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Tandem Mass Spectrometric Collision-induced Dissociation Study of *s*-Triazines in an Ion Trap Mass Spectrometer

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The collision-induced dissociation, (CID) mass spectra of 11 common *s*-triazine herbicides were investigated using gas chromatography/tandem mass spectrometry on an ion trap mass spectrometer with a temperature-programmable injector. The precursor ions of the CID mass spectra studied included both the molecular ions and the major electron ionization (EI) fragment ions. Typical fragmentation processes were observed, including simple cleavages, cleavages with hydrogen transfer rearrangements and skeletal rearrangements, involving opening of the triazine ring. Based on these results, EI fragmentation pathways of the triazines studied were derived. The better understanding of the dissociation processes and pathways should improve target compound analysis of these herbicides in environmental samples. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Synthetic 1,3,5-*s*-triazines are being extensively used for agricultural and other weed control purposes. These compounds are of environmental concern, as they might find their way into groundwater.[1,2] Consequently, sensitive and reliable analytical methods are necessary for their monitoring. Mass spectrometry is one of the major methods which is being used for the analysis of these herbicides. Solid probe electron ionization (EI) mass spectra have been studied and fragmentation pathways suggested.[3,4] Early gas chromatographic/mass spectrometric (GC/MS) analyses of atrazine and its metabolites in oats used packed columns.[5] Liquid chromatography/MS with thermospray ionization[6–8] and recently with electrospray[9] has also been applied for the analysis of triazines. Nevertheless, there is continuing interest in GC/MS and GC/MS/MS because GC/MS is still more readily available to environmental analytical chemists.[10] Many investigators use EI, since triazines produce very good spectra under these conditions. There has been continuous development of GC/MS methods for atrazine analysis[11] and various types of mass spectrometers, including ion traps, have been used for this purpose.[12]

Ion trap MS/MS studies have been recently reported by Abraham and Lynn[13] and Charreteur *et al.*[14] The majority of MS/MS work reported was performed using triple quadrupole[15,16] or hybrid mass spectrometers.[17] MS/MS-CID studies typically describe fragment ion spectra of the molecular species, M^+ or MH^+ or $[M - CH_3]^+$.[13,14,16,17]

We have undertaken a CID study of a group of *s*-triazines (Scheme 1), using MS/MS in an ion trap mass spectrometer, in order to investigate the fragment ion spectra of the molecular ion and of the EI fragment ions, and to derive fragmentation processes and pathways.

EXPERIMENTAL

The GC/MS instrumentation consisted of a Varian Saturn 4D GC/MS/MS ion trap. The gas chromatograph was fitted with a septum-equipped programmable injector (SPI) and a J&W (Folsom, CA, USA) DB-1 column (15 m × 0.255 mm i.d., 0.25 μm film thickness). The temperature of the column was 80 °C for 2 min, programmed to 200 °C at 15 °C min^{-1} with a final hold of 2 min. The temperature of the SPI was 0 °C for 0.5 min, programmed to 150 °C at 150 °C min^{-1} with a final hold time of 10.7 min. The injector was cooled with liquid CO_2. The helium flow rate was 1 ml min^{-1}. The ion trap was kept at 170 °C. The ionization mode was EI at an electron energy of 70 eV. GC/MS/MS-CID was performed in the resonant excitation mode, using the helium buffer gas in the ion trap as the CID collision gas. In the resonant excitation mode, a high-frequency supplemental dipole field was applied to the end-caps of the ion trap. The frequency must match the oscillation frequency of the trapped ion. As it is difficult to calculate its value precisely, the amplitude of the r.f. trapping field was modulated over a specified range. The resonance frequency of the trapped ion depends on

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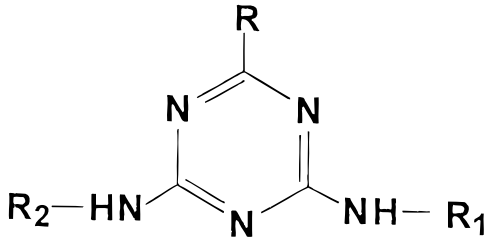
TRIAZINES



	M. W.	R	R_1	R_2
Atrazine	215	Cl	CH_2CH_3	$CH(CH_3)_2$
Simazine	201	Cl	CH_2CH_3	CH_2CH_3
Propazine	229	Cl	$CH(CH_3)_2$	$CH(CH_3)_2$
Terbutylazine	229	Cl	$C(CH_3)_3$	CH_2CH_3
Atraton	211	OCH_3	$CH(CH_3)_2$	CH_2CH_3
Prometon	225	OCH_3	$CH(CH_3)_2$	$CH(CH_3)_2$
Desmetryn	213	SCH_3	$CH(CH_3)_2$	CH_3
Ametryn	227	SCH_3	$CH(CH_3)_2$	CH_2CH_3
Prometryn	241	SCH_3	$CH(CH_3)_2$	$CH(CH_3)_2$
Terbutryn	241	SCH_3	$C(CH_3)_3$	CH_2CH_3
Methoprotryn	271	SCH_3	$(CH_2)_3OCH_3$	$CH(CH_3)_2$

Scheme 1

the magnitude of the r.f. field; therefore, modulating the r.f. field amplitude results in a modulation of the resonant frequency of the ion. The CID voltage and time were 0.6 V and 20 ms, respectively. The pressure of the helium was of the order of 10^{-3} Torr (1 Torr = 133.3 Pa).

Materials

The triazines investigated were obtained from the following sources: atrazine, simazine, propazine, terbutylazine, atraton, desmetryn, prometryn, terbutryn and methoprotryn from Riedel-de Haën, Seelze, Germany, and prometon and ametryn from Ultra Scientific, North Kingstown, RI, USA.

Solutions were prepared in analytical-grade acetone. A 1 μl volume of the solution was injected into the GC/MS system.

RESULTS AND DISCUSSION

Table 1 shows the CID ions of all the triazines investigated. The initial process is EI and all the precursor ions in the CID processes are EI ions. From these results fragmentation pathways can be drawn. Some typical fragmentation pathways are shown in Fig. 1–5 for atrazine, simazine, atraton, ametryn and methoprotryn, respectively.

