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GAS CHROMATOGRAPHY AND MASS SPECTROMETRY OF BIS(ALKYLAMINO)-*s*-TRIAZINES

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SUMMARY

The retention behaviour of 22 2-chloro, 2-methoxy- and 2-methylthio-4,6-bis(alkylamino)triazines was studied on four gas chromatographic columns with different polarities. The most polar stationary phase, Carbowax 20M, was found to be the best suited for the separation of these compounds. The differences in the retention indices of the same triazines on columns with different polarities were found to be proportional to the pK_a values and the dipole moments of these compounds.

Electron-impact mass spectra and deduced fragmentation schemes are given. The stability of the compounds under electron impact increases in the order chloro < methoxy < methylthio derivatives.

Chemical-ionization mass spectra, using methane as reagent gas, are tabulated. It has been found that the ease of fragmentation of the protonated molecular ions of chlorotriazines is related to the low proton affinity of the leaving neutral HCl group. In the isobutane chemical-ionization mass spectra all triazines exhibited the protonated molecular ion as the base peak with only relatively minor fragmentations.

INTRODUCTION

s-Triazine derivatives are important compounds in agriculture and industry because of their herbicidal properties. These compounds are 1,3,5-triazines substituted in positions 2, 4 and 6. Most properties of the *s*-triazine derivatives are determined by the substituents; the ring itself is not involved except for its effect on the charge distribution.

The character of *s*-triazines is determined primarily by the substituent in position 2, commonly chlorine (the commercial name ends with -azine), methoxy (ending in -tone) or thiomethyl (ending in -tryne). Positions 4 and 6 are usually substituted by various alkylamino groups.

The physico-chemical properties of *s*-triazines are very variable, even within the restricted group of the commercially available derivatives. The *s*-triazines are weak bases, their pK_a values ranging from 1.65 for simazine to 4.46 for terbutone. The dissociation constant is strongly affected by the substituent in position 2. The basicity increases in the order $Cl < SCH_3 < OCH_3$. The groups in positions 4 and 6 have smaller but still pronounced effects on the basicity of *s*-triazines: the greater the number of ethyl groups in place of hydrogen atoms, the more basic are the compounds.

Different properties of *s*-triazines are reflected in both their biological and chromatographic behaviour. The availability of a wide range of derivatives offers a great opportunity to study extensively the relationships between the structure and the chromatographic, spectrometric, electrochemical and mass spectrometric behaviour.

Gas chromatography has become the prevailing method for the analysis of *s*-triazines[1–18]. Most of the papers published to date deal with the application of gas chromatography for the determination of residues in soil, grain, etc.[3,4,6–8,11–14]. In this work the gas chromatographic and mass spectrometric behaviour of *s*-triazine derivatives has been studied and the structural correlations are discussed.

EXPERIMENTAL

All *s*-triazines studied were products of Ciba-Geigy (Basle, Switzerland) and are listed in Table I.

The following stationary phases and column packings for gas chromatography were used: XE-60 (Applied Science Labs., State College, Pa., U.S.A.); SE-30 and Carbowax 20M (Carlo Erba, Milan, Italy); Reoplex 400 and Versamid 900 (Hewlett-Packard, Avondale, Pa., U.S.A.); Chromaton N-AW, 60–80 mesh (Lachema, Brno, Czechoslovakia); Chromosorb W, silanized, 60–80 mesh (Carlo Erba).

Other chemicals used included the following: C_{22}–C_{28} *n*-alkanes (Applied Science Labs.); sodium hydroxide, p.a., without glycerol (Lachema); perchloric acid, p.a., 70% (Carlo Erba); buffers pH 4.00 and pH 7.02 (Radiometer, Copenhagen, Denmark).

As reagent gases for chemical-ionization mass spectrometry, methane of 99.995% purity (code N45) and isobutane of 99.95% purity (code CH35) were obtained from L'Air Liquide (Liège, Belgium).

For pH measurements a PHM 64 pH meter (Radiometer) was employed.

Gas chromatography

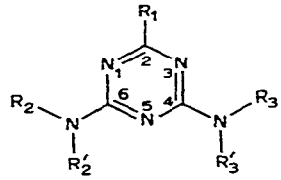
The measurements were carried out on a Hewlett-Packard (Palo Alto, Calif., U.S.A.) Model 5700 gas chromatograph equipped with a flame-ionization detector. Stainless-steel columns (140 cm × 3 mm I.D.) were used.

Column A was packed with 3% Carbowax 20M on Chromosorb W, column B with 5% XE-60 on Chromaton N-AW, column C with 5% Versamid 900 on Chromosorb W, and column D with 5% SE-30 + 2% Reoplex 400 on Chromosorb W.

Nitrogen was used as the carrier gas at a flow-rate of 40 ml/min. Columns B, C and D were operated isothermally at 195° and column A at 215°. The injection block temperature was maintained at 230°. The detector temperature was 210° (column B, C and D) and 230° (column A).

