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Spectral elucidation of some biologically important heterocyclic compounds by mass spectrometry

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Abstract: A series of m-terphenyl and biaryl derivatives have been investigated by EI mass spectrometry because of due to their versatile wide applications such as laser dyes, OLED, liquid crystals, solar cells and NLO properties. Mass spectral fragmentation of m-terphenyl and biaryl derivatives were thoroughly analyzed in this article. In general, all the compounds except **3b**, showed the molecular ion peak. Loss of CH_3 group from the Ar-CH_2CH_3 or N-CH_2CH_3 has been observed from their parent skeleton compounds **2a-g**. The most common loss of CN,NH_2,HCN,C_2H_4 groups were observed from the compounds **1a-e, 2a-g, 3a-c**, which are depicted in the **scheme (I, II, III & IV)**. The loss of CHO group is the characteristic of furfuryl moiety has been observed in compound **3c** (m/z 194). As a representative fragmentation pattern of compound **1a** depicted in **Scheme - V**. A number of heterocyclic compounds have been investigated by EI mass spectrometry because of due to their versatile wide applications such as laser dyes, OLED, liquid crystals, solar cells, NLO properties and biological applications. Mass spectral fragmentation of some heterocyclic compounds (**4a-b, 5a-d, 6 a-c, 7a-b,8**) were thoroughly analyzed (**Scheme VI – IX**) in this article.

Key words: M-terphenyl, biaryl, OLED, NLO, furfuryl, HCN, CN, CHO, Quinoacridine, quinoxanthene, pyridinedinitrile, pyranopyridine, quinoxaline.

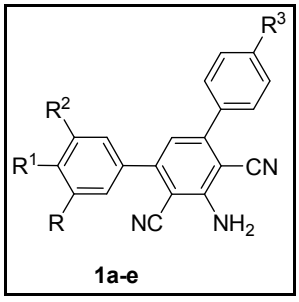
Introduction

Mass spectrometry (MS) is unequivocally a powerful tool of characterization of organic compounds. In recent years, we have witnessed a significant development in the utilization of the terphenyls, particularly m-terphenyl[1] which are useful intermediate for building blocks for cyclophanes[2] to create a large molecular cavity[3]and host-guest complexes[4]. The biaryl unit is represented in several types of compounds of current interest including natural products, polymers, advanced materials, liquid crystals, ligands and molecules of medicinal interest[5]. In continuation of our work on the synthesis of m- terphenyl and biaryl compounds having laser dyes[6] and NLO properties[7], in this paper we would like to report the mass spectral fragmentation pattern of m-terphenyl and biaryl compounds **1 a-e , 2 a-g** and **3 a-c**. Similar loss of CH_3, HCHO and HCN groups were observed both methyl substituted compounds **1b** and **1d**.The characteristic loss of CHO group was observed in compound **3c**, it shows presence of furfuryl moiety. In recent years, we have witnessed a significant development in the utilization of the Quinoacridine and quinoxanthene which are very useful in anti-HIV activity[9], Ca^{2+} release activity[10] and intercalation of DNA[11] . The substituted pyridinedinitrile and pyranopyridine derivatives are shows significant attention in the fields of electrical materials[12] , biological activities[13] and quinoxalines show antimalarial activity against gallinaceum in chicks[14,15] in addition, we would like to report the mass spectral fragmentation pattern of quiniacridine (**4a)**,quinoxanthene **(4b)**, pyridinedinitrile compounds **(5 a-d)**, pyranopyridine derivatives (**6 a-c)** and quinoxaline derivatives(**7a-b, 8**) The loss of H,

isobutylene and ketene groups were observed in quinoacridine(**1a**). Similar loss of H, C_2H_2, NH_2, CN, groups were observed both pyridinedinitrile compounds **(5a-d)** and pyranopyridine derivatives (**6a-c**) .The common loss of H, CO, C_2H_4, HCN groups were observed in quinoxaline derivatives (**7a-b,8**).

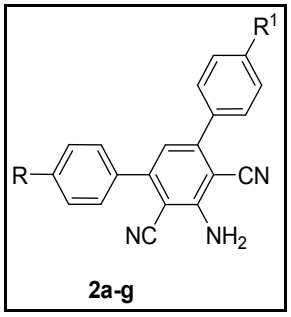
Experimental

The mass spectra were recorded with Jeol-JMS-DX 303 HF and GCMS QP 5000 Shimadzu instruments. Synthesis of m-terphenyl and biaryl compounds **1a-e, 2a-g, 3a-c** were previously reported[8] by our research group.