Atrazine

In the CID mass spectrum of M^+ the highest mass fragment ion is at *m/z* 200, formed through loss of a methyl radical. The molecular ion loses preferentially propylene and propyl to form ions at *m/z* 173 and 172. There is loss of 77 u which is that of C_3H_6 and Cl. A similar loss was reported previously in single-stage EIMS.[3,4]

The lowest mass fragment ion in the CID spectrum of atrazine's molecular ion is at *m/z* 58, the isopropylamino side-chain. The $[M - CH_3]^+$ ion at *m/z* 200, as precursor ion, because of its numerous fragment ions, has been used as the precursor ion of choice for analytical purposes.[10,15,16] Unlike $M^{+\cdot}$, $[M - CH_3]^+$ loses C_2H_4 and C_2H_5 to form the fragment ions at *m/z* 172 and 171. C_2H_4 can be lost from either the 4-$NHCHCH_3$ or the 6-aminoethyl group. However, as one observes also the loss of C_3H_6 and C_3H_7, some of the population of the $[M - CH_3]^+$ precursor ion must

Table 1. CID ions of the triazines investigated

Triazine	M_r	Precursor ion *m/z*	Ion	CID mass spectrum [*m/z* (%)]
Atrazine	215	215	$[M]^+$	200 (100), 173 (57), 172 (38), 138 (28), 58 (24)
		200	$[M - CH_3]^+$	172 (8), 171 (17), 164 (16), 158 (5), 157 (18), 132 (16), 131 (52), 130 (20), 122 (21), 121 (100), 105 (16), 104 (53), 94 (68), 71 (11), 69 (12), 68 (38)
		173	$[M - C_3H_6]^+$	144 (33), 137 (62), 136 (37), 130 (53), 104 (52), 94 (41), 79 (100), 69 (53), 68 (41)
		172	$[M - C_3H_7]^+$	145 (21), 136 (22), 130 (82), 105 (19), 104 (63), 94 (78), 79 (100), 69 (53), 68 (51)
		158	$[M - NC_3H_7]^+$	131 (17), 115 (9), 104 (23), 91 (100), 90 (20), 68 (10)
		138	$[M - Cl - C_3H_6]^+$	111 (100), 96 (20), 71 (14), 70 (12), 69 (33), 68 (9)
Simazine	201	201	$[M]^+$	186 (77), 173 (100), 172 (73), 157 (14), 138 (81), 137 (17)
		186	$[M - CH_3]^+$	158 (15), 150 (56), 131 (38), 122 (41), 104 (30), 96 (30), 95 (21), 91 (100), 71 (25), 68 (88)
		173	$[M - C_2H_4]^+$	145 (28), 138 (32), 136 (57), 130 (57), 104 (61), 94 (61), 79 (100), 69 (58), 68 (42)
		172	$[M - C_2H_5]^+$	145 (10), 144 (22), 136 (11), 135 (30), 130 (34), 129 (88), 105 (18), 104 (71), 94 (76), 79 (100), 69 (51), 68 (49)
		158	$[M - NC_2H_5]^+$	143 (17), 104 (26), 91 (100), 90 (22), 68 (17)
		138	$[M - Cl - C_2H_4]^+$	111 (100), 110 (8), 96 (22), 71 (8), 70 (13), 69 (44), 68 (10)
Propazine	229	229	$[M]^+$	214 (10), 187 (22), 186 (100), 144 (32), 104 (32)
		214	$[M - CH_3]^+$	172 (100), 171 (11), 136 (5), 130 (6), 104 (17), 94 (8), 79 (7)
		187	$[M - C_3H_6]^+$	172 (18), 152 (20), 151 (55), 150 (22), 145 (38), 144 (100), 104 (56), 103 (23), 83 (28), 79 (22), 68 (27)
		186	$[M - C_3H_7]^+$	145 (100), 144 (25), 107 (35), 104 (70), 103 (26), 83 (38), 79 (29), 68 (29)
		172	$[M - CH_3 - C_3H_6]^+$	145 (8), 144 (21), 136 (18), 130 (85), 129 (12), 105 (30), 104 (76), 94 (89), 79 (100), 69 (63), 68 (56)
		152	$[M - Cl - C(CH_3)_2]^+$	150 (62), 135 (19), 125 (100), 124 (28), 111 (20), 110 (20), 109 (45), 108 (20), 85 (20), 83 (85), 70 (52), 68 (38), 58 (26), 56 (31)
Terbutylazine	229	229	$[M]^+$	216 (11), 214 (55), 187 (11), 186 (13), 174 (16) 173 (40), 172 (100), 138 (22)
		214	$[M - CH_3]^+$	197 (20), 178 (37), 174 (10), 173 (72), 150 (11), 136 (66), 132 (100), 119 (61), 104 (42), 96 (23), 83 (13), 71 (12), 68 (10)
		173	$[M - C_4H_8]^+$	145 (19), 144 (42), 136 (51), 130 (77), 111 (11), 105 (42), 104 (100), 94 (58), 79 (92), 69 (33), 68 (12), 59 (23)
		172	$[M - C(CH_3)_3]^+$	145 (37), 137 (9), 136 (36), 130 (77), 111 (11), 105 (44), 104 (100), 94 (52), 79 (93), 69 (35), 68 (15), 62 (5), 59 (24)
		138	$[M - Cl - C_4H_8]^+$	138 (29), 111 (100), 96 (21), 71 (18), 70 (12), 69 (22)
Atraton	211	211	$[M]^+$	196 (58), 183 (10), 169 (100), 168 (17), 155 (17), 154 (40), 58 (12)
		196	$[M - CH_3]^+$	169 (10), 168 (23), 155 (42), 154 (35), 153 (10), 139 (7), 128 (16), 127 (15), 126 (22), 122 (12), 121 (38), 114 (21), 112 (100), 101 (36), 100 (11), 98 (15), 97 (38), 94 (20), 85 (71), 83 (55), 71 (10), 70 (10), 69 (20), 59 (27), 57 (46)
		169	$[M - C_3H_6]^+$	154 (100), 140 (5), 112 (14), 86 (3), 83 (3), 70 (2)
		168	$[M - C_3H_7]^+$	153 (12), 150 (17), 141 (11), 140 (26), 126 (89), 125 (12), 112 (42), 111 (100), 110 (11), 100 (11), 86 (20), 85 (12), 84 (17), 83 (50), 70 (14), 69 (17), 57 (17), 56 (14)
		154	$[M - NCH(CH_3)_2]^+$	139 (12), 137 (5), 112 (100), 111 (11), 98 (8), 95 (10), 86 (19), 85 (10), 70 (19), 69 (7)
		139	$[M - NCH(CH_3)_2 - CH_3]^+$	122 (8), 121 (18), 112 (22), 111 (92), 98 (26), 97 (11), 96 (20), 95 (13), 71 (18), 70 (100), 69 (40), 55 (11)
Prometon	225	225	$[M]^+$	210 (24), 183 (14), 182 (42), 181 (100), 142 (35), 140 (46), 126 (21), 58 (21), 57 (21)

