Electron Ionization Mass Spectrometric Studies of 1,2-Dihydro-2-[2-(1',3'-benzo-thiazolyl)]-3H-indazol-3-one and 1,2-Dihydro-2-(3',4'-dimethylphenyl)-6,7-dimethoxy-3H-indazol-3-one

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Summary:Electron ionization mass spectra of 1,2-dihydro-2-[2-(1',3'-benzothiazo-lyl)]-3H-indazol-3-one (**2a**) and 1,2-dihydro-2-(3',4'-dimethylphenyl)-6,7-dimethoxy-3H-indazol-3-one (**2b**) and their related compounds (**1a-b**) are described with the help of LREIMS. The molecular formulae are further confirmed by high resolution peak matching of molecular ion peaks exhibited by EIMS.

Introduction

2-Substituted indazolones [1] are an important class of hetrocycles which find a number of useful applications. Colour couplers of indazolinone type had long been used to produce colour photographic images. Thus, 5-(steraroylamino)-3-indazolinone is major ingredient of an emulsion for positive motion picture films [2]. Indazolone derivatives have been tested for antihyperlipodemic activity [3] in male mice. The N-2-butylindazolone was the most active compound. 4-Carbamoylindazol-3-ones [4] are potent 5-lipoxygenase (5-LPO) inhibitors. Thus 1,2-dihyro-2-methyl-4-(pentylcarbamoyl)-3H-indazol-3-one had ED_{50} of 30-100 mg/kg orally in rats for 5-LPO inhibitation. Thermal transfer sheets containing inks coloured with indazolone derivatives have been patented [5].

We have reported [6,7] already the synthesis of 1,2-dihydro-2-[2-(1',3'-benzothiazolyl)]-3H-indazol-3-one (**2a**) and 1,2-dihydro-2-(3,4-dimethyl-phenyl)-6,7-dimethoxy -3H-indazol-3-one (**2b**) and their related compounds (**Ia-b**) . In this article we wish to report low resolution electron ionization mass spectral (LREIMS) studies of these compounds [**1a-b** & **2a-b**]. The molecular formulae of these compounds were further confirmed by high resolution electron ionization mass spectral (HREIMS) and peak matching of molecular ion

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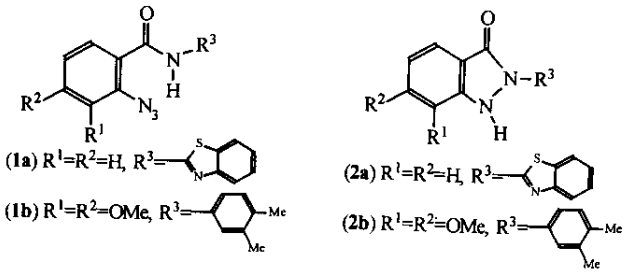
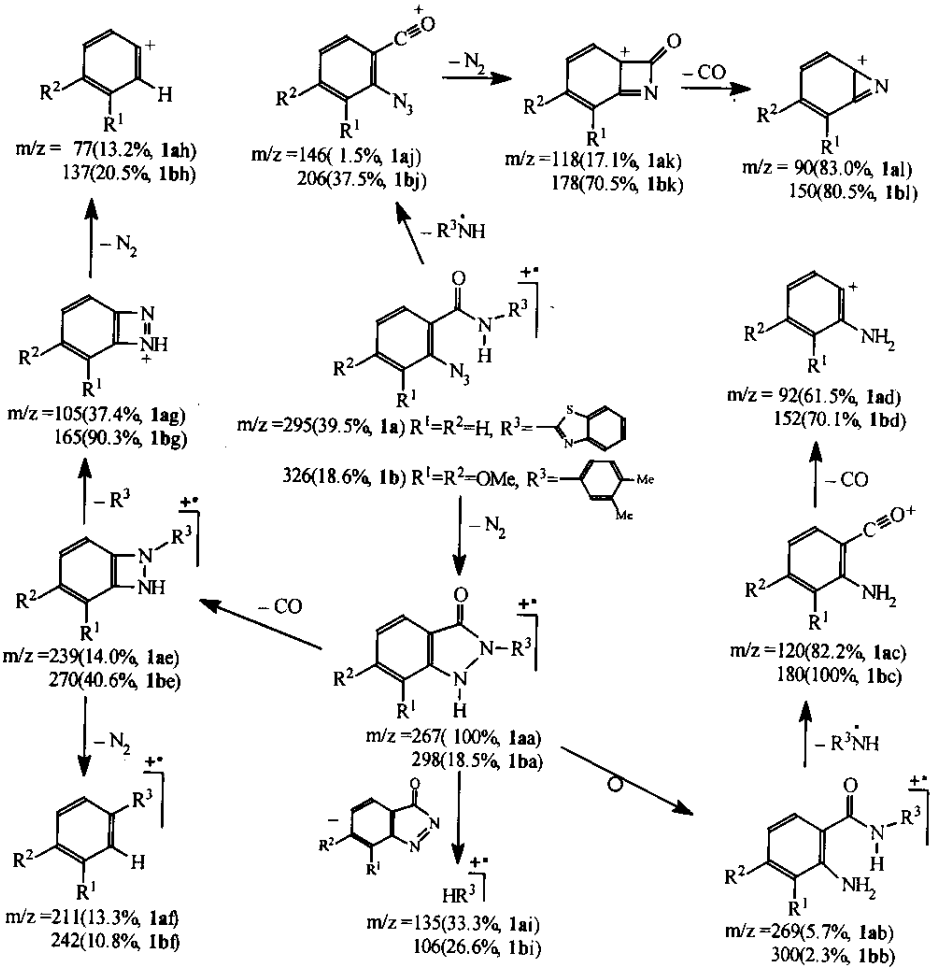


