ARTICLE INFO
Received 29 June 2023
Accepted 03 August 2023
Available online August 2023

DECAY SEQUENCES - IONIC SERIES OF MASS SPECTRA FOR
2,4,6-TRIS(PERFLUOROALKYL)-1,3,5-TRIAZINES

N. D. Kagramanov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
119991, GSP-1, Moscow, B-334, Vavilov St. 28
e-mail: ndkagram@gmail.com

Abstract: This report presents the ion series of mass spectra for eight homologues of
2,4,6-tris(perfluoroalkyl)-1,3,5-triazines from NIST libraries, including the ion series of two isomers:
triazine \((C_3F_7)_3C_3N_3\) with symmetrical substituents \(C_7F_15\) and triazine \((CF_3)_2C_3N_3(C_7F_15)\) with
unsymmetrical substituent \(C_7F_15\). The influence of molecular weight of substituents and their
symmetry on fragmentation of 1,3,5-triazines is discussed. Using \([(CF_3)_3CO]_3C_3N_3\) homologue with
oxaperfluoroalkyl substituents as an example, the effect of \((CF_3)_3C\) groups and oxygen atoms on
fragmentation is discussed.

Keywords: 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines, ion series of mass spectra, effect of molecular
weight of substituents and their symmetry on peak intensities of fragment ions.

Ionic series of mass spectra for 2,4,6-trifluoro-1,3,5-triazine and 1,3,5-triazine

The first triazine homologues - 1,3,5-triazine and 2,4,6-trifluoro-1,3,5-triazine - are trimers of
HCN [1] and, respectively, FCN [2]. Its ionic series are presented separately from other homologues,
since it reflects the decays of triazine rings, not complicated by fragmentation of perfluoroalkyl
substituents, which have large masses. Figs. 1 and 2 show the ion series of mass spectra for
1,3,5-triazine and 2,4,6-trifluoro-1,3,5-triazine.

In Fig. 1 the main ionic series of trifluorotriazine is marked with red lines, and two side
series - with dotted lines.
In Fig. 2 the main ionic series of 1,3,5-triazine is marked with blue line, and the side fragmentation series - with dotted lines.

Unlike two consecutive emissions of \( \cdot F \) and \( \cdot CN \) occurring during decomposition of fluorine-substituted triazine cycle (see Fig. 1), the fragmentation of molecular \( ^*\cdot M \) radical cation of hydrogen-substituted cycle (see Fig. 2) occurs in three parallel ways, namely with detachments of HCN, NCN and NCHN.
The intensities of peaks for trimeric, dimeric and monomeric ions in the spectra of 1,3,5-triazine and 2,4,6-trifluoro-1,3,5-triazine have similar values (see Table 1).

<table>
<thead>
<tr>
<th>Ion</th>
<th>MW</th>
<th>Percent</th>
<th>Ion</th>
<th>MW</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_3\text{H}_3\text{N}_3]^+)</td>
<td>81</td>
<td>100%</td>
<td>([\text{C}_3\text{F}_3\text{N}_3]^+)</td>
<td>135</td>
<td>100%</td>
</tr>
<tr>
<td>([\text{C}_2\text{H}_2\text{N}_2]^+)</td>
<td>54</td>
<td>75%</td>
<td>([\text{C}_2\text{F}_2\text{N}_2]^+)</td>
<td>90</td>
<td>55%</td>
</tr>
<tr>
<td>([\text{HCN}]^+)</td>
<td>27</td>
<td>42%</td>
<td>([\text{FCN}]^+)</td>
<td>45</td>
<td>35%</td>
</tr>
</tbody>
</table>

In NIST library#: 284289 ID#: 17428 DB: mainlib also presents the mass spectrum of (E)-2,3-difluoroprop-2-ennitrile, which is a formal dimer of FCN.

Figure 3. Mass spectrum of ion series for (E)-2,3-difluoroprop-2-ennitrile, MW:90 \(\text{C}_2\text{F}_2\text{N}_2\)

NIST#: 284289 ID#: 17428 DB: mainlib.

The peak intensity of molecular ion for such a dimer (m/z 90) is (92%), and the peak intensity of monomeric ion \([\text{FCN}]^+\) (m/z 45) is (100%).
Ionic series of mass spectra of homologues of 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines

Fig. 4 shows the ion series of the mass spectrum of 2,4,6-tris(trifluoromethyl)-1,3,5-triazine.