Table 1. Continued

Triazine	M_r	Precursor ion *m/z*	Ion	CID mass spectrum [*m/z* (%)]
		210	$[M - CH_3]^+$	168 (48), 167 (100), 127 (11), 112 (13), 111 (42), 100 (7), 83 (13), 69 (8), 57 (10)
		183	$[M - C_3H_6]^+$	180 (77), 141 (100), 126 (76), 125 (38), 112 (31), 100 (52), 99 (37), 83 (77), 57 (77)
		182	$[M - C_3H_7]^+$	180 (100), 123 (82), 111 (73), 110 (41)
		168	$[M - CH_3 - C_3H_6]^+$	151 (8), 141 (32), 126 (68), 125 (31), 112 (100), 111 (32), 100 (16), 86 (23), 85 (15), 83 (91), 69 (33), 68 (12), 58 (100), 57 (33), 56 (11), 55 (24)
Ametryn	227	227	$[M]^+$	185 (25), 184 (100), 136 (41), 96 (17), 68 (20)
		228	$[M + H]^+$	228 (100), 212 (96), 194 (48), 186 (23), 185 (77), 184 (91), 170 (34), 166 (25), 157 (29), 156 (15), 152 (94), 151 (13), 137 (15), 111 (5), 58 (24)
		212	$[M + H - CH_4]^+$	184 (17), 179 (12), 171 (11), 170 (14), 165 (23), 142 (21), 139 (21), 137 (8), 122 (100), 121 (33), 96 (18), 94 (66), 69 (21), 68 (59)
		184	$[M - C_3H_7]^+$	142 (38), 125 (87), 111 (38), 109 (73), 69 (73), 68 (100)
		170	$[M + H - NHC_3H_7]^+$	128 (48), 111 (100), 110 (7), 86 (48), 69 (23), 69 (9)
		155	$[M - NC_3H_8 - CH_2]^+$	153 (100), 152 (33), 111 (8), 97 (41), 96 (25), 85 (41), 68 (42), 54 (25)
Desmetryn	213	213	$[M]^+$	198 (16), 197 (54), 180 (12), 179 (22), 171 (27), 170 (100), 156 (7), 138 (11), 125 (12), 58 (19)
		198	$[M - CH_3]^+$	157 (16), 150 (8), 125 (21), 116 (19), 108 (31), 107 (100), 83 (9), 82 (38), 81 (12), 57 (22)
		171	$[M - C_3H_6]^+$	156 (32), 155 (96), 125 (40), 124 (100), 114 (27), 108 (20), 98 (32), 82 (28)
		170	$[M - C_3H_7]^+$	128 (22), 89 (77), 82 (100), 57 (22)
		156	$[M - NC_3H_7]^+$	140 (48), 128 (32), 114 (100), 85 (41), 68 (26), 62 (41)
		141	$[M - NC_3H_7 - CH_3]^+$	115 (33), 99 (73), 83 (68), 82 (100), 72 (38), 55 (19)
Prometryn	241	241	$[M]^+$	226 (100), 208 (40), 199 (25), 198 (67), 197 (70), 184 (14), 183 (36), 166 (85), 157 (21), 58 (30)
		226	$[M - CH_3]^+$	184 (32), 183 (100), 143 (5), 142 (4), 111 (8),
		199	$[M - C_3H_6]^+$	183 (100), 157 (91), 156 (91), 111 (42)
		198	$[M - C_3H_7]^+$	157 (63), 156 (100), 125 (19), 83 (30)
		184	$[M - NHC_3H_6]^+$	168 (10), 150 (22), 142 (36), 141 (100), 127 (20), 125 (89), 115 (22), 111 (44), 110 (12), 102 (69), 100 (40), 94 (31), 85 (47), 83 (22), 74 (29), 69 (92), 68 (55), 58 (45)
Terbutryn	241	241	$[M]^+$	226 (28), 208 (28), 186 (16), 185 (32), 184 (100), 152 (21)
		226	$[M - CH_3]^+$	209 (37), 197 (11), 186 (15), 185 (98), 184 (14), 156 (28), 153 (56), 143 (37), 136 (100), 135 (22), 96 (52), 83 (31), 71 (58), 70 (22), 68 (57), 58 (53)
		185	$[M - C_5H_8]^+$	170 (100), 169 (15), 157 (20), 156 (21), 152 (25), 138 (11), 127 (15), 111 (22), 71 (26), 69 (14), 68 (15)
		170	$[M - C_4H_8 - CH_3]^+$	128 (26), 127 (63), 111 (100), 86 (42), 85 (15), 69 (23), 68 (8)
		156	$[M - C_4H_8 - C_2H_5]^+$	139 (45), 138 (100), 129 (18), 123 (58), 122 (45), 114 (66), 112 (50), 89 (86), 68 (80), 62 (37)
Methoprotryn		271	$[M]^+$	256 (100), 240 (100), 198 (24)
		256	$[M - CH_3]^+$	224 (15), 212 (100), 211 (12), 200 (80), 158 (27)
		240	$[M - OCH_3]^+$	198 (100)
		226	$[M - CH_2OCH_3]^+$	184 (40), 183 (100)
		224	$[M - SCH_3]^+$ or $[M - (CH_3)_2OH]$	196 (100)
		212	$[M - (CH_2)_2OCH_3]^+$	170 (100), 103 (15)
		198	$[M - (CH_2)_3OCH_3]^+$	170 (24), 165 (20), 156 (72), 142 (28), 125 (60), 108 (100), 91 (55), 83 (63), 82 (52), 74 (28), 56 (20),
		184	$[M - (CH_2)_3CH_2OCH_3]^+$	156 (18), 142 (63), 125 (36), 116 (36), 111 (66), 102 (58), 94 (32), 91 (21), 74 (30), 69 (100), 68 (48), 58 (23)
		171	$[M - (CH_2)_3OCH_3 - C_2H_3]^+$	156 (100), 125 (53), 114 (35), 98 (27)
		170	$[M - (CH_2)_3OCH_3 - C_2H_4]^+$	137 (35), 116 (35), 103 (42), 82 (63), 74 (84), 68 (100), 61 (64)

