Mass Spectral Fragmentation Patterns of Various 6-Substituted 2,4-*bis*-(*m*-Aminoanilino)-*s*-triazines

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The mass spectra of 6-substituted-2,4-*bis*-(*m*-aminoanilino)-*s*-triazines were determined and found to be dominated by intense molecular ions (base peak), strong M-H peaks and fragment ions diagnostic for the arylamino and C-6 substituents. Mechanisms have been proposed for the formation of the major peaks in the spectra. Fragmentation pathways involving hydrogen transfer reactions have been rationalized by concomitant opening of the triazine ring rather than an amino-imino tautomerization as previously suggested. Fragmentation reactions accompanied by rearrangement modes have also been encountered in some of the compounds studied.

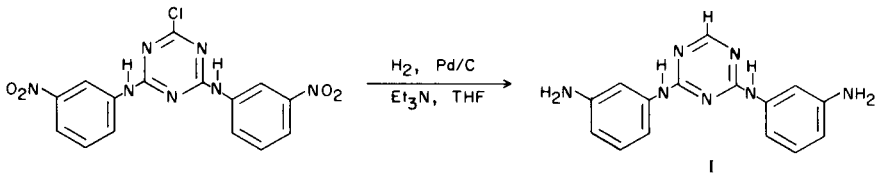
Introduction

Mass spectrometry has been amply demonstrated to be a diagnostic tool for the identification of various *s*-triazines (1-3). Thus, Spiteller and co-workers presented an early account of the mass spectral properties of chloro-, thiomethyl- and methoxyl-*bis*-(alkylamino)-*s*-triazines (1) while a more current report has dealt with chlorinated compounds bearing amino and alkylamino substituents (2). The most comprehensive treatise has been presented recently by Preston and co-workers, in which a variety of *s*-triazine derivatives has been analyzed (3). To date, electron-impact studies of *s*-triazines bearing arylamino substituents have not been reported. Hence, we wish to present the results of our investigations with the title compounds.

Results and Discussion.

The preparation of the compounds under discussion is shown in Chart I. They all contain a *m*-aminoanilino substituent at C-2 and C-4, but vary in the nature of the substituent at C-6. The individual mass spectra are reproduced in Figures 1-5 and are characterized by intense molecular ions, strong M-H peaks accompanied by appropriate metastable peaks, doubly charged molecular ions, and weaker fragment ions which serve to identify the arylamino and C-6 substituents.

CHART I



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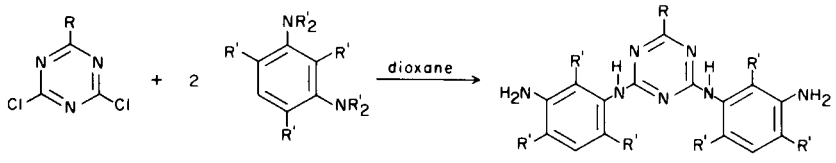


II R = NH_2 R' = H
III R = $(CH_3)_2N$ R' = H
IV R = $(C_6H_5)_2N$ R' = H
IVa R = $(C_6H_5)_2N$ R' = D
V R = C_6H_5 R' = H