![Figure 4. Ion series of the mass spectrum for 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, C_6F_9N_3 MW: 285 NIST#: 13755 ID#: 36197 DB: mainlib.](image_url)

As a result of successive detachments of fluorine atom and ·CF_2CN, [CF_3(CN)_2CF_3]^+ dimeric ion with m/z 190 (38%) appears. Surprisingly, the intensities of +M, +M·F and -CF_2CN peaks do not change and are equal to 37-38%. At the next detachment, the ion-monomer [CF_3CN]^+ with m/z 95 is not formed. The ejection of ·CF_3 leads to the ion with m/z 121, which loses a fluorine atom, turning into +C_3F_2N_2 with m/z 102. As a result, instead of monomeric ion, the +CF_2CN ion with m/z 76 (50%) appears. Peaks of ions with m/z 69 +CF_3 (100%), 50 +CF_2 (35%) and 31 +CF (23%) result from decay of ions with m/z 121 and m/z 76 (marked with red dotted lines).

Fig. 5 shows the ion series of mass spectrum for 2,4,6-tris(pentafluoroethyl)-1,3,5-triazine.
As a result of detachments of F and CF₂, the first intense peak of spectrum appears with m/z 366 (C₂F₅)₂[C₃N₃]+CF₂ (77%). Subsequent ejections of CF₂ and CN are completed by dimeric ion +[(C₂F₅)(CN₂C)C₂F₅] with m/z 290 (1%).

The ion with m/z 290 ejects F and CF₂ with formation of C₂F₅(C₂N₂)+CF₂ ion weak peak with m/z 221 (1%). The ion with m/z 221 fragments both by successive detachments of CF₂ and F, and F and CF₂, forming a radical cation with m/z 152 (3%). However, the detachment from the ion with m/z 221 with only CF₂ (without F radical) leads to a peak (with medium intensity) of C₂F₅-CN⁺ ion with m/z 171 (22%).

The ion with m/z 171 fragments in two ways. As a result of detachment of F, CN and CF₂ atoms from it, the base peak of mass spectrum with m/z 76 appears. As a result of ejection of ethanedicarbonitrile NC-CN molecule, the +C₂F₅ ion, its fragment ion +CF₃ and so the +C₂F₄ and +CF₂ ions (marked with red dotted line) are formed (marked with a red dotted line).

Figure 6 shows the ion series of mass spectrum of symmetrical (relative threefold symmetry axis) 2,4,6-tris(heptafluoropropyl)-1,3,5-triazine.
The ionic series C$_{12}$F$_{21}$N$_3$ (see Fig. 6) are similar to C$_9$F$_{15}$N$_3$ series (see Fig. 5).

As a result of detachment of F and C$_2$F$_4$, the first intense peak appears with m/z 466 (C$_3$F$_7$)$_2$[C$_3$N$_3$]$^+$/CF$_2$ (70%). It fragments in two ways. Detachment from the ion with m/z 466 (-2 CF$_2$) leads to ion with m/z 366 (3%), forming a series of ions: with m/z 176 (3%), 126 (7%) and 76 (83%) (marked with blue lines).

As a result of detachment of rearrangement molecule (-$^+$CF$_2$=C=NF) from the ion with m/z 466, the ion with m/z 371 (2%) appears. It fragments with ejection of -C$_3$F$_6$, forming the C$_3$F$_7$-CN$_2$+$^+$C ion with m/z 221 (5%). The ion with m/z 221 fragments to form both a perfluoroallyl ion with m/z 131 (2%) and a series of perfluoroalkyl ions ending in $^+$CF$_3$ base ion (marked with red lines).