Table-1: HREIMS of molecular ion peaks of the compounds (**1a-b & 2a-b**).

Compd.	Mol. Formulae	M(m/z)	
		Calc.	Found
1a	$C_{14}H_9ON_5S$	295.0528	295.0523
1b	$C_{17}H_{18}O_3N_4$	326.1379	326.1380
2a	$C_{14}H_9ON_3S$	267.0466	267.0460
2b	$C_{17}H_{18}O_3N_2$	298.1317	298.1312



Scheme-1

peaks exhibited by electron ionization mass spectra (EIMS) are listed in Table-1.

Results and Discussions

The mass fragmentation patterns of these compounds (**1a-b** & **2a-b**) are assigned with the help of LREIMS and are depicted in Schemes **1-3.**

2-Azido-N-2-(1',3'-benzothiazolyl)benzanilide (1a) and 2-Azido-3,4-dimethoxy-N-(3',4'-dimethylphenyl) benzanilide (1b)

The EIMS of (**1a-b**) afforded radical cations at m/z 295 ($C_{14}H_9N_5OS$, **1a**) and 326 ($C_{17}H_{18}N_4O_3$, **1b**) The loss of N_2 molecule from (**1a-b**) yielded radical cations at m/z 267 ($C_{14}H_9N_5OS$, **1aa**) and 298 ($C_{17}H_{18}N_2O_3$, **1ba**) followed by the reduction and ring opening afforded other raidcal cations at m/z 269 ($C_{14}H_{11}N_5OS$, **1ab**) and 300 ($C_{17}H_{20}N_2O_3$, **1bb**). The loss of 2-amino-1,3-benzothiazolyl radical from (**1ab**) and 3,4-dimethylaniline radical from (**1bb**) yielded cations at m/z 120 (C_7H_6NO, **1ac**) and 180 ($C_9H_{10}NO_3$, **1bc**) followed by the loss of CO molecule afforded other cations at m/z 92 (C_6H_6N **1ad**) and 152 ($C_8H_{10}NO_2$ **1bd**). The loss of CO molecule from (**1aa-ba**) yielded radical cations at m/z 239 ($C_{13}H_9N_3S$, **1ae**) and 270 ($C_{16}H_{18}N_2O_2$ **1be**) followed by the loss of N_2 molecule afforded radical cations at m/z 211 ($C_{13}H_9NS$, **1af**) and 242 ($C_{16}H_{18}O_2$, **1bf**). The loss of 1,3-benzothiazolyl radical from (**1ae**) and 3,4-dimethylbenzene radical from (**1be**) yielded cations at m/z 105 ($C_6H_5N_2$ **1ag**) and 165 ($C_8H_9N_2O_2$, **1bg**) followed by the loss of N_2 molecule afforded cations at m/z 77 (C_6H_5 **1ah**) and 137 ($C_8H_9O_2$, **1bh**) and the loss of 1,2-benzodiazol-3-one from (**1aa**) and 6,7-dimethoxy-1,2-benzadiazol-3-one from (**1ba**) yielded radical cations at m/z 135 (C_7H_5NS, **1ai**) and 106 (C_8H_{10}, **1bi**). The loss of 2-amino-1,3-benzodiazolyl radical from (**1a**) and 3,4-dimethylaniline radical from (**1b**) afforded cations at m/z 146 ($C_7H_4N_3O$, **1aj**) and 206 ($C_9H_8N_3O_2$, **1bj**). The loss of N_2 molecule from (**1aj-bj**) yielded cations at m/z 118 (C_7H_4NO, **1ak**) and 178 ($C_9H_8NO_3$, **1bk**) followed by the loss of CO molecule afforded cations at m/z 90 (C_6H_4N, **1al**) and 150 ($C_8H_8NO_2$ **1bl**). (Scheme-**1**).

