (Table 1), there is a significant although small loss of 25 mass units which is absent in the corresponding MI spectra. As such a loss is exclusively observed with ions having an ethynyl group,[12] this can be considered as indicative of this substituent.

Under electron impact conditions, the second most abundant fragment ion from 2-vinylimidazole (**2**) appears at *m/z* 68 (Fig. 1), with an elemental composition of $C_3H_4N_2$, and it is not unreasonable to suppose that it would have the same structure as the imidazole radical cation. Comparison of the CCAD spectrum of the *m/z* 68 ion with that of the imidazole molecular ion (Table 2) clearly shows that the structures must be different. Notably, the presence of *m/z* 42 in the CCAD spectrum from 2-vinylimidazole (17% of all fragments formed) is striking, whereas from imidazole (**12**) it is hardly formed at all (Table 2, Fig. 2(a) and (e)). In the metastable (MI) spectrum of the molecular ion of **2**, *m/z* 68 is hardly present, from which we conclude that under EI conditions this fragment is formed through a relatively fast process. In the CCAD spectrum of the molecular ion of **2** it is the most abundant fragment, which is found at *m/z* 71 in the labelled analogue **5**. It is, therefore, generated by loss of C_2H_2 from the vinyl substituent with a hydrogen transfer from this group to the imidazole ring. All these observations are consistent with a conformation of the molecular ion in which a hydrogen is shared, by hydrogen bonding, between the free nitrogen atom and the vinyl group. The product ion formed (g) as well as the already postulated $[M-H]^+$ ion *d* are easily generated from this configuration (Scheme 2).

Table 2. CCAD spectra of the molecular ion of imidazole (12), and of the fragment ions $[M-C_2H_2]^{+\cdot}$, formed from compounds 2 and 4 (2-vinylimidazole) and 6 (4(5)-vinylimidazole). The spectra have been normalized as in Table 1.[a]

				
	12	2	4	6
m/z				
69	—	—	1.0	—
68	—	—	14.2	—
67	18.7	18.3	1.2	8.2
66	1.1	1.0	0.2	1.0
65	0.2	0.4	—	0.4
64	—	0.2	—	0.2
54	—	0.2	0.4	—
53	0.3	0.4	0.7	0.6
52	0.4	1.0	0.7	2.0
51	0.4	0.7	0.1	1.4
50	0.1	0.2	0.1	0.9
49	—	—	—	0.3
44	—	—	0.1	—
43	—	—	14.3	—
42	0.5	17.0	33.7	0.7
41	27.9	18.4	14.4	22.7
40	31.7	20.9	4.2	16.7
39	6.4	5.9	1.4	14.7
38	4.6	4.6	3.0	9.4
37	—	1.0	0.1	5.6
36	—	0.2	—	1.4
30	—	—	0.4	—
29	—	—	5.0	0.2
28	4.4	5.5	2.5	7.2
27	1.8	2.1	1.4	2.6
26	0.9	1.2	0.7	2.0
25	0.4	0.6	0.1	1.2
24	0.2	0.2	0.1	0.6

[a] Due to experimental errors, introduced by the subtraction procedure and by incomplete labelling, the results in Table 1 are less accurate than in this table. All CCAD spectra are the average of at least two series of three spectra recorded at different days. For experimental details, see also Ref. 1.



Scheme 2

The behaviour of analogue **4** supports this mechanism, since in its EI spectrum *m/z* 68 is shifted to 70, with an elemental composition of $C_3H_2D_2N_2$. Therefore the vinyl group is involved in the C_2H_2 loss. The CCAD spectrum of this $[M-C_2H_2]^{+\cdot}$ fragment ion (Table 2) is in agreement with the proposed structure g. The H$^\cdot$ lost from this ion is almost exclusively from the 4(5)-position, like in the imidazole (**12**) molecular ion upon electron impact.[5] The fragment at *m/z* 42 is caused by a second C_2H_2 loss, and this expulsion can only occur when C(4) and C(5) are involved. Then, in **4**, C_2D_2 should be lost, and the product ion still observed at *m/z* 42, which is in agreement with the data (Table 2). It should be noted that the fragment *m/z* 43 in **4** represents a loss of 27 mass units, reflecting loss of HCN, and not that of (un)labelled acetylene. This C_2H_2 expulsion is not observed in imidazole (**12**) itself (Fig. 2). An explanation for this difference in behaviour might be that from the first compound the molecular ion of the stable carbodiimide, $[H—N=C=N—H]^{+\cdot}$,[13] is formed, whereas from imidazole a rearrangement is required to arrive at the same ion. Here the energetically favourable cleavage of the N(1)—C(2) and N(3)—C(4) bonds leaves a stable $[C_2H_3N]^{+\cdot}$ ion[14,15] upon expulsion of HCN.