Fig. 7 shows the ion series of mass spectrum for asymmetric (relative first-order symmetry axis) 2-perfluoroheptyl-4,6-bis(trifluoromethyl)-1,3,5-triazine.
The ionic series of unsymmetrical homologue C$_{12}$F$_{21}$N$_3$ (see Fig. 7) differ from those of symmetrical triazine C$_{12}$F$_{21}$N$_3$ (see Fig. 6). The molecular radical cation (see Fig. 7) fragments in two ways. Upon detachment of rearrangement radical (CF$_2$)$_2$N, the rearrangement ion appears with m/z 471 (5%), which retains the C$_7$F$_{15}$ substituent. The subsequent ejection of C$_4$F$_8$ leads to formation of the ion +C$_6$F$_8$N$_2$ with m/z 271 (1%), which fragments both with formation of a series of perfluoroalkyl ions +C$_3$F$_7$, +C$_2$F$_5$ with the base peak +CF$_3$, and the series of perfluoroalkenyl ions with perfluoroallyl ion +C$_3$F$_5$ (m/z 131) (22%) (marked with red lines). Another way of M$^+$ fragmentation includes the detachment of fluorine atom and subsequent ejections of +C$_5$F$_{10}$ and CF$_2$ with formation of intense ion peak with m/z 266 (97%). Detachment of -CF$_2$CN from the ion with m/z 266 (as it happens in spectrum of (CF$_3$)$_3$C$_3$N$_3$, where the intensity of peak with m/z 266 is only 38%, see Fig. 4), does not occur in spectrum of unsymmetrical isomer (see Fig. 7). As a result, the dimeric ion [CF$_3$(CN)$_2$CF$_3$]$^+$ with m/z 190 is not formed.

The ion with m/z 266 (100%) (see Fig. 7) rejects -CF$_2$CN and -CF$_2$ (Σ-140), turning into C$_3$F$_4$N$^+$ ion with m/z 126 (7%) and fragment ion +CF$_2$CN with m/z 76 (41%).

Fig. 8 shows the ion series of mass spectrum for 2,4,6-tris(perfluoro-tert-butoxy)-1,3,5-triazine C$_{15}$F$_{27}$O$_3$, the compound with three substituents -OC(CF$_3$)$_3$ (m/z 235).
After primary detachment of fluorine atom, the $^+\text{C}_{15}\text{F}_{26}\text{O}_3$ ion with m/z 764 (98%) ejects OC$_4$F$_8$, losing one of the three OC(CF$_3$)$_3$ substituents and turning into [(CF$_3$)$_3$CO]$_2$C$_2$N$_3$+$^+\text{C}$ ion with m/z 548 (55%).

The loss of $^·\text{OC(CF}_3)_3$ substituent also occurs in three successive detachments: $^-\text{CF}_3$, $^-\text{CF}_3\text{CO}$ and $^·\text{CF}_3$ (marked with dotted blue lines).

The ion with m/z 548 fragments in three ways:

- with detachment of second substituent together with CN group of triazine ring of (CF$_3$)$_3$COCN molecule, turning into the ion with m/z 287(100%);
- with detachment of $^-\text{C}_4\text{F}_9$ from second substituent, and $^-\text{F}$ atom from third substituent, turning into the ion with m/z 310 (8%);
- with detachment of $^·\text{CF}_3$ and O-C$_3$N$_2$ group of triazine ring or F$_3$COC$_3$N$_2$ rearrangement molecule (marked with dotted red lines), forming the ion with m/z 399 (12%).

The ion with m/z 287 (100%) fragments as if with ejection of C$_4$F$_6$N$_2$ (-190) rearrangement molecule, turning into CF$_3^+$C=O ion with m/z 97(12%), which is characteristic of spectra for polyoxaperfluoroalkanes [3] (marked with dotted red lines), and with detachment of CN$_2$C=O molecule and two fluorine atoms, turning into rearrangement ion CF$_3$-CF=$^+$CF with m/z 181 (4%).

Fragmentation of ion with m/z 181 yields an analogue of CF$_3$-CF=$^+$CF perfluoroallyl ion with m/z 131 (45%) and its fragment ion $^+$CF$_3$ (90%).
The ion with m/z 310 fragments with detachment of OC$_4$F$_8$, forming the ion with m/z 94 (32%) with CsN$_3$O triazine ring containing an additional oxygen atom. The ion with m/z 94 fragments with detachment of CN and formation of C$_2$N$_2$O ion with m/z 68 (10%).

The ion with m/z 399 fragments with ejection of (CF$_3$)$_2$C=N-OCF$_3$ molecule and formation of perfluoroolefin ions, i.e. $^+$C$_3$F$_6$ and $^+$C$_2$F$_4$ (marked with red dotted lines).

Fig. 9 shows the ion series of mass spectrum for 2,4,6 tris(pentadecafluoroheptyl)-1,3,5-triazine.