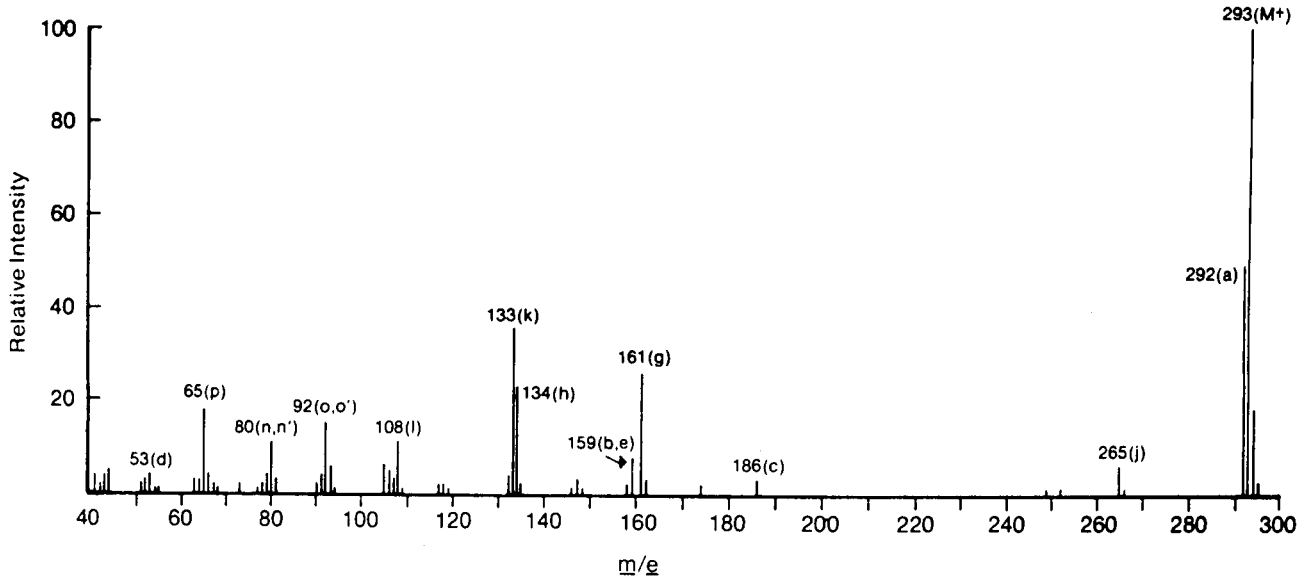


Figure 1. Mass spectrum of 2,4-*bis*-(*m*-aminoanilino)-*s*-triazine (I).

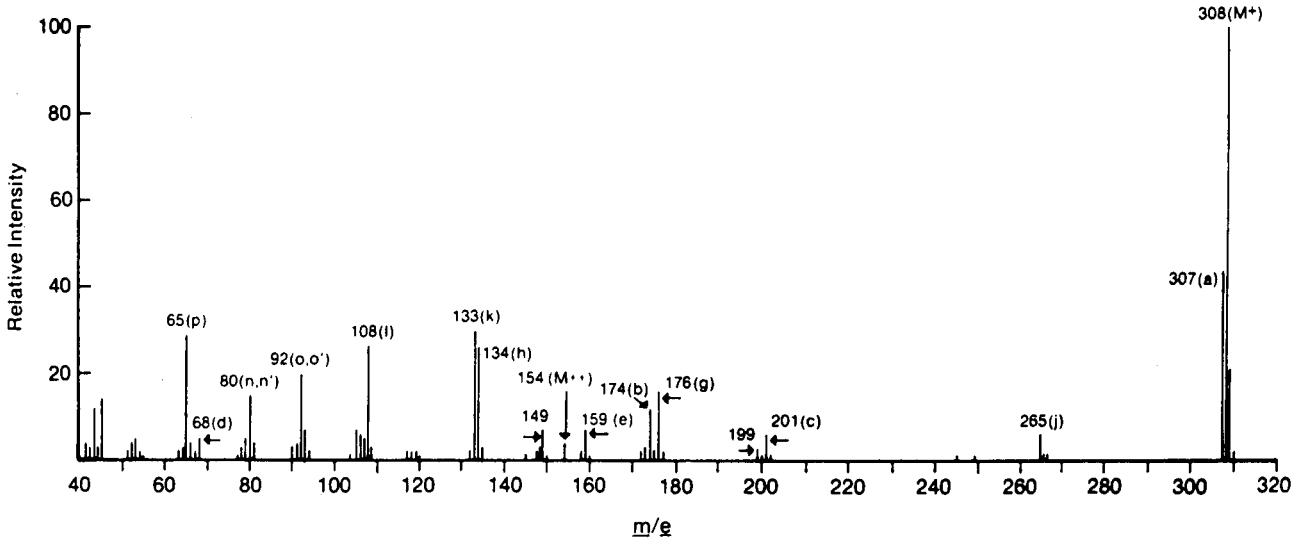


Figure 2. Mass spectrum of 2,4-*bis*-(*m*-aminoanilino)-6-amino-*s*-triazine (II).

