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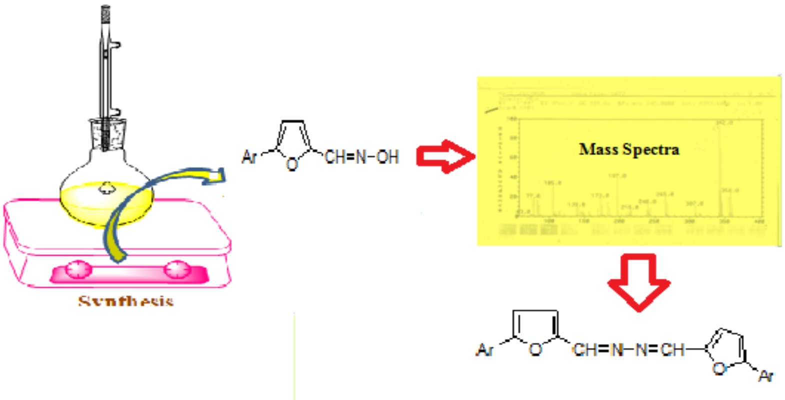
Unexpected Dimerizations of Arylfurfural Oximes in their Mass Spectra

Samina Aslam* [a,b], Aroog Fatima[a], Sidra Mustafa [a], Ansa Madeeha Zafar [c], Noreen Aslam [b,c], Mussarat Jabeen [c], Munawar Ali Munawar [d], and Misbahul Ain Khan [c,e]

Various oximes of arylfurfural were found to eliminate an OH radical and dimerize during their mass spectral fragmentaion. A tentative fragmentation pattern is presented.

Graphical abstract



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1. Introduction

Oximes are important class of organic compounds [1, 2] and are used not only for the characterization of carbaldehydes but are also important for the synthesis of nitrogen heterocyclic compounds [‘3] and undergo Beckmann rearrangements [4] etc. They are also useful ligands [5] and find uses as herbicides and fungicides among others [6,7]. With our continuous interest in the chemistry of arylfurans, we had earlier reported the synthesis of arylfurfuryl chalcones [8] and synthesis and biological screening of oximes of various arylfuran-2-carbaldehyde oximes. The oximes were characterized through their usual spectra (FTIR, ^{1}H NMR, ^{13}C NMR) and CHN elemental analyses which were consistent with the expected structure and presented in our earlier communication [9]. Their mass spectra however showed an anomalous behaviour. The mass spectra of the newly prepared arylfuran-2-carbaldehyde oximes did not exhibit the expected molecular ion peak and so were further investigated. We would like to report this mass spectral behavior of these oximes in the present communication.

2. Material and Methods

General

All reagents and solvents were used as obtained from the supplier. However, when required these were purified by recrystallization (for solids) or by redistillation (for liquids) as necessary. Thin Layer chromatography was performed using aluminium sheets (Merck) coated with silica gel 60 F_{254}. Elemental analyses for C, H and N were recorded with Perkin-Elmer 2400 Series II CHN Analyzer. Melting points were recorded on a GallenKamp apparatus and are uncorrected.

[a] Department of Chemistry, The Women University Multan, Multan. [b] Department of Chemistry, The Islamia University of Bahawalpur, Bahawalpur, Pakistan. [c] Department of Chemistry, Government Sadiq Women University, Bahawalpur, Bahawalpur, Pakistan. [d] Institute of Chemistry, University of the Punjab, Quaid e Azam Campus, Lahore, Pakistan. [e] Research and Development Labs, Shafi Reso, Ferozepur Road, Lahore, Pakistan. *Corresponding author. E-mail: **drsamina.chem@wum.edu.pk, Ph# 0092-331-9735474**

The mass spectra were recorded on VG AutoSpec M series (EBE) MS spectrometer.

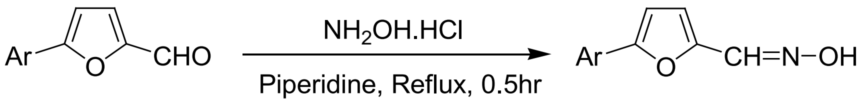
5-Arylfuran 2-carbldehydes: These were prepared as described in an earlier publication [8].