During their work on 2-substituted imidazoles Bowie *et al.*[16] found that some undergo a fragmentation process yielding an ion at *m/z* 68, and that the fragments, formed from 2-imidazolecarboxylic acid (**13**)

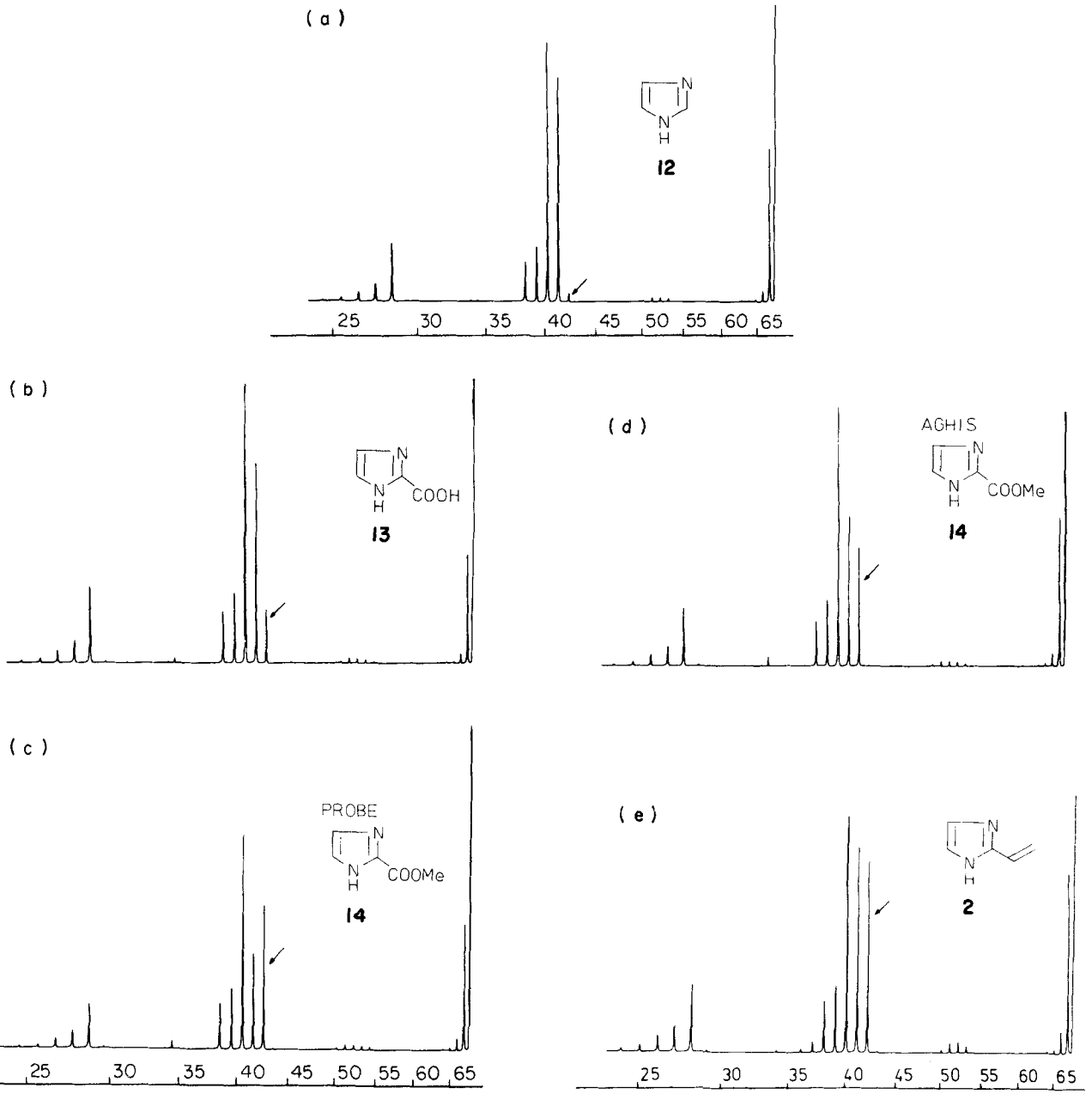
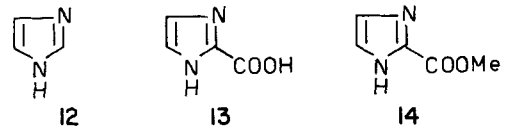


Figure 2. Collisionally activated dissociation (CAD) spectra (70 eV) of *m/z* 68, produced from (a) **12**, (b) **13** (DI probe), (c) **14** (DI probe), (d) **14** (AGHIS) and (e) **2**, in the cluster *m/z* 36 to 42, *m/z* 42, has been marked by an arrow.

and its methyl ester (**14**) are, at least for 90% $[C_3H_4N_2]^{+\cdot}$ ions. We found that this contribution is



even higher. As the acid is thermally unstable, we checked the stability of the methyl ester by introduction through the all-glass heated inlet system (AGHIS) as well as via the direct insertion (DI) probe, and observed that *m/z* 68 was more abundant when introduced in the first manner. This means that the ester undergoes a thermal rearrangement to imidazole. In Fig. 2 the CAD spectra of *m/z* 68 from the methyl ester, when introduced in both ways, are shown. The difference in abundance of *m/z* 42 is obvious; also the AGHIS spectrum is more resemblant of imidazole than the DI probe spectrum. Apart from a possible thermal rearrangement, the difference between the CAD spectra of the acid **13** and the ester **14** can be understood in terms of the available mechanisms for formation of the imidazole (**12**) molecular ion versus ion g (Scheme 3). In the acid, formation of ion g is