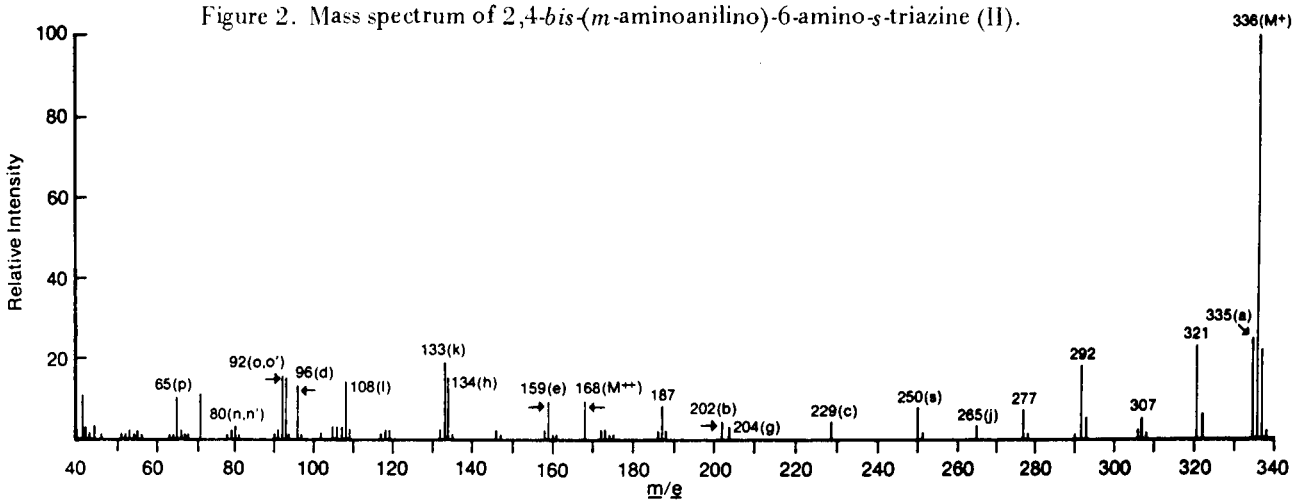


Figure 3. Mass spectrum of 2,4-*bis*-(*m*-aminoanilino)-6-dimethylamino-*s*-triazine (III).

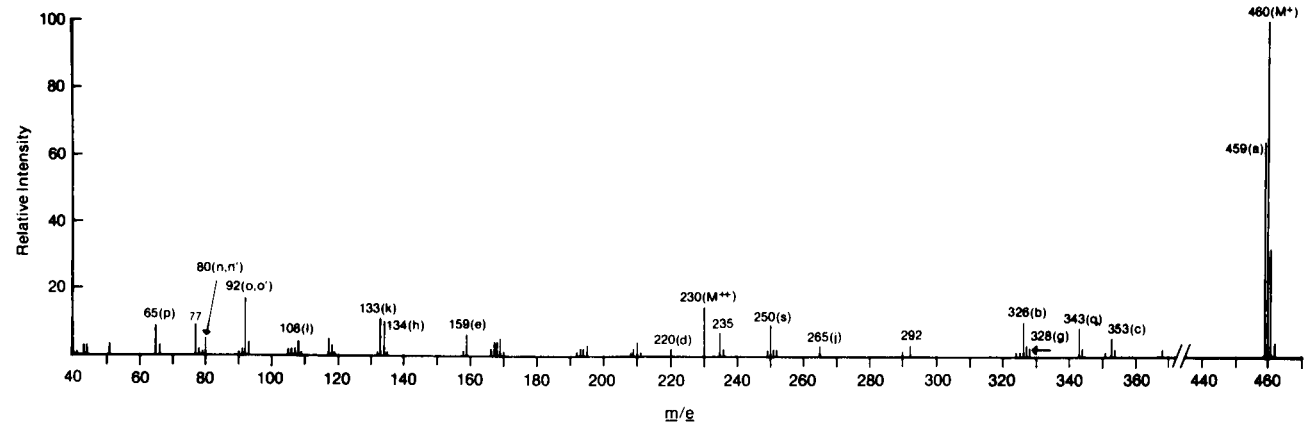


Figure 4. Mass spectrum of 2,4-*bis*-(*m*-aminoanilino)-6-diphenylamino-*s*-triazine (IV).