General procedure for the preparation of oximes

Equimolecular quantities (5 mmoles) of a 5-arylfuran-2-carbaldehyde and hydroxylamine hydrochloride was refluxed in Ethanol for 30 min in the presence of 2, 3 drops of piperidine as a catalyst. On cooling precipitates were formed which were filtered, dried and recrystallized from Ethanol. The following oximes were prepared following these general methods [9]. The mass spectral data are given in the Table 1.

3. Results and Discussion

The oximes were prepared by the reaction of the respective carbaldehydes with hydroxylamine hydrochloride in the presence of pyridine (Scheme 1). Although the IR, CHN and NMR show the expected analytical values consistent with their structure, however the mass spectra showed somewhat anomalous behavior. Although the mass spectra of these oximes displayed the expected molecular ion peaks but invariably in all the spectra an intense (100%) peak was observed at higher values which were almost the double value of their molecular weight. On closer examination it became evident that these m/z ion peaks coincided with the process of a loss of OH radical from the molecular ion peak concomitant with its dimerization. Oximes are well known to eliminate an OH radical from their molecular radical ions [10-12]. In the case of these oximes the dimer further fragments by the elimination of a nitrogen molecule (m/z 28). At this stage the possibility of a CO, which is frequently observed as the fragment for the furans [12]. can also not be ruled out.



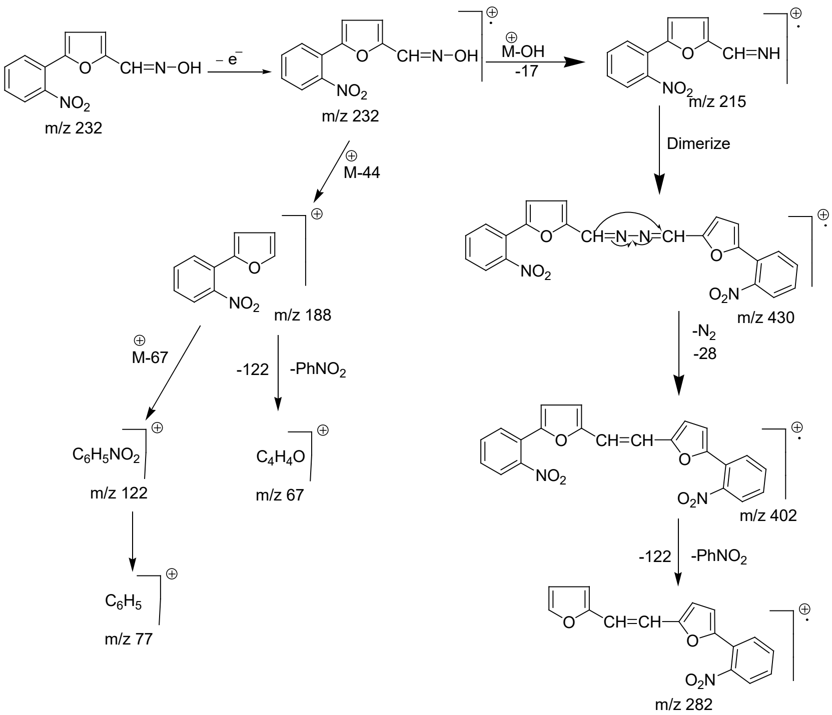
Ar = 2-$NO_2C_6H_4$**(1)**, 3-$NO_2C_6H_4$**(2)**, 4-$NO_2C_6H_4$**(3)**, 2-ClC_6H_4**(4)**, 3-ClC_6H_4**(5)**, 4-ClC_6H_4**(6)**, 4-BrC_6H_4**(7)**, 5-Cl-2-$NO_2C_6H_3$ **(8)**, 4-Cl-2-$NO_2C_6H_3$ **(9)**, 2-Cl-4-$NO_2C_6H_3$ **(10)**, 2,4-$(NO_2)_2C_6H_3$ **(11)**, 2,4-$(Cl)_2C_6H_3$ **(12)**, 2,5-$(Cl)_2C_6H_3$ **(13)**, 2,3-$(Cl)_2C_6H_3$ **(14)**, 3,5-$(Cl)_2C_6H_3$ **(15)**, 4-$COOC_2H_5C_6H_4$ **(16)**, 2-CH_3-3-$NO_2C_6H_3$ **(17)**, 2-CH_3-5-$NO_2C_6H_3$ **(18)**, 3-$COOHC_6H_4$ **(19)**, 2-Cl-5-$NO_2C_6H_3$ **(20)**,

Scheme 1

Normally oximes have been reported to fragment by first a "dehydration" step to form a nitrile which subsequently undergoes further breakdown according to the type of oximes under study. In some cases the oximes fragments by first losing an OH radical and then follows its fragmentation route. For the present case this high molecular mass present in all the oximes mass spectra is, for convenience sake, termed as an "Oxime Dimer". The fragmentation scheme for a couple of these oximes is discussed in the following and presented in the Scheme no 2-3. The most common fragments are collected in the Table 2.