Scheme 3

achieved through a five-centre, and of the imidazole molecular ion through a four-centre, mechanism. Apparently the last is energetically more favourable since the process **13**→ g is relatively unimportant; a small peak at *m/z* 42 is observed in the CAD spectrum of *m/z* 68 (Fig. 2(a)). In the methyl ester, ion g will be formed through a six-centre mechanism, and here the contribution of *m/z* 42 will be more predominant (Fig. 2(c)). In conclusion, comparison of the available data (Fig. 2(e); Table 2) leads us to propose a mixture of ions *m/z* 68 from 2-vinylimidazole, the majority having structure g. A smaller proportion will have the imidazole structure (**12**), with a possible contribution of a third ion, as will be discussed below.

4(5)-Vinylimidazole (6)

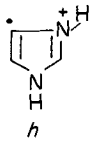
As shown in Fig. 1, the EI spectrum of this compound, as in the case of the 2-isomer (**2**), has strong fragment ions at *m/z* 93 and 68, but less abundant than in the latter. The origin of these ions, is also as in **2**, due to the occurrence of an intramolecular hydrogen bonded precursor. Here, *m/z* 67, $[C_4H_5N]^{+\cdot}$, is somewhat stronger than in **2**. The structure of these ions will be discussed in a forthcoming paper.

Due to H/D exchange kinetics[17] it is not possible to obtain the labelled compounds **7–9** in a pure state since under more drastic conditions exchange of the vinylic hydrogens occurs. With the aid of NMR spectroscopy exact label positions could be determined, and in the labelled compounds the amount of exchanged ring hydrogens always exceeded 90%.

B/E linked scans of molecular ions decomposing in the first field free region showed a D˙ loss of less than 5% with respect to H˙ loss, indicating that in this compound also a vinylic hydrogen is involved in the $[M-H]^+$ formation. The CCAD spectra of this ion, obtained from the compounds **6**, **7** and **9** (Table 1), cannot be interpreted in a satisfactory manner. Probably this is due to the lower symmetry, notably of the labelled ions, such as from **7**, as compared with **2**.

In the CCAD spectrum of the unlabelled ion $[M-H]^+$ from **6** (Table 1), a small, but significant, peak is found at *m/z* 68, as in the ions *d*, *e* and *f* from the 2-isomer, and indicative of the presence of a C_2H group. In the labelled analogues **7** and **9** it is shifted to *m/z* 69 and 71, respectively. The elemental composition of the fragment *m/z* 39 might either be C_2HN or C_3H_3. As in **7** this ion is still found at *m/z* 39, the latter possibility appears to be the most likely, otherwise there would have occurred a partial shift to *m/z* 40 due to a $[C_2DN]^{+\cdot}$ contribution. In neither case could the fragment ion be explained from ring-closed ions, and probably we are dealing here with a mixture of ion structures, one of which is ring-opened. This is in agreement with the findings for the *m/z* 68 ion (*vide infra*).

As with the 2-isomer **2**, this ion, *m/z* 68 from 4(5)-vinylimidazole (**6**), consists of $[C_3H_4N_2]^{+\cdot}$ ions. Its CCAD spectrum (Table 2) is totally different from that of either the *m/z* 68 ion from **2** or from the imidazole (**12**) molecular ion, the most abundant fragments at *m/z* 41 and 40 being probably due to loss of HCN and HCNH˙, respectively. The presence of peaks at *m/z* 36 and 37 can only be ascribed to $[C_3]^{+\cdot}$ and $[C_3H]^+$ fragments. These are absent in the CAD spectra of imidazole (**12**) and of the ion g, where the imidazole ring is intact (Fig. 2). This is incompatible with a ring-closed ion structure *h*, the analogue of g from the 2-isomer. We therefore have to conclude that here we have an ion with a ring-opened structure.



h

CONCLUSIONS

A method of recording and processing CAD spectra, published before,[1] has been used to study the fragment ions *m/z* 68 and 93, formed from 2-vinyl-(**2**) and 4(5)-vinyl-imidazole (**6**). The first ion, formed from **2**, is present as an imidazolium-2 radical cation that does not readily isomerize to the imidazole molecular ion. The $[M-H]^+$ ion from **2** can be described as the apparently stable 2-ethynylimidazolium cation (*d*).

For the corresponding ions from the 4(5)-isomer (**6**), such structures appear not to play an important role. The formation of a $[M-H]^+$ ion, analogous with *d* in **2**, will undoubtedly be less easily formed, as in **6** there is only one nitrogen attainable as an internal proton acceptor. As a consequence, the abundance of the $[M-H]^+$ ion is much decreased. Note that in the 1-isomer (**1**) this ion is virtually absent (Fig. 1).

The ion *m/z* 68 from the 4(5)-isomer must at least partially occur as an ion having an open structure.

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