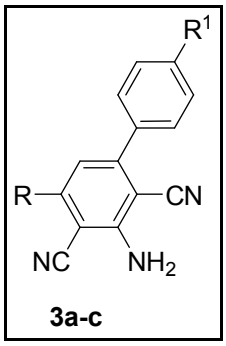
1a-e

Compounds	R	R^1	R^2	R^3
1a	H	H	H	H
1b	OCH_3	OCH_3	OCH_3	H
1c	H	Cl	H	H
1d	OCH_3	OCH_3	OCH_3	CH_3
1e	H	H	H	CH_3



2a-g

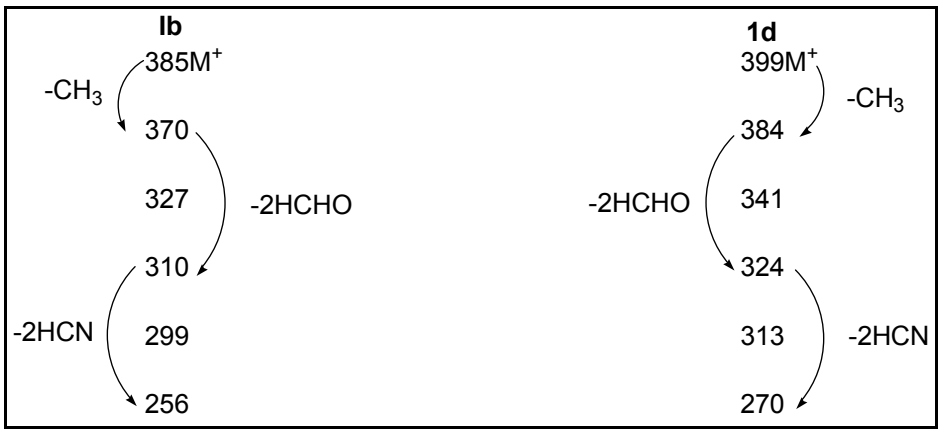
Compound	R	R^1
2a	$N(CH_2CH_3)_2$	CH_3
2b	$N(CH_2CH_3)_2$	CH_2CH_3
2c	$N(CH_3)_3$	CH_2CH_3
2d	OCH_3	CH_3
2e	CH_3	CH_3
2f	CH_3	CH_2CH_3
2g	H	CH_2CH_3