Fragmentation pattern of 5-(2'-nitrophenyl) furan-2-carbaldehyde oxime (1)

The fragmentation pattern of **1** is presented in Scheme 2. It gives an M^+ peak at m/z 232, which by the loss of an OH radical gives a peak at m/z 215 then it dimerize to give a peak at m/z 430 followed by the loss of N_2. Then it loses $PhNO_2$ resulting in a peak at m/z 282.



Scheme 2

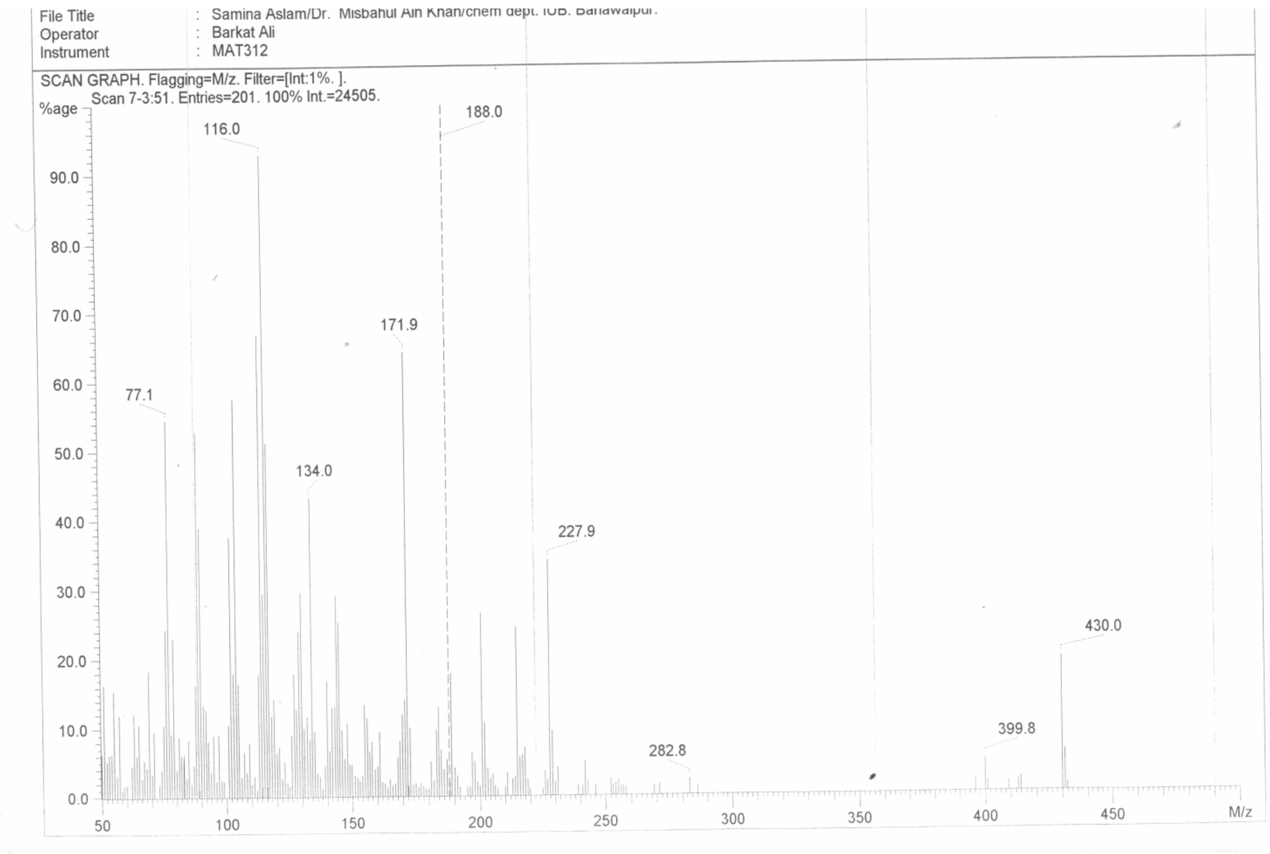
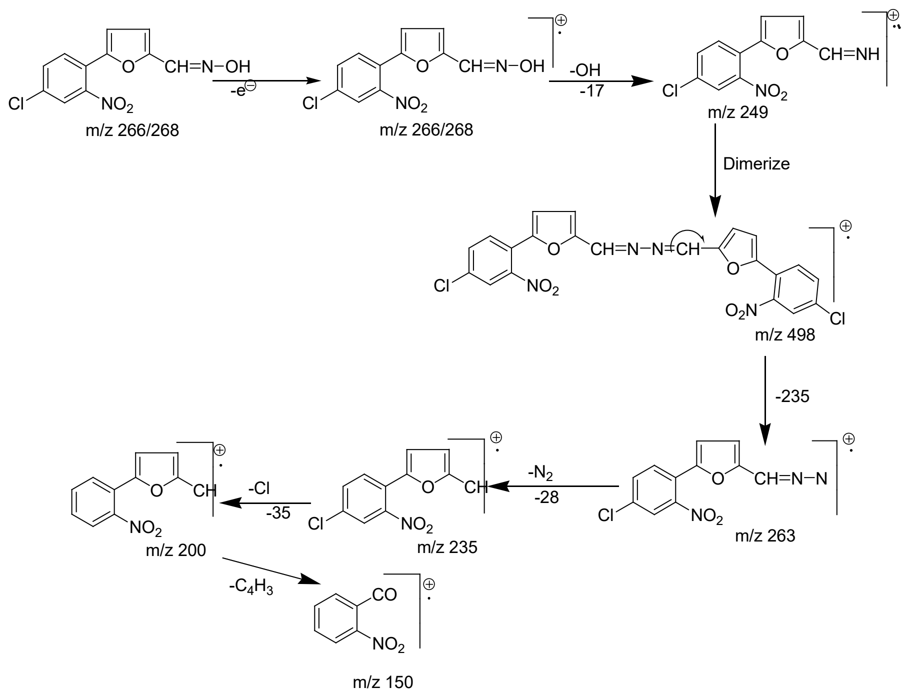