![Figure 9. Mass spectrum of ion series for 2,4,6-tris(pentadecafluoroheptyl)-1,3,5-triazine](image)

As a result of primary detachment of fluorine atom and subsequent ejections of six CF$_2$ groups, the first intense peak of triazine ion with m/z 866 (62%) with two C$_7$F$_{15}$ substituents and one $^+$CF$_2$ group is formed. The ion with m/z 866 fragments in three ways (marked in Fig. 9 with dotted lines), with formation of three ionic series.

The first way of fragmentation of the ion with m/z 866 begins with ejection of C$_4$F$_8$ molecule from second substituent C$_7$F$_{15}$, which has not yet fragmented, to form the ion (C$_7$F$_{15}$)(C$_3$F$_7$)[C$_3$N$_3$]$^+$CF$_2$ with m/z 666 (1%).

The second way of fragmentation of the ion with m/z 866 is detachment of $^+$CF$_2$CN (with ring break and detachment of CN) from the first already fragmented substituent and additional ejection of the $^+$F atom from second substituent, or ejection of CF$_2$C=NF or CF$_3$CN molecule with formation of rearrangement ion with m/z 771 (12%). The additional detachment of $^+$F atom probably comes from...
CF₂ group of C₇F₁₅ substituent, which is directly linked to fragmenting triazine ring. The subsequent ejection of -CF₂ ends with C₇F₁₅(C₃N₃)(C₃F₆CF₂)*CF₂ ion with m/z 721(1%).

The third way of fragmentation of ion with m/z 866 is detachment of fluorine atom from second, not yet fragmented substituent, with formation of radical C₇F₁₅(C₃N₃)(C₆F₁₂CF₂)(*CF₂) with m/z 847 (0.5%). The next detachment of C₃F₆ molecule probably also occurs from the second one, which began to fragment the C₆F₁₂CF₂ substituent. Detachment of C₃F₆ also leads to radical cation C₇F₁₅(C₃N₃)(C₃F₆CF₂)⁺CF₂ with m/z 697 (0.1%).

The ion with m/z 666 (C₇F₁₅)(C₃F₇)[C₃N₃]*CF₂ (first way) after detachment of two CF₂ groups, is formed by (C₇F₁₅)(CF₃)[C₃N₃]*CF₂ ion with m/z 566 (4%). The ion with m/z 566 fragments with ejection of CF₂CN (-90) molecule and detachment of C₃F₄, turning into C₃F₁₁C*NCCF₃ ion, which rearranges into *CF₂C₆F₁₂CN ion with m/z 376 (8%). The series of six further CF₂ detachments: (326, 276, 226, 176) is completed by *CF₂CN ion with m/z 76 (11%).

The ion with m/z 721(1%) (second way) ejects the C₅F₁₀ (-250) molecule turning into *CF₂(CN₂C)(CF₂)ₐCF₃ ion with m/z 471 (12%). The next detachment of CF₂ gives rise to the ion with m/z 421 (1%), which fragments in two ways: both with ejection of cyanogen NC-CN and formation of *C₃F₇ ion with m/z 369 (1%), a series of perfluoroalkyl ions, with detachment of *CF₂CN₂, leading to *C₇F₁₃ ion with m/z 331(1 %) and series of perfluoroalkenyl ions, the most intense peak of which is the peak of perfluoroallyl ion CF₂=CF⁻*CF₂ with m/z 131 (21%).

The cation-radical with m/z 697 (0.1%) (third way) C₇F₁₅(C₃N₃)(C₃F₆CF₂)*CF₂ ejects four CF₂ groups, transforming it into cation-radical C₇F₁₅[CN-CNCN]*CF₂ 497 (1%). The detachment of *CF₂CN (-76) with breakdown of triazine ring terminates C₇F₁₅[CN₂*C] ion with m/z 421 (1%), which fragments in two ways, which we have considered above.

Fig. 10 shows the ion series of mass spectrum for 2,4,6-tri-(perfluorononyl)-1,3,5-triazine C₃₀F₅₇N₃. Like C₂₄F₄₅N₃ homologue (see Fig. 9).