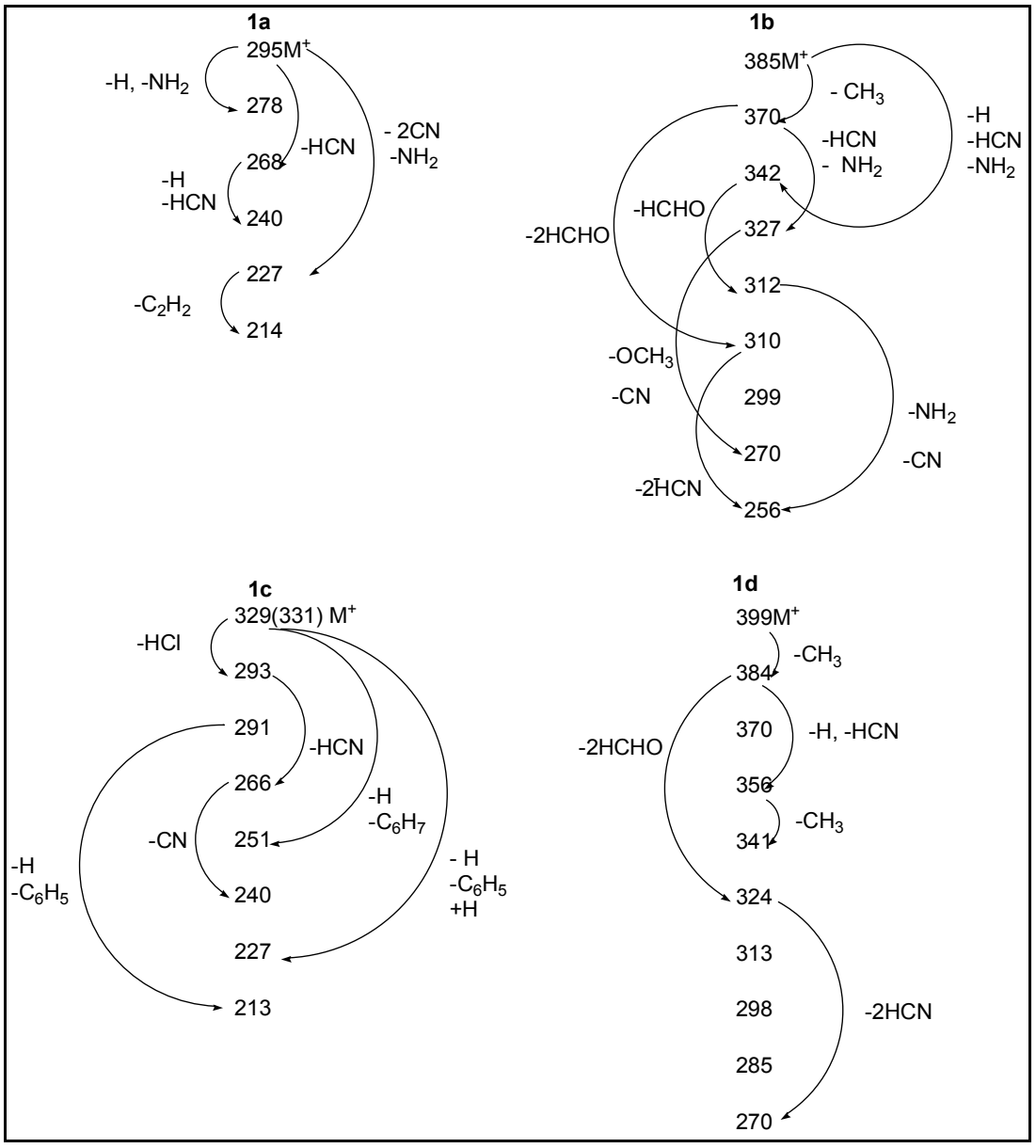
3a-c

Compound	R	R^I
3a	C_6H_5	H
3b	C_6H_5	CH_3
3c	Furfuryl	CH_3

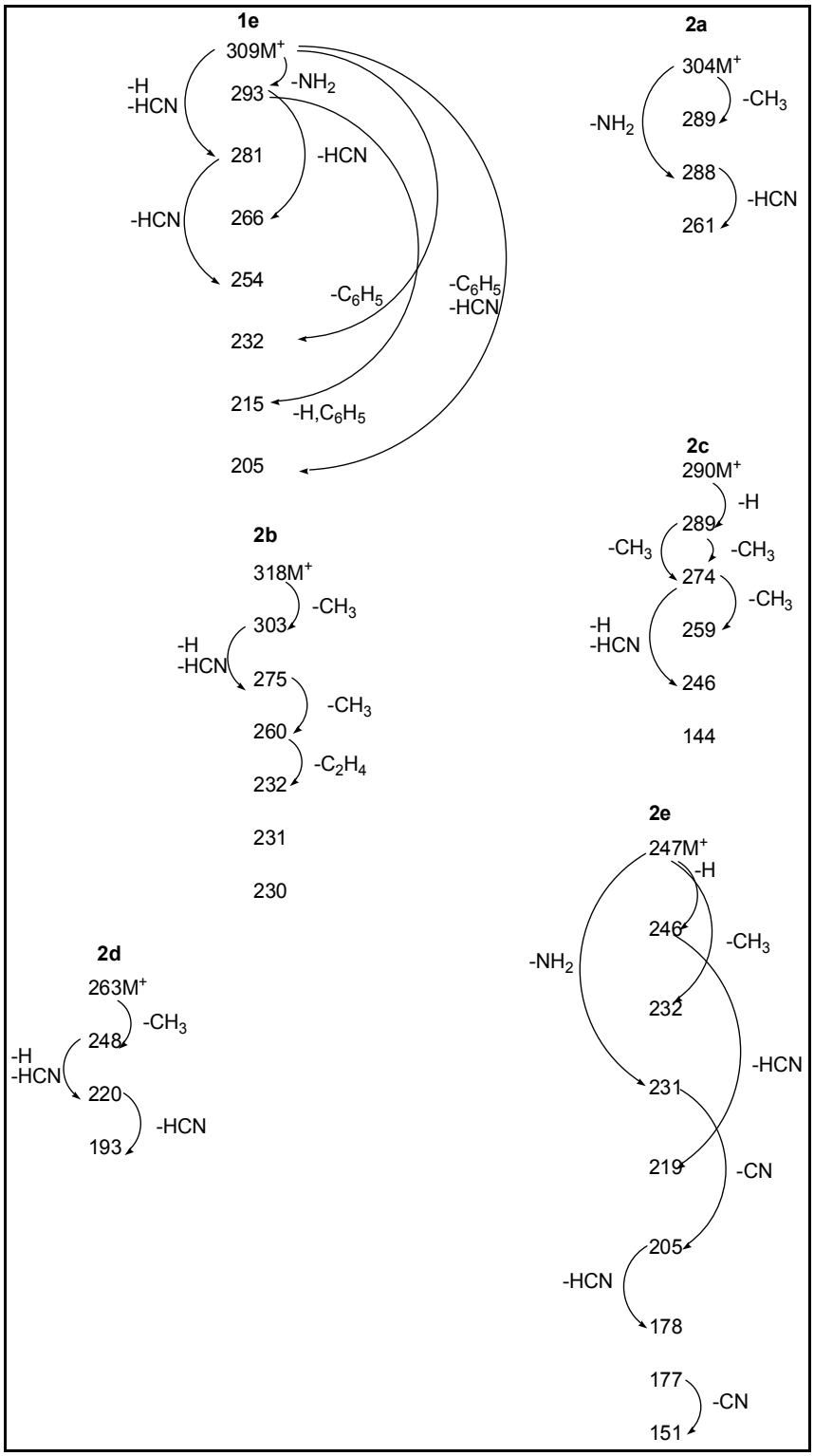
Similar loss of CH_3 , HCHO and HCN was observed both methyl substituted compounds **1b** and **1d** from the molecular ion shown in **scheme -I.** A successive loss of phenyl groups were observed compound **1c** and fragmentation pattern of m-terphenyl compounds **1b** and **1c** is depicted in **scheme** –II.