Fig. 1. Mass spectra of 5-(2'-nitrophenyl) furan-2-carbaldehyde oxime.

Fragmentation pattern 5-(4'-chloro-2'-nitrophenyl) furan-2-carbaldehyde oxime (9)

The fragmentation pattern of **9** is presented in scheme **3**. It gives M+ and M++2 peaks at m/z 266 and 268 respectively, which by the loss of OH group gives peak at m/z 249 then it dimerizes to gives a fragment at m/z 498. A fragment loss with the molecular weight 235 and gives another peak at m/z 263. Then by lose of N_2 gives a peak at m/z 235. Then by the successive loss of a Cl atom and a furan ring, it gives peaks at m/z 200 and 150 respectively.



Scheme 3

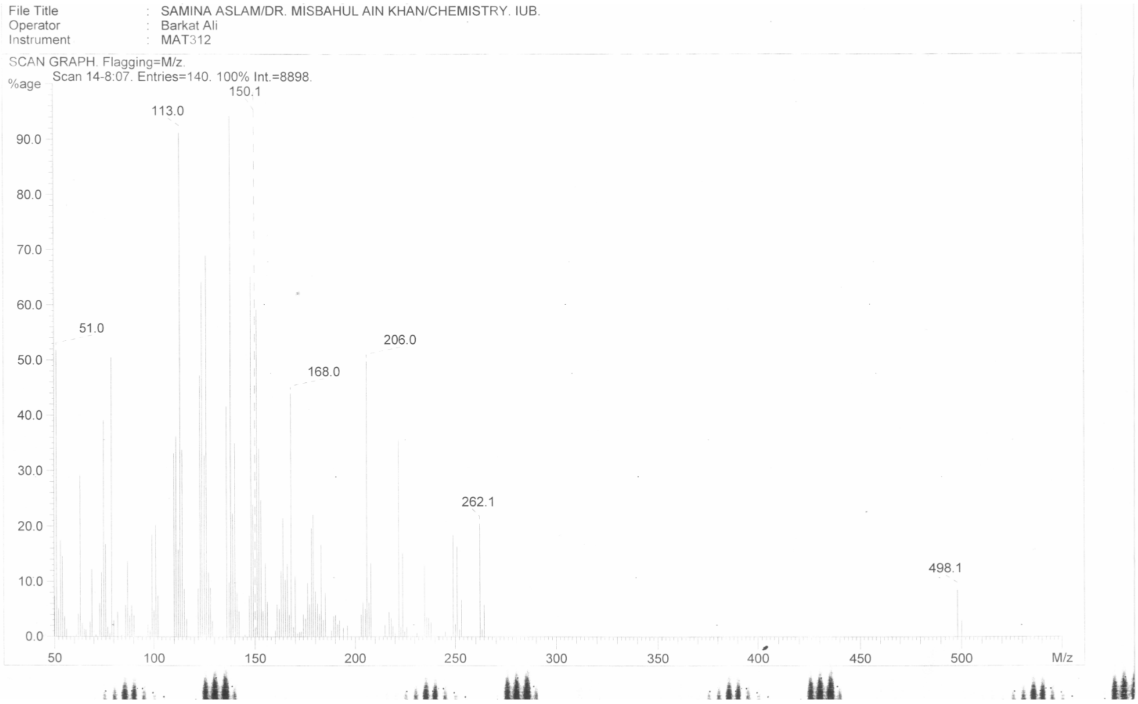
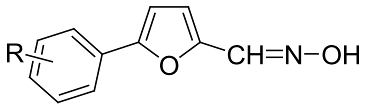


Fig. 2. Mass spectra of 5-(4'-chloro-2'-nitrophenyl) furan-2-carbaldehyde oxime (**9**).

Table 1. Mass spectra of 5-arylfuran 2-carbldehydes oxime.



Compound no.	Substituent R	Mass Spectra m/z (relative intensity)
1	2-NO_2	431 (6), 430 (19), 402 (2), 229 (9), 228 (34), 215 (24), 202 (11), 201 (26), 189 (18), 188 (100), 184 (13), 172 (64), 171 (14), 155 (13), 148 (11), 145 (25), 140 (17), 134 (43), 130 (30), 122 (18), 63 (12), 55 (16), 116 (93), 114 (67), 104 (58), 102 (38), 91 (13), 90 (39), 89 (53), 79 (23), 77 (55), 76 (24), 67 (18), 65 (11), 57 (12), 55 (15)
2	3-NO_2	431 (16), 430 (56), 402 (12), 298 (9), 217 (4), 215 (6), 201 (4), 169 (4), 150 (13), 127 (12), 115 (23), 114 (49), 113 (14), 104 (11), 88 (13), 79 (100), 76 (13), 75 (8), 63 (11), 51 (21)
3	4-NO_2	432 (100), 430 (50), 351 (30), 277 (20), 315 (18), 195 (18), 185 (35), 168 (20), 155 (35), 140 (45), 114 (20), 88 (8), 76 (30), 63 (10), 44 (20)
4	2-Cl	413 (3), 412 (12), 411 (20), 410 (62), 409 (32), 408 (100), 382 (24), 380 (33), 241 (14), 205 (15), 204 (11), 178 (12). 162 (24), 151 (25), 149 (74), 141 (23), 139 (62), 127 (23), 114 (28), 111 (22), 79 (50), 75 (11), 51 (27)