TABLE I

COMPOUNDS STUDIED



(a) Di(monoalkylamino) derivatives ($R_2 = R_3' = H$)

No.	*Trivial name*	R_1	R_2	R_3
1	—	Cl	H	*tert.*-Bu
2	—	Cl	*tert.*-Bu	*tert.*-Bu
3	Propazine	Cl	*i*-Pr	*i*-Pr
4	Terbutylazine	Cl	Et	*tert.*-Bu
5	Atrazine	Cl	Et	*i*-Pr
6	Norazine	Cl	Me	*i*-Pr
7	Simazine	Cl	Et	Et
8	Prometone	OMe	*i*-Pr	*i*-Pr
9	Terbutone	OMe	Et	*tert.*-Bu
10	Atratone	OMe	Et	*i*-Pr
11	Noratone	OMe	Me	*i*-Pr
12	Simetone	OMe	Et	Et
13	Prometryne	SMe	*i*-Pr	*i*-Pr
14	Terbutryne	SMe	Et	*tert.*-Bu
15	Ametryne	SMe	Et	*i*-Pr
16	Desmetryne	SMe	Me	*i*-Pr
17	Simetryne	SMe	Et	Et
18	Metoprotryne	SMe	$(CH_2)_3OMe$	*i*-Pr

(b) Diethylamino and sec.-butylamino derivatives

No.	*Trivial name*	R_1	R_2	R_2	R_3	R_3'
19	Ipazine	Cl	*i*-Pr	H	Et	Et
20	Trietazine	Cl	Et	H	Et	Et
21	Chlorazine	Cl	Et	Et	Et	Et
22	*sec.*-Bumetone	OMe	Et	H	*sec.*-Bu	H

UV spectrophotometry

For the measurement of dissociation constants the procedure of Albert and Serjeant[19] was adopted. The measurements were carried out on a Specord UV VIS spectrophotometer (Carl Zeiss, Jena, G.D.R.).

Mass spectrometry

Electron-impact (EI) mass spectra were obtained on an AEI MS-12 single-focusing magnetic sector instrument (AEI, Manchester, Great Britain) under the following conditions: electron energy, 70 eV; electron current, 0.50 mA; ion accelerating voltage, 4 kV; scan time, 2 sec per decade; source temperature, 250°.

Chemical-ionization (CI) mass spectra were produced with a Model 4000 (Finnigan, Sunnyvale, Calif., U.S.A.) quadrupole instrument under the following

TABLE II

pK_a VALUES AND RETENTION INDICES (I) ON FOUR STATIONARY PHASES

A = Carbowax 20M (215°); B = XE-60; C = Versamid 900; D = SE-30 + Reoplex 400 (5:2). Columns B, C and D were operated at 195°.

No.	*Trivial name*	*Mol.wt.*	pK_a*	I_A	I_B	I_C	I_D
1	—	201.5	—	2336	—	—	1766
19	Ipazine	243.6	1.99[22]	2461	2378	2142	1907
2	—	257.8	—	2501	2418	2185	1938
21	Chlorazine	257.8	1.74	2309	2286	1935	1791
20	Trietazine	229.7	1.88	2557	2415	2196	1932
3	Propazine	229.7	1.85	2633	2462	2262	1973
4	Terbutylazine	229.7	1.94[22]	2664	2504	2288	1999
5	Atrazine	215.7	1.68	2722	2509	2318	2023
6	Norazine	201.5	1.88[22]	2761	2518	2320	2029
7	Simazine	201.5	1.65	2806	2553	2375	2078
8	Prometone	225.3	4.28	2539	2350	2199	1916
9	Terbutone	225.3	4.46[22]	2570	2396	2205	1938
22	*sec.*-Bumetone	225.3	4.23[22]	2676	2470	2302	2015
10	Atratone	211.3	4.20	2610	2418	2212	1972
11	Noratone	197.2	4.15	2620	2411	2204	1966
12	Simetone	197.2	4.17	2680	2435	2270	1990
13	Prometryne	241.3	4.05	2758	2558	2378	2099
14	Terbutryne	241.3	4.38[22]	2793	2608	2403	2122
15	Ametryne	227.3	4.00	2837	2610	2418	2139
16	Desmetryne	213.3	3.92[22]	2868	2623	2452	2141
17	Simetryne	213.3	4.00[22]	2915	2656	2465	2185
18	Metoprotryne	271.4	3.98[22]	3202	2983	2726	2457

* Values from ref. 21, except where indicated otherwise from ref. 22.

conditions: electron energy, 25–40 eV; electron current, 0.20 mA; scan time, 1 sec per scan; source temperature, 250° (methane) and 150° (isobutane). The ion source pressure was maintained at 0.15 Torr gauge reading.

Samples were always introduced through a direct introduction probe and heated to 250°. The spectra given were obtained at probe temperatures of 40–120°.