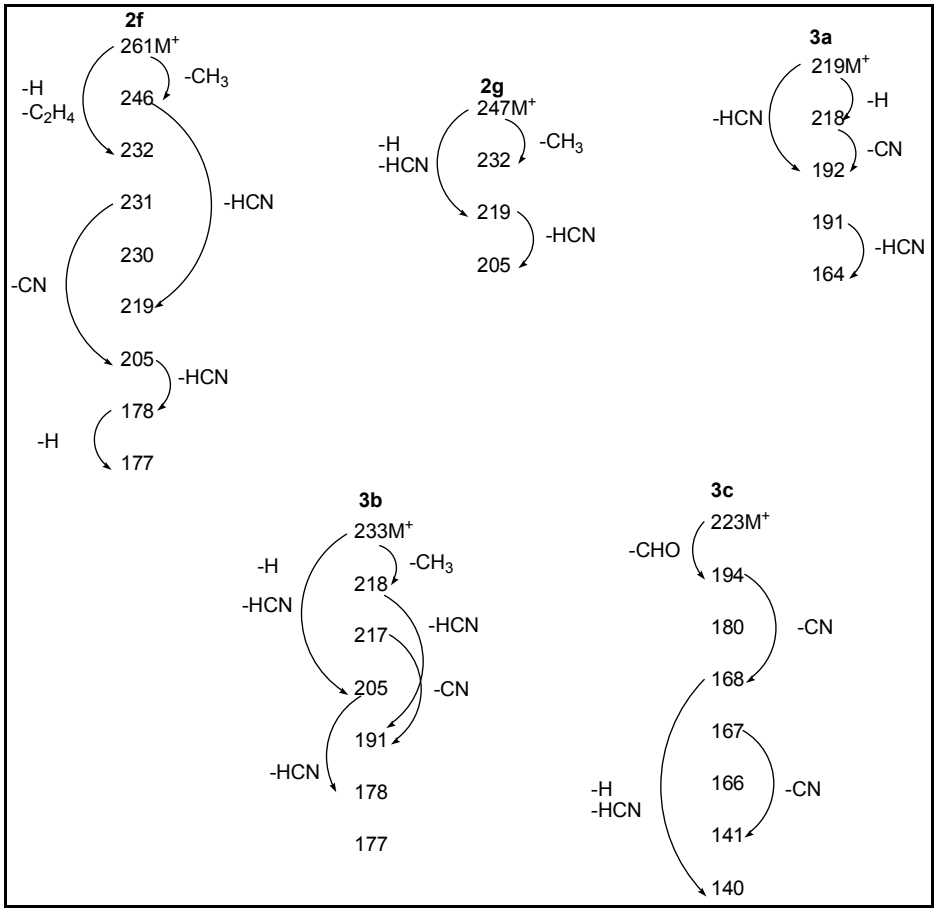
Scheme - I


1a
295M+
-H, -NH2
278
-HCN
- 2CN
-NH2
268
-H
-HCN
240
227
-C2H2
214
1b
385M+
- CH3
370
-HCN
- NH2
-H
-HCN
-NH2
342
-HCHO
-2HCHO
327
312
310
-OCH3
-CN
299
-NH2
270
-CN
-2HCN
256
1c
329(331) M+
-HCl
293
291
-HCN
266
-H
-C6H7
-CN
251
-H
-C6H5
240
- H
-C6H5
+H
227
213
1d
399M+
-CH3
384
370
-H, -HCN
-2HCHO
356
-CH3
341
324
313
298
-2HCN
285
270