5	3-Cl	410 (3), 408 (5), 222 (13), 220 (44), 205 (7), 203 (9), 178 (13), 156 (23), 151 (10), 149 (34), 141 (11), 140 (20), 139 (33), 129 (9), 128 (13), 127 (11), 124 (21), 123 (13), 115 (12), 111 (29), 92 (70), 91 (100), 83 (49), 79 (48), 65 (55), 63 (37), 51 (58), 50 (26)
6	4-Cl	410 (30), 409 (11), 408 (45), 382 (19), 380 (30), 241 (14), 205 (10), 178 (10), 162 (30), 151 (30), 149 (100), 141 (25), 140 (16), 139 (76), 136 (13), 127 (21), 114 (35), 113 (31), 111 (35), 79 (40), 75 (21), 63 (17), 51 (38)
7	4-Br	498 (70), 496 (66), 470 (28), 361 (10), 285 (16), 249 (30), 206 (22), 195 (82), 190 (74), 155 (60), 127 (92), 114 (100), 105 (15), 79 (94),
8	5-Cl-2-NO_2	498 (6), 262 (14), 249 (15), 235 (16), 224 (10), 222(30), 218 (11), 208 (16), 206 (56), 205 (12), 179 (26), 178 (30), 168 (42), 166 (20), 164 (25), 155 (17), 153 (26), 152 (35), 151 (58), 150 (100), 148 (59), 138 (84), 136 (35), 113 (67), 111 (41), 101 (20), 99 (25), 91 (9), 89 (11), 83 (20), 79 (54), 75 (32), 63 (29), 55 (26), 51 (44)
9	4-Cl-2-NO_2	500 (3), 498 (8), 262 (20), 251 (16), 249 (18), 235 (13), 224 (15), 222 (36), 206 (49), 183 (16), 179 (22), 178 (19), 170 (10), 168 (43), 166 (13), 165 (10), 164 (21), 163 (12), 155 (13), 153 (24), 152 (33), 151 (59), 150 (100), 149 (23), 148 (65), 140 (34), 139 (22), 138 (94), 136 (41), 127 (11), 126 (69), 125 (32), 124 (64), 123 (47), 114 (33), 113 (91), 101 (20), 99 (18), 87 (13), 79 (50), 76 (16), 75 (39), 74 (11), 69 (12), 63 (29), 54 (14), 53 (17), 51 (52)
10	2-Cl-4-NO_2	500 (9), 498 (20), 335 (13), 333 (27), 332 (11), 331 (100), 253 (10), 250 (15), 219 (22), 172 (13), 164 (11), 148 (25), 141 (9), 126 (20), 123 (12), 113 (43), 98 (26), 90 (15), 83 (18), 79 (36), 75 (10), 70 (30), 68 (18), 63 (35), 55 (13), 51 (16)
11	2,4-$(NO_2)_2$	502 (11), 500 (32), 499 (13), 470 (11), 184 (10), 161 (8), 150 (11), 149 (11), 148 (34), 138 (20), 136 (10), 126 (34), 114 (10), 113 (60), 79 (100), 75 (12), 63 (20), 51 (40)

