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**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*

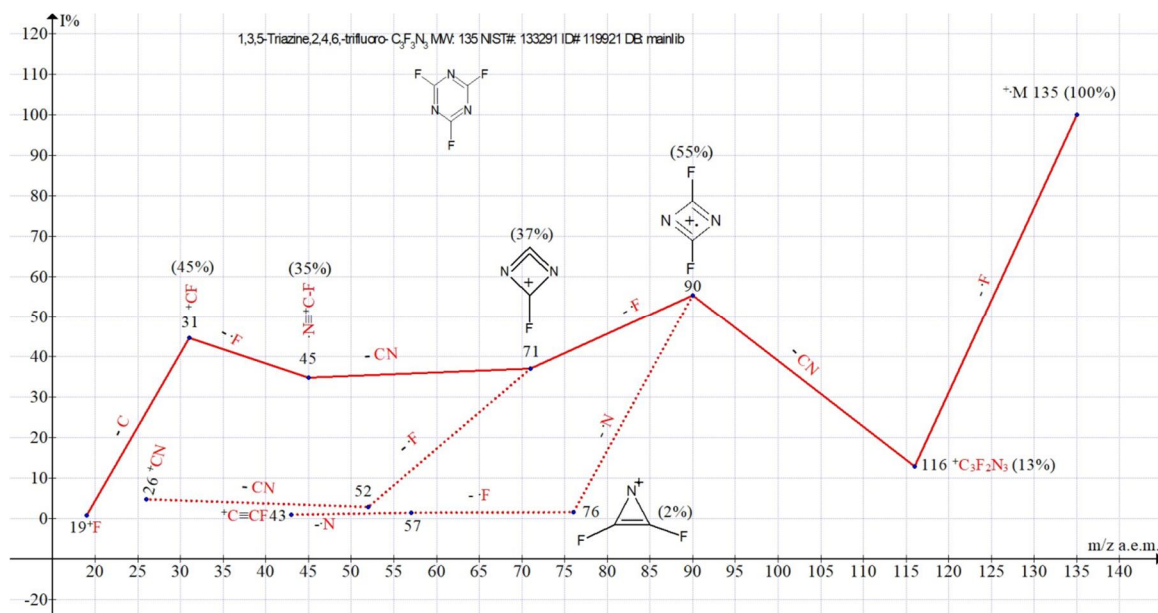
**Abstract:** This report presents the ion series of mass spectra for eight homologues of 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines from NIST libraries, including the ion series of two isomers: triazine  $(C_3F_7)_3C_3N_3$  with symmetrical substituents  $C_3F_7$  and triazine  $(CF_3)_2C_3N_3(C_7F_{15})$  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.

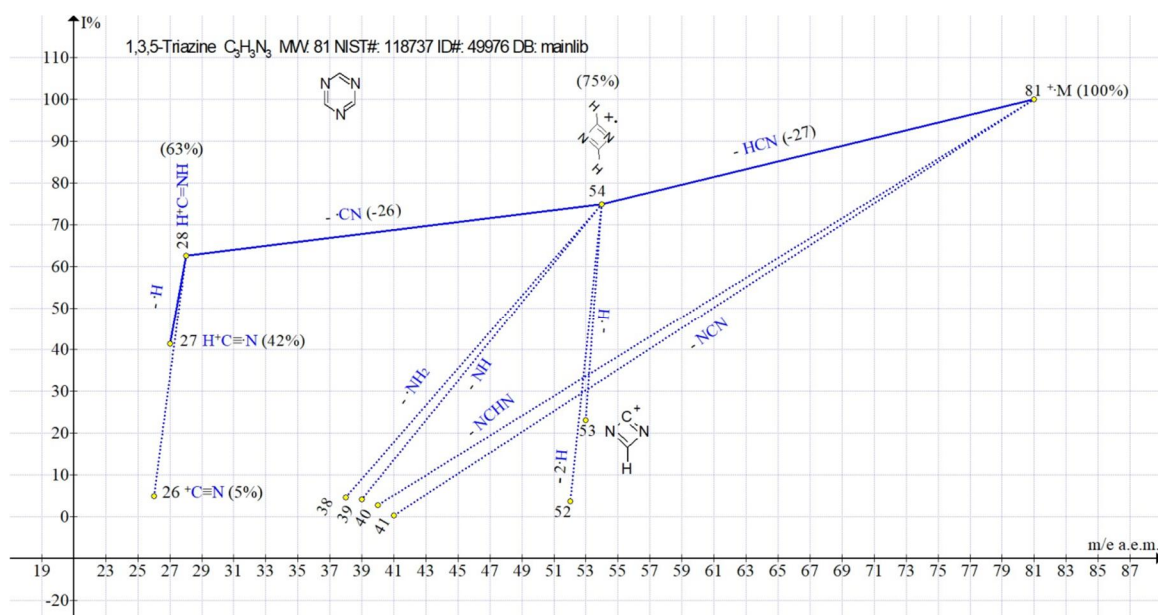
**Ionic series of mass spectra for 2,4,6-trifluoro-1,3,5-triazine and 1,3,5-triazine**

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.



**Figure 1.** Mass spectrum of ion series for 2,4,6-trifluoro-1,3,5-triazine,  $C_3F_3N_3$  MW: 135 NIST#: 133291 ID#: 119921 DB: mainlib



**Figure 2.** Mass spectrum of ion series for 1,3,5-triazine,  $C_3H_3N_3$  MW: 81 NIST#: 118737 ID#: 49976 DB: mainlib.

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.