Scheme- II

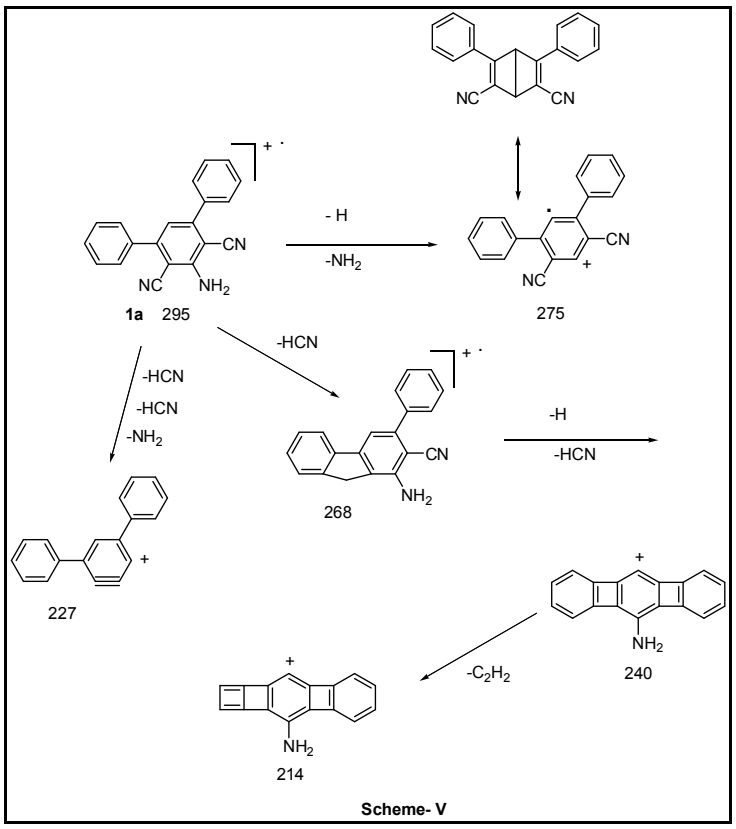

1e
309M+
-H
-HCN
293
-NH2
281
-HCN
-HCN
266
254
-C6H5
-C6H5
-HCN
232
215
-H,C6H5
205
2a
304M+
-CH3
-NH2
289
288
-HCN
261
2b
318M+
-CH3
303
-H
-HCN
275
-CH3
260
-C2H4
232
231
230
2c
290M+
-H
289
-CH3
-CH3
274
-CH3
-H
-HCN
259
246
144
2d
263M+
-CH3
248
-H
-HCN
220
-HCN
193
2e
247M+
-H
246
-CH3
-NH2
232
-HCN
231
219
-CN
205
-HCN
178
177
-CN
151

Scheme –III

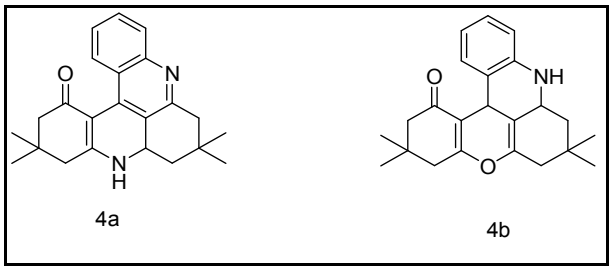


Scheme –IV

The representative fragmentation pattern of m- terphenyl compound **1a** is furnished in **scheme-V**.



A successive loss of Hydrogen followed by loss of isobutylene, ketene and carbon monoxide groups were observed compound **4a** and fragmentation pattern depicted in **scheme** –VI.



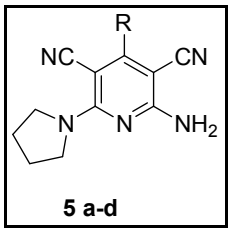


Table - I

Compound	R
5a	p-OH-C_6H_4
5b	o-OH-C_6H_4
5c	p-NO_2-C_6H_4
5d	2-Thienyl

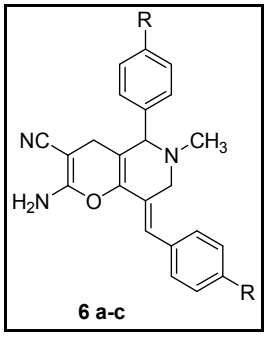
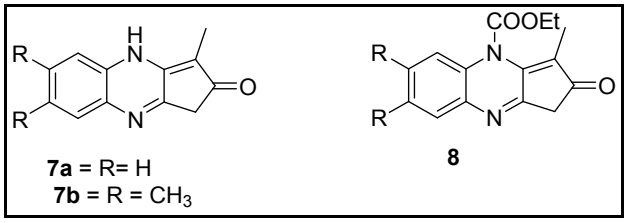