RESULTS AND DISCUSSION

Gas chromatography

The retention indices (I) on four stationary phases were measured (Table II). Some of the results has been already published[16]. The polarity of the stationary phases used is given by the McReynolds constants[20]. The most polar stationary phase, Carbowax 20M ($\Sigma I = 2308$), is best suited for the separation of triazines. The other three liquid stationary phases, XE-60 ($\Sigma I = 1785$), Versamid 900 ($\Sigma I = 969$) and the mixed phase SE-30 + Reoplex 400 (5:2) ($\Sigma I = 940$), can also be used for the analysis of *s*-triazines.

The chromatographic data depend primarily on the nature of the substituent in position 2. The order of elution is first methoxy, then chloro and finally thiomethyl derivatives. In a series of *s*-triazines with the same substituent in position 2, the retention order is chiefly influenced by the spatial shielding of the substituted NH

groups in positions 4 and 6 (see Table II). The weakest shielding, causing the longest retention, is exerted by the ethyl group, the strongest by the *tert.*-butyl group and isopropyl lies in between.

The retention data for the *s*-triazines are influenced by their basic character. In order to complete the list of pK_a data given in the literature[21], we measured [22] the dissociation constants of *s*-triazines by UV spectrophotometry according to Albert and Serjeant[19]. The results are given in Table II. The differences between Cl, OCH_3 and SCH_3 derivatives can be attributed to the activating mesomeric effect of the methoxy and thiomethyl groups and the deactivating inductive effects of the chlorine atom.

XE-60 seems to be the most suitable liquid stationary phase for structural correlations. The differences in the basicity of the compounds contribute to the higher retention indices of terbutylazine and terbutryne on XE-60 in comparison with atrazine and ametryne, and to their poor separation.

The differences between the retention indices on XE-60 and on the mixed phase SE-30/Reoplex 400 can be correlated with pK_a values and dipole moments. As can be seen from Table III, the ΔI values are proportional to pK_a.

TABLE III

COMPARISON OF ΔI AND pK_a VALUES

No.	*Trivial name*	ΔI_{B-D}	pK_a
4	Terbutylazine	505	1.94
5	Atrazine	485	1.68
7	Simazine	475	1.65
14	Terbutryne	486	4.38
15	Ametryne	471	4.00
17	Simetryne	471	4.00
9	Terbutone	456	4.46
10	Atratone	446	4.20
12	Simetone	445	4.17

Data on dipole moments are scarce in the literature[21]. The correlations between ΔI and the dipole moments can be performed only in the series propazine, prometryne and prometone, and for atrazine and ametryne. It follows (Table IV) that ΔI is proportional to the dipole moments.

TABLE IV

COMPARISON OF ΔI VALUES AND DIPOLE MOMENTS

No.	*Trivial name*	ΔI_{B-D}	μ
3	Propazine	489	4.52
13	Prometryne	459	3.54
8	Prometone	434	2.94
5	Atrazine	485	4.63
15	Ametryne	471	3.15

TABLE V

RELATIVE ABUNDANCES (%) OF THE MAIN IONS ABOVE *m/z* 40 IN THE MONOISOTOPIC EI MASS SPECTRA OF MONOALKYLAMINO DERIVATIVES (*cf.*, SCHEME 1)

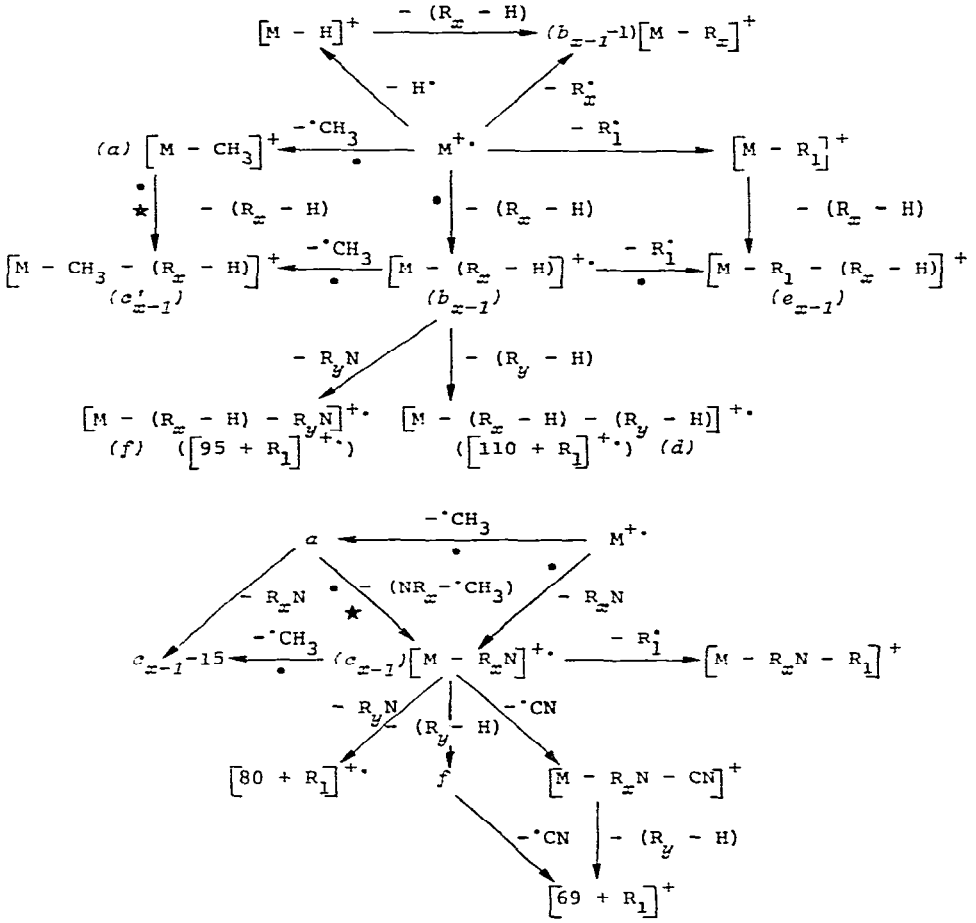
Superscripts +1 and −2 indicate that these peaks were found at 1 a.m.u. higher or 2 a.m.u. lower, respectively. ? = Not measured; − = not present or less than 0.5%.