The spectrum of C₃₀F₅₇N₃ consists of three ionic series: perfluoroalkyl ion series *CF₃ with m/z 369-69, CF₂=CF-*CF₂ perfluoroalkenyl ion series with m/z 381-131 and *CF₂ (CF₂)ₐCN ion series with m/z 476-76. Its difference is that the peak intensities of perfluoroalkyl ions and *CF₂CN ion series in C₃₀F₅₇N₃ spectrum (see Fig. 10) are one and a half times weaker than in C₂₄F₄₅N₃ spectrum (see Fig. 9), while the peak intensities of its perfluoroalkenyl series are the same.
Figure 10. Mass spectrum of ion series for 2,4,6-tris(perfluoronyl)-1,3,5-triazine $C_{30}F_{57}N_3$ MW: 1485 ID#: 391974 DB: wiley_nist98.

Detachment of fluorine atom from first intense ion with m/z 866, which occurs in spectrum of $C_{24}F_{45}N_3$ (see Fig. 9), does not occur (or does not appear) in spectrum of $C_{30}F_{57}N_3$ (see Fig. 10) with m/z 1066 -F.

Conclusions

A review of ion series of mass spectra for 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines allows us to compare the primary processes of its fragmentation, as well as the intensities of resulting peaks, depending on substituents of triazine ring and its molecular weights.

Fig. 11 shows: the intensities graph of molecular peaks $^+M$ of triazine homologues (marked with red dotted lines), the graph of $^+M$-F peaks (marked with blue dotted lines), as well as the graph of first intense fragment peaks after the ejection of fluorine atom (marked with green dotted lines).
Figure 11. Intensity graph of triazine homologue molecular ion peaks, +M-F peaks and first intense fragment peaks.

The graphs of primary detachments in spectra of two C_{12}F_{21}N_{3} isomers with m/z 585 differ in color: the graph of symmetric isomer (C_{3}F_{7})_{3}C_{3}N_{3}, like all graphs of symmetric isomers, is marked with blue lines). The plot of unsymmetrical (CF_{3})_{2}C_{3}N_{3}(C_{7}F_{15}) isomer is marked with purple lines.

With rising in molecular weight of homologue (i.e. in total mass of substituents in triazine ring), the intensity of molecular ion peak decreases from 100% for C_{3}F_{3}N_{3} to 2% for C_{7}F_{15})_{3}C_{3}N_{3}. However, for (C_{9}F_{19})_{3}C_{3}N_{3} homologue, the intensity of molecular ion peak increases to 6% (marked with red dotted lines in Fig. 11).

During ionization, the peak of +C_{3}F_{3}N_{3} molecular ion (which has a minimum mass of 135 a.m.u.) acquires the maximum energy and maximum intensity. However, detachment of one fluorine atom from +C_{3}F_{3}N_{3} leads to a sharp decrease in peak intensity of +M-F with m/z 116 (13%). The reason for destabilization of triazine cycle is the loss of one of three symmetrical fluorine atoms. The next ejection of CN radical leads to formation of a stable symmetrical dimer +[FCNNCF] with m/z 90 (55%).

The peak intensity of molecular ion +[(CF_{3})_{3}[C_{3}N_{3}]] with a mass of 285 a.m.u., 2.1 times greater than that of +C_{3}F_{3}N_{3}, decreases in 2.7 times to 37%. However, when a fluorine atom is detached from +[(CF_{3})_{3}[C_{3}N_{3}]], the intensity of resulting +M-F peak remains at level of 37% and only slightly increases to 38% upon detachment of CF_{2}CN and in appearance of dimeric ion CF_{3}+(C_{2}N_{2})CF_{3}. For homologs of (C_{2}F_{5})_{3}C_{3}N_{3} and (C_{3}F_{7})_{3}C_{3}N_{3} (C_{2}F_{5}) the intensity of +M-F peak decreases from 30% to 17%. It remains constant at 17%-18% for homologue (C_{7}F_{15})_{3}C_{3}N_{3}. 
After detachment of fluorine atom from \(^{+}(C_{9}F_{19})_{3}C_{3}N_{3}\) with molecular weight of 1485 a.m.u. (see Fig. 11) there is unprecedented increase in peak intensity \(^{+}M-F\) with m/z 1466 (51%) - three times greater than that of \((C_{7}F_{15})_{3}C_{3}N_{3}\) homologue. It is possible that this is the result of threefold increase in intensity of \(^{+}(C_{9}F_{19})_{3}C_{3}N_{3}\) molecular ion peak (6%) compared to (2%) for \((C_{7}F_{15})_{3}C_{3}N_{3}\) molecular peak with m/z 1166. After appearance of M–F peaks the possibility of subsequent stabilizing detachments of CF\(_{2}\) is realized, up to formation of most intense peaks of fragment ions with two initial substituents and one \(^{+}CF_{2}\) group. With successive detachments of CF\(_{2}\), the insignificant successive increase in peaks of emerging ions occurs. However, only the final ejection of CF\(_{2}\) with formation of ion with two initial triazine ring substituents and one \(^{+}CF_{2}\) group leads to the first intense fragmentary peaks.

