Primary Ethynamines ($HC{\equiv}CNH_2$, $PhC{\equiv}CNH_2$), Aminopropadienone ($H_2NCH{=}C{=}C{=}O$), and Imidoylketene ($HN{=}CHCH{=}C{=}O$). Preparation and Identification of Molecules of Cosmochemical Interest

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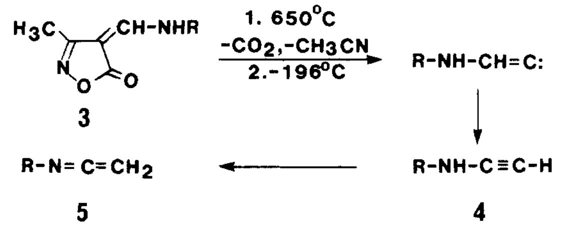
Abstract: Ethynamine ($HC{\equiv}CNH_2$) has been prepared from three different precursors (**7a**, **7b**, and **8**) by flash vacuum pyrolysis and observed by low-temperature infrared spectroscopy for the first time. The collision activation mass spectra (CAMS) strongly support the assignments. The Meldrum's acid derivative **8** also gives rise to equilibrating imidoylketene (**10**) and aminopropadienone (**9**), observable by both IR and CAMS. **9** decarbonylates above 680 °C to ethynamine. Ethynamine isomerizes in part to acetonitrile in the gas phase but polymerizes in the solid state between −70 and −50 °C. Both ketene imine ($H_2C{=}C{=}NH$) and acrylonitrile are formed on FVP of 3-hydroxypropionitrile. 2-Phenylethynamine ($PhC{\equiv}CNH_2$) is readily produced by FVP of the isoxazolone **11**.

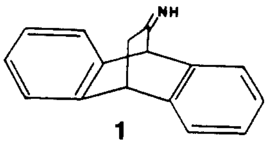
Some 68 interstellar molecules, radicals, and ions are known, and the list is growing.[2-4] Many of these compounds contain amine, imine, nitrile, and/or acetylenic moieties, and indeed ammonia was the first polyatomic molecule to be discovered, in 1968, in the interstellar medium.[2] Nitriles, from the CN radical to acetonitrile[5] to undecapentaynonitrile ($HC_{11}N$), are widespread. While the mechanism of interstellar synthesis of acetonitrile is uncertain, it is considered that methyl isocyanide and the unstable isomers ethynamine ($HC{\equiv}CNH_2$) and ketene imine ($H_2C{=}C{=}NH$) may well be formed in related processes.[6] Once formed, the extremely low temperature (<10–100 K) and pressure (1–10^6 particles/cm^3) in diffuse and dark molecular clouds[7] would ensure the preservation of these terrestrially exceedingly unstable molecules.

Ab initio calculations[8] place ethynamine some 40–48 kcal/mol above acetonitrile, with ketene imine some 6–16 kcal/mol more stable than ethynamine. N- and C-protonated ethynamines are computationally (6-31G*) 49 and 72 kcal/mol more stable than isolated CH_3^+ + HCN, which are the likely source of the C_2H_3N isomers.[6c] Rotational constants and vibrational frequencies for ethynamine have been calculated (6-31G*).[9,10]

Scheme I



Ketene imine is a known molecule. It was tentatively identified by Jacox and Milligan as the product of the reaction of NH with acetylene in solid argon[11] and more recently definitively identified by IR spectroscopy at 14 K as the product of the reaction of acetonitrile with excited argon.[12] The IR spectrum was also obtained by flash vacuum pyrolysis of 11-iminodibenzo[*be*]bicyclo[2.2.2]octane (**1**) or 5-iminonorborn-2-ene with isolation of the ketene imine at 77 K.[13] The microwave spectrum of ketene imine was obtained following pyrolysis of **1** at 800 °C or by pyrolysis of 3-hydroxypropionitrile (**2**) at 800–1100 °C (10^{-2}–10^{-3} Torr); acetonitrile, the rearrangement product of ketene imine, and formaldehyde, the byproduct of its formation from **2** were also observed.[14]



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While microwave, millimeterwave, and submillimeterwave spectroscopies are of direct relevance to radioastronomy, ethynamine has thus far proved too unstable and/or too difficult to

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[1] (a) University of Queensland. (b) Briehl, H. Ph.D. Thesis, University of Marburg, 1984. (c) Lorencak, P. Ph.D. Thesis, University of Marburg, 1985. (d) Winter, H.-W. Ph.D. Thesis, University of Marburg, 1980. (e) University of Mons.

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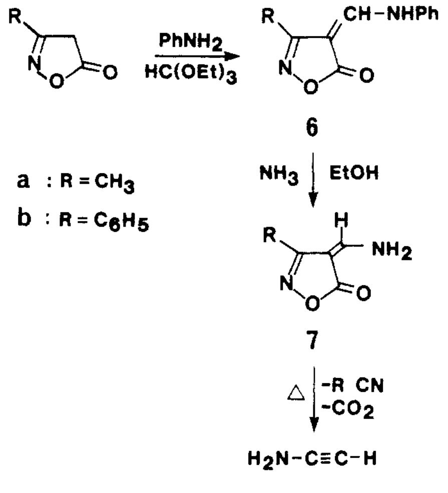
Scheme II



produce in sufficient quantity for these observational methods. However, infrared spectroscopy and mass spectrometry are rapidly gaining importance in the investigation of planetary atmospheres and comets, which contain molecules in many ways reminiscent of the interstellar clouds from which the stellar nebulae are believed to form.[15,16]

We report here an infrared–mass spectrometric identification of ethynamine. This molecule was hitherto very scantily known. Lasne and Ripoll observed a "weak and transitory" band at 2160 cm^{-1} in the pyrolysis of an aminoethanobisanthracene, but only acetonitrile was detectable by mass spectrometry.[17] Schwarz,[18] Holmes,[19] and their co-workers generated the molecular ion of ethynamine by CO loss from the molecular ion of acetylenecarboxamide in the mass spectrometer. By tandem mass spectrometry they were able to distinguish the $HC{\equiv}CNH_2^{\bullet+}$ ions from the isomeric $H_2C{=}C{=}NH^{\bullet+}$, $H_3CC{\equiv}N^{\bullet+}$ and $H_2C{=}N{=}CH^{\bullet+}$ ions. Ketene imine ions ($H_2C{=}C{=}NH^{\bullet+}$) had been produced previously by fragmentation of $C_3H_7CN^{\bullet+}$.[20] Moreover, by neutralization–reionization mass spectrometry (NRMS), it was shown[18,19] that neutral $HC{\equiv}CNH_2$ is capable of existence and reionization to afford the same collision activation (CA) mass spectrum (CAMS) of $HC{\equiv}CNH_2^{\bullet+}$ as before. This can hardly be said to be a preparative method for ethynamine, and the technique is not amenable to the application of other spectroscopies. Yet, the CA mass spectrum is a crucial piece of evidence that permits the identification of ethynamine in our systems.