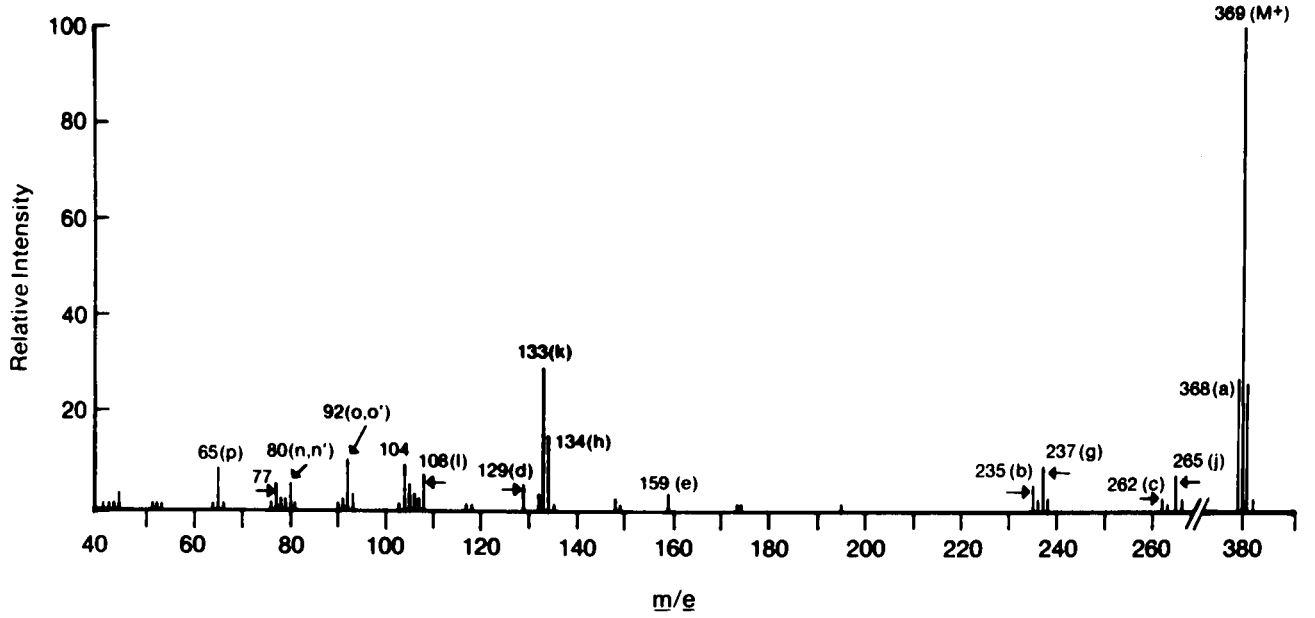
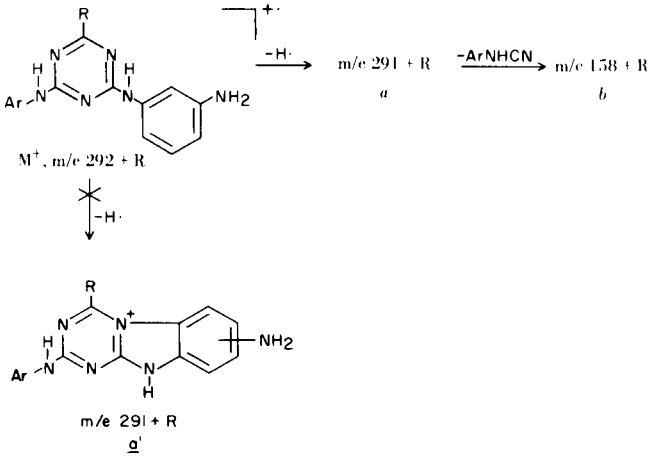


Figure 5. Mass spectrum of 2,4-*bis*-(*m*-aminoanilino)-6-phenyl-*s*-triazine (V).

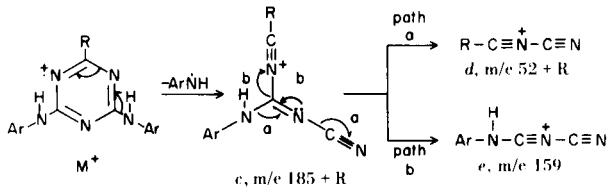
Common Fragmentation Pathways.

The second most intense peak in the mass spectra of compounds I-IV and the third most abundant ion in the spectrum of V results from loss of a hydrogen radical from the molecular ion to form a peak at m/e 291 + R (*a*). The source of this hydrogen loss can be from the primary or secondary amino group, the aromatic protons of the *m*-aminoanilino substituent, the C-6 substituent or a combination of these loci. Involvement of the aromatic protons *ortho* to the primary amino group seemed a likely possibility since the driving force for this cleavage could be the formation of the ammonium ion *a'*. In order to test this hypothesis in the case of the diphenylamino compound, IV, we examined the mass spectrum of the corresponding deuterated compound IVa. Examination of the m/e 460-m/e 470 region in the mass spectrum of IVa and comparison with calculated peak intensities to be expected with hydrogen or deuterium loss from the molecular ion revealed that expulsion of a hydrogen atom from one of the *ortho* positions does not contribute significantly to the formation of the M-H species. Hence, the latter must involve loss of a hydrogen radical from one or both of the amino groups. Compounds I-III contain substituents at C-6 which probably also provide a source for hydrogen expulsion in addition to the aforementioned amino groups.

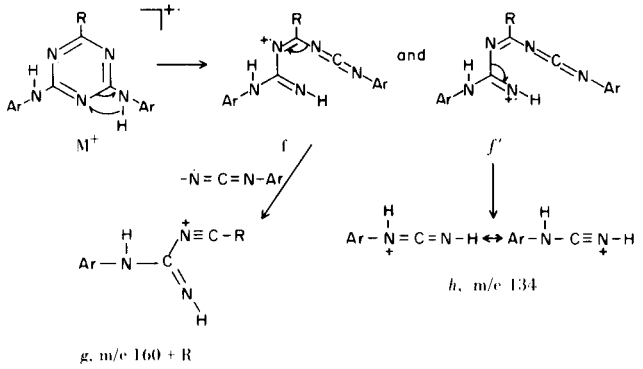


Loss of a neutral cyanamide molecule from the M-H species (*a*) results in the formation of the peak at m/e 158 + R (*b*).