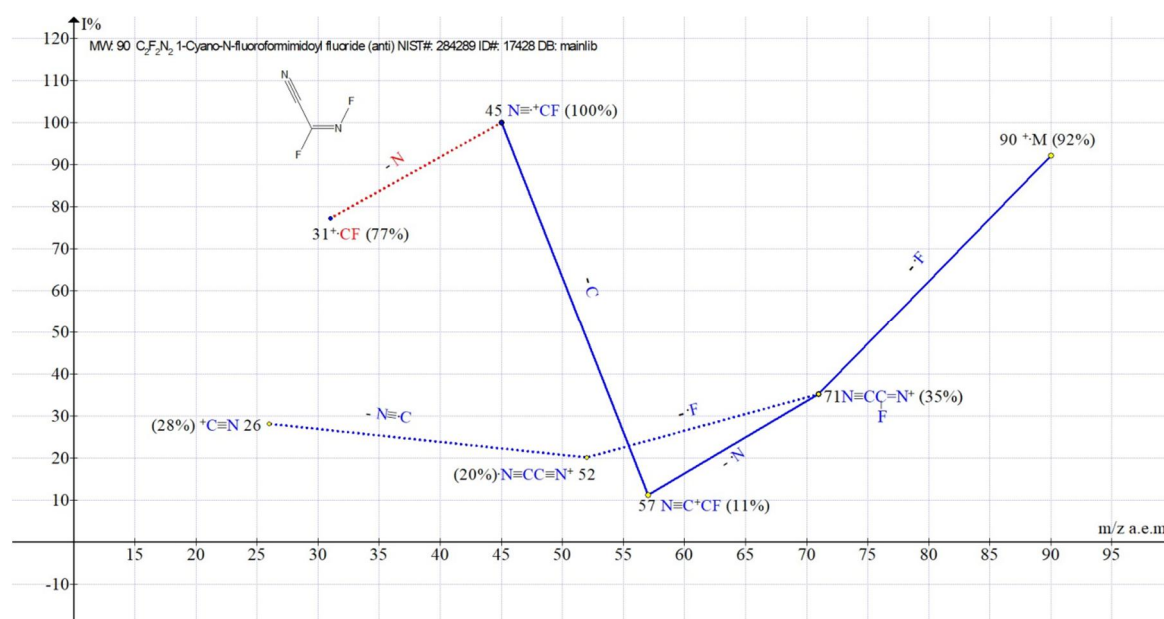
Unlike two consecutive emissions of  $\cdot F$  and  $\cdot CN$  occurring during decomposition of fluorine-substituted triazine cycle (see Fig. 1), the fragmentation of molecular  $\cdot M$  radical cation of hydrogen-substituted cycle (see Fig. 2) occurs in three parallel ways, namely with detachments 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 1**

$[\text{C}_3\text{H}_3\text{N}_3]^+$	MW: 81	100%	$[\text{C}_3\text{F}_3\text{N}_3]^+$	MW: 135	100%
$[\text{C}_2\text{H}_2\text{N}_2]^+$	MW: 54	75%	$[\text{C}_2\text{F}_2\text{N}_2]^+$	MW: 90	55%
$[\text{HCN}]^+$	MW: 27	42%	$[\text{FCN}]^+$	MW: 45	35%

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

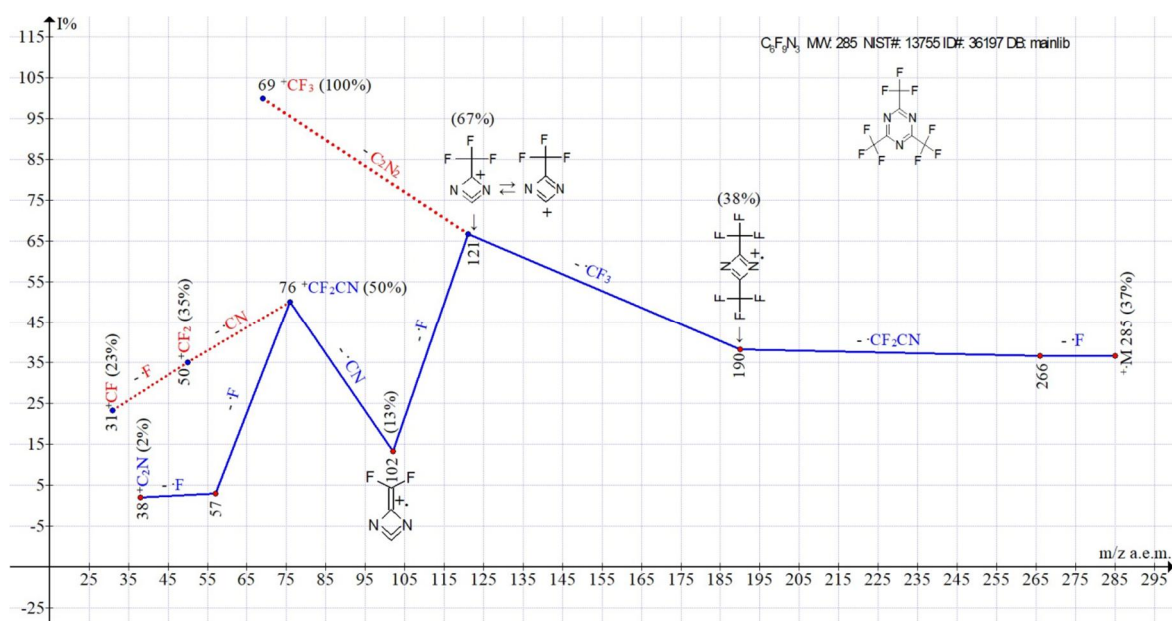


**Figure 3.** Mass spectrum of ion series for (*E*)-2,3-difluoroprop-2-enitrile, MW:90  $\text{C}_2\text{F}_2\text{N}_2$   
NIST#: 284289 ID#: 17428 DB: mainlib.