No.	*Trivial name*	$M^{+\bullet}$	$[M - CH_3]^+$ *(a)*	$M^{+\bullet} - (R_{2/3} - H)$ $(b_{1/2})$	$M^{+\bullet} - R_{2/3}N$ *and/or* $a - (R_{2/3} - H)$ $(c_{1/2})$	$c_{1/2} - {}^{\bullet}CH_3$	$M^{+\bullet} - (R_2 - H) - (R_3 - H)$ *(d)*	$b_{1/2} - R_1^{\bullet}$ $(e_{1/2})$	$H_2N(HN)C\overset{+}{N}CR_1$ $[69 + R_1]^+$	$[R_{2/3}NH]^+$	$[M - 2{}^{\bullet}CH_3]^{2+}$
2	−	13	33	29	100	−	51^{+1}	7	21	−	13
3	Propazine	39	74	25	50	2	10	10	20	100	25
4	Terbutylazine	21	100	−/51	4/12	2/−	12	$-/20^{-2}$	16	28/−	15
5	Atrazine	40	91	5/31	18*/14	4/2	11	3/15	17	48/100	15
6	Norazine	12	29	2/15	1/3	1/2	1	−/10	3	?/100	14
7	Simazine	65	48	40	23	5	12	19	11	100	26
8	Prometone	46	74	47	75	20	34	−	23	100	30
9	Terbutone	18	100	2/89	4/28	3/7	28	−	10	17/2	20
10	Atratone	55	65	5/40	15*/24	4/15	15	−	10	60/100	13
11	Noratone	28	40	9/30	10/15	2/22	9	−	8	?/100	27
12	Simetone	100	47	42	55	74	27	−	11	61	20
13	Prometryne	66	55	29	87	18	16	15	−	100	18
14	Terbutryne	36	95	−/100	6/58	−/−	17	$-/13^{+1}$	−	23/−	23
15	Ametryne	100	75	4/34	21*/36	9/18	11	8/14	−	30/76	33
16	Desmetryne	100	78	−/48	−/18	−/18	−	−/25	−	?/75	2
17	Simetryne	100	22	17	41	41	8	20	−	37	20

* These ions are coincident with $b_2 - 1$.

Mass spectrometry

Electron-impact spectra. The positive ion electron-impact (EI) mass spectra of the di(monoalkylamino)-*s*-triazine derivatives 2–17 are summarized in Table V. From these spectra a fragmentation scheme was deduced (Scheme 1).



Scheme 1. Fragmentation pathways for bis(monoalkylamino)triazine derivatives under EI conditions. $x = 2$ or 3; $y = 2$ if $x = 3$ and $y = 3$ if $x = 2$. *: Transition is confirmed by metastable peaks. ★: As *c* and *c'* have the same nominal mass, it is unknown whether the metastable peak corresponds to the decomposition $a \rightarrow c$ or $a \rightarrow c'$ or to both.

Only prominent peaks from the monoisotopic mass spectra are listed in Table V. Notable omissions include the following. Ions $M^{+\cdot}$ and *b* are accompanied by satellites at 1 a.m.u. lower with 10–20% of the abundance of the former ions. $M^{+\cdot}$ loses $R_1^{\cdot}$ [or $(R_1 - H)$ in the case of methylthiotriazines], and *c* loses R_1H to some extent (less than 5% relative to these peaks). *c* loses CN· readily (up to 25% for chloro-, less than 10% for methoxy- and methylthiotriazines). In most spectra, the peaks corresponding in mass to *d*—15 and *d*—30 occur {$[95 + R_1]^{+\cdot}$ (*f*) and $[80 + R_1]^{+\cdot}$ in Scheme 1}.