Continuation of Table 1

12	2,4-Cl₂	481 (9), 480 (30), 479 (19), 478 (55), 476 (41),
13	2,5-Cl₂	479 (25), 478 (39), 476 (27), 452 (11), 450 (24), 448 (18), 275 (11), 240 (11), 239 (13), 198 (13), 196 (19), 185 (43), 183 (70), 175 (31), 174 (10), 173 (47), 170 (10), 161 (15), 149 (16), 148 (33), 147 (20), 145 (17),126 (13), 113 (38), 87 (10), 79 (100), 75 (10), 63 (17), 51 (53)
14	2,3-Cl₂	480 (21), 478 (40), 476 (33), 452 (10), 450 (25), 448 (19), 275 (12), 239 (13), 198 (13), 196 (24), 185 (45), 183 (70), 175 (28), 174 (13), 173 (47), 161 (14), 149 (16), 148 (28), 147 (21), 145 (17), 126 (12), 113 (40), 87 (12), 79 (100), 63 (17), 51 (52)
15	3,5-Cl₂	483 (3), 482 (12), 480 (48), 479 (25), 478 (100), 477 (21), 476 (75), 452 (22), 450 (44), 448 (33), 277 (12), 275 (19), 239 (22), 237 (12), 196 913), 185 (20), 183 (32), 173 (23), 148 (11), 113 (10), 79 (25), 44 (13)
16	4-COOC₂H₅	486 (26), 484 (100), 457 (25), 456 (80), 439 (28), 429 (14), 428 (44), 400 (37), 258 (44), 243 (17), 242 (28), 219 (10), 214 (10), 198 (16), 197 (28), 196 (23), 183 (13), 159 (22), 155 (10), 149 (18), 115 (10), 114 (18), 79 (10),
17	2-CH₃-3-NO₂	459 (22), 458 (74), 183 (110, 174 (18), 168 (11), 164 (27), 157 (16), 156 (21), 155 (18), 146 (18), 141 (16), 139 (19), 129 (35), 128 (100), 127 (68), 118 (20), 115 (80), 103 (21), 102 (37), 91 (21), 90 (25), 79 (41), 77 (27), 63 (13), 55 (16), 51 (27)
18	2-CH₃-5-NO₂	459 (28), 458 (100), 430 (24), 338 (6), 311 (2), 266 (3), 229 (8), 198 (3), 174 (17), 164 (17), 141 (19), 129 (12), 128 (67), 147 (45), 118 (11), 115 (45), 102 (20), 89 (12), 79 (31), 77 (13), 55 (11), 51 (18)
19	3-COOH	430 (3), 429 (11), 428 (42), 400 (26), 318 (15), 251 (12), 216 (15), 215 (76), 214 (28), 213 (29), 172 (12), 160 (11), 159 (100), 155 (15), 149 (76), 140 (15), 127 (21), 115 (59), 114 (37), 113 (25), 105 (20), 89 (16), 85 (20), 83 (29), 79 (72), 77 (58), 65 (54), 63 (27), 52 (12), 51 (43)
20	2-Cl-5-NO₂	499 (10), 498 (43), 470 (13),m331 915), 194 (11), 184 (12), 150 (12), 149(18), 148 (32), 138 (15), 126 (19), 113 (54), 79 (100), 75 (10), 63 (17), 51 (37)