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

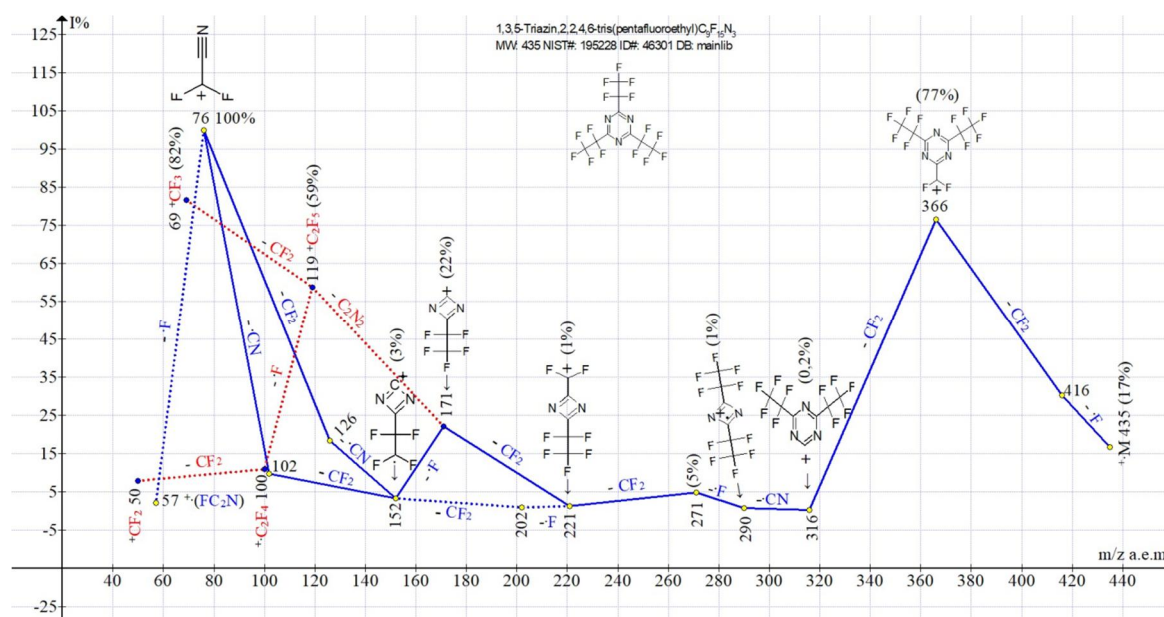
Fig. 4 shows the ion series of the mass spectrum of 2,4,6-tris(trifluoromethyl)-1,3,5-triazine.



**Figure 4.** Ion series of the mass spectrum for 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, C<sub>6</sub>F<sub>9</sub>N<sub>3</sub> MW: 285 NIST#: 13755 ID#: 36197 DB: mainlib.

As a result of successive detachments of fluorine atom and  $\cdot\text{CF}_2\text{CN}$ ,  $[\text{CF}_3(\text{CN})_2\text{CF}_3]^+$  dimeric ion with m/z 190 (38%) appears. Surprisingly, the intensities of  $^+\text{M}$ ,  $^+\text{M}\cdot\text{F}$  and  $-\text{CF}_2\text{CN}$  peaks do not change and are equal to 37-38%. At the next detachment, the ion-monomer  $[\text{CF}_3\text{CN}]^+$  with m/z 95 is not formed. The ejection of  $\cdot\text{CF}_3$  leads to the ion with m/z 121, which loses a fluorine atom, turning into  $^+\text{C}_3\text{F}_2\text{N}_2$  with m/z 102. As a result, instead of monomeric ion, the  $^+\text{CF}_2\text{CN}$  ion with m/z 76 (50%) appears. Peaks of ions with m/z 69  $^+\text{CF}_3$  (100%), 50  $^+\text{CF}_2$  (35%) and 31  $^+\text{CF}$  (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.



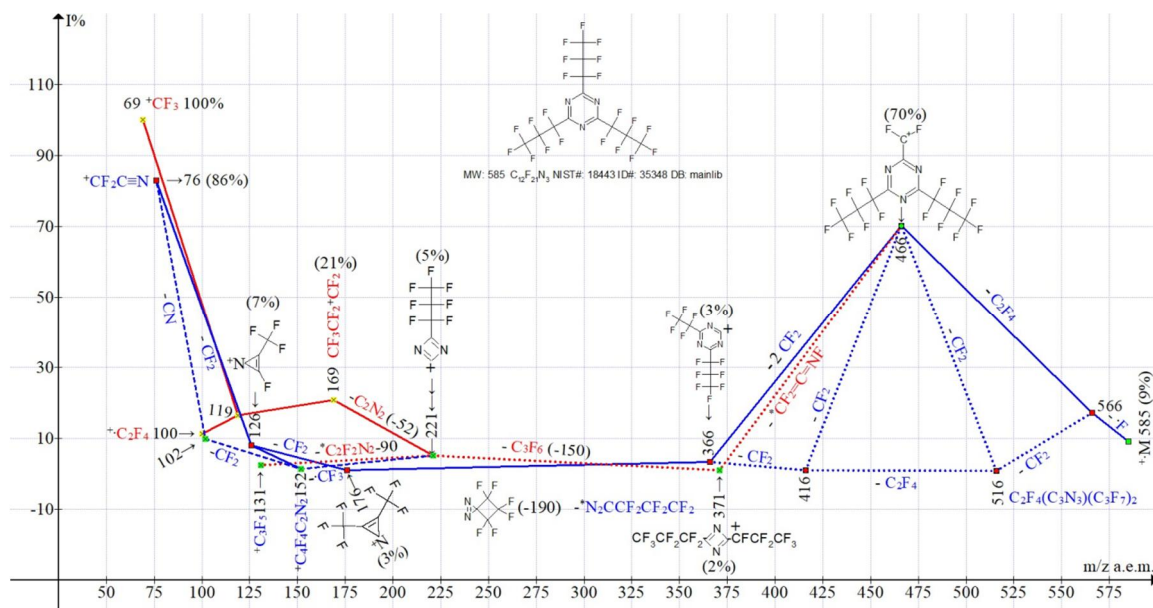
**Figure 5.** Mass spectrum of ion series for 2,4,6-tris(pentafluoroethyl)-1,3,5-triazine,  $C_9F_{15}N_3$  MW: 435 NIST#: 195228 ID#: 46301 DB: mainlib.