Results and Discussion

Our approach is based on the previously reported successful synthesis of secondary and tertiary ethynamines of the types $RNHC{\equiv}CH$, $R_2NC{\equiv}CH$, and $R_2NC{\equiv}CR'$ by flash vacuum pyrolysis (FVP) of 4-[(arylamino)methylene]-3-methylisoxazol-5(4*H*)-ones (**3**) (Scheme I) and substituted analogues.[21]

The secondary ethynamines **4** were observed by IR spectroscopy at −196 °C (2120–2136 (C≡C), 3290 (C≡CH), 3200–3300 (NH) cm^{-1}) and isomerized to the isolable ketene imines **5** on warming to −70 to −60 °C.[21]

The required primary (aminomethylene)isoxazolones **7a** and **7b** were best prepared by displacement of aniline from 4-[(phenylamino)methylene]isoxazolones **6** with ammonia (Scheme II).[22]

Flash vacuum pyrolysis of **7a** at 560–690 °C (10^{-5}–10^{-4} Torr) with condensation of the products on the cold end of a cryostat at either 77 or 15–30 K resulted in new peaks in the IR spectrum at 2155, 3240, 3336, and 3390 cm^{-1}, which are assigned to ethynamine (vide infra). (The C≡C stretch at 2155 cm^{-1} (neat) appeared at 2162 cm^{-1} in an Ar matrix at 10 K.) Additional peaks due to CH_3CN (2252, 2288 cm^{-1}) and CO_2 (2334 cm^{-1}) were also present. The bands assigned to the acetylene disappeared on warmup between −70 and −50 °C, being replaced by a new band at 2188 cm^{-1}, which remained stable at room temperature and belonged to a polymeric material. This 2188-cm^{-1} band was present with varying intensities even in the "cold" spectra at pyrolysis temperatures above 560 °C. At a pyrolysis temperature of 700 °C, the 2155-cm^{-1} band was barely produced any more, and the 2188-cm^{-1} band and acetonitrile were now the main features of the spectrum throughout the temperature range from −196 °C to room temperature. The optimal temperature for the production of the 2155-cm^{-1} band was 625 °C. In all the experiments, *only* acetonitrile and a brown polymer were isolable after warming to room temperature. The polymer featured the aforementioned medium band at 2188 cm^{-1} together with a broad amine absorption (3200, 3380 cm^{-1}) in the IR. The ^1H NMR showed only a vinylic proton at δ 7.8 and two broad NH absorptions at δ 8.8 and 9.2 (1:1:1) apart from acetonitrile. The ^{13}C NMR showed acetonitrile (δ 1.6 and 117.0) and two weak peaks at δ 123 and 149. No distinct mass spectrum was obtainable. These data are consistent with the material being of polymer of ethynamine.

Similar pyrolysis of **7b** gave exactly the same, albeit much weaker, band at 2155 cm^{-1} (30 K). Weak bands at 2040–2035 cm^{-1} were present in some of the spectra from both **7a** and **7b**, but any assignment of these to ketene imine[11-13] would be hazardous. More importantly, acetonitrile was formed not only from **7a** (where it is a necessary byproduct) but also from **7b** (together with benzonitrile). It was definitively identified in the pyrolysis of **7b** by both IR spectroscopy and millimeterwave spectroscopy, in the latter case by measuring inter alia the transition $J_{8\leftarrow7}$ ($K = 3$) at 147 149.0756 MHz.[23,24]

The IR bands assigned to ethynamine are in surprisingly good agreement with Radom's predictions[9] (2152 (C≡C), 3344 (C≡CH), 3258, 3346 (NH) cm^{-1}. Confidence limit: 10 cm^{-1} for C≡C and C≡CH). Furthermore, 3-methyl-4-[(*N*-methylamino)methylene]isoxazol-5(4*H*)-one (**3**, R = CH_3) has been prepared by our method and pyrolyzed at 700 °C to *N*-methylethynamine (**4**, R = CH_3), which absorbs at 2152 cm^{-1}, in the gas phase.[25a]

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(22) Lower yields of **7** were obtained in a one-pot three-component reaction between 3-methyl- or 3-phenylisoxazolone, ethyl orthoformate, and ammonia. This method works well for the preparation of N-substituted (aminomethylene)isoxazolones, including **6**.[21]

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Table I. Mass Spectra of Isoxazolone **7a** (400 °C) and Its Decomposition Products (760 °C)[a]

	m/z																			
temp, °C	127	126	125	82	81	80	69	68	67	66	55	54	53	44	43	42	41	40	39	38
400	7	*100*	3	7	10	6	12	15	6	4	3	4	4	8	3	8	15	6	6	3
760		25		5	3		3	6	3			4		50		6	*100*	41	12	7

[a] *B/E* spectrometer with internal oven (see the Experimental Section), 3 kV, 1 mA, 70 eV.