1,2-Dihydro-2-[2-(1',3'-benzthiazolyl)]-3H-indazol-3-one (2a)

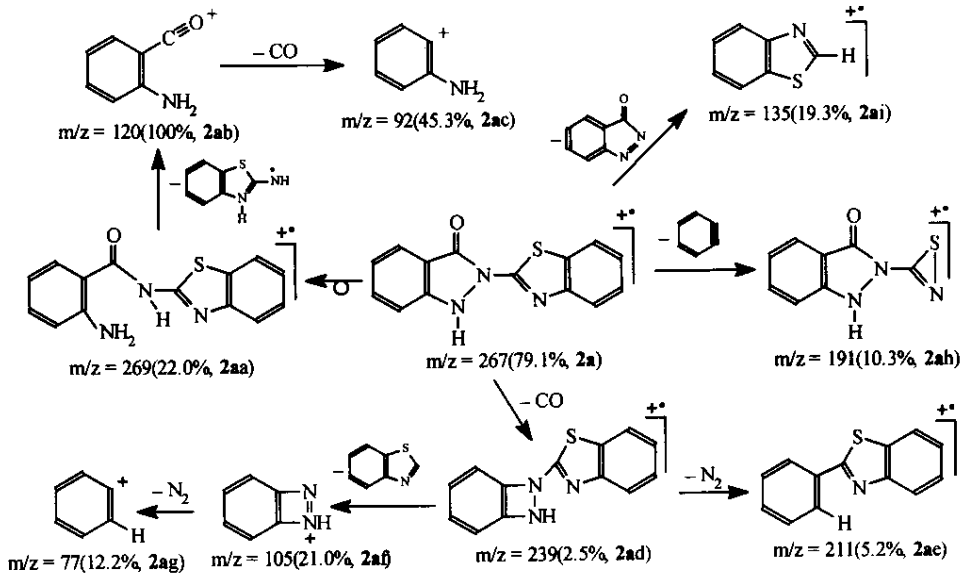
The EIMS of (**2a**) afforded radical cation at m/z 267 ($C_{14}H_9N_3OS$, **2a**). The reduction and ring opening of (**2a**) at high temperature during EI (+Ve) yielded another radical cation at m/z 269 ($C_{14}H_{11}N_3OS$, **2aa**) followed by the loss of 2-amino-1,3-benzothiazolyl radical afforded a cation at m/z 120 (C_7H_6NO, **2ab**). The loss of CO molecule from (**2ab**) yielded another cation at m/z 92 (C_6H_6N, **2ac**). The loss of CO molecule from (**2a**) afforded a radical cation at m/z 239 ($C_{13}H_9N_3S$, **2ad**) followed by the loss of N_2 molecule yielded another radical cation at m/z 211 ($C_{13}H_9NS$, **2ae**). The loss of 1,3-benzothiazol from (**2ad**) afforded a cation at m/z 105 ($C_6H_5N_2$, **2af**) followed by the loss of N_2 molecule yielded phenyl cation at m/z 77 (C_6H_5, **2ag**). The loss of benzyne from (**2a**) afforded a radical cation at m/z 191($C_8H_5N_3OS$, **2ah**) and the loss of 1,2-benzodiazol-3-one molecule from (**2a**) yielded another radical cation at m/z 135 (C_7H_5NS, **2ai**). (Scheme-**2**).