As a result of detachments of  $\cdot F$  and  $CF_2$ , the first intense peak of spectrum appears with  $m/z$  366  $(C_2F_5)_2[C_3N_3]^+CF_2$  (77%). Subsequent ejections of  $CF_2$  and  $\cdot CN$  are completed by dimeric ion  $^+[C_2F_5(CN_2C)C_2F_5]$  with  $m/z$  290 (1%).

The ion with  $m/z$  290 ejects  $\cdot F$  and  $CF_2$  with formation of  $C_2F_5(C_2N_2)^+CF_2$  ion weak peak with  $m/z$  221 (1%). The ion with  $m/z$  221 fragments both by successive detachments of  $CF_2$  and  $\cdot F$ , and  $\cdot F$  and  $CF_2$ , forming a radical cation with  $m/z$  152 (3%). However, the detachment from the ion with  $m/z$  221 with only  $CF_2$  (without  $\cdot F$  radical) leads to a peak (with medium intensity) of  $C_2F_5-CN_2^+C$  ion with  $m/z$  171 (22%).

The ion with  $m/z$  171 fragments in two ways. As a result of detachment of  $\cdot F$ ,  $\cdot CN$  and  $CF_2$  atoms from it, the base peak of mass spectrum with  $m/z$  76 appears. As a result of ejection of ethanedinitrile  $NC-CN$  molecule, the  $^+C_2F_5$  ion, its fragment ion  $^+CF_3$  and so the  $^+C_2F_4$  and  $^+CF_2$  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.



**Figure 6.** Mass ion series of 2,4,6-tris(heptafluoropropyl)-1,3,5-triazine,  $\text{C}_{12}\text{F}_{21}\text{N}_3$  MW: 585 NIST#: 18443 ID#: 35348 DB: mainlib.

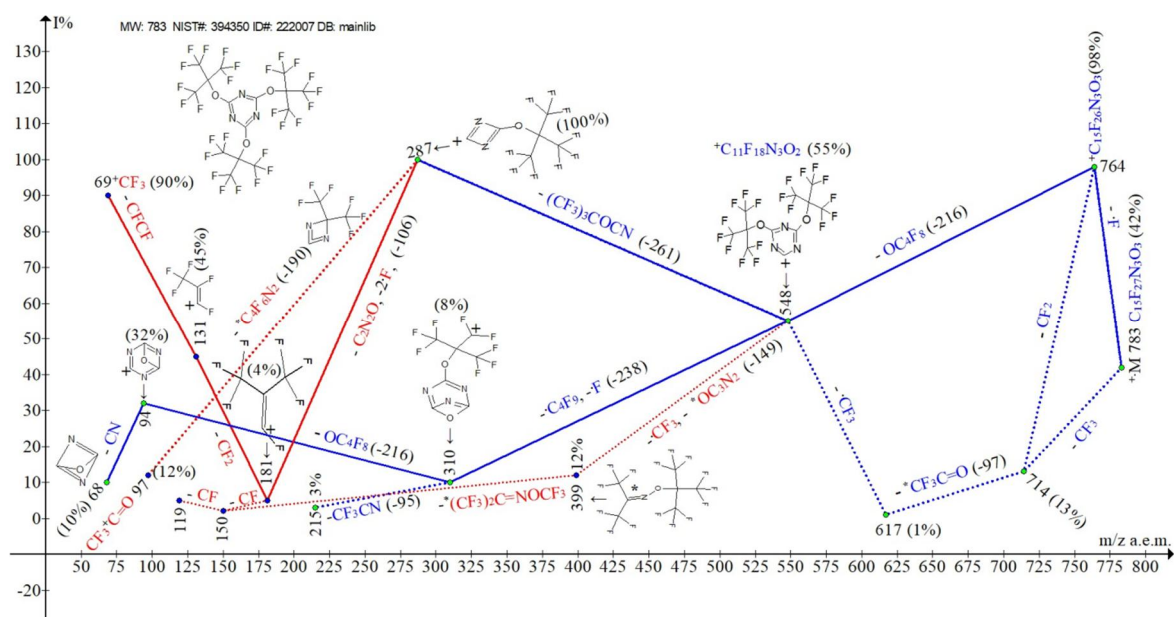
The ionic series  $\text{C}_{12}\text{F}_{21}\text{N}_3$  (see Fig. 6) are similar to  $\text{C}_9\text{F}_{15}\text{N}_3$  series (see Fig. 5).

As a result of detachment of  $\cdot\text{F}$  and  $\text{C}_2\text{F}_4$ , the first intense peak appears with m/z 466  $(\text{C}_3\text{F}_7)_2[\text{C}_3\text{N}_3]^+\text{CF}_2$  (70%). It fragments in two ways. Detachment from the ion with m/z 466 ( $-2\text{CF}_2$ ) 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 ( ${}^-\text{CF}_2=\text{C}=\text{NF}$ ) from the ion with m/z 466, the ion with m/z 371 (2%) appears. It fragments with ejection of  $-\text{C}_3\text{F}_6$ , forming the  $\text{C}_3\text{F}_7\text{-CN}_2^+\text{C}$  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  ${}^+\text{CF}_3$  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.





**Figure 8.** Mass spectrum of ion series for 2,4,6-tris(perfluoro-tert-butoxy)-1,3,5-triazine  $C_{15}F_{27}N_3O_3$  MW: 783 NIST#: 394350 ID#: 222007 DB: mainlib.

After primary detachment of fluorine atom, the  ${}^+C_{15}F_{26}O_3$  ion with  $m/z$  764 (98%) ejects  $OC_4F_8$ , losing one of the three  $OC(CF_3)_3$  substituents and turning into  $[(CF_3)_3CO]_2C_2N_3^+C$  ion with  $m/z$  548 (55%).