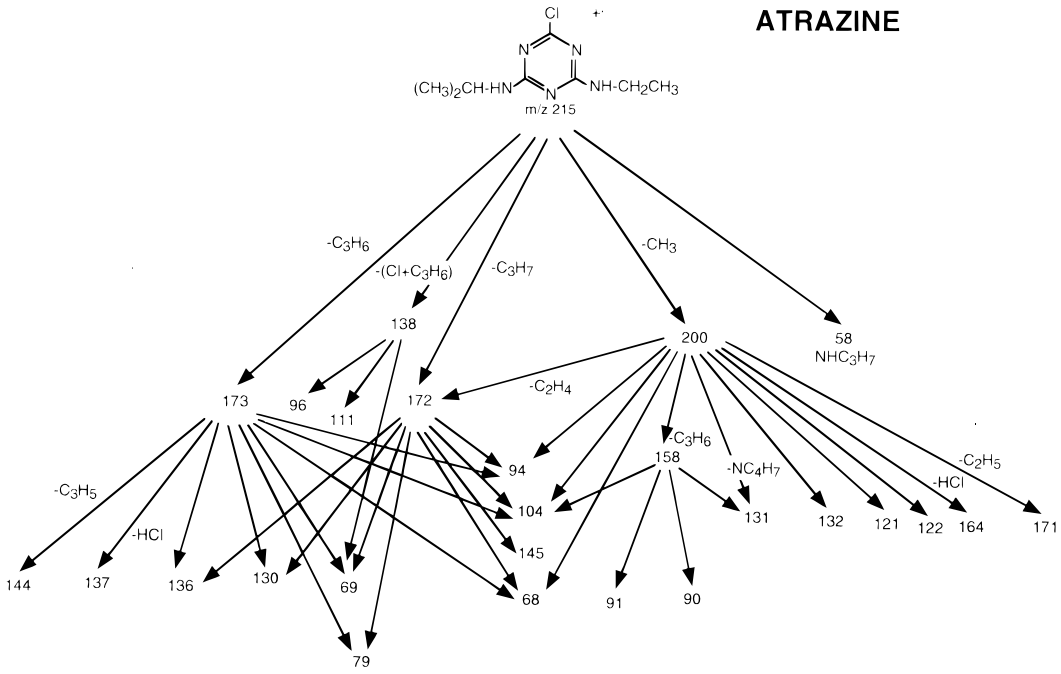


Figure 1. CID fragmentation pathway map for atrazine.

apparently have an intact isopropyl substituent. This will have to be proved unequivocally with appropriately labeled compounds. The loss of 36 u from this precursor ion to form the fragment ion at *m/z* 164 must be that of an HCl molecule. The fragment ion at *m/z* 131 is formed by the loss of NC_4H_7 (Scheme 2, **a**). The base peak in the CID mass spectrum of $[M - CH_3]^+$ is at *m/z* 121, which can be explained as loss of $[HCl + C_3H_7]$. It is accompanied by *m/z* 122 due to the loss of $[Cl + C_3H_7]$ or $[HCl + C_3H_6]$. The previously reported[6,8] fragment ion at *m/z* 104 is also a product of a skeletal rearrangement. This fragment ion appears in all the CID mass spectra of the precursor ions lower than $M^{+\cdot}$, except *m/z* 138 and 152, of the four 2-chloro-1,3,5 triazines, and only in them. It has been described by Voyksner *et al.*[6] as the opened ring $ClC^+{=}NC{=}NH(NH_2)$. This fragment ion has been proved to contain Cl, by the CID mass spectrum of the ^{37}Cl-containing ion at *m/z* 175 of simazine, where it is shifted to *m/z* 106.

Three low-mass fragment ions of *m/z* 200 are the ions at *m/z* 71, 69 and 68. The ion at *m/z* 71 is suggested to be $[C_2H_5NH + CNH]^+$,[4] whereas those at *m/z* 68 and

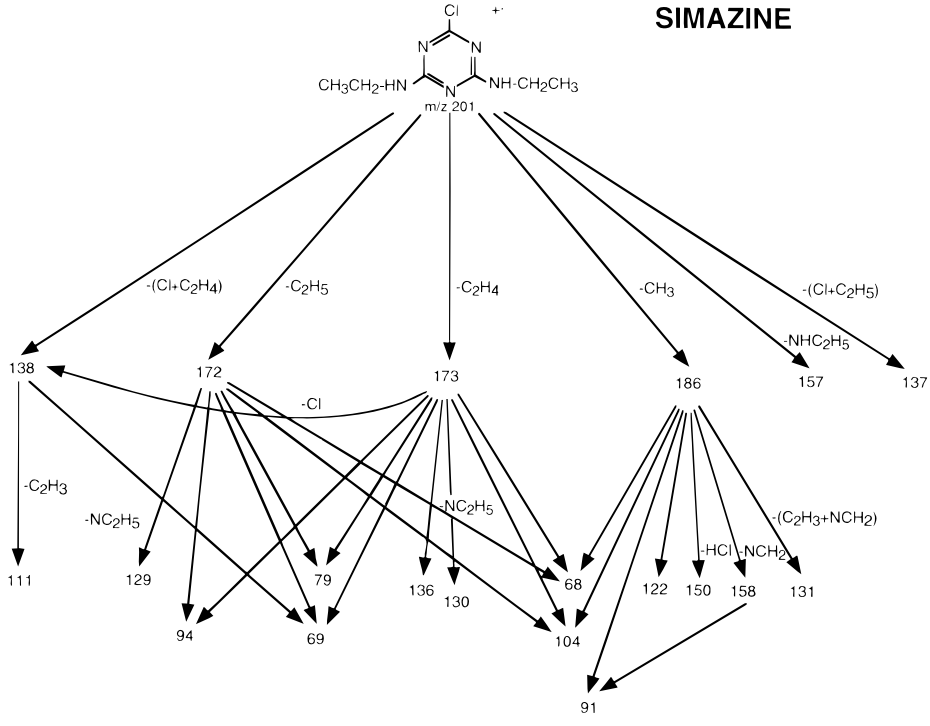


Figure 2. CID fragmentation pathway map for simazine.