Table II. CAMS of Isomeric $C_2H_3N^{\bullet+}$ Ions (*m/z* 41) from Various Precursors[a]

	m/z												
precursor	29	28	27	26	25	24	20.5	16	15	14	13	12	ion structures
$CH_3C{\equiv}N$[b]	3	100	53	46	14	4	3		14	52	17	9	$CH_3{-}C{\equiv}N^{\bullet+}$
$CH_3CH_2CH_2C{\equiv}N$[c]		100	64	42	18	5	18		8	73	17	7	$CH_2{=}C{=}NH^{\bullet+}$
$HC{\equiv}CCONH_2$[d]	4	100	23	10	21	8	20	6	4	44	15	6	$HC{\equiv}CNH_2^{\bullet+}$
7b[e]	3	100	30	17	25	7	13	4	6	42	14	6	$HC{\equiv}CNH_2^{\bullet+} + C_3H_5^+$ (90:10)[f]
7a[e]	2	100	40	28	25	7	11	4	11	53	15	8	$HC{\equiv}CNH_2^{\bullet+} + CH_3C{\equiv}N^{\bullet+}$
8[e]	46	100	34	30	25	8	11	2	6	49	60	12	$HC{\equiv}CNH_2^{\bullet+} + C_2HO^+$ (75:25)[g]

[a] *B/E* spectrometer at 3 kV. [b] By direct ionization; cf. ref 20. [c] By ionization followed by dissociation; cf. ref 20. [d] By ionization followed by dissociation; cf. ref 18 and 19. [e] By pyrolysis; see text. [f] Composition determined by high-resolution measurement for pyrolysis at 740 °C; the presence of $C_3H_5^+$ causes the slight differences observed by adding intensity to the signals at *m/z* 27, 26, and 15. [g] From high-resolution measurements; see text.

Likewise, we obtained the known and isolable *N*,*N*-dimethylethynamine ($HC{\equiv}CN(CH_3)_2$) by similar pyrolysis of 4-[(dimethylamino)methylene]-3-phenylisoxazol-5(4*H*)-one.[25b] Thus, the generality of this method of preparation of ethynamines seems secured. The weak band observed by Lasne and Ripoll[17] at 2160 cm^{-1} may have been identical with our 2155-cm^{-1} (2162 in Ar) band for ethynamine. The compound would be deposited in the presence of large amounts of anthracene in the Ripoll work, and this could account for the 5-cm^{-1} discrepancy.

It follows from the observations made so far that ethynamine is not easy to generate in quantity. At the optimal temperature of 625 °C, there is still much undecomposed starting material, obscuring much of the spectrum. The compound isomerizes to acetonitrile in the gas phase (indeed, this is the *only* compound detectable by millimeterwave spectroscopy), but there is little or no evidence for any tautomerization of ethynamine in the condensed phase; instead, it polymerizes between −70 and −50 °C. This is consistent with results obtained for 2-phenylethynamine (**12**) (vide infra). The secondary ethynamines **4** are much less prone to polymerization, readily tautomerizing to ketene imines **5**.

In view of these difficulties, it was essential to identify ethynamine with another method. The CA mass spectra referred to above[18,19] permit a clear-cut differentiation of the C_2H_3N isomers. Pyrolyses were therefore carried out in a reactor situated immediately in front of the ion source of either a dual-sector (*B/E*) or a triple-sector (*E/B/E*) mass spectrometer. The ions of interest were selected and subjected to collisional activation (air) in the second or third field free region. This has the advantage that undesired ions of different masses, e.g. due to undecomposed starting material, do not appear. When the normal electron ionization mass spectra are monitored as a function of temperature, the onset and progress of pyrolysis can be determined. The results are presented in Tables I and II.

In agreement with the IR study, **7a** is stable toward pyrolysis above 400 °C; the spectrum given for this temperature in Table I is due to the undecomposed starting material ($M^{\bullet+} = 126$). At 760 °C the compound is still not totally decomposed, but the principal masses are now *m/z* 41 (C_2H_3N) and 44 (CO_2). The ions at *m/z* 40–38 are due to loss of hydrogen from $C_2H_3N^{\bullet+}$. Minor byproducts are seen at *m/z* 82 and 68; these are present in the spectrum of the starting material also, but their intensity decrease does not follow that of *m/z* 126 exactly. They correspond to methylpyrazole and pyrazole, respectively, which could be formed by thermal ring opening and recyclization of **7a** to 3-methylpyrazole-4-carboxylic acid followed by decarboxylation and demethylation, a process described elsewhere for related systems.[26] Clearly, however, the major ion current is carried by the desired species, $C_2H_3N^{\bullet+}$.

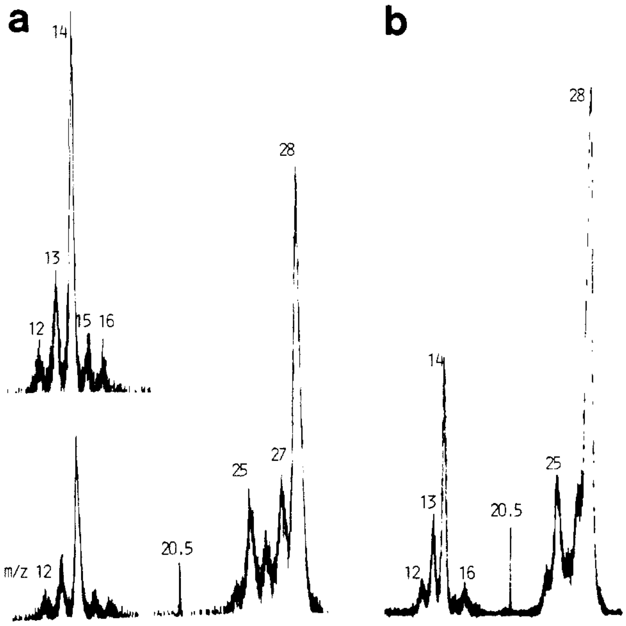

Figure 1. (a) CAMS of ethynamine (*m/z* 41) produced by FVP of **7b** at 740 °C. Inset: higher resolution scan of *m/z* 12–16. (b) CAMS of *m/z* 41 ($HC{\equiv}CNH_2^{\bullet+}$) produced by dissociation of $HC{\equiv}CCONH_2^{\bullet+}$ in the *B/E* mass spectrometer (see the Experimental Section). The spectra in (a) and (b) were recorded on slightly different scales.