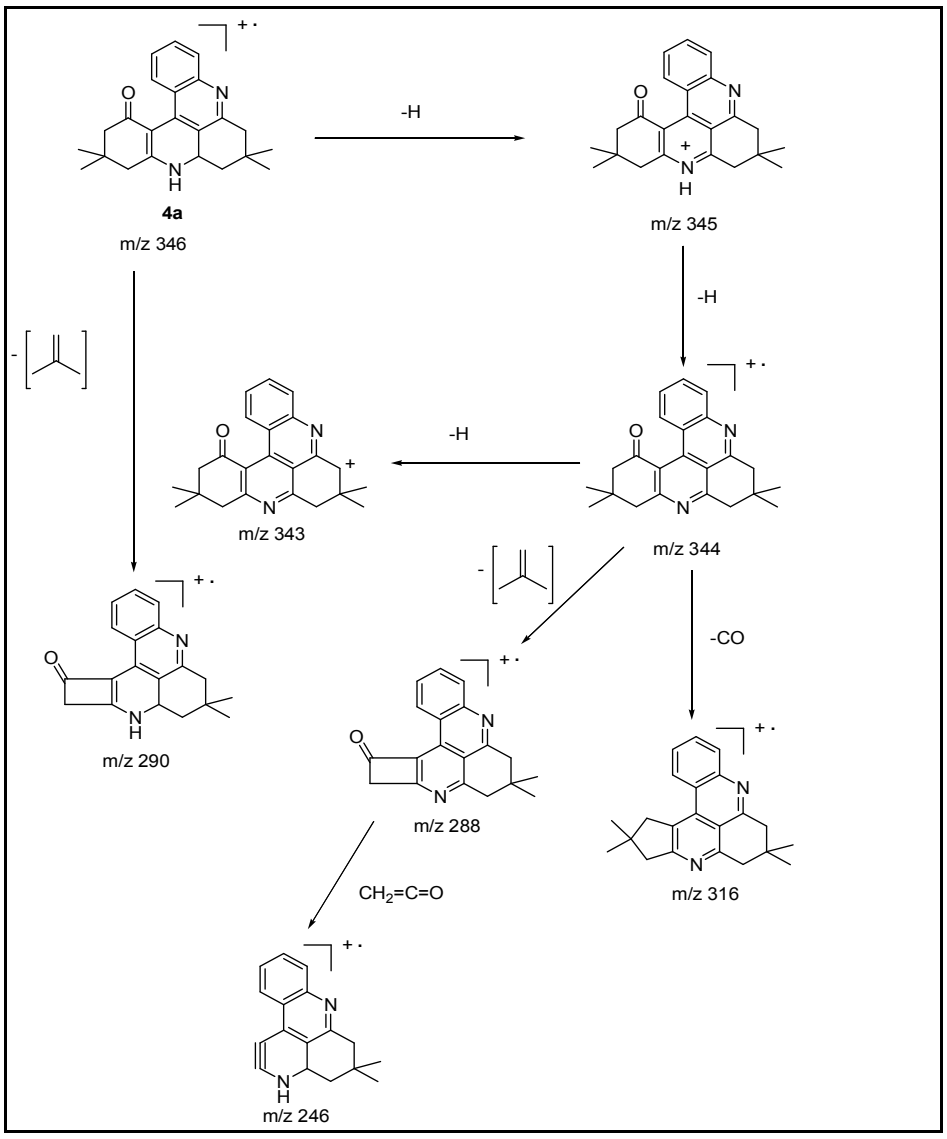
Table –II

Compound	R
6a	CH_3
6b	CH_3
6c	OCH_3

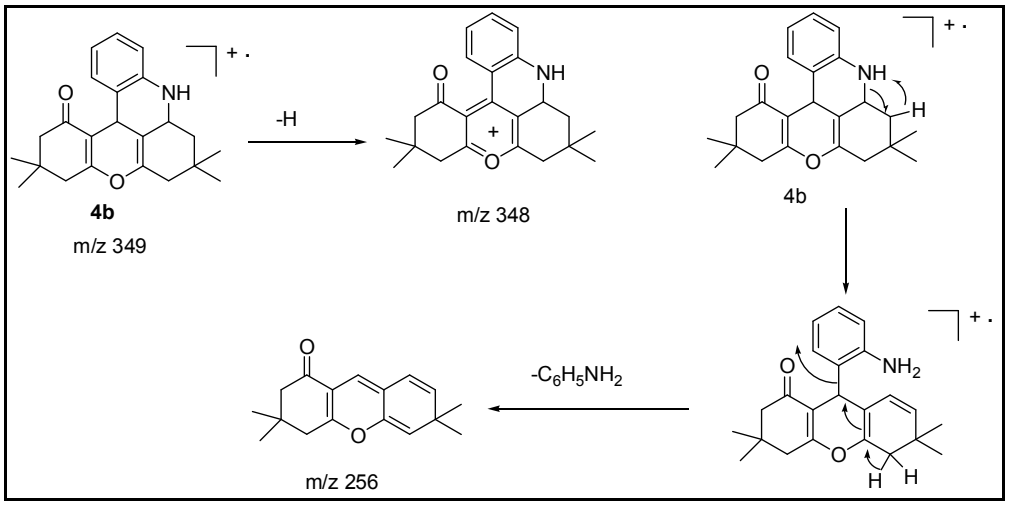


The loss of H and followed by cleavage of benzylamine groups was observed in compound **4b** and the fragmentation pattern shown in **Scheme-VII**. Similar loss of H , C_2H_4, CN, NH_2 groups was observed in compounds **5a-d** and the characteristic