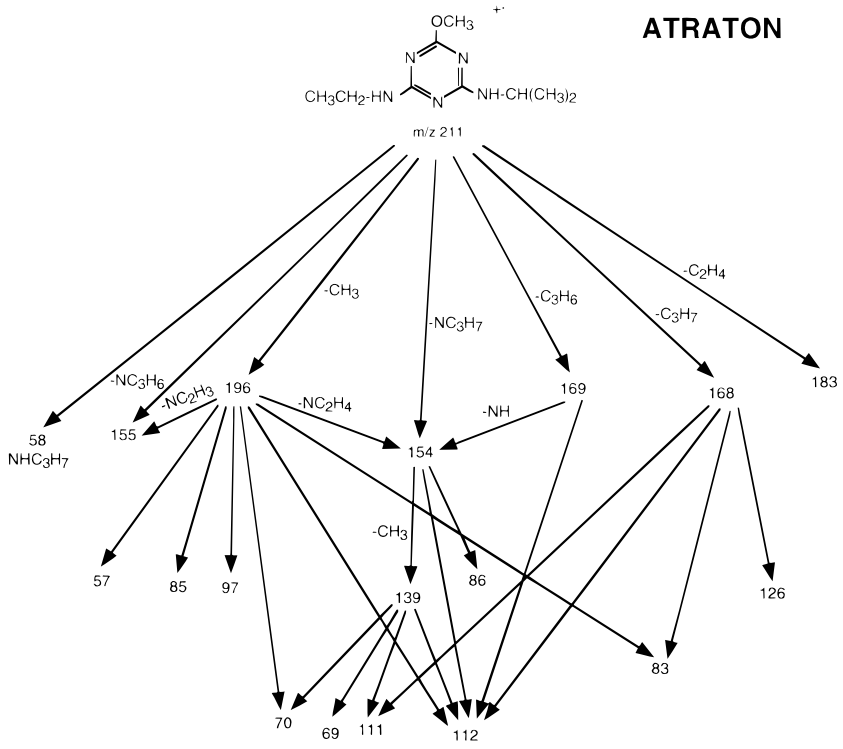


Figure 3. CID fragmentation pathway map for atraton.

69 can be cyclic structures (Scheme 2, **c** and **d**), as suggested previously.[3] Both precursor ions at *m/z* 173 and 172 have a highly abundant fragment ion at *m/z* 79, $[Cl + NHC_2H_5]^+$. In the CID of the ^{37}Cl containing precursor ion at *m/z* 175, this ion is shifted to *m/z* 81, corroborating this assignment. The precursor ion at *m/z* 172 loses 42 u to form a fragment ion at *m/z* 130 (Scheme 2, **b**).

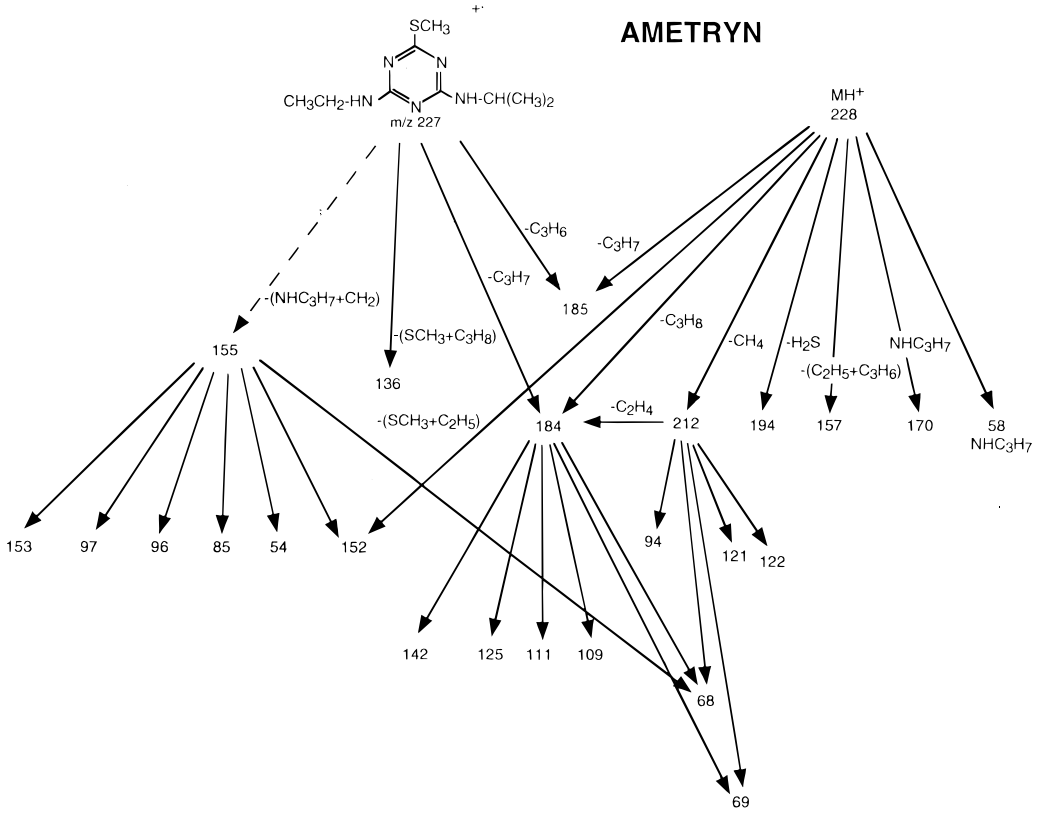


Figure 4. CID fragmentation pathway map for ametryn. The dotted line represents assumed fragmentation path not proved by experimental CID results.