The CA spectrum of this species is compared with those of $CH_3CN^{\bullet+}$ and $CH_2{=}C{=}NH^{\bullet+}$ in Table II. Other isomeric ion structures ($CH_3NC^{\bullet+}$ and $H_2C{=}N{=}CH^{\bullet+}$) are ruled out by comparison with literature data.[18-20] CH_3CN is, of course, a mandatory byproduct of the pyrolysis of **7a**. In **7b**, any CH_3CN present must be formed by rearrangement of another C_2H_3N species. The CA spectrum of ethynecarboxamide was also recorded on our instrument for direct comparison. It is seen from Table II that the CA spectrum of $HC{\equiv}CNH_2^{\bullet+}$ is characterized by the simultaneous presence of *m/z* 16, 25, and the charge stripping peak at 20.5. In particular, *m/z* 16 is *only* seen in the spectra of $HC{\equiv}CNH_2^{\bullet+}$.[18,19] The close similarity between the CA spectra of *m/z* 41 from **7b** and $HC{\equiv}CCONH_2^{\bullet+}$ identifies the carrier as ethynamine, $HC{\equiv}CNH_2$ (Table II; Figure 1). In

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Table III. CAMS of m/z 41 ($CH_2{=}C{=}NH$) Produced by FVP of 3-Hydroxypropionitrile (**2**), by Dissociation of the Molecular Ion of Butyronitrile, and Comparison with the Molecular Ion of Acetonitrile[a]

	m/z											
precursor (temp, °C)	29	28	27	26	25	24	20.5	15	14	13	12	14/15
$CH_3CH_2CH_2CN$ (100)	2	100	54	46	25	10	38	7	49	11	9	7
2 (300)	3	100	50	37	24	9	33	5	45	14	9	9
2 (800)	2	100	51	40	21	8	8	10	34	11	9	3.4
2 (1000)	2	100	52	48	23	8	7	10	35	12	10	3.5
$CH_3C{\equiv}N$	2	100	54	45	21	8	8	9	26	9	7	2.9

[a] *E/B/E* spectrometer (see the Experimental Section). Due to the different spectrometer used, intensities should not be directly compared with those given in Table II.

Table IV. Mass Spectra of 3-Hydroxypropionitrile (**2**) without Pyrolysis (300 °C) and with Pyrolysis to Acrylonitrile (m/z 53), Ketene Imine (m/z 41), and Formaldehyde (m/z 30)[a]

	m/z																			
temp, °C	80	79	71	54	53	52	51	50	42	41	40	39	38	31	30	29	28	27	26	25
300			<1		2	15	15	7	12	85	10	5	5	*100*	5	20	9	9	18	3
800					4	4	2		4	*100*	51	19	14	13	33	49	19	4	9	3
1000	1	2		4	10	5	4		4	*100*	60	21	15	3	33	51	44	15	11	3

[a] See Table III.. Intensities should not be directly compared with those given in Table I.

Table V. Mass Spectra of Meldrum's Acid Derivative **8** at Various Temperatures[a]

	m/z													
temp, °C	171	156	114	96	85	70	69	59	58	44	43	42	41	40
150	44	46	67	8	12	35	*100*	45		15	52	13	26	9
580							45		33	75	*100*	19	11	21
735							39		37	*100*	73	15	14	16

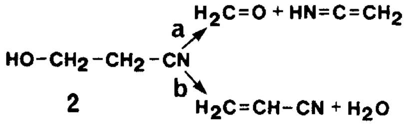
[a] *B/E* spectrometer, 3 kV,,1 mA, 70 eV.

the case of **7a**, the spectrum is necessarily due to a mixture of ethynamine and acetonitrile.

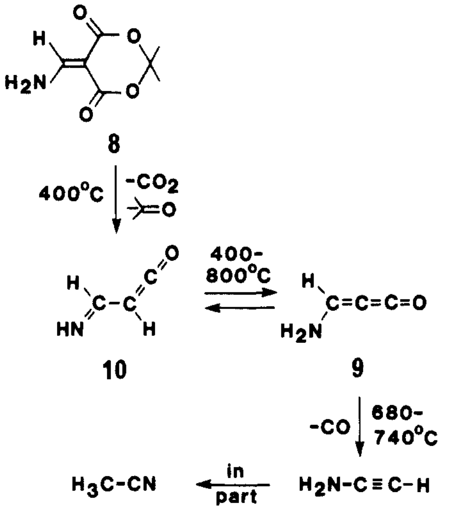
The assignment of the CA spectrum of ketene imine, $CH_2{=}C{=}NH$, so far relied on the mass spectrometric fragmentation of butyronitrile.[18,20] Since a correct assignment is mandatory for the purpose of comparison, we sought an alternative, thermal route to ketene imine. The pyrolysis of **1** was not suitable due to its low vapor pressure; the ion current was carried mainly by anthracene. For the same reason, it is difficult to obtain the microwave spectrum of ketene imine from **1**.[14] 3-Hydroxypropionitrile (**2**), however, pyrolyzes to ketene imine at 800–1100 °C.[14] The CAMS of this pyrolysate confirms the assignment of m/z 41 for $CH_3CH_2CH_2CN^{\bullet+}$ as $CH_2{=}C{=}NH^{\bullet+}$. However, it should be noted that ketene imine generated at 500–1000 °C is not stable, but it too isomerizes to acetonitrile. Thus, a constant evolution of the CA spectrum toward that of acetonitrile is observed (Table III). We have confirmed this by IR spectroscopy and millimeterwave spectroscopy and find that, due to the high temperature required, the pyrolysis of **2** gives, in fact, only a small amount of $CH_2{=}C{=}NH$ in the presence of much CH_3CN. Furthermore, the electron ionization mass spectra (Table IV). demonstrate that not only $CH_2{=}C{=}NH/CH_3CN$ (m/z 41) and $CH_2{=}O$ (m/z 30) are formed but also acrylonitrile ($CH_2{=}CHCN$, m/z 53). Weak signals at m/z 80 and 79 indicate that also succinonitrile may be produced. Since acrylonitrile was said *not* to be a product,[14] we reexamined this pyrolysis by millimeterwave spectroscopy also[24] and definitively identified acrylonitrile as a minor constituent together with formaldehyde, acetonitrile, and ketene imine. The measured frequencies for ketene imine[14] were confirmed.[1c] The now complete pyrolysis scheme for **2** is presented in Scheme III.

5-Aminomethylene derivatives of Meldrum's acid constitute another potential source of aminoacetylenes.[27] However, in view of our earlier results,[27-29] we should expect 3-aminopropadienone (**9**) and/or the imidoylketene (**10**), as the principal products; ethynamine formation might be a secondary pathway. Indeed, this is what we observe (Scheme IV).