loss of H, Schiff's base and substituted acetylene moiety groups was observed in compounds **6a-c** and the schematic fragmentation pattern is depicted in **scheme-VIII**. The common

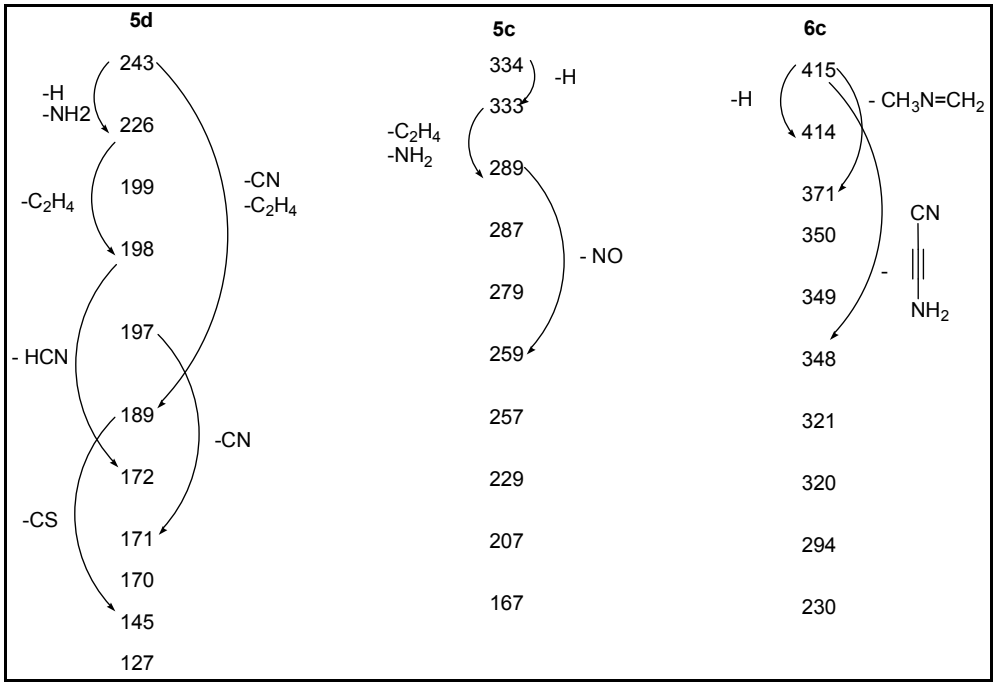
loss of H, CO, C_2H_4, HCN groups were observed in quinoxaline derivatives (**7a-b, 8**) and the fragmentation pattern is depicted in **Scheme - IX**