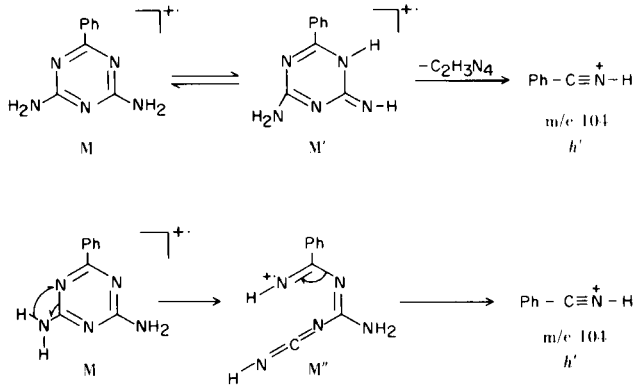
Simple cleavage on an arylamino group furnishes ion *c* (4). The mechanism shown below appears to be preferred over an aryne structure for the charged fragment as proposed by Ross and Tweedy (2) since further fragmentation of the more stable ion *c* could readily account for the subsequent formation of ions *d* (m/e 52 + R) and *e* (m/e 159). The nature of the C-6 substituent can be determined from the mass of fragment *d*.



Opening of the triazine ring with concomitant transfer of the hydrogen atom from a secondary amine results in the rearranged molecular ions *f* or *f'* depending on the site of the positive charge. Ion *f*, by expulsion of a cyanamide radical can give rise to the species *g* at m/e 160 + R, while α-cleavage of the *f'* molecular ion affords the resonance stabilized cyanamide cation *h* (m/e 134).

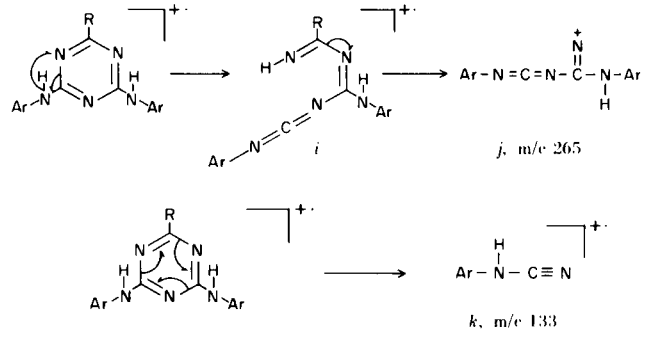


The ion *h* (m/e 134) is analogous to the protonated benzonitrile cation at m/e 104 reported by Preston and co-workers to be characteristic of all amino substituted *s*-triazines (3). These investigators proposed that the *s*-triazine molecular ion tautomerizes to the imino form and the latter cleaves to furnish the protonated benzonitrile cation, *e.g.* M → M' → *h'* (3). However, the driving force for the M' → *h'* fragmentation is difficult to envision and this point was not commented upon by the authors. We do not see the need for invoking the imino tautomer as an

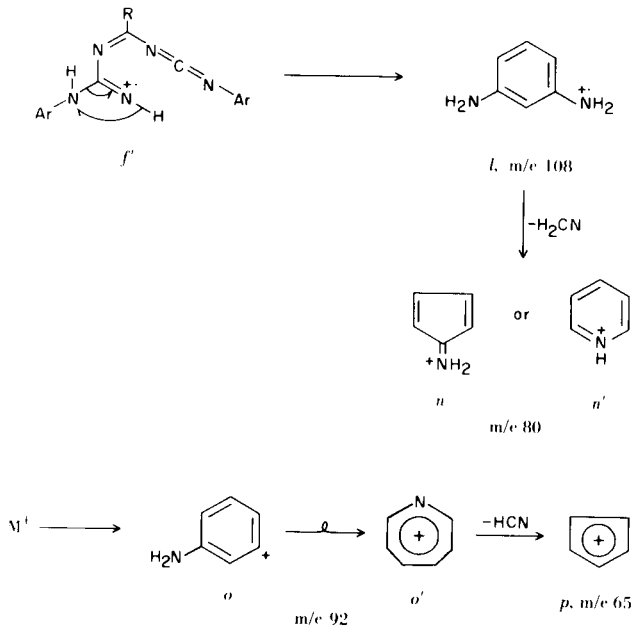


intermediate, but prefer a mechanism involving concerted ring opening with hydrogen transfer to generate M'' since the latter is ideally suited for fragmentation by α-cleavage to provide the m/e 104 species (h'). An exactly analogous situation pertains in the case of the *bis*-arylamino-*s*-triazines (*i.e.*, M+ → *f'* → *h*)