Scheme III



Scheme IV



The base peak in the mass spectrum of **8** is m/z 69 (Table V). The CA spectrum of this ion features a prominent peak for the loss of the amino group at m/z 53 in agreement with the (aminomethylene)ketene structure $9^{\bullet+}$ (Figure 2a). As the temperature is raised to 580 °C, **8** is completely pyrolyzed as seen in the disappearance of the molecular ion (m/z 171) and the generation of intense signals for acetone (m/z 58 and 43) and CO_2 (m/z 44), whereas m/z 69 is still present (Table V). The CA spectrum of the new m/z 69 in the high-temperature regime (680 °C) (Figure 2b) clearly demonstrates that it is totally different from that

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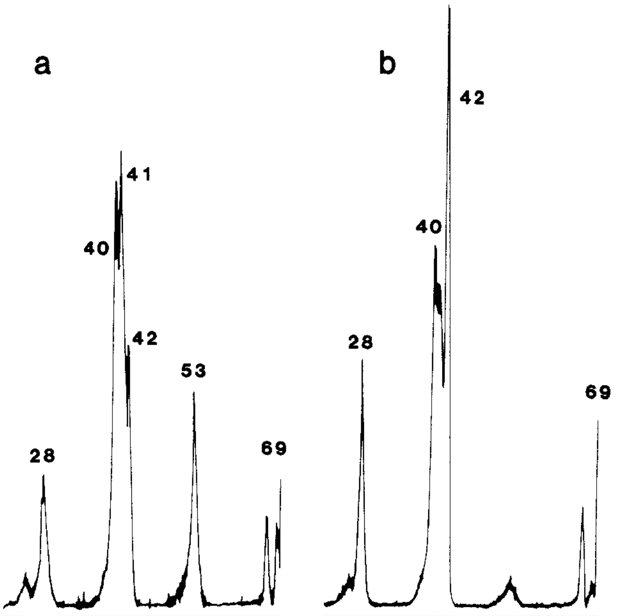


Figure 2. (a) CAMS of *m/z* 69 ($9^{\bullet+}$) produced by dissociation of $8^{\bullet+}$ in the *B/E* mass spectrometer at an inlet temperature of 150 °C. (b) CAMS of *m/z* 69 ($10^{\bullet+}$) produced by FVP of **8** at 680 °C (*B/E* instrument).

formed in the cold. Only a trace of NH_2 loss remains, and the new ion eliminates instead 27 mass units (HCN), which would be in agreement with the imidoylketene structure $\mathbf{10}^{\bullet+}$. This ion (and hence its neutral parent) is very stable, remaining essentially unchanged until 735 °C.

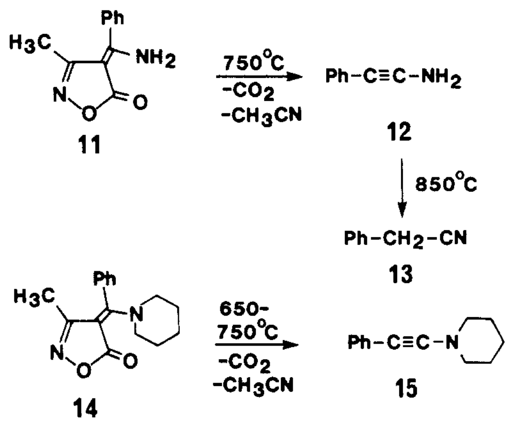
The IR spectra support this conclusion. Two strong bands at 2080 and 2130 cm^{-1} are seen in the −196 °C spectra of the products of pyrolyses in the range 400–680 °C (10^{-5} Torr). Both compounds are stable until −120 °C in the solid state. The 2080-cm^{-1} absorption is characteristic of methyleneketenes[27,30] and is assigned to compound **9**. The 2130-cm^{-1} absorption is in the region typical of imidoylketenes[27] and is attributed to **10**. Both **9** and **10** polymerize above −120 °C, and no solid-state tautomerization was observed. The imidoylketene **10** actually appears first, being visible already at a pyrolysis temperature of 390 °C. As the temperature is raised, **10** rapidly interconverts with **9**. Reasons for this[1c] will be given in a separate publication. The gas-phase reaction **9** ⇄ **10** formally constitutes a 1,3 hydrogen shift. We have shown elsewhere that 1,3-shifts are thermally allowed and readily occurring in ketenes (and in cumulenes generally) in the gas phase above 400 °C but not in the condensed phase at ordinary temperatures.[27,31] However, there are reasons to believe that the reaction **9** → **10** is not a direct process but involves instead a 1,5-shift of hydrogen from the amino group to oxygen, giving first 2-imidoylethynol.

$$H_2NCH{=}C{=}C{=}O \rightarrow HN{=}CHC{\equiv}COH \rightarrow HN{=}CHCH{=}C{=}O$$

We have observed the related 2-vinylethynols in the rearrangements of alkylideneketenes to vinylketenes by IR spectroscopy.[1c]

It is seen in Table V that a fragment at *m/z* 41 is also present in the high-temperature pyrolysis of **8**. High-resolution measurements indicate that this is due to a mixture of isobaric ions $C_2H_3N^{\bullet+}$ and C_2HO^+ in the ratio 3:1 (mass ratio: 1.00054). The CA spectrum of this ion mixture is included in Table II. The C_2HO^+ ions are undoubtedly responsible for the relatively strong signals at *m/z* 13 and 29. The presence of *m/z* 16, 25, and 21.5 indicates that $C_2H_3N^{\bullet+}$ is derived from neutral $HC{\equiv}CNH_2$, which, at the higher temperatures, will isomerize in part to CH_3CN. The presence of the latter was confirmed by millimeterwave spectroscopy of the pyrolysis gas from **8** at 900 °C (0.075 Torr) where the transition $J_{6\leftarrow5}$ ($K = 2$) was measured at 110 374.998 MHz.[23,24]

Scheme V



After the presence of $H_2NC{\equiv}CH$ in the pyrolysis of **8** was determined by CAMS, this molecule was now clearly identifiable by IR spectroscopy also, appearing at 2155 (2162 in Ar), 3240, 3330, and 3400 cm^{-1} (neat solid, −196 °C) and polymerizing to the above-mentioned 2188-cm^{-1} species on warmup. Ethynamine formation was prominent in the temperature range 680–740 °C, and it was accompanied by a sharp decrease in the intensity of the absorption of **9** at 2080 cm^{-1}, whereas the imidoylketene **10** was less so affected. This is the likely reason why **9** almost disappears in the CAMS at 680 °C (Figure 2b). (Note that the furnaces used for IR and MS are different so that a slightly higher temperature appears to be necessary to decompose **9** for IR purposes.) With three thermal sources of ethynamine now in hand, its identification is secure.