The low mass ends of the EI spectra are crowded with peaks corresponding to the homologous ion series ($n = 0,1,2,...$):

C_nH_{2n+1}-$CH{=}\overset{+}{N}H$-$C{\equiv}N$ (m/z 55,69,83,...,40+R_x)

C_nH_{2n+1}-HN-$C{\equiv}\overset{+}{N}H$ (m/z 43,57,71,...,42+R_x)

C_nH_{2n+1}-NH-$C{\equiv}\overset{+}{N}$-$C{\equiv}N$ (m/z 68,82,96,...,67+R_x)

C_nH_{2n+1}-$CH{=}\overset{+}{N}H_2$ (m/z 44,58,72,...,15+R_x)

Ions of m/z 68 (H_2N-$C\overset{+}{N}$-CN), 43 (H_2N-$C\overset{+}{N}H$), 42 ($[H_2N$-$CN]^{+\cdot}$) and 41 ($[H_3C$-$CN]^{+\cdot}$) are abundant in all of the spectra. The intensity of the ions R_xHN-$C\overset{+}{N}H$ ($[42 + R_x]^+$) and R_xHN-$C\overset{+}{N}$-CN ($[67 + R_x]^+$) decreases with increasing size of the substituent R_x. These ions are especially abundant in methylamino derivatives (m/z 57, 65–95%; m/z 82, 20–50%).

Ions R_1^+ or $R_1H^{+\cdot}$ were not measured (below m/z 40), except in case of methylthio derivatives, where SCH_3^+ intensities of 6–8% were found.

In addition to $[M - 2{\cdot}CH_3]^{2+}$ as listed in Table V, the doubly charged ions $[M - {\cdot}H - {\cdot}CH_3]^{2+}$ occur with an about 3% intensity in most cases. $[M - HR_1]^{2+}$ was observed only in the spectra of methylthio derivatives .

The EI mass spectra of simazine[23,24] and propazine[23] have been published earlier. Some fragmentation patterns were also reported for atrazine, prometone, ametryne, prometryne[23] and simetryne[25], but the spectra were not given. Jörg *et al.*[23] have already explained the genesis of ions *a*, *b*, *c*, *d*, and *e* for simazine (Scheme 1). The occurrence of $[M - 2{\cdot}CH_3]^{2+}$ was observed and m/z 68 was assigned to the imidazole cation. Ross and Tweedy[24] had shown that in the spectrum of simazine, ion $[M - R_x - 14]^+$ is a mixture of $b_{x-1} - {\cdot}CH_3$ (= *c'*, 21%) and $M^{+\cdot} - R_xN$ (= *c*, 79%).

In our study, metastable peaks were recorded in almost all instances for the transitions $M^{+\cdot} \rightarrow a$, $M^{+\cdot} \rightarrow b$, $M^{+\cdot} \rightarrow c$, $a \rightarrow c$ (or $a \rightarrow c'$?), $b \rightarrow c'$, $c \rightarrow c - 15$ supporting the proposed fragmentation pathways in Scheme 1.

From the mass spectral data of three series of homologous *s*-triazines in Table V, conclusions can be drawn regarding the relative stabilities of the compounds. As the abundance of the molecular ion reflects its stability, it can be seen that the

TABLE VI

RELATIVE ABUNDANCES (%) OF THE MAIN IONS ABOVE m/z 40 IN THE MONOISOTOPIC EI MASS SPECTRA OF DIETHYLAMINO DERIVATIVES AND *sec.*-BUMETON (*cf.*, SCHEME 2)

For compounds 20 and 21, ions *r* and *s* are coincident. – = Not present or less than 0.5%.

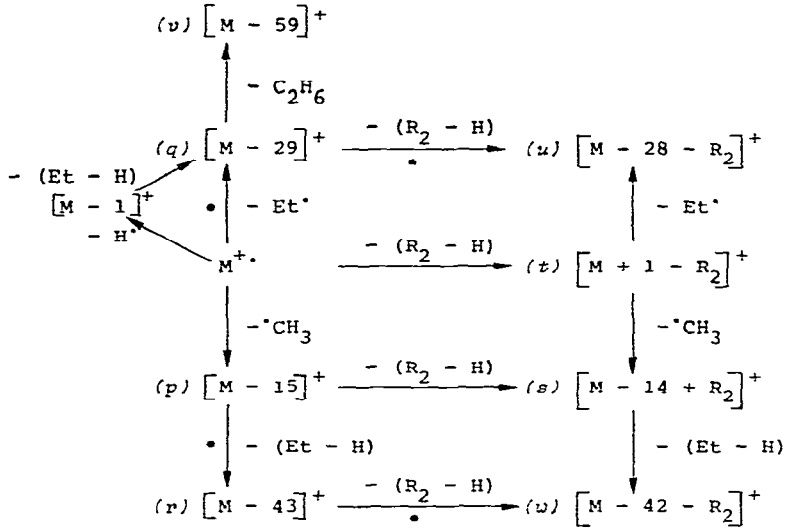
No.	*Trivial name*	$M^{+\cdot}$	$[M - CH_3]^+$ (*p*)	$[M - C_2H_5]^+$ (*q*)	$p - C_2H_4$ (*r*)	$p - (R_2 - H)$ (*s*)	$M^{+\cdot} - (R_2 - H)$ (*t*)*
19	Ipazine	62	85	100	54	13	19
20	Trietazine	46	55	100	65	*r*	15
21	Chlorazine	37	29	100	57	*r*	17
22	*sec.*-Bumetone	7	12	100	–	–	6

* Not corrected for the isotopic contribution of *q* (compounds 20, 21, 22) and *r* (compound 19).