Comparison of \(^{+}M\) peaks intensities of two isomers (symmetric \((C_{3}F_{7})_{3}[C_{3}N_{3}]\) (9%) and unsymmetrical \((CF_{3})_{2}[C_{3}N_{3}](C_{7}F_{15})\) (0%)) allows us to conclude that, in contrast to \(^{+}M\) symmetrical isomer, the \(^{+}M\) of unsymmetrical isomer with substituent C\(_{7}F_{15}\) is unstable (0%).

The minimum difference between the masses of its C\(_{3}F_{7}\) and CF\(_{3}\) substituents is 100 a.m.u., and the maximum difference between the masses of C\(_{3}F_{7}\) and C\(_{7}F_{15}\) is 200 a.m.u. for C\(_{4}F_{8}\).

In mass spectra of \((C_{2}F_{5})_{3}[C_{3}N_{3}]\) with m/z 435, \((C_{4}F_{7})_{3}[C_{3}N_{3}]\) with m/z 585, as well as in mass spectra of unsymmetrical isomer \((CF_{3})_{2}[C_{3}N_{3}](C_{7}F_{15})\) with m/z 585 after detachment of fluorine atom and ejection CF\(_{2}\), C\(_{2}F_{4}\), and, accordingly, C\(_{5}F_{10}\) +CF\(_{2}\) molecules, the first intense peaks of stable fragment ions appear: with m/z 366 (77%), m/z 466 (70%) and m/z 266 (97% ) with two symmetrical substituents and one \(^{+}CF_{2}\) group. The maximum intensity of 97% (stability) is acquired by peak of the \((CF_{3})_{2}[C_{3}N_{3}]^{+}CF_{2}\) ion with a minimum mass of m/z 266, which occurs during fragmentation of asymmetric isomer \((CF_{3})_{2}[C_{3}N_{3}](C_{7}F_{15})\) with m/z 585. That is, with the same molecular weight of two isomers with different substituents of triazine ring, it is precisely the minimum mass of fragment ion with m/z 266 a.m.u. corresponds to maximum intensity of emerging peak (97%). The lower a molecular weight of fragment ion with two initial substituents and one \(^{+}CF_{2}\)group, the greater a peak intensity of its fragment ion. Decreasing the intensities of first fragment peaks with m/z 366 (77%), 466 (70%) and 866 (62%) correspond to detachments of increasing masses: CF\(_{2}\) (50), C\(_{2}F_{4}\) (100) and C\(_{5}F_{10}\) +CF\(_{2}\) (300) (see Fig. 11). However, the dependence graph is disturbed by the peak of fragment ion with m/z 1066 (100%), since expected decrease in its intensity (by analogy with fragment ions of other homologues) does not occur. The peak intensity of fragment ion \(^{+}M-F\) with m/z 1466 (51%), which is three times higher than peak intensity of \(^{+}M-F\) with m/z 1166 (18%), seems strange at first glance.

However, this increase in intensity is probably the result of threefold increase in intensity of peak for molecular ion \((C_{9}F_{19})_{3}^{+}[C_{3}N_{3}]\) (6%) compared to peak intensity of molecular ion
(C\textsubscript{7}F\textsubscript{15})\textsuperscript{3+}C\textsubscript{3}N\textsubscript{3}) (2\%). The reason for intensity increasing of molecular peak with m/z 1485 a.m.u. there may be an increase in its effective ionization cross section compared to homologue with m/z 1185.