In addition to peaks at m/e 134 (*g*) and 159 (*e*) discussed above, fragment ions at m/e 265, 133, 108, 92, 80, and 65 were observed in all the mass spectra. The peak at m/e 265 can be accounted for by ring cleavage of the parent ion to give *i*, followed by homolytic scission of the C-N bond to the species *j*. The remaining ions are derived from the cyanamide portion of molecule. Thus, m/e 133 corresponds to the cyanamide radical cation *k* and is probably formed by concerted opening of the triazine ring.



Ion *f'* by fragmentation with hydrogen transfer, leads to the phenylenediamine structure, *l*, m/e 108. The latter by extrusion of H_2CN affords the m/e 80 peak which may be represented as either of the isomeric structures *n* or *n'* (5).



Direct cleavage of the aryl-nitrogen bond of the molecular ion affords the $C_6H_6N^+$ species *o*, which by analogy with the M-H peak in aniline (6,7) could possibly rearrange to the azepinium ion *o'*. Further loss of an HCN molecule affords the cyclopentadienyl cation *p*.

High resolution measurements of the characteristic peaks in the mass spectrum of the amino compound II support the aforementioned assignments and are listed in Table I.

Compound-Specific Fragmentation Pathways.

Peaks analogous to m/e 149 and 199 in the spectrum of II were not noted in the other *bis*-(arylamino)-*s*-triazines under investigation, which would suggest that their origin involves the amino substituent either as a source of iterant hydrogen radicals or a migrating group. Thus, m/e 149 (calculated for $C_7H_9N_4$: 149.0836; observed: 149.0832) can be formed by opening of the triazine ring with simultaneous transfer of the amino substituent from carbon to nitrogen. Although a $C_7H_9N_4$ cation could also be obtained by multistep pathways involving succes-

sive hydrogen transfers, we prefer the simpler mechanism shown above since it leads to a relatively stable species by a more direct route. The m/e 199 ion was found to be comprised of a $C_9H_7N_6$ species by high resolution analysis (calculated: 199.0732; found: 199.0748). Since analogous ions were not observed in the spectra of other derivatives, this would seem to implicate the C-6 amino group in this fragmentation process. A possible precursor to the m/e 199 species could be fragment ion c, which

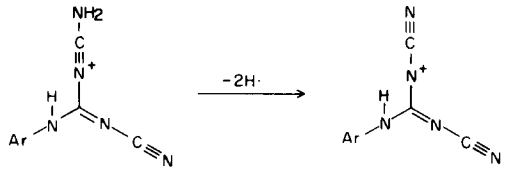
TABLE I

High Resolution Data for
2,4-*bis*-(*m*-Aminoanilino)-6-Amino-*s*-Triazine

Ion	m/e	Elemental Composition	Observed Mass	Calculated Mass
M^+	308	$C_{15}H_{16}N_8$	308.1494	308.1497
j	265	$C_{14}H_{13}N_6$	265.1203	265.1202
c	201	$C_9H_9N_6$	201.0896	201.0889
g	176	$C_8H_{10}N_5$	176.0932	176.0936
b	174	$C_8H_8N_5$	174.0783	174.0780
e	159	$C_8H_7N_4$	159.0672	159.0671
	154	$C_{15}H_{16}N_8$ (a)	154.0738	154.0748
h	134	$C_7H_8N_3$	134.0695	139.0717
k	133	$C_7H_7N_3$	133.0628	133.0639
l	108	$C_6H_8N_2$	108.0665	108.0686
o or *o'*	92	C_6H_6N	92.0505	92.0500
n or *n'*	80	C_5H_6N	80.0493	80.0499

(a) Doubly charged molecular ion.

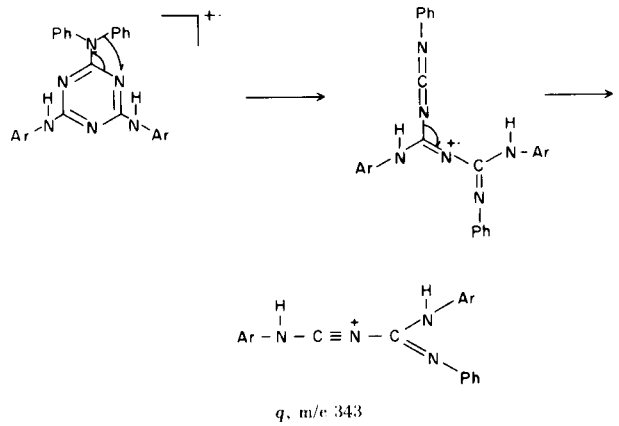
by expulsion of two hydrogen atoms would afford the m/e 199 species as shown below.