The loss of  $\cdot OC(CF_3)_3$  substituent also occurs in three successive detachments:  $\cdot CF_3$ ,  $\cdot CF_3CO$  and  $\cdot CF_3$  (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  $(CF_3)_3COCN$  molecule, turning into the ion with  $m/z$  287(100%);
- with detachment of  $\cdot C_4F_9$  from second substituent, and  $\cdot F$  atom from third substituent, turning into the ion with  $m/z$  310 (8%);
- with detachment of  $\cdot CF_3$  and  $O-C_3N_2$  group of triazine ring or  $F_3COC_3N_2$  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  $C_4F_6N_2$  (-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  $CN_2C=O$  molecule and two fluorine atoms, turning into rearrangement ion  $CF_3-CF=^+CF$  with  $m/z$  181 (4%).

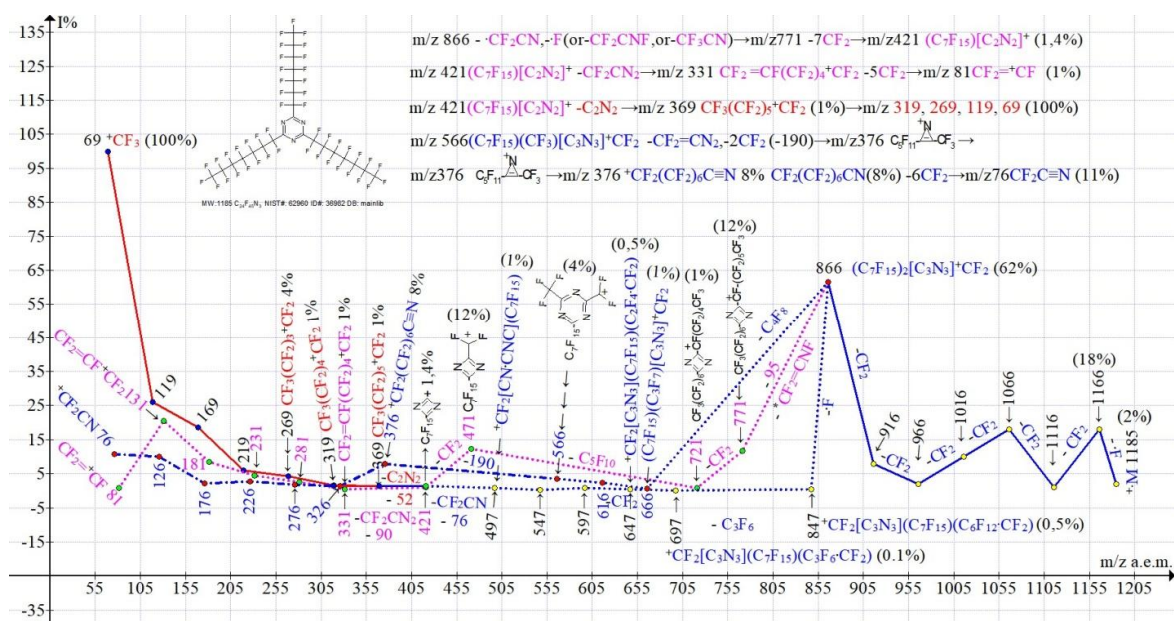
Fragmentation of ion with  $m/z$  181 yields an analogue of  $CF_3-CF=^+CF$  perfluoroallyl ion with  $m/z$  131 (45%) and its fragment ion  ${}^+CF_3$  (90%).



The ion with  $m/z$  310 fragments with detachment of  $\text{OC}_4\text{F}_8$ , forming the ion with  $m/z$  94 (32%) with  $\text{C}_3\text{N}_3\text{O}$  triazine ring containing an additional oxygen atom. The ion with  $m/z$  94 fragments with detachment of  $\text{CN}$  and formation of  $\text{C}_2\text{N}_2\text{O}$  ion with  $m/z$  68 (10%).

The ion with  $m/z$  399 fragments with ejection of  $(\text{CF}_3)_2\text{C}=\text{N}-\text{OCF}_3$  molecule and formation of perfluoroolefin ions, i. e.  $^+\text{C}_3\text{F}_6$  and  $^+\text{C}_2\text{F}_4$  (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  $\text{C}_{24}\text{F}_{45}\text{N}_3$  MW: 1185 NIST#: 62960 ID#: 36982 DB: mainlib.

As a result of primary detachment of fluorine atom and subsequent ejections of six  $\text{CF}_2$  groups, the first intense peak of triazine ion with  $m/z$  866 (62%) with two  $\text{C}_7\text{F}_{15}$  substituents and one  $^+\text{CF}_2$  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  $\text{C}_4\text{F}_8$  molecule from second substituent  $\text{C}_7\text{F}_{15}$ , which has not yet fragmented, to form the ion  $(\text{C}_7\text{F}_{15})(\text{C}_3\text{F}_7)[\text{C}_3\text{N}_3]^+\text{CF}_2$  with  $m/z$  666 (1%).

The second way of fragmentation of the ion with  $m/z$  866 is detachment of  $\cdot\text{CF}_2\text{CN}$  (with ring break and detachment of  $\text{CN}$ ) from the first already fragmented substituent and additional ejection of the  $\cdot\text{F}$  atom from second substituent, or ejection of  $\text{CF}_2\text{C}=\text{NF}$  or  $\text{CF}_3\text{CN}$  molecule with formation of rearrangement ion with  $m/z$  771 (12%). The additional detachment of  $\cdot\text{F}$  atom probably comes from