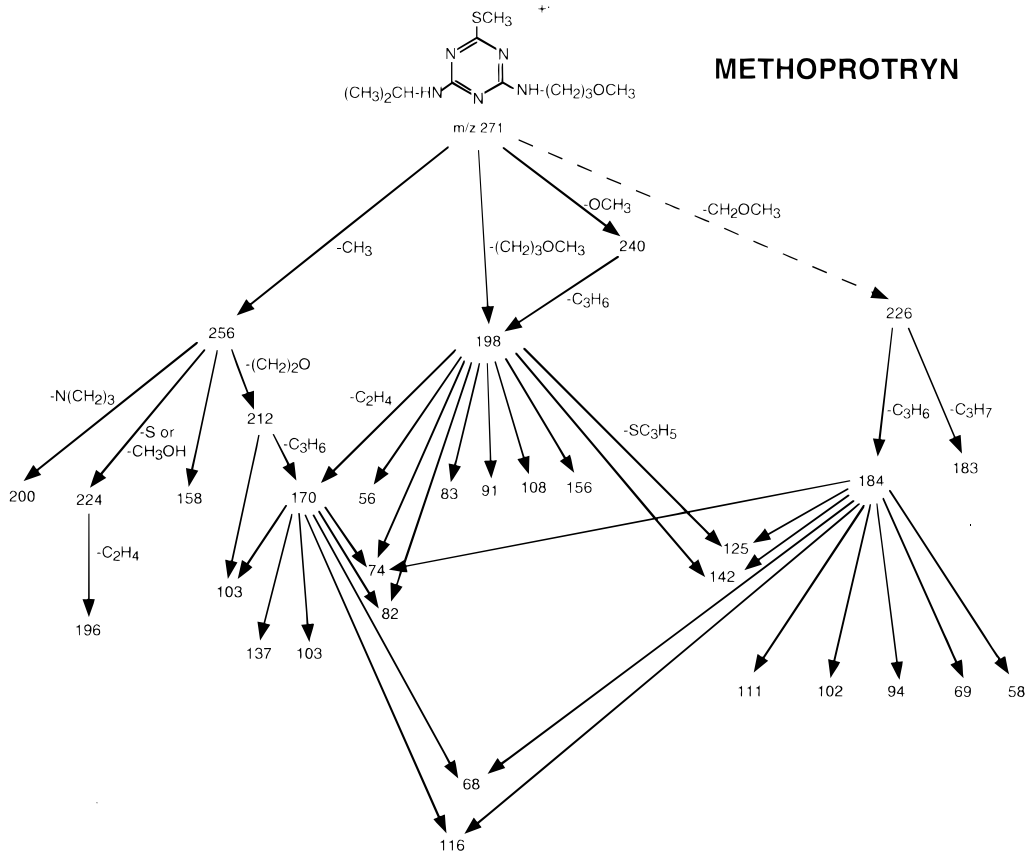


Figure 5. CID fragmentation pathway map for methoprotryn. The dotted line represents assumed fragmentation path not proved by experimental CID results.

The fragment ion at *m/z* 94 is a major fragment ion in the CID mass spectra of $[M - CH_3]^+$, $[M - C_3H_6]^+$ and $[M - C_3H_7]^+$. We could not show this ion to contain chlorine and therefore consider it to be $C_4H_4N_3^+$ (or $C_3N_4H_2^+$).

The precursor ion at *m/z* 158 loses C_2H_3, presumably from the remaining *N*-ethyl substituent, to form the fragment ion at *m/z* 131 (Scheme 2, **a**). It breaks down to the Cl-containing ion at *m/z* 104 and 91, $C_2H_4N_2Cl$, accompanied by *m/z* 90. The most abundant fragment ion in the CID mass spectrum of the precursor ion at *m/z* 138 is that at *m/z* 111, which we believe to be the symmetric 4,6-diamino-1,3,5-triazine (Scheme 2, **g**). If this is so, then this precursor ion should be the 4-amino-6-ethylaminotriazine radical ion (Scheme 2, **f**).

Simazine

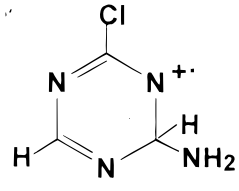
Simazine behaves similarly to atrazine and there are many common fragment ions from precursors having the same mass.

The fragment ions of M^+ (*m/z* 201) at *m/z* 173 (loss of C_2H_4) and 172 are more abundant here than in atrazine because simazine has two *N*-ethyl substituents. An additional abundant fragment ion at *m/z* 138, due to loss of 63 u from $M^{+\bullet}$, can be explained as loss of $[C_2H_4 + Cl]$. This is supported by the CID mass spectrum of the ^{37}Cl-containing *m/z* 203 precursor ion, which forms the same fragment ion. Loss of CH_3 in simazine accounts for the fragment ion at *m/z* 186. Here too, no fragment ions arising from ring opening have been found in the CID spectrum of M^+. It is worth noting that $M^{+\bullet}$ does not lose 43 u to form the *m/z* 158 fragment ion, which is a major fragment in the EI mass spectrum of simazine,[3] where it was shown by exact mass measurement[4] to be a mixture of $[M - C_2H_5N]^+$ (79%) and $[M - CH_3 - C_2H_4]^+$ (21%). Our data show that it is a fragment ion in the CID mass spectrum of the precursor ion $[M - CH_3]^+$ (*m/z* 186), were it can be accounted for by loss of NCH_2 or C_2H_4, the former being more likely.

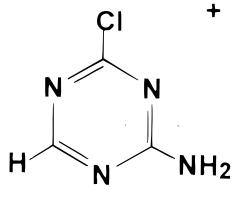
The base peak in the CID mass spectrum of *m/z* 186 is at *m/z* 91, suggested to be $C_2H_4N_2Cl^+$, which may have a four-membered ring structure (Scheme 2, **e**). The fragment ion at *m/z* 131 is due to the loss of $[C_2H_3 + CH_2N]$ (Scheme 2, **a**) The ion at *m/z* 122 is most likely $[P - Cl - C_2H_5]^+$, that at *m/z* 104 is the chlorine-containing ion $[ClC{=}NC{=}NH(NH_2)]^+$ and that at *m/z* 96 is $[C_2H_5NHCNCN]^+$.[4] The precursor ions at *m/z* 173 and 172 have several common fragments in their respective CID mass spectra. The base peak in both CID mass spectra is at *m/z* 79 due to $[ClCNH_2(NH_2)]^+$. An ion at *m/z* 81 was observed in the CID mass spectra of the ^{37}Cl-containing precursor ions. The ion at *m/z* 94, as in atrazine, is $C_4H_4N_3^+$ (or $C_3N_4H_2^+$).

Propazine

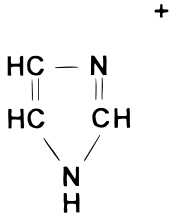
The most abundant ion in the CID mass spectra of propazine is that arising by loss of an isopropyl radical.



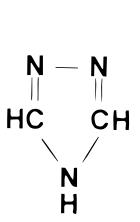
a: m/z 131



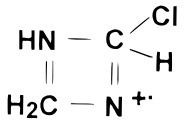
b: m/z 130



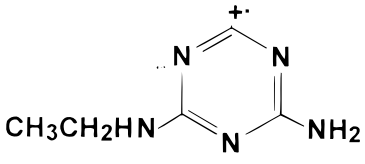
c: m/z 68



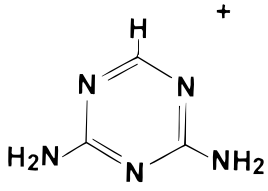
d: m/z 69



e: m/z 91



f: m/z 138



g: m/z 111

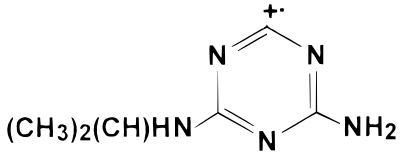
Scheme 2

As in simazine, the amino substituents are identical and probably therefore this pathway is favored. The loss of propylene from the molecular ion, leading to the fragment ion at *m/z* 187, is of much lower abundance, and it can therefore be concluded that despite the hydrogen transfer reaction involved, in this case the simple cleavage prevails. The ion at *m/z* 144 is the result of loss of $[C_3H_7 + C_3H_6]$ leading to $C_3H_5N_5Cl^+$. This seems more likely than $C_4H_5N_4Cl^+$, which would necessitate excision of C_2H_3 from the *N*-isopropylamino side-chain. Here the fragment ion at *m/z* 104, due to skeletal rearrangement, is formed directly from the molecular ion.