c, m/e 201 m/e 199

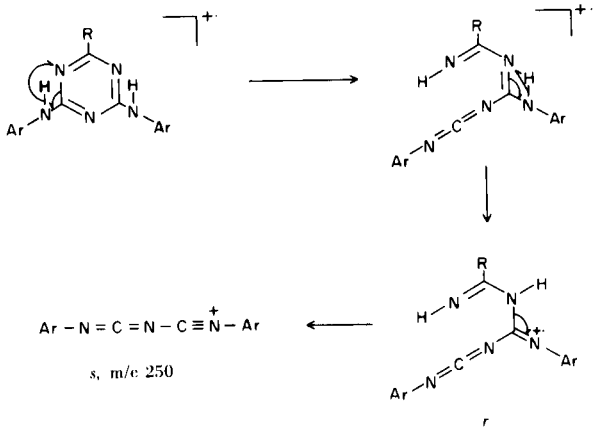
Compound III, bearing a dimethylamino group, exhibits rearrangement ions at m/e 307 and 277. The former was shown by high resolution measurements to consist of a $C_{16}H_{17}N_7$ species (calculated: 307.1545; observed: 307.1551) and therefore corresponds to expulsion of CH_3N from the molecular ion. Similar rearrangement reactions have been reported to occur in other heterocyclic systems containing a dimethylamino substiuent (8,9). Formation of the m/e 277 ion necessitates a loss of $C_2H_7N_2$ from the parent molecule (calculated for $C_{15}H_{13}N_6$: 277.1201; observed: 277.1209) and thereby requires a rearrangement mechanism possibly involving migration of the dimethylamino moiety to a ring nitrogen atom.

Another interesting rearrangement was uncovered in the mass spectrum of the diphenylamino compound IV (Figure 4). The peak at m/e 343 arises by loss of a $C_7H_5N_2$ fragment as judged by high resolution data (calculated for $C_{20}H_{19}N_6$: 343.1671: observed: 343.1662) and must therefore involve transfer of a phenyl group. A plausible mechanism is shown below. Thus, 1,3-phenyl migration with concerted ring opening followed by cleavage α to the charge-bearing nitrogen atom results in the stable even electron ammonium ion *q* at m/e 343.



q, m/e 343

A peak at m/e 292, formed by loss of the C-6 substituent of the triazine ring, is present in the mass spectra of compounds III and IV. Both the dimethylamino (III) and diphenylamino (IV) derivatives afford an ion at m/e 250. The composition of the latter was established by high resolution measurements as $C_{14}H_{12}N_5$ (calculated: 250.1093; observed: 250.1096). A plausible mechanism can be represented by two successive hydrogen transfer with ring opening steps to afford the species *r*, the latter undergoing α-cleavage to the resonance stabilized immonium ion *s*, for which one resonance form is drawn.



s, m/e 250 *r*

Conclusions.

The mass spectra of 6-substituted-2,4-*bis*-(*m*-aminoanilino)-*s*-triazines exhibit intense molecular ions, abundant M-H peaks and weaker peaks incorporating the C-6 and arylamino substituents. Fragmentation pathways are initiated by simple cleavage of the arylamino substituent and by opening of the *s*-triazine ring, with and without hydrogen transfer, and do not require the intervention of an amino ⇋ imino tautomerization of the molecular ion prior to the fragmentation sequence.

Rearrangement reactions involving methyl and phenyl migration occur during the fragmentation of the dimethylamino (III) and diphenylamino (IV) derivatives, respectively.

EXPERIMENTAL

Mass spectra were determined by Mr. E. Gessler with an MS-902 mass spectrometer. Samples were analyzed with a direct insertion probe at a temperature close to their melting points and at an ionizing current of 70eV. Elemental compositions were obtained by the peak matching method for selected ions in a spectrum or by an automated data processing system utilizing an IBM 1800 computer for complete high resolution analysis of an entire spectrum.

2,4-*bis*-(*m*-Aminoanilino)-*s*-triazine (I).

To a solution of 15.5 g. (0.04 mole) of 2,4-*bis*-(*m*-nitroanilino)-6-chloro-*s*-triazine (10) and 4.04 g. (0.04 mole) of triethylamine in 200 ml. of THF was added 10 g. of 5% Pd/C. The mixture was hydrogenated overnight at 50 psi, and then filtered. The residue was washed with 400 ml. of THF and then with water until chloride free. These washings were discarded, and the residue washed with

DMF until the filtrate was colorless. The DMF solution was added to 1 l. of water to precipitate the product. After isolation by filtration, the product was washed with water, and then purified by washing with 200 ml. of boiling acetone, yield 8.20 g. (70%), m.p. 269-271°.