CF<sub>2</sub> group of C<sub>7</sub>F<sub>15</sub> substituent, which is directly linked to fragmenting triazine ring. The subsequent ejection of -CF<sub>2</sub> ends with C<sub>7</sub>F<sub>15</sub>[C<sub>3</sub>N<sub>3</sub>](C<sub>3</sub>F<sub>6</sub>·CF<sub>2</sub>)<sup>+</sup>CF<sub>2</sub> 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 C<sub>7</sub>F<sub>15</sub>[C<sub>3</sub>N<sub>3</sub>](C<sub>6</sub>F<sub>12</sub>·CF<sub>2</sub>)(<sup>+</sup>CF<sub>2</sub>) with m/z 847 (0.5%) . The next detachment of C<sub>3</sub>F<sub>6</sub> molecule probably also occurs from the second one, which began to fragment the C<sub>6</sub>F<sub>12</sub>·CF<sub>2</sub> substituent. Detachment of C<sub>3</sub>F<sub>6</sub> also leads to radical cation C<sub>7</sub>F<sub>15</sub>[C<sub>3</sub>N<sub>3</sub>](C<sub>3</sub>F<sub>6</sub>·CF<sub>2</sub>)<sup>+</sup>CF<sub>2</sub> with m/z 697 (0.1%).

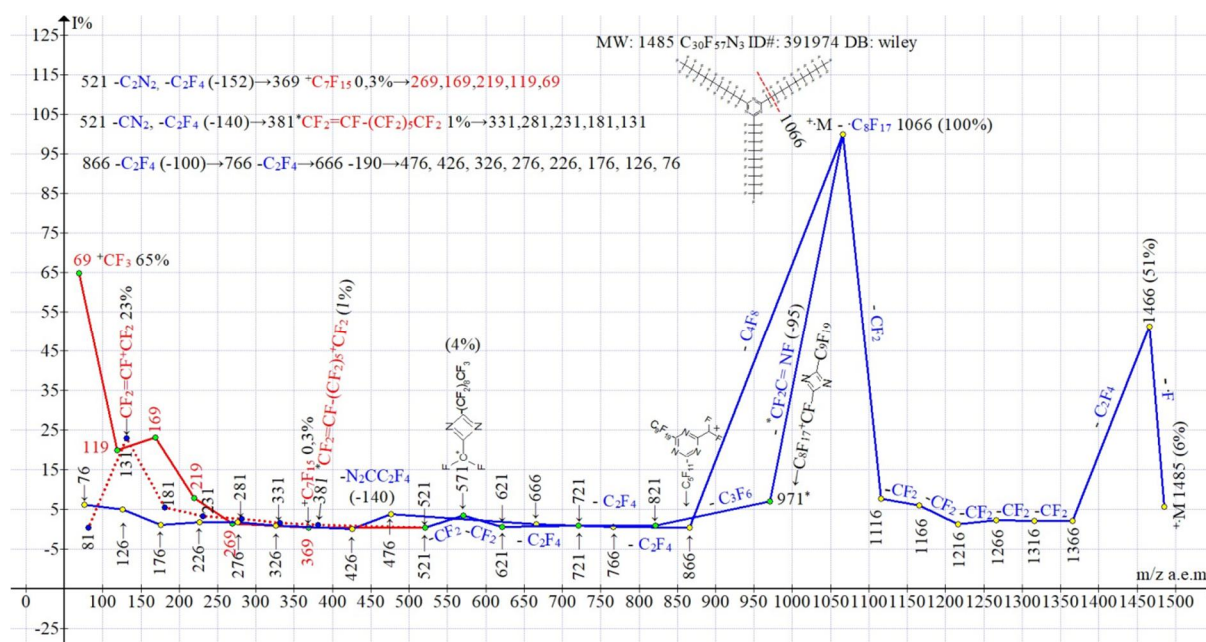
The ion with m/z 666 (C<sub>7</sub>F<sub>15</sub>)(C<sub>3</sub>F<sub>7</sub>)[C<sub>3</sub>N<sub>3</sub>]<sup>+</sup>CF<sub>2</sub> (first way) after detachment of two CF<sub>2</sub> groups, is formed by (C<sub>7</sub>F<sub>15</sub>)(CF<sub>3</sub>)[C<sub>3</sub>N<sub>3</sub>]<sup>+</sup>CF<sub>2</sub> ion with m/z 566 (4%). The ion with m/z 566 fragments with ejection of CF<sub>2</sub>CN<sub>2</sub> (-90) molecule and detachment of C<sub>2</sub>F<sub>4</sub>, turning into C<sub>5</sub>F<sub>11</sub>C<sup>+</sup>NCCF<sub>3</sub> ion, which rearranges into <sup>+</sup>CF<sub>2</sub>C<sub>6</sub>F<sub>12</sub>CN ion with m/z 376 (8%). The series of six further CF<sub>2</sub> detachments: (326, 276, 226, 176) is completed by <sup>+</sup>CF<sub>2</sub>CN ion with m/z 76 (11%).

The ion with m/z 721(1%) (second way) ejects the C<sub>5</sub>F<sub>10</sub> (-250) molecule turning into <sup>+</sup>CF<sub>2</sub>(CN<sub>2</sub>C)(CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub> ion with m/z 471 (12%). The next detachment of CF<sub>2</sub> 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 <sup>+</sup>C<sub>3</sub>F<sub>7</sub> ion with m/z 369 (1%), a series of perfluoroalkyl ions, with detachment of ·CF<sub>2</sub>CN<sub>2</sub>, leading to <sup>+</sup>C<sub>7</sub>F<sub>13</sub> ion with m/z 331(1 %) and series of perfluoroalkenyl ions, the most intense peak of which is the peak of perfluoroallyl ion CF<sub>2</sub>=CF-<sup>+</sup>CF<sub>2</sub> with m/z 131 (21%).