** This ion, appearing at 1 a.m.u. above *u*, is actually ion b_2 from Scheme 1.

stability, as function of R_2 and R_3, decreases in the order Et,Et > Et,*i*-Pr > *i*-Pr, *i*-Pr > Et,Bu (> Bu,Bu). The position of Me,*i*-Pr compounds in this series is not clear because it is apparently influenced by the nature of R_1. A comparison of the spectra of corresponding compounds with different R_1 groups shows that the stability of the compounds increases on electron impact in the order Cl < OCH_3 < SCH_3.

The EI mass spectra of the diethylamino derivatives, triazines 19, 20 and 21, are given in Table VI. The deduced fragmentation pattern is depicted in Scheme 2.



Scheme 2. Fragmentation pathways for diethylaminotriazine derivatives and of *sec.*-bumeton under EI conditions. *: Transition is confirmed by metastable peaks. Et equals R_3 (compounds 19, 20 and 21) or part of R_3 (triazine 22).

Because *sec.*-bumetone (compound 22) fragments similarly on electron impact, this derivative is included in Table VI. However, its fragmentation also exhibits the pathways proposed in Scheme 1.

Important peaks not included in Table VI involve the following ions. The loss of H• from $M^{+\bullet}$ results in an ion beam with about 10% of the intensity of $M^{+\bullet}$.

q − (*R*₂ − *H*) (*u*)	*q* − C_2H_6 (*v*)	*r* − (*R*₂ − *H*) (*w*)	$[(C_2H_5)_2N]^+$	$[R_{2/3}NH]^+$	$[M - 2{\bullet}CH_3]^{2+}$	$[M - {\bullet}CH_3 - {\bullet}Et]^{2+}$
51	11	28	48	62/19	11	9
8	9	6	36	23	6	—
8	11	6	88	24	2	3
25[+1**]	1	5	—	9/—	1	7

TABLE VII

RELATIVE ABUNDANCES (%) OF THE MAIN IONS ABOVE *m/z* 50 IN THE MONOISOTOPIC CI(CH_4) MASS SPECTRA OF MONOALKYLAMINO DERIVATIVES

— = Not present or less than 0.5%.

No.	*Trivial name*	$[M + C_2H_5]^+$	MH^+	$M^{+\cdot}$	$MH^+ - H_2$	$MH^+ - CH_4$	$MH^+ - R_1H$	$MH^+ - R_3$*	$MH^+ - (R_{2/3} - H)$	$MH^+ - HNR_3$*	$MH^+ - R_1H - (R_3 - H)$*
2	—	10	95	9	4	12	100	13	46	10	3
3	Propazine	13	70	9	3	11	100	5	13	3	2
4	Terbutylazine	7	80	17	7	41	100	29	28/81	11	64
5	Atrazine	19	98	11	6	11	100	7	1/9	1	3
6	Norazine	15	100	7	2	3	94	2	—/5	—	1
7	Simazine	9	77	8	3	2	100	—	3	1	1
8	Prometone	11	100	7	5	6	—	3	5	2	—
9	Terbutone	10	100	6	7	7	2	6	10/30	1	1
10	Atratone	13	100	6	5	4	—	2	—/3	—	—
11	Noratone	12	100	5	5	4	1	2	—/3	—	—
12	Simetone	11	100	8	7	3	1	—	3	2	—
13	Prometryne	15	100	9	5	6	1	2	5	2	1
14	Terbutryne	14	100	5	4	5	—	5	4/24	1	1
15	Ametryne	15	100	7	6	4	2	2	—/4	—	1
16	Desmetryne	14	100	7	5	4	1	2	—/6	1	1
17	Simetryne	15	100	7	5	2	1	1	1	1	—

* Corresponding losses of R_2 were not found.

TABLE VIII

RELATIVE ABUNDANCES (%) OF THE MAIN IONS ABOVE *m/z* 50 IN THE MONOISOTOPIC CI(CH_4) MASS SPECTRA OF DIETHYLAMINO DERIVATIVES AND *sec.*-BUMETON

– = Not present or less than 0.5%.

No.	*Trivial name*	$[M + C_2H_5]^+$	MH^+	$M^{+\bullet}$	$MH^+ - H_2$	$MH^+ - CH_4$	$MH^+ - R_1H$	$MH^+ - C_2H_6$*	$MH^+ - (R_2 - H)$	$MH^+ - R_3$*	$MH^+ - (R_3 - H)$
19	Ipazine	13	83	12	5	8	100	7	5	–	–
20	Trietazine	15	75	13	5	6	100	7	4**	–	***
21	Chlorazine	12	100	9	6	4	82	3	1**	–	***
22	*sec.*-Bumetone	14	100	4	7	6	–	8	5**	4	9

* C_2H_6 equals R_3H (compounds 19, 20, 21) or part of R_3 (compound 22).