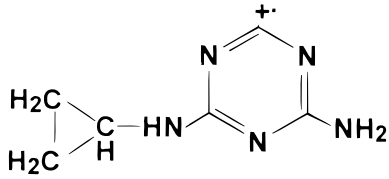
The most abundant fragment ion of the precursor at *m/z* 186 is that at *m/z* 145, which arises through loss of C_3H_5. We believe this ion to have the structure of 2-chloro-4,6-diamino-1,3,5-*s*-triazine.

It is noteworthy that the CID mass spectrum of the precursor ion at *m/z* 186 ion in this case is different from that obtained in simazine. On the other hand, the CID mass spectra of the precursor ion at *m/z* 172 in atrazine, propazine and simazine are similar, indicating that this ion has the same structure in all three compounds.

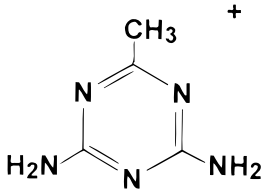
The CID mass spectrum of the precursor ion at *m/z* 152 (Scheme 3, **a**) loses 2 u to form a fragment ion at *m/z* 150 (62%), which can be portrayed as the 4-amino-6-*N*-cyclopropylaminotriazine ion (Scheme 3, **b**). This fragment ion is apparently peculiar to propazine. The most abundant fragment ion is at *m/z* 125 (Scheme 3, **c**),



a: m/z 152



b: m/z 150



c: m/z 125

Scheme 3

resulting from the loss of C_2H_3. This ion has a symmetric structure similar to that of the ion at *m/z* 145 in the CID mass spectrum of *m/z* 186, namely 2-methyl-4, 6-diamino-1,3,5-triazine, which must evidently be the result of a rearrangement process with transfer of CH_3 to the 2-position. Interestingly, it is accompanied by a fragment ion at *m/z* 124, which has one hydrogen atom less. This behavior is paralleled by the ions at *m/z* 111 and 110.

Terbutylazine

The most abundant fragment ion in the CID mass spectrum of the molecular ion of terbutylazine is at *m/z* 172, formed through loss of $C(CH_3)_3$ by simple cleavage. This fragment ion is accompanied by one at *m/z* 173, which includes a hydrogen transfer. The lowest mass CID fragment ion of terbutylazine's molecular ion is at *m/z* 138 (Scheme 2, **f**). The ion at *m/z* 104, the familiar Cl-containing ring-opened structure, is the base peak in the CID mass spectra of both precursor ions at *m/z* 173 and 172 and an abundant fragment ion of the precursor ion at *m/z* 214.

Atraton

Atraton is the OCH_3 analog of atrazine. The base peak in the CID mass spectrum of $M^{+\cdot}$ is the ion at *m/z* 169, resulting from isopropylene loss with H transfer. The *N*-ethyl side-chain also loses ethylene, forming *m/z* 183. Another CID fragmentation of $M^{+\cdot}$, which includes hydrogen rearrangement, is loss of C_3H_6N to form an ion at *m/z* 155. This is accompanied by loss of C_3H_7N to yield the ion at *m/z* 154. While the losses of methyl, isopropylene and ethylene are similar to those in atrazine, the losses of C_3H_6N and C_3H_7N appear only in atraton and not in atrazine.

In the CID mass spectrum of $[M - CH_3]^+$ at *m/z* 196, the fragment ions at *m/z* 112, 85 and 83 are interrelated. Abundant fragment ions, at *m/z* 85 and 83, are rearrangement ions produced through a hydrogen atom transfer to and from the species at *m/z* 84, and the *m/z* 112 fragment is left as the neutral fragment.

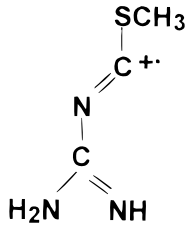
Prometon

Prometon is the OCH_3 analog of propazine, the *N*-alkyl substituents being the same. The CID fragmentation is therefore very similar to that of propazine.

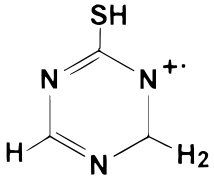
Desmetryn

The CID mass spectrum of the molecular ion of desmetryn has about twice as many fragment ions as the chlorine-substituted triazines. The most abundant fragment ion at *m/z* 170 is formed by loss of C_3H_7, while the parallel loss of C_3H_6 forming a rearrangement fragment ion at *m/z* 171 amounts to an abundance of only 27% relative to the former ion.

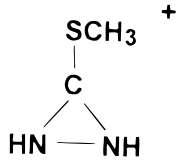
The fragment ion at *m/z* 116 (Scheme 4, **a**), formed from the precursor ion at *m/z* 198, $[M - CH_3]^+$ is the analog of the ion at *m/z* 104 in the Cl-substituted triazines. The fragment ion at *m/z* 81 could be the 1,3,5-triazine ring (Scheme 4, **d**), while the ion at *m/z* 82 could



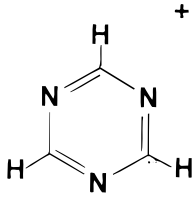
a: m/z 116



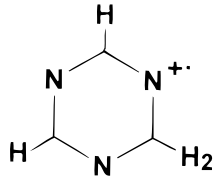
b: m/z 114



c: m/z 89



d: m/z 81



e: m/z 82

Scheme 4

be the protonated triazine ring (Scheme 4, **e**). The *m/z* 82 ion appears also as a fragment ion in the CID mass spectra of the ions at *m/z* 171, 170 and 141.

The CID mass spectrum of the precursor ion at *m/z* 170 contains, in addition to the base peak at *m/z* 82, fragment ions at *m/z* 128 (due to loss of C_2H_4N) and *m/z* 89 (Scheme 4, **c**). The ion at *m/z* 114 (Scheme 4, **b**) is the base peak in the CID mass spectrum of the precursor ion at *m/z* 156.

Ametryn

Ametryn is the SCH_3 analog of atrazine. The most abundant fragment ion at *m/z* 184 (100%) results from loss of C_3H_7 from the molecular ion, while the loss of C_3H_6, with hydrogen transfer to the ion, has only a 25% relative abundance.