The cation-radical with m/z 697 (0.1%) (third way) C<sub>7</sub>F<sub>15</sub>[C<sub>3</sub>N<sub>3</sub>](C<sub>3</sub>F<sub>6</sub>·CF<sub>2</sub>)<sup>+</sup>CF<sub>2</sub> ejects four CF<sub>2</sub> groups, transforming it into cation-radical C<sub>7</sub>F<sub>15</sub>[CN·CNCN]<sup>+</sup>CF<sub>2</sub> 497 (1%). The detachment of ·CF<sub>2</sub>CN (-76) with breakdown of triazine ring terminates C<sub>7</sub>F<sub>15</sub>[CN<sub>2</sub><sup>+</sup>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 C<sub>30</sub>F<sub>57</sub>N<sub>3</sub>. Like C<sub>24</sub>F<sub>45</sub>N<sub>3</sub> homologue (see Fig. 9).

The spectrum of C<sub>30</sub>F<sub>57</sub>N<sub>3</sub> consists of three ionic series: perfluoroalkyl ion series <sup>+</sup>CF<sub>3</sub> with m/z 369-69, CF<sub>2</sub>=CF-<sup>+</sup>CF<sub>2</sub> perfluoroalkenyl ion series with m/z 381-131 and <sup>+</sup>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>CN ion series with m/z 476-76. Its difference is that the peak intensities of perfluoroalkyl ions and <sup>+</sup>CF<sub>2</sub>CN ion series in C<sub>30</sub>F<sub>57</sub>N<sub>3</sub> spectrum (see Fig. 10) are one and a half times weaker than in C<sub>24</sub>F<sub>45</sub>N<sub>3</sub> spectrum (see Fig. 9), while the peak intensities of its perfluoroalkenyl series are the same.



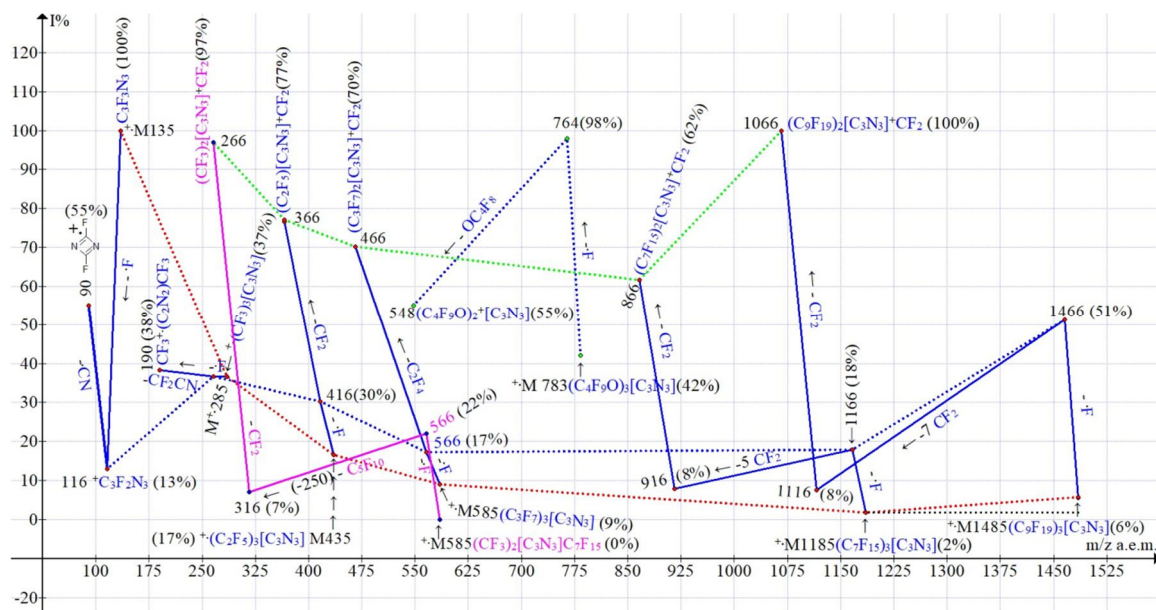
**Figure 10.** Mass spectrum of ion series for 2,4,6-tris(perfluoronyl)-1,3,5-triazine  $C_{30}F_{57}N_3$  MW: 1485 ID#: 391974 DB: wiley\_nist98.

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  $(C_3F_7)_3C_3N_3$ , like all graphs of symmetric isomers, is marked with blue lines). The plot of unsymmetrical  $(CF_3)_2C_3N_3(C_7F_{15})$  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  $C_3F_3N_3$  to 2% for  $(C_7F_{15})_3C_3N_3$ . However, for  $(C_9F_{19})_3C_3N_3$  homologue, the intensity of molecular ion peak increases to 6% (marked with red dotted lines in Fig. 11).

During ionization, the peak of  $^+C_3F_3N_3$  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  $^+C_3F_3N_3$  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  $^+(CF_3)_3[C_3N_3]$  with a mass of 285 a.m.u., 2.1 times greater than that of  $^+C_3F_3N_3$ , decreases in 2.7 times to 37%. However, when a fluorine atom is detached from  $^+(CF_3)_3[C_3N_3]$ , the intensity of resulting  $^+M-F$  peak remains at level of 37% and only slightly increases to 38% upon detachment of  $CF_2CN$  and in appearance of dimeric ion  $CF_3^+(C_2N_2)CF_3$ . For homologs of  $(C_2F_5)_3C_3N_3$  and  $(C_3F_7)_3C_3N_3$  ( $C_2F_5$ ) the intensity of  $^+M-F$  peak decreases from 30% to 17%. It remains constant at 17%-18% for homologue  $(C_7F_{15})_3C_3N_3$ .