** Not corrected for isotopic contributions of $MH^+ - C_2H_6$.

*** Coincident with $MH^+ - (R_2 - H)$.

Molecular ions $M^{+\bullet}$ also lose $R_1^{\bullet}$, yielding ions with an abundance of 5–10% of $M^{+\bullet}$. In the spectra of diethylaminotriazines 19, 20 and 21, the following peaks in the low mass region were not included in Table VI: *m/z* 99 [$(C_2H_5)_2\overset{+}{N}HCN$], 10–49%; *m/z* 71 ($[C_2H_5N{=}CH_2]^{+\bullet}$), 15–36%; *m/z* 69, 29–50%; *m/z* 68, 43–68%; *m/z* 55, 32–53%; *m/z* 43, 51–75%; *m/z* 42, 28–43% and *m/z* 41, 7–28%. The elemental composition of the latter ions is presumably the same as that described earlier for di(monoalkylamino) compounds. All of these ions were far less abundant in the spectrum of *sec.*-bumetone (less than 4%, except *m/z* 68, 8% and *m/z* 43, 11%).

The spectrum of *sec.*-bumetone does not show a peak corrresponding to ion *u* from Scheme 2 [$M^{+\bullet} - {}^{\bullet}C_2H_5 - (R_2 - H^{\bullet})$] but rather to $M^{+\bullet} - (R_3 - H)$ at 1 a.m.u. higher (b_2, Scheme 1).

TABLE IX

RELATIVE ABUNDANCES (%) OF THE MAIN IONS ABOVE *m/z* 70 IN THE MONOISOTOPIC CI (ISOBUTANE) MASS SPECTRA OF MONOALKYLAMINO DERIVATIVES

— = Not present or less than 0.5%.

No.	*Trivial name*	$[M + C_4H_9]^+$	$[M + C_3H_7]^+$	$[M + C_3H_5]^+$	$[M + C_3H_3]^+$	MH^+	$M^{+\bullet}$
2	—	—	1	1	3	100	9
3	Propazine	—	1	1	3	100	7
4	Terbutylazine	—	1	1	3	100	7
5	Atrazine	—	1	1	2	100	7
6	Norazine	—	1	1	2	100	7
7	Simazine	—	1	1	2	100	7
8	Prometone	1	2	1	3	100	7
9	Terbutone	1	1	1	3	100	7
10	Atratone	1	1	1	2	100	7
11	Noratone	1	2	1	2	100	6
12	Simetone	1	2	1	3	100	7
13	Prometryne	1	2	1	3	100	8
14	Terbutryne	1	2	1	3	100	8
15	Ametryne	1	2	1	3	100	7
16	Desmetryne	1	2	1	3	100	7
17	Simetryne	1	2	1	3	100	6

* Corresponding losses of R_2 were not found.

TABLE X

RELATIVE ABUNDANCES (%) OF THE MAIN IONS ABOVE *m/z* 70 IN THE MONOISOTOPIC CI (ISOBUTANE) MASS SPECTRA OF DIETHYLAMINO DERIVATIVES AND *sec.*-BUMETON

— = Not present or less than 0.5%.

No.	*Trivial name*	$[M + C_4H_9]^+$	$[M + C_3H_7]^+$	$[M + C_3H_5]^+$	$[M + C_3H_3]^+$	MH^+	$M^{+\bullet}$
19	Ipazine	—	2	2	3	100	8
20	Trietazine	1	2	2	3	100	8
21	Chlorazine	—	2	1	1	100	5
22	*sec.*-Bumetone	1	1	1	3	100	7

* Coincident with $MH^+ - C_2H_6$.
** $MH^+ - C_4H_8$.
*** $MH^+ - C_4H_9$.

Ions *q*, *r*, *u* and *w* are presumably identical with the corresponding ions $M^{+\bullet} - H^{\bullet}$, *a*, *b* — H and *c* from Scheme 1. Metastable peaks were observed for several transitions, as indicated in Scheme 2. The main fragmentation process is the loss of $^{\bullet}C_2H_5$ from $M^{+\bullet}$, yielding the base peak in all instances.

A comparison of the spectra of triazines 21, 20 (Table VI) and 7 (Table V) shows that the abundance of the molecular ions decreases with increasing number of ethyl substituents. In other words, simazine is more stable on electron impact than trietazine, which in turn is more stable than chlorazine. This substituent effect is reversed, however, with ipazine, which seems to be more stable than atrazine. A reason for this phenomenon has not been found.