We present one further example to demonstrate that the isoxazolone method is generally applicable to the generation of tertiary, secondary,[21] and primary ethynamines and, thus far, it is the best method available.

4-(Aminophenylmethylene)-3-methylisoxazol-5(4*H*)-one (**11**) started decomposing on FVP at 650 °C (10^{-3} Torr), and the pyrolysis was almost complete at 750 °C. At this temperature, new signals at 2230 (s) (disubstituted C≡C),[32] 3200–3400 (−N-H_2), 1545, and 750 cm^{-1} together with CO_2 and CH_3CN were recorded in the IR spectrum (−196 °C). Only a trace amount of benzyl cyanide (**13**) appeared under these conditions. The acetylene (**12**) polymerized to a brown tar at −45 to −40 °C, but *no* isomerization to a ketene imine or to **13** (Scheme V) was observed on slow warming from −196 to −40 °C. Obviously, polymerization is faster than tautomerization in primary ethynamines, in contrast to the situation in the secondary case.[21] Yet, such tautomerization readily occurs in the gas phase at high temperature and low pressure where polymerization is retarded for reasons of low concentration. Thus, the preparative pyrolysis of **11** at 850 °C gave benzyl cyanide (**13**) in 76% isolated yield. The reaction **12** → **13** formally constitutes two consecutive 1,3-shifts of hydrogen, passing through phenylketene imine, but since these two shifts will not have very different activation energies and the reaction is thermodynamically driven toward **13**, the ketene imine cannot be intercepted. These 1,3-shifts are electronically equivalent to those operating in ketenes and referred to above.[27,31]

$$PhC{\equiv}CNH_2 \xrightarrow{1,3\text{-H}} PhCH{=}C{=}NH \xrightarrow{1,3\text{-H}} PhCH_2CN$$

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In contrast to ordinary disubstituted acetylenes where the $C\equiv C$ stretching vibration near 2220 cm^{-1} is very weak in the IR,[32a] the phenylethynamines absorb strongly due to the increased rate of change of the dipole moment.[32b] For comparison, the piperidyl analogue **14**[25b] gave a tertiary phenylethynamine (**15**), now stable until room temperature and absorbing at 2225 (s), 1545, and 750 cm^{-1} in the IR. Altogether, the IR spectrum of **15** is very similar to that of **12** except for the obvious lack of a primary amine function.

Conclusion

Ethynamine has been produced thermally from three different sources (**7a**, **7b**, and **8**) and identified by low-temperature IR and in particular gas-phase collision activation mass spectrometry. Comparisons with the spectra of isomeric and isobaric species and with published ab initio calculations, together with the method of synthesis itself, which is shown to be general, support the assignments. Ethynamine is a very fleeting substance, difficult to produce in quantity. Seven years of supporting investigations of related chemistry[1b–d] and sophisticated instrumentation was necessary in order to substantiate the existence of the title compounds, first generated in our laboratory in 1980.[1d] Numerous attempts to obtain the millimeterwave spectrum of ethynamine[24] were unsuccessful. The reason is that the vapor pressure of the starting materials **7** and the velocity of their pyrolysis are insufficient at medium temperatures to produce measurable gas-phase concentrations of ethynamine in the flowing medium at ca. 10^{-2} Torr. At high temperatures the required pressure will be reached, but now the isomerization to acetonitrile becomes too rapid. However, IR spectroscopy permits the slow buildup of pyrolysis product even in the presence of large amounts of undecomposed starting material, and CAMS allows the selection of ions even in low relative abundance. 2-Phenylethynamine (**12**) is significantly more stable and a microwave/millimeterwave investigation of this and other 2-substituted primary ethynamines should be possible by using the methods described here.

While secondary ethynamines tautomerize to the spectroscopically identifiable and often isolable ketene imines at ca. −70 °C, primary ethynamines polymerize faster than they tautomerize in the solid phase, but they tautomerize to the corresponding nitriles in the gas phase at elevated temperatures.

The Meldrum's acid derivative **8** undergoes FVP to imidoylketene (**10**) and aminopropadienone (**9**), which interconvert in the gas phase only. Both polymerize in the solid state. Decarbonylation of **9** to ethynamine takes place in the high-temperature regime. This method should even allow the microwave spectroscopic detection of ethynamine.

Experimental Section

General Methods. The pyrolysis apparatus used for preparative, infrared, and mass spectral purposes were as previously described.[27,29,33] A triple-sector (*E*/*B*/*E*) modified AEI MS902 mass spectrometer (8 kV)[34] or a dual-sector (*B*/*E*) Varian MAT 311A spectrometer (3 kV) was used. IR spectra were recorded on a Perkin-Elmer 281 or Mattson Sirius 100 FT-IR spectrometer. Millimeterwave spectra were recorded at the Justus Liebig University of Giessen.[24,35]

3-Methyl-4-[(phenylamino)methylene]isoxazol-5(4*H*)-one (6a). To a mixture of freshly distilled aniline (3.7 g, 40 mmol) and triethyl orthoformate (9 g, 60 mmol) in a 100-mL flask equipped with reflux condenser, drying tube, and a magnetic stirring bar was added free 3-methylisoxazol-5(4*H*)-one (4.0 g, 40 mmol). The yellow solution was gently heated to reflux with stirring and within 5 min solidified to an orange mass, which after recrystallization from ethyl acetate gave 5 g of yellow crystals (65%): mp 158–160 °C (lit.[36] mp 158 °C); IR (KBr) 3240 (w), 3080 (w), 1715 (sh), 1700 (vs), 1655 (vs), 1635 (vs), 1595 (vs), 1500 (s), 1450 (m), 1435 (m), 1410 (m), 1380 (vw), 1360 (w), 1325 (vs), 1220 (m), 1165 (m), 1020 (m), 1010 (m), 880 (m), 845 (w), 830 (w), 800 (s), 770 (w), 755 (s), 690 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.52 (s, 3 H, CH$_3$), 7.21–7.42 (m, 5 H, phenyl), 8.01 (d, *J* = 14 Hz, 1 H, vinyl), 10.54 (br d, *J* = 14 Hz, 1 H, NH); MS, *m*/*z* 203 ($[M + 1]^+$, 10), 202 ($[M^{\bullet+}]$, 84), 158 (8), 157 (72), 144 (14), 143 (14), 142 (23), 117 (20), 116 (13), 115 (15), 110 (46), 104 (29), 93 (35), 90 (19), 89 (17), 82 (32), 78 (14), 77 (100), 66 (34), 65 (17), 52 (12), 51 (68), 50 (10), 43 (14), 39 (45), 26 (25), 25 (11). Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.23; H, 4.80; N, 13.71.