After detachment of fluorine atom from  $^{+}(\text{C}_9\text{F}_{19})_3\text{C}_3\text{N}_3$  with molecular weight of 1485 a.m.u. (see Fig. 11) there is unprecedented increase in peak intensity  $^{+}\text{M}-\text{F}$  with  $m/z$  1466 (51%) - three times greater than that of  $(\text{C}_7\text{F}_{15})_3\text{C}_3\text{N}_3$  homologue. It is possible that this is the result of threefold increase in intensity of  $^{+}(\text{C}_9\text{F}_{19})_3\text{C}_3\text{N}_3$  molecular ion peak (6%) compared to (2%) for  $(\text{C}_7\text{F}_{15})_3\text{C}_3\text{N}_3$  molecular peak with  $m/z$  1166. After appearance of  $\text{M}-\text{F}$  peaks the possibility of subsequent stabilizing detachments of  $\text{CF}_2$  is realized, up to formation of most intense peaks of fragment ions with two initial substituents and one  $^{+}\text{CF}_2$  group. With successive detachments of  $\text{CF}_2$ , the insignificant successive increase in peaks of emerging ions occurs. However, only the final ejection of  $\text{CF}_2$  with formation of ion with two initial triazine ring substituents and one  $^{+}\text{CF}_2$  group leads to the first intense fragmentary peaks.

Comparison of  $^{+}\text{M}$  peaks intensities of two isomers (symmetric  $(\text{C}_3\text{F}_7)_3[\text{C}_3\text{N}_3]$  (9%) and unsymmetrical  $(\text{CF}_3)_2[\text{C}_3\text{N}_3](\text{C}_7\text{F}_{15})$  (0%)) allows us to conclude that, in contrast to  $^{+}\text{M}$  symmetrical isomer, the  $^{+}\text{M}$  of unsymmetrical isomer with substituent  $\text{C}_7\text{F}_{15}$  is unstable (0%).

The minimum difference between the masses of its  $\text{C}_3\text{F}_7$  and  $\text{CF}_3$  substituents is 100 a.m.u., and the maximum difference between the masses of  $\text{C}_3\text{F}_7$  and  $\text{C}_7\text{F}_{15}$  is 200 a.m.u. for  $\text{C}_4\text{F}_8$ .

In mass spectra of  $(\text{C}_2\text{F}_5)_3[\text{C}_3\text{N}_3]$  with  $m/z$  435,  $(\text{C}_3\text{F}_7)_3[\text{C}_3\text{N}_3]$  with  $m/z$  585, as well as in mass spectra of unsymmetrical isomer  $(\text{CF}_3)_2[\text{C}_3\text{N}_3](\text{C}_7\text{F}_{15})$  with  $m/z$  585 after detachment of fluorine atom and ejection  $\text{CF}_2$ ,  $\text{C}_2\text{F}_4$ , and, accordingly,  $\text{C}_5\text{F}_{10} + \text{CF}_2$  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  $^{+}\text{CF}_2$  group. The maximum intensity of 97% (stability) is acquired by peak of the  $(\text{CF}_3)_2[\text{C}_3\text{N}_3]^{+}\text{CF}_2$  ion with a minimum mass of  $m/z$  266, which occurs during fragmentation of asymmetric isomer  $(\text{CF}_3)_2[\text{C}_3\text{N}_3](\text{C}_7\text{F}_{15})$  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  $^{+}\text{CF}_2$  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:  $\text{CF}_2$  (50),  $\text{C}_2\text{F}_4$  (100) and  $\text{C}_5\text{F}_{10} + \text{CF}_2$  (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  $^{+}\text{M}-\text{F}$  with  $m/z$  1466 (51%), which is three times higher than peak intensity of  $^{+}\text{M}-\text{F}$  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  $(\text{C}_9\text{F}_{19})_3^{+}[\text{C}_3\text{N}_3]$  (6%) compared to peak intensity of molecular ion

$(C_7F_{15})_3^+[C_3N_3]$  (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  $C_{24}F_{45}N_3$  and  $C_{30}F_{57}N_3$  after detachment of fluorine atom, only the ejection of six  $CF_2$  groups and, accordingly, the ejection of  $C_2F_4$  and six  $CF_2$  groups leads to intense peaks of fragment ions with two symmetrical substituents and one  $CF_2$  group:  $((C_7F_{15})_2[C_3N_3]^+CF_2$  with  $m/z$  866 (62%) and  $(C_9F_{19})_2[C_3N_3]^+CF_2$  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  $(CF_3)_2C_3N_3(C_7F_{15})$ , as well as the mass spectrum of triazine  $(C_4F_9O)_3C_3N_3$  with three  $\cdot OC(CF_3)_3$  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  $(C_4F_9O)_3C_3N_3$  (see Fig. 11), as it were, falls out of the graphs of triazines that do not contain oxaperfluoroalkyl groups.

The intensity of peak of  $(C_4F_9O)_3C_3N_3$  molecular ion with  $m/z$  783 (42%) is higher than the intensity of peak of  $(CF_3)_3C_3N_3$  molecular ion with  $m/z$  285 (37%), but less than that for  $C_3F_3N_3$  with  $m/z$  135 (100%). In contrast to linear perfluoroalkyl substituents, three  $OC(CF_3)_3$  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  $(C_4F_9O)_3C_3N_3$  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  $^+CF_2$  terminal group and oxygen atom of substituent. This is indicated by

ejection of  $\text{OC}_4\text{F}_8$  molecule, although successive but less intense detachments also occur along with  $\text{CF}_2$ ,  $\text{CF}_3\text{C}=\text{O}$  and  $\text{CF}_3$ . As a result, the ion  $(\text{C}_4\text{F}_9\text{O})_2^+\text{C}_3\text{N}_3$  with  $m/z$  548 (55%) appears with preserved triazine cycle (see Fig. 8). Its analogs are the low-intensity peak  $(\text{C}_2\text{F}_5)_2^+\text{C}_3\text{N}_3$  with  $m/z$  316 (0.2%), mass-spectrum of  $(\text{C}_2\text{F}_5)_3^+\text{C}_3\text{N}_3$  and  $(\text{C}_3\text{F}_7)_2^+\text{C}_3\text{N}_3$  peak with  $m/z$  416 (1%) of symmetrical  $(\text{C}_3\text{F}_7)_3^+\text{C}_3\text{N}_3$  mass spectrum. The  $^+\text{CF}_2\text{CN}$  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  $\text{C}_{15}\text{F}_{27}\text{N}_3\text{O}_3$ .

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