$MH^+ - H_2$	$MH^+ - CH_4$	$MH^+ - (R_1 - H)$	$MH^+ - R_1H$	$MH^+ - (R_3 - H)^{\bullet}$	$MH^+ - R_3^{\bullet}$	$MH^+ - (R_3 - H) - (R_1 - H)/ - R_1H^{\bullet}$
—	1	3	1	5	1	1/1
—	1	2	1	1	—	1/1
—	1	2	1	4	—	1/1
—	1	2	1	—	—	—/—
—	1	1	1	—	—	—/—
—	—	1	1	—	—	—/1
—	1	—	—	1	1	—/—
1	1	—	—	3	1	—/—
—	1	—	—	—	1	—/—
—	1	—	—	—	1	—/—
1	—	—	—	—	1	—/—
1	1	1	—	—	—	—/—
1	1	1	—	3	1	—/—
1	1	1	—	—	—	—/—
1	—	1	—	—	—	—/—
—	—	1	—	—	—	—/—

$MH^+ - CH_4$	$MH^+ - (R_1 - H)$	$MH^+ - R_1H$	$MH^+ - C_2H_4$	$MH^+ - C_2H_6$	$MH^+ - (R_1 - H) - C_2H_4/ - C_2H_6$
2	2	1	—	1	—/1
1	3	1	1	1	—/1
—	2	2	1	1	—/—
1	*	—	1	2	1**/1***

Chemical-ionization spectra. The chemical-ionization (CI) mass spectra, using methane as reagent gas, are summarized in Tables VII and VIII. In these tables adduct ions $[M + C_3H_5]^+$ have been omitted; their abundance was less than 4% in all instances . Ions $MH^+ - C_2H_4$, observed in the spectra of triazines 2 (13%), 6 (3%) and 11 (14%), also have not been included. Finally, triazine 2 displayed a peak corresponding to $MH^+ - (R_2 - H) - (R_3 - H)$:16%.

For the protonation in the gas phase, the negative enthalpy of the reaction ($-\Delta H^0$) is defined as the proton affinity (*PA*) of the molecule. The enthalpy for the reaction $CH_5^+ + M \rightarrow MH^+ + CH_4$ then equals the difference in the proton affinities of the sample and the reagent gas molecules: $\Delta H^0 = PA(CH_4) - PA(M)$. The degree of fragmentation of protonated molecular ions MH^+ can generally be correlated with the amount of the energy exchanged in the protonation reaction (ΔH^0) and hence with the proton affinities of the sample and the reagent gas molecules. Table VII shows that 2-chloro-*s*-triazines fragment much more easily than the methoxy and thiomethyl derivatives. The conclusion that the *PA* of the triazines decreases in the order $Cl > OCH_3 > SCH_3$ is, however, false. The proton affinities are proportional to the gas-phase basicities[26,27]. Although they are influenced by solvent effects, the solution phase basicities (pK_a values) show a different order: $OCH_3 > SCH_3 > Cl$. The *PA* data available for RCl, $ROCH_3$ and $RSCH_3$ compounds are analogous to the order of the solution-phase basicities[28] (see also Table XI). Another possible conclusion, that fragmentation of a given MH^+ decreases whenever reactant gases with higher *PA* are applied, is correct, as can be seen, *e.g.*, for the methane (Tables VII and VIII) and isobutane (Tables IX and X) CI mass spectra [$PA(CH_4) = 129$ kcal/mol; $PA(i\text{-}C_4H_{10}) = 195$ kcal/mol].

Other factors govern the fragmentation mechanism. Field[29] has already suggested that the leaving ability of a group R from a given compound M is inversely proportional to the proton affinity of RH. This has been confirmed for a series of cyclohexyl derivatives[30] and for series of substituted 1,4-oxathiins and derivatives[31].

The following rationale is proposed for the fragmentation of the triazines under CI (methane) conditions, by analogy with the cited reports. Protonation takes place preferentially on the alkylamino groups (the *PA* of H_2NR is very high: Table XI), or possibly on the triazine-ring nitrogen atoms. Hydrogen rearrangements may occur in protonated molecular ions before decomposition occurs[30]. The loss of a neutral molecule R_1H from MH^+ may then occur. The importance of this fragmentation (Table VII) is indeed inversely correlated with the proton affinity of the departing R_1H molecule (Table XI).

TABLE XI
PROTON AFFINITIES (*PA*) OF SOME SELECTED MOLECULES
R = alkyl.

Compound	*PA (kcal/mol)*	*Ref.*
H_2NR	218–226	25
CH_3SH	185	27
CH_3OH	180	27
HCl	141	27–29

The electron-releasing inductive effect of alkyl groups is proportional to the proton affinity of the nitrogen atom attached to them[26]. This explains the abundance of the ions $MH^+ - (R_3 - H)$ in the case of *tert.*-butylamino derivatives.

CI mass spectra, obtained with isobutane as reagent gas, are listed in Tables IX and X. Ions MH^+ are the base peaks in all of the spectra. Adduct ions and fragment ions contribute relatively little to the total ion current. Apart from $M^{+\bullet}$, the only fragment ions of importance correspond to the loss of isobutene from MH^+ in the spectra of *tert.*-butyl derivatives. Remarkable, but not yet understood, is the loss of $(R_1 - H)$ from MH^+, especially with chlorotriazines.

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