The EI mass spectrum of ametryn has a highly abundant MH^+ ion at *m/z* 228 formed by self-chemical ionization. The most abundant fragment ion in the CID mass spectrum of this MH^+ ion is at *m/z* 212, formed by loss of CH_4 (but there is no loss of CH_3 from the M^+ ion). Another abundant fragment ion is formed by the loss of an alkane, C_3H_8, to form the ion at *m/z* 184. The fragment ion at *m/z* 152 is formed through the loss of 76 u, which can be the combined loss of SCH_3 and C_2H_5. It is accompanied by the ion at *m/z* 151, $[P - (SCH_3 + C_2H_6)]^+$. Similarly, *m/z* 137 could be $[P - (SCH_3 + C_3H_8)]^+$.

Prometryn

Loss of a methyl group from the molecular ion at *m/z* 241 results in the formation of the base peak at *m/z* 226 in the CID mass spectrum.

One of the isopropyl groups is cleaved off the molecular ion as such, but also isopropylene and isopropane, namely isopropyl plus and minus a hydrogen atom,

respectively, are lost, resulting in a triplet of fragment ions at *m/z* 197, 198 and 199. The loss of isopropyl and of isopropylene is found also in ametryn, but not the loss of isopropane.

An abundant fragment ion of the molecular ion is at *m/z* 166, probably due to the combined loss of SCH_3 and ethylene. The CID mass spectra of precursor ions at *m/z* 226, 199 and 184 contain a fragment ion at *m/z* 111 (Scheme 2, **g**).

The CID mass spectrum of the ion at *m/z* 184 contains a large number of fragment ions. The most abundant fragment ion is due to loss of C_3H_7. Abundant fragment ions are at *m/z* 125, formed by loss of 59 u, likely to be isopropylamine, and at *m/z* 69 and 68.

Terbutryn

The highest mass fragment ion in the CID mass spectrum of the molecular ion is at *m/z* 226, due to loss of a methyl group. The fragment ion at *m/z* 208 is probably due to loss of SH. The base peak is at *m/z* 184, produced by cleavage of *tert*-butyl. In addition, rearrangement fragment ions are observed at *m/z* 185 and 186, due to loss of C_4H_8 and C_4H_7, respectively.

The CID mass spectrum of the $[M - CH_3]^+$ precursor ion contains 16 fragment ions. The base peak, at *m/z* 136, is due to $[P - NHC_3H_9 - NHCH_3]^+$.

Abundant fragment ions are at *m/z* 185, $[P - C_3H_5]^+$, *m/z* 153, $[P - (SCH_2 + CHN)]^+$ (Scheme 5, **a**), and *m/z* 96 (Scheme 5, **b**).

The CID mass spectrum of the $[M - C_4H_8]^+$ ion at *m/z* 185 contains a major fragment ion at *m/z* 170, due to loss of CH_3. Additional fragment ions are due to loss of SH, at *m/z* 152, and to loss of SCH at *m/z* 138.

The CID mass spectrum of the precursor ion at *m/z* 170 contains a major fragment ion at *m/z* 111 (Scheme 2, **h**). Major additional fragment ions are observed at *m/z* 128, $[P - NCH_2 - N]^+$, *m/z* 127, $[P - NCH_2 - NH]^+$, and *m/z* 86 (Scheme 5, **c**).

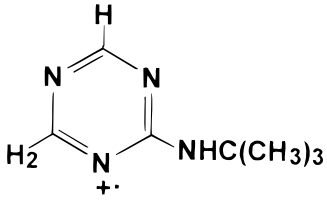
Methoprotryn

This compound is different, having a $(CH_2)_3OCH_3$ substituent on one of the amino groups. Here one observes the loss of OCH_3 from $M^{+\cdot}$ to form the fragment ion at *m/z* 240 (100%). The fragment ion $[M - CH_3]^+$ at *m/z* 256 has a similar relative abundance. The $(CH_2)_3OCH_3$ group is cleaved off, forming an ion at *m/z* 198. The CID mass spectrum of the $[M - CH_3]^+$ precursor ion contains ions at *m/z* 212 and 200, due to losses of $(CH_2)_2O$ and $N(CH_2)_3$, respectively, from the precursor ion.

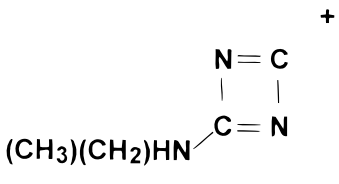
The fragment ion at *m/z* 224 arises through loss of CH_3OH or S from the $[M - CH_3]^+$ precursor. The precursor ion $[M - OCH_3]^+$ at *m/z* 240 loses C_3H_6 to form the ion at *m/z* 198. The precursor ion $[M - (CH_2OCH_3)]^+$ at *m/z* 226 loses C_3H_6 and C_3H_7 to form ions at *m/z* 184 and 183, respectively. Both EI fragment ions at *m/z* 224 and 212 form abundant fragment ions by losing C_2H_4 and C_3H_6, respectively.

CONCLUSIONS

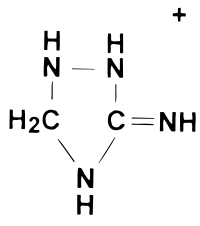
The CID mass spectra of the triazines are characterized by loss of methyl from the molecular ion. Most of them also have fragment ions formed by loss of C_3H_6



a: m/z 153



b: m/z 96



c: m/z 86

Scheme 5

(rearrangement) and C_3H_7 (cleavage) from the molecular ion. In addition, the CID spectra of the Cl-substituted triazines contain fragment ions formed by loss of Cl together with another group, such as C_2H_4, C_3H_6 or C_4H_8, from the molecular ion. The CID mass spectra of the SCH_3-substituted triazines are characterized by loss of SCH_3 together with another group, such as C_2H_4, C_3H_5 or C_3H_8, from the molecular ion, in addition to loss of SCH_3, HS and H_2S, from either the molecular ion or a fragment ion. Many pairs of cleavage and rearrangement fragment ions are formed, such as *m/z* 172, 173 in atrazine, *m/z* 172, 173 and *m/z* 137, 138 in simazine, *m/z* 186, 187 in propazine, *m/z* 172, 173 in terbutylazine, *m/z* 168, 169 in atraton, *m/z* 182, 183 in prometon, *m/z* 170, 171 in desmetryn, *m/z* 168, 169 in ametryn, *m/z* 198, 199 in prometryn, *m/z* 184, 185 in terbutryn and *m/z* 183, 184 in methoprotryn. The relative abundances of both cleavage and rearrangement ions in the CID spectra are high.

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