4-(Aminomethylene)-3-methylisoxazol-5(4*H*)-one (7a). **6a** (2.02 g, 10 mmol) dissolved in 100 mL of ethanol was placed in a 250-mL three-neck flask equipped with reflux condenser, inner thermometer, gas inlet tube, and magnetic stirrer. Ammonia gas was introduced for 5.5 h with stirring and heating at 50–60 °C. The light yellow solution was concentrated to 30 mL, and the light yellow precipitate thus formed was filtered and washed with cold ethanol to give 0.78 g (62%) of colorless crystals, mp 209–210 °C from ethanol. The compound can be further purified without decomposition by sublimation at 200–210 °C (10^{-4} Torr): IR (KBr) 3370 (m), 3125 (br), 1695 (s), 1660 (w), 1570 (s), 1435 (m), 1390 (w), 1320 (s), 1135 (m), 1030 (m), 1000 (m), 860 (m), 760 (m), 740 (w), 675 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.08 (s, 3 H, CH$_3$), 7.82 (dd, *J* = 15.9 and 16.2 Hz); 8.71 (br, 1 H, NH), 9.24 (br, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 10.5 (CH$_3$), 89.7 (C-4), 153.7 ($^1J_{CH}$ = 168.5 Hz, C-6), 159.7 (C-3), 173.0 ($^3J_{CH}$ = 9.8 Hz, C-5). Anal. Calcd for $C_5H_6N_2O_2$: C, 47.62; H, 4.80; N, 22.21. Found: C, 47.75; H, 4.67; N, 22.17.

3-Phenyl-4-[(phenylamino)methylene]isoxazol-5(4*H*)-one (6b). 3-Phenylisoxazol-5(4*H*)-one (8.05 g, 50 mmol) was dissolved with gentle heating in 25 mL of triethyl orthoformate in a 100-mL flask equipped with reflux condenser, dropping funnel, and a magnetic stirring bar. Aniline (4.65 g, 50 mmol) was added all at once, and the mixture was stirred at reflux at 80 °C for 30 min, causing the initially light yellow solution to turn dark red to brown. The mixture was stirred for a further 10 min without external heating and then concentrated on the rotary evaporator. The brown solid residue was recrystallized first from ethyl acetate and then from ethyl acetate–petroleum ether (1:1) to give 8.2 g (62%) of yellow crystals: mp 144–145 °C (lit.[36] mp 145 °C); IR (KBr) 3210 (w), 3055 (w), 1700 (s), 1630 (s), 1585 (s), 1520 (m), 1490 (s), 1390 (m), 1360 (m), 1300 (s), 1125 (m), 975 (m), 965 (m), 870 (m), 785 (m), 760 (m), 705 (m), 685 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.25–7.80 (m, 10 H, aromatic), 8.34 (d, *J* = 13.5 Hz, 1 H), 11.18 (d, *J* = 13.5 Hz, NH); ^{13}C NMR (DMSO-d_6) δ 90.3 (C-4), 148.9 ($^1J_{CH}$ = 173.3 Hz, C-6), 161.6 (C-3), 172.9 ($^3J_{CH}$ = 9.5 Hz, C-5); MS, *m*/*z* 265 ($[M + 1]^+$, 10), 264 ($M^{\bullet+}$, 52), 219 (43), 196 (36), 105 (14), 104 (19), 103 (17), 93 (100), 77 (64), 66 (13), 51 (24), 47 (19), 46 (14), 45 (31), 31 (78), 29 (20), 27 (22), 26 (24). Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.52; H, 4.51; N, 10.71.

4-(Aminomethylene)-3-phenylisoxazol-4(5*H*)-one (7b). **6b** (4.75 g, 18 mmol) was dissolved in 350 mL of ethanol, and ammonia gas was introduced with stirring at 60 °C for 5 h. The yellow solution was evaporated, and the yellow solid so obtained was recrystallized twice from absolute ethanol, giving 2.0 g (59%) of white to light yellow crystals, mp 196–199 °C. The compound sublimes without decomposition at temperatures up to 200 °C (10^{-5} Torr): IR (KBr) 3450 (m), 3380 (w), 3320 (w), 3260 (w), 3050 (w), 1735 (s), 1715 (m), 1670 (s), 1555 (s), 1515 (m), 1495 (m), 1425 (m), 1325 (s), 1195 (m), 1045 (m), 1025 (m), 860 (s), 785 (s), 755 (s), 685 (m), 665 (m), 650 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.52–7.54 (m, 3 H, aromatic), 7.62–7.63 (m, 2 H, aromatic), 7.84 (d, *J* = 15 Hz, H-C(6)), 9.07 (d, *J* = 15 Hz, 1 H, NH), 9.41 (br, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 87.9 (C-4), 154.8 ($^1J_{CH}$ = 169.5 Hz, C-6), 161.7 (C-3), 173.4 ($^3J_{CH}$ = 9.2 Hz, C-5); MS, *m*/*z* 189 ($[M + 1]^+$, 11), 188 ($[M^{\bullet+}]$, 100), 170 (17), 144 (12), 143 (14), 109 (32), 104 (20), 103 (11), 77 (50), 51 (15), 45 (15), 31 (26). Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.29; N, 14.89. Found: C, 63.74; H, 4.22; N, 14.89.