Table 2. Mass fragmentation of 5-arylfuran 2-carbldehydes oximes.

S.no	Substituent	Major Fragments (Relative intensities)					
		2M⁺	2M⁺-N₂	M⁺	M⁺-OH	M⁺-44	M⁺-72
1	2-NO₂	430 (25)	402 (4)	232 (6)	215 (26)	188 (100)	-
2	3-NO₂	430 (60)	-	-	215 (10)	-	-
3	4-NO₂	430 (100)	-	232 (10)	215 (20)	-	-
4	2-Cl	408 (100)	380 (36)	221 (8)	205 (16)	177 (12)	149 (74)
5	3-Cl	408 (8)	380 (4)	221 (44)	205 (10)	-	149 (32)
6	4-Cl	408 (50)	380 (36)	-	205 (14)	177 (12)	149 (100)
7	4-Br	496 (60)	468 (30)	-	248 (30)	-	193 (82)
8	5-Cl-2-NO₂	498 (10)	469 (5)	266 (5)	249 (15)	222 (30)	150 (100)
9	4-Cl-2-NO₂	498 (10)	-	266 (8)	249 (20)	-	150(100)
10	2-Cl-4-NO₂	498 (30)	-	-	249 (15)	222 (10)	150(10)
11	2,4-(NO₂)₂						
12	2,4-Cl₂	476 (40)	448 (22)	255 (4)	238 (36)	221 (8)	183 (100)
13	2,5-Cl₂	476 (44)	448 (28)	-	238 (18)	-	183 (70)
14	2,3-Cl₂	476 (40)	448 (30)	-	-	-	183 (74)
15	3,5-Cl₂	476 (100)	448 (44)	255 (2)	238 (24)	221 (21)	183 (36)
16	4-COOC₂H₅	484 (100)	456 (80)	259 (44)	238 (28)	215 (15)	177 (18)
17	2-CH₃-3-NO₂	458 (78)	430 (10)	246 (8)	229 (8)	202 (6)	164 (28)
18	2-CH₃-5-NO₂	458 (100)	430 (30)	-	229 (10)	-	164 (10)
19	3-COOH	428 (50)	400 (30)	231 (10)	215 (76)	214 (78)	149 (76)
20	2-Cl-5-NO₂	498 (50)	469 (15)	--	249 (10)	-	150 (38)

To our knowledge, such a mass spectral behaviour for oximes has not been reported and needs further study.

4. Conclusions

In this communication, we have presented a possible mass fragmentation pattern of 5-Arylfuran-2-carbaldehyde oximes. These oximes showed unexpected behavior of dimerization and further fragmentation pattern.

Supporting Information

Mass spectra of the studied compounds.

Acknowledgments

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Author Contributions

Aslam. S.: Data curation; Funding acquisition, Writing - review & editing, Fatima, A. Project supervision, Mustafa, S. performed the experiment Zafar, A.M. Data analysis, Aslam, N. Data analysis and write up Jabeen, M. Contributed reagents and tools, Munawar, M.A. Draft write up and modification, and Khan, M.A. Conceptualization and Project administration.

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