Anal. Calc. for $C_{15}H_{15}N_7$: C, 61.40; H, 5.16; N, 33.44. Found: C, 61.16; H, 5.17; N, 33.24.

2,4-*bis*-(*m*-Aminoanilino)-6-amino-*s*-triazine (II).

To a stirred mixture of 108.0 g. (1.0 mole) of *m*-phenylenediamine and 21.2 g. (0.20 mole) of sodium carbonate in refluxing dioxane (200 ml.) under nitrogen was added dropwise over a 4.5 hour period, a solution of 16.9 g. (0.10 mole) of 2-amino-4,6-dichloro-*s*-triazine (11) in dioxane (250 ml.). After refluxing for an additional 6 hours, the mixture was poured into 1 l. of ice water. The resulting gummy material was removed, triturated with water and filtered. On standing, 18.8 g. of solid crystallized from the filtrate. Recrystallization from 2-propanol gave 10.4 g. (34%) of product, m.p. 198-200°.

Anal. Calcd. for $C_{15}H_{16}N_8$: C, 58.44; H, 5.19; N, 36.36. Found: C, 58.72; H, 5.35; N, 36.30.

2,4-*bis*-(*m*-Aminoanilino)-6-dimethylamino-*s*-triazine (III).

Compound III was prepared following the procedure described for II from 108.0 g. (1.0 mole) of *m*-phenylenediamine, 21.0 g. (0.20 mole) of sodium carbonate and 19.3 g. (0.10 mole) of 2-dimethylamino-4,6-dichloro-*s*-triazine (12). The crude product was isolated by filtering the solid obtained by pouring the reaction mixture into ice water. After washing chloride free with water, the residue was washed with 2 x 300 ml. of methanol in an electric blender to give 28.1 g. (84%), m.p. 195-198°. Recrystallization from acetonitrile gave a m.p. of 196-198°; a mixed m.p. with an analytical sample of III gave no depression. The ir spectrum was identical to the spectrum of authentic III.

2,4-*bis*-(*m*-Aminoanilino)-6-diphenylamino-*s*-triazine (IV).

Compound IV was prepared following the procedure for II from 432.0 g. (4.0 mole) of *m*-phenylenediamine, 84.8 g. (0.80 mole) of sodium carbonate and 126.8 g. (0.40 mole) of 2-diphenylamino-4,6-dichloro-*s*-triazine (11). However, the reaction mixture was refluxed overnight before working up the reaction. The crude product (181.0 g.) was stirred in 1.8 l. of refluxing acetone for 30 minutes and filtered. The acetone was stripped from the filtrate leaving 158.7 g. of solid. Recrystallization from 350 ml. of dioxane and 800 ml. of benzene (Darco) gave 102.8 g. (51%) of pure product, m.p. 138-142°. Compound IV was isolated as a 1:1 complex with dioxane.

Anal. Calcd. for $C_{31}H_{32}N_8O_2$: C, 67.86; H, 5.88; N, 20.42. Found: C, 67.67; H, 5.93; N, 20.32.

Compound IVa.

Three hundred mg. of *m*-phenylenediamine was refluxed in 20 ml. of deuterium oxide for 24 hours. The deuterium oxide was removed using a Rinco Evaporator. The residue, deuterated *m*-phenylenediamine, was reacted with 2-diphenylamino-4,6-dichloro-*s*-triazine as indicated above. Deuterium bound to nitrogen atoms was removed during the work-up procedure, *i.e.* pouring the reaction mixture into water.

Anal. Mass Spectrum: 2% d_2, 6% d_3, 12% d_4, 20% d_5, 31% d_6, 17% d_7, 9% d_8, 3% d_9.

2,4-*bis*-(*m*-Aminoanilino)-6-phenyl-*s*-triazine (V).

Compound V was prepared following the procedure described for II from 86.0 g. (0.80 mole) of *m*-phenylenediamine, 25.0 g. (0.23 mole) of sodium carbonate and 18.0 g. (0.23 mole) of 2-phenyl-4,6-dichloro-*s*-triazine (13). The crude product (30.0 g.) was recrystallized from 2-propanol to give 16.5 g. (56%), m.p. 176° dec.

Anal. Calcd. for $C_{21}H_{19}N_7$: C, 68.29; H, 5.18; N, 26.55. Found: C, 68.38; H, 5.04; N, 26.27.

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