5-(Aminomethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (8). This compound could not be prepared by directly following the literature procedure.[37] A mixture of methyl formimidate hydrochloride[38] (9.6 g, 0.1 mol), Meldrum's acid (14.4 g, 0.1 mol), and triethylamine (0.12 mol) in 100 mL of chloroform was refluxed for 15 h and worked up as described.[37] However, **8** was consistently isolated in 10% yield from the aqueous and not as reported[37] from the organic phase. It is also not necessary to carry out the reaction at reflux temperature; **8** is obtained also by stirring the above mixture for 15 h at 20 °C. A higher yield is achieved from methoxymethylene–Meldrum's acid:[39] mp 215 °C dec

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(lit.[37,39] mp 214–215 °C); IR (KBr) 3415 (m), 3280 (br), 2990 (w), 1725 (m), 1685 (s), 1645 (s), 1535 (m), 1400 (m), 1375 (w), 1350 (w), 1265 (m), 1230 (w), 1200 (m), 1150 (m), 1100 (m), 1065 (w), 1010 (w), 995 (m), 920 (s), 820 (m), 740 (m), 700 (br), 645 (w) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.60 (s, 6 H, CH$_3$), 8.03 (d, J = 17 Hz, vinyl H), 9.14 (br, 1 H, NH), 9.36 (br, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 26.4 (CH$_3$), 84.2 (C-5), 103.4 (C-2), 159.0 ($^1J_{CH}$ = 166.8 Hz, C-7, vinyl), 163.5 ($^3J_{CH}$ = 0.0 Hz, C-6, *E*-carbonyl), 163.8 ($^3J_{CH}$ = 9.6 Hz, C-4, *Z*-carbonyl); MS *m/z* 171 ([M$^{\bullet+}$], 52), 156 (33), 114 (66), 85 (10), 70 (28), 69 (100), 59 (56), 43 (42), 41 (17), 28 (10).

4-(Aminophenylmethylene)-3-methylisoxazol-5(4*H*)-one (11). The compound described by Betti[40a] as an amide and by Speroni[40b] as 4-benzoyl-5-imino-3-methylisoxazoline is in fact the title compound **11**.[41] 4-Benzylidene-3-methylisoxazol-5(4*H*)-one (40 g, 0.21 mol) was dissolved with warming in 2.3 L of ethanol, and the solution was saturated with ammonia gas for 30 min. Benzaldehyde (26 g, 0.24 mol) was added, and air was bubbled through the solution at reflux for 30 min, causing a color change from yellow-orange to brown. The presence of benzaldehyde is essential, mediating the air oxidation of the initial Michael addition product. The mixture was left in the open air at room temperature for 2 days, diluted with 300 mL of ethanol, and then stirred for 15 min. The light yellow to rose crystals thus formed were filtered off. The mother liquor was saturated once again with ammonia gas, and the above procedure was repeated four times. The combined crystals were recrystallized from ethanol, giving 5.2 g (12%); mp 262–263 °C dec (lit.[40a] mp 256–257 °C from AcOH); IR (KBr) 3270 (s), 3050 (s, br), 1705 (s), 1650 (s, br), 1560 (s, br), 1490 (s), 1415 (s, br), 1260 (m), 1125 (m), 1010 (s), 890 (m), 860 (s), 760 (s), 700 (s) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.41 (s, 3 H, CH$_3$), 7.43–7.66 (m, 5 H, aromatic), 9.26 (2 H, br, independent of concentration); ^{13}C NMR (DMSO-d_6) δ 13.7 (CH$_3$), 88.6 (C-4), 128.0 (*m*-phenyl), 128.5 (*o*-phenyl), 131.0 (*p*-phenyl), 133.1 (phenyl C-1′), 158.3 (C-3), 167.0 (exocyclic vinyl), 173.9 (C-5); MS, *m/z* 203 ([M + 1]$^+$, 10), 202 ([M$^{\bullet+}$], 100), 201 (5), 183 (8), 144 (21), 130 (5), 117 (5), 104 (17), 77 (12), 66 (11). Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.63; H, 4.89; N, 13.97.

Compound **11** sublimed without decomposition at 220–230 °C (4 × 10^{-5} Torr). Pyrolysis at 850 °C (4 × 10^{-5} Torr) gave benzyl cyanide in 76% yield, identified by IR, ^{1}H NMR, mass spectrometry, and chromatographic comparison with authentic material.

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Ion/Surface Collisions for Distinction of Isomeric $[C_6H_6]^{\cdot+}$ and $[C_6H_6]^{2+}$ Ions

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Abstract: Ion/surface collisions have been employed to dissociate $[C_6H_6]^{\bullet+}$ ions generated from benzene, 2,4-hexadiyne, and 1,5-hexadiyne. Experiments covering a range of collision energies (25–150 eV) demonstrate that the $[C_6H_6]^{\bullet+}$ ions retain distinct structures under the conditions of this experiment, which preferentially samples ions of low internal energy. Fragmentation efficiencies, as well as associative ion/surface reactions, provide additional means for differentiation of these isomers. It is also shown that high internal energy deposition is not necessarily desirable for isomeric ion distinction. The $[C_6H_6]^{2+}$ ions generated from benzene by electron impact have the same (cyclic) structure as singly ionized benzene.

A widely used method of distinguishing isomeric ions in the gas phase is collision-activated dissociation (CAD).[1-3] CAD is usually implemented in the kiloelectron volt range for high-energy collisions[4,5] or in the energy range below 100 eV.[6,7] The average internal energies deposited in ions upon high- and low-energy collisions can be surprisingly similar.[8] In cases where isomeric ions are particularly difficult to distinguish, it is often beneficial to obtain data under different experimental conditions, e.g., to monitor the dissociation of the ions as their internal energy is systematically varied. This can be achieved by varying the collision energy (energy-resolved mass spectrometry (ERMS))[9,10] or, less frequently, the scattering angle (angle-resolved mass spectrometry (ARMS)).[10,11]

Several authors[12-14] have expressed the view that access to ions of very high internal energy is often desirable in order to maximize differences in dissociation behavior. The use of solid surfaces as collision targets represents one method of achieving high internal energy.[15,16] We present results that show that structural distinction between isomeric $[C_6H_6]^{\bullet+}$ ion are readily made by surface-induced dissociation (SID). Results that demonstrate the value of SID in isomeric ion distinction have recently been reported for several other ions.[17,18]

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