In spectra of homologues C\textsubscript{24}F\textsubscript{45}N\textsubscript{3} and C\textsubscript{30}F\textsubscript{57}N\textsubscript{3} after detachment of fluorine atom, only the ejection of six CF\textsubscript{2} groups and, accordingly, the ejection of C\textsubscript{2}F\textsubscript{4} and six CF\textsubscript{2} groups leads to intense peaks of fragment ions with two symmetrical substituents and one CF\textsubscript{2} group: ((C\textsubscript{7}F\textsubscript{15})\textsubscript{2}C\textsubscript{3}N\textsubscript{3})\textsuperscript{+} CF\textsubscript{2} with m/z 866 (62\%) and (C\textsubscript{9}F\textsubscript{19})\textsubscript{2}C\textsubscript{3}N\textsubscript{3}\textsuperscript{+} CF\textsubscript{2} with m/z 1066 (100\%). The increase in peak intensity with m/z 1066 (100\%) compared to intensity of peak at m/z 866 (62\%) is the result of difference in intensities of its molecular and fragment peaks +M-F. Ions with intense peaks are fragmented in several ways, which leads to branching of ionic series.

The branching of ionic series of fragment ions is apparently the result of variants of its isomerization that are close in energy.

In most of presented spectra, the branching of ionic series begins only after detachment of one of triazine ring substituents. The exceptions are: the mass spectrum of triazine with unsymmetrical substituent (CF\textsubscript{3})\textsubscript{2}C\textsubscript{3}N\textsubscript{3}(C\textsubscript{7}F\textsubscript{15}), as well as the mass spectrum of triazine (C\textsubscript{4}F\textsubscript{9}O)\textsubscript{3}C\textsubscript{3}N\textsubscript{3} with three OC(CF\textsubscript{3})\textsubscript{3} groups. In its spectra, the branching of ion series begins immediately upon fragmentation of molecular ions. This may also be the result of isomerization of its +M. Reliable examples of isomerization of molecular ion are: five ion series of benzene spectrum, resulting from rearrangement of its carbon backbone, in accordance with five variants of \(\pi\)-conjugations, eight ion series of 1,3,5,7-cyclooctatetraene and 15 ion series of 18-annulene [4].

It should be noted that peak intensities graph of mass spectrum (C\textsubscript{4}F\textsubscript{9}O)\textsubscript{3}C\textsubscript{3}N\textsubscript{3} (see Fig. 11), as it were, falls out of the graphs of triazines that do not contain oxaperfluoroalkyl groups.

The intensity of peak of (C\textsubscript{4}F\textsubscript{9}O)\textsubscript{3}C\textsubscript{3}N\textsubscript{3} molecular ion with m/z 783 (42\%) is higher than the intensity of peak of (CF\textsubscript{3})\textsubscript{3}C\textsubscript{3}N\textsubscript{3} molecular ion with m/z 285 (37\%), but less than that for C\textsubscript{3}F\textsubscript{3}N\textsubscript{3} with m/z 135 (100 \%). In contrast to linear perfluoroalkyl substituents, three OC(CF\textsubscript{3})\textsubscript{3} groups probably promote more efficient ionization processes and redistribution of excitation energy. The efficiency of ionization and transfer of excitation energy depends on effective ionization cross section of molecule, but its determination requires special equipment [5].

In (C\textsubscript{4}F\textsubscript{9}O)\textsubscript{3}C\textsubscript{3}N\textsubscript{3} spectrum, the detachment of fluorine atom leads to a sharp increase in intensity of +M-F peak (98\%). There is no such intense +M-F peak in spectra of any considered homologues.

It is possible that such stabilization, which occurs when a fluorine atom is detached, is associated either with increase in effective ionization cross section of molecule, or with appearance of interaction between the +CF\textsubscript{2} terminal group and oxygen atom of substituent. This is indicated by
ejection of OC₄F₈ molecule, although successive but less intense detachments also occur along with CF₂, CF₃C=O and CF₃. As a result, the ion (C₄F₉O)₂⁺C₃N₃ with m/z 548 (55%) appears with preserved triazine cycle (see Fig. 8). Its analogs are the low-intensity peak (C₂F₅)₂⁺C₃N₃ with m/z 316 (0.2%), mass-spectrum of (C₃F₇)₃⁺C₃N₃ and (C₃F₇)₂⁺C₃N₃ peak with m/z 416 (1%) of symmetrical (C₃F₇)₃⁺C₃N₃ mass spectrum. The *CF₂CN ion with m/z 76, characteristic for spectra of triazines with perfluoroalkyl substituents that do not contain oxygen atoms, is not formed in spectrum of C₁₅F₂₇N₃O₃.

**Acknowledgements**

This work was supported by the Ministry of Science and Higher Education of the Russian Federation and was performed employing the equipment of Center for Molecular Composition Studies of INEOS RAS.

**References**