1,2-Dihydro-2-(3',4'-dimethylphenyl)-6,7-dimethoxy-3H-indazol-3-one (2b)

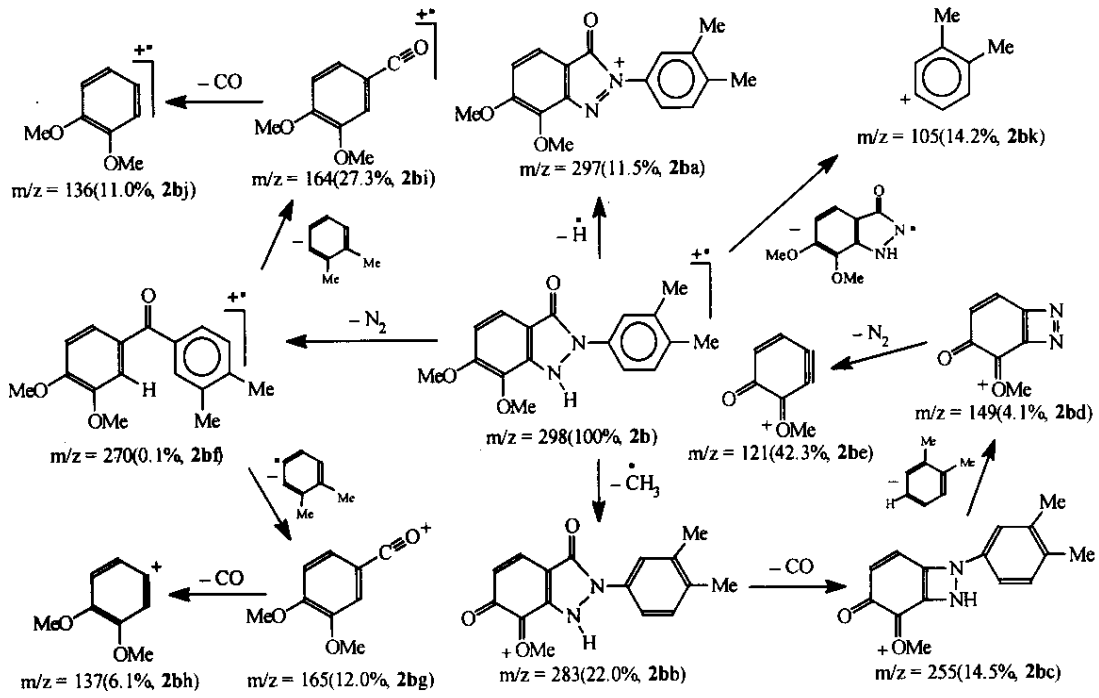
The EIMS of (**2b**) afforded radical cation at m/z 298 ($C_{17}H_{18}N_2O_3$, **2b**). The loss of H radical from (**2b**) yielded a cation at m/z 297 ($C_{17}H_{17}N_2O_3$, **2ba**). The loss of methyl radical from (**2b**) afforded a cation at m/z 283 ($C_{16}H_{15}N_2O_3$, **2bb**) followed by the loss of CO molecule yielded another cation at m/z 255 ($C_{15}H_{15}N_2O_2$, **2bc**). The loss of *o*-xylene from (**2bc**) afforded a cation at m/z 149 ($C_7H_5N_2O_2$, **2bd**) followed by the loss of N_2 molecule yielded another cation at m/z 121 ($C_7H_5O_2$, **2be**). The loss of N_2 molecule from (**2b**) afforded a radical cation at m/z 270 ($C_{17}H_{18}O_3$, **2bf**) followed by the loss of *o*-xylene radical yielded a cation at m/z 165 ($C_9H_9O_3$, **2bg**). The loss of CO molecule from (**2bg**) afforded a cation at m/z 137 ($C_8H_9O_2$, **2bh**) and the loss of *o*-xylene molecule from (**2bf**) yielded a radical cation at m/z 164 ($C_9H_8O_3$, **2bi**) followed by the loss of CO molecule afforded a radical cation at m/z 136 ($C_8H_8O_2$, **2bj**). The loss of 6,7-dimethoxy-1,2-dihydro-1,2-benzodiazol-3-one from (**2b**) yielded a cation at m/z 105 (C_8H_9, **2bk**). (Scheme-**3**).

Experimental

Compounds (**1a-b** and **2a-b**) were prepared according to the literature procedure [6,7]. All of them were characterized by IR and ^{1}H-NMR spectral data. The EIMS were recorded on MAT-311 instrument with an accelerating voltage of 3 kV and ionization energy of 70 eV. The temperature of the ion source was maintained at 250°C.



Scheme-2



Scheme-3

Conclusion

The above fragmentation patterns show that the loss of N_2 from molecular ions of compounds (**1a** & **1b**) furnish the radical cations which are similar to (**2a** &**2b**) and their further fragmentation patterns are similar.

References

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