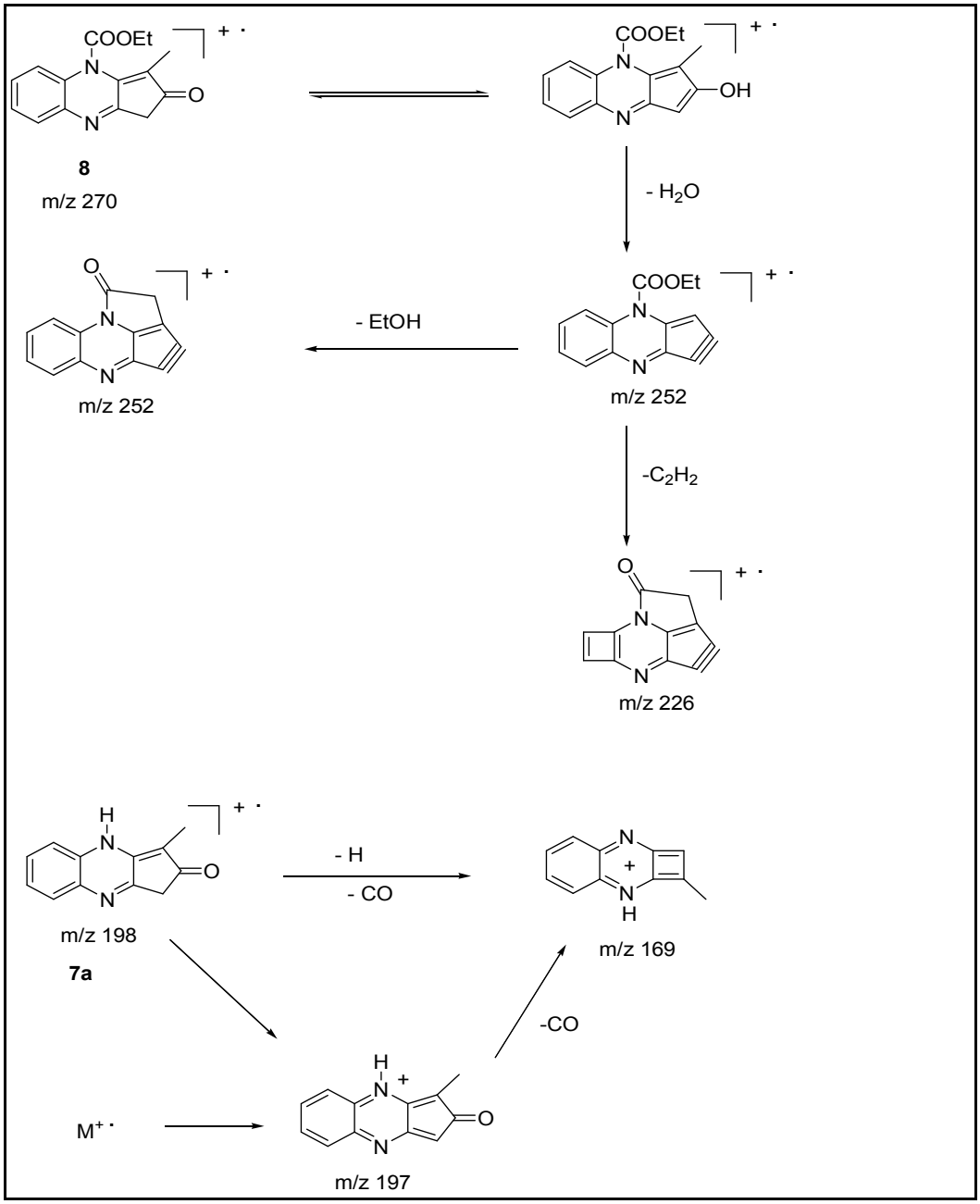
Scheme –VI



Scheme - VII


5d
243
-H
-NH2
226
-C2H4
199
198
-CN
-C2H4
- HCN
197
189
-CN
172
-CS
171
170
145
127
5c
334
-H
333
-C2H4
-NH2
289
287
- NO
279
259
257
229
207
167
6c
415
-H
- CH3N=CH2
414
371
350
CN
-
349
NH2
348
321
320
294
230

Scheme-V III



Scheme- IX Compound 4a loss of H, CO groups in two different routes was observed and showed in Scheme-IV.

Conclusion

Totally **25** m-terphenyl , biaryl derivatives and nitrogen containing heterocyclic compounds were studied for their mass spectral fragmentation pattern. Molecular mass information and fragmentation pattern are easily obtained under the electron ionization (EI) condition. The most common loss of CN, NH_2, HCN, C_2H_4 groups were observed from all the compounds **1a-e, 2a-g, 3a-c**. Similar loss of CH_3, HCHO and HCN groups were identified both methyl substituted compounds **1b** and **1d** from the molecular ions. Successive loss of phenyl groups were observed in compound **1c** and the loss of CHO group is the characteristic of furfuryl moiety has been observed in compound **3c** (m/z 194). The loss of H, isobutylene and ketene groups were observed in quinoacridine (**4a**). Similar loss of H, C_2H_2, NH_2, CN, groups were observed both pyridinedinitrile compounds **(5a-d)** and pyranopyridine derivatives (**6a-c**) .The common loss of H, CO, C_2H_4, HCN groups were observed in quinoxaline derivatives (**7a-b, 8**).

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