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Synthesis and investigation of mass spectra of some nitrogen heterocycles and salycylaldazine derivatives

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ABSTRACT

*Reaction of cynoacetic acid hydrazide (**1**) with thiophene-2- carboxaldehyde, phthalic anhydride, 5-bromosalicylaldehyde and 2-hydroxyacetophenone yielded the corresponding hydrazone derivative (**2**), phthalazin-1,4-diones (**5**) and salicylaldazine derivatives (**10**$_{a-b}$). Pyrazolo[5-,1-a] pyrimidinone (**4**) was prepared via the reaction of hydrazone (**2**) with malononitrile in the presence of triethyl amine. Bromination and hydrazonylsis of phthalazin-1,4-diones derivative (**5**) with bromine and hydrazine hydrate gave the corresponding 2-(bromo cyanomethyl) carbonyl phthalazin-1,4- dione (**6**) and phthalazin-1,4-dione (**8**). The electron impact mass spectra of both of the above some series of compounds have also recorded and their fragmentation pattern are discussed.*

Keywords: Synyhesis, Mass spectra, nitrogen heterocycles, salycylaldazine derivatives.

INTRODUCTION

Many publications[1-7] report the synthesis of different heterocyclic compounds using cyanoacetic acid hydrazide as key starting material. The biological properties of some heterocyclic compounds were prepared from cyanoacetic acid hydrazide is reported[8-15].

In this work, reported the preparation of some hetero-cyclic compounds containing nitrogen atoms and salicylaldazine derivatives using cyanoacetic acid hydrazide (**1**) as a key starting material which was obtainable in the reaction of ethyl cyanoacetate with hydrazine hydrate according to literature methods. The electron impact (EI) mass spectral fragmentation patterns of some synthesized compounds are described.

MATERIALS AND METHODS

The melting points were determined in capillaries with MEL-TEMP II laboratory Devices, USA, and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 337 Spectrophotometer using KBr wafers. Proton NMR spectra were obtained on a Varian EM 360 spectrometer using solution in hexadeuteriodimethyl sulphoxide with tetramethyl silane as the internal standard. Mass spectra were recorded on a VG Autspec GEIFAB and a Hewlett Packard MS-Engine thermospray and ionization by electron impact at 70 eV. The acceleration voltage was 6 kV, the emission current ≈ 100 MA. Microanalysis was conducted using a Perkin-Elmer 2408 CHN analyzer.

1-(Thiophen-2-carboaldehyde)-cyanoacetic acid hydrazone (2)
A mixture of cyanoacetic acid hydrazide (0.01 mole) and thiophene-2-caboxaldehyde (0.01 mole) in methanol (30 ml) was heated under reflux for 2 hrs. The solid formed after cooling was filtered off, dried and purified by recrystallization with ethanol to give **2** as yellow crystals, yield 76% mp 165°C. IR (KBr): 3222(NH), 2254(CN), 1678(C=O), 1625 (C=N) cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 3-25(s, 2H, $COCH_2CN$), 7.35-7.86(s, 3H, thiophene-H), 8.62(s, 1H, CH= N), 10.83(s, 1H, NH). Anal. Calcd for $C_8H_7N_3OS$: C, 49.74; H, 3.63; N, 21.76; S, 16.58. Found: C, 49.48; H, 3.36; N, 21.4; S, 16.29.

2-Amino-6-thinyl-7-cyano-4-oxo-3-hydropyrazolo[5,1-a]pyrimidine (4)
A mixture of **2** (0.01 mole), malonoitrile (0.01 mole) and triethyl amine (0.03mole) in ethanol (50 ml) was heated under reflux for 3 hrs. The solid formed after hot was frittered off, dried and purified by recrystallization from acetic acid to give **4** as yellow crystals, yield 56%, m.p.30°C, IR (KBr): 3396, 3249(NH_2), 3303(NH), 2208(CN), 1683(CO), 1631(C=N) cm^{-1} . ^{1}H-NMR (DMSO-d_6): δ 5.71 (s, 2H, $COCH_2$), 7.20-7.90(m, 3H, Thiophene-H), 8.41-8.63(br.s, 2H, NH_2) ppm. Anal. Calcd for $C_{11}H_7N_5OS$: C, 51.36; H, 2.72; N, 27.24; S, 12.45. Found: C, 51.08; H, 2.47; N, 27.02; S, 12.22.

2-(Cyanomethyl)carbonyl-phthalazien-1,4-dione (5)
A mixture of **2** (0.01 mole) and phthalic anhyaride (0.01 mole) in methanol (30 ml) was heated under reflux for 3 hrs. The solid obtained after cooling was filtered off, dried and purified by recrystallization from ethanol to give **5** as colourless crystals, yield 81%, m.p. 186 °C. IR (KBr): 3294(NH), 2257(CN), 1748, 1680 (CO), 1611, 1583 (C=C) cm^{-1}. ^{1}H-NMR (DMSO-d_6):δ 3.22 (s, 2H, $COCH_2CN$), 7.21-7.83 (m, 4H, Ar-H), 10.63 (s, 1H, NH) ppm. Anal. Calcd for $C_{11}H_7N_3O_3$: C, 57.64; H, 3.06; N, 18.34. Found: C, 57.41; H, 2.89; N, 18.17.

1-(Bromo cyano methyl)carbonyl-phthalazine-1,4-dione (6)
A solution of **5** (0.01 mole) in glacial acetic acid (30 ml) was added to a solution of bromine (0.01 mole) in glacial acetic acid (10 ml) with stirring at room temperature for 2hrs. The solid formed was filtered off, washed with water, dried and recrystallized from ethanol to give **6** as colorless crystals , yield 63%, m.p. 240 °C, IR (KBr): 3229 (NH) , 2254 (CN), 1744, 1687 (CO) , 1605, 1588 (C = C) cm^{-1}. ^{1}H-NMR (DMSO-D_6): δ 5-91 (s, 1H, CHBrCN), 7.62-8.01 (m, 4H, Ar-H), 11.68 (s, 1H, NH) ppm. Anal. Calcd For $C_{11}H_6BrN_3O_3$: C, 42.99; H, 1.95; N, 13.68. Found: C, 42.71; H, 1.69; N, 13.36.

Phthalazine-1,4-dione (8)
A mixture of **5** (0.01 mole) and hydrazine hydrate (0.03 mole) was fused on a hot plate for 10-15 min. The reaction mixture was added to boiling methanol (50ml) and heated under reflux for 2hr, then cooled. The solid formed was filtered off, washed with methanol, dried and purified by recrystallization with acetic acid to give **8** as colorless crystals, yield 47%, m.p. 256 °C, IR (KBr): 3165 (NH), 3300-2582 (br , OH), 1662 (CO), 1601, 1556 (C=C), 1261, 1080 (C-O) cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 7.61-8.10 (m, 4H, Ar-H), 10.80-11.01 (br. s, 2H, NH) ppm. Anal. Calcd For $C_8H_6N_2O_2$: C, 59.26; H, 3.70; N, 17.28. Found; C, 59.04; H, 3.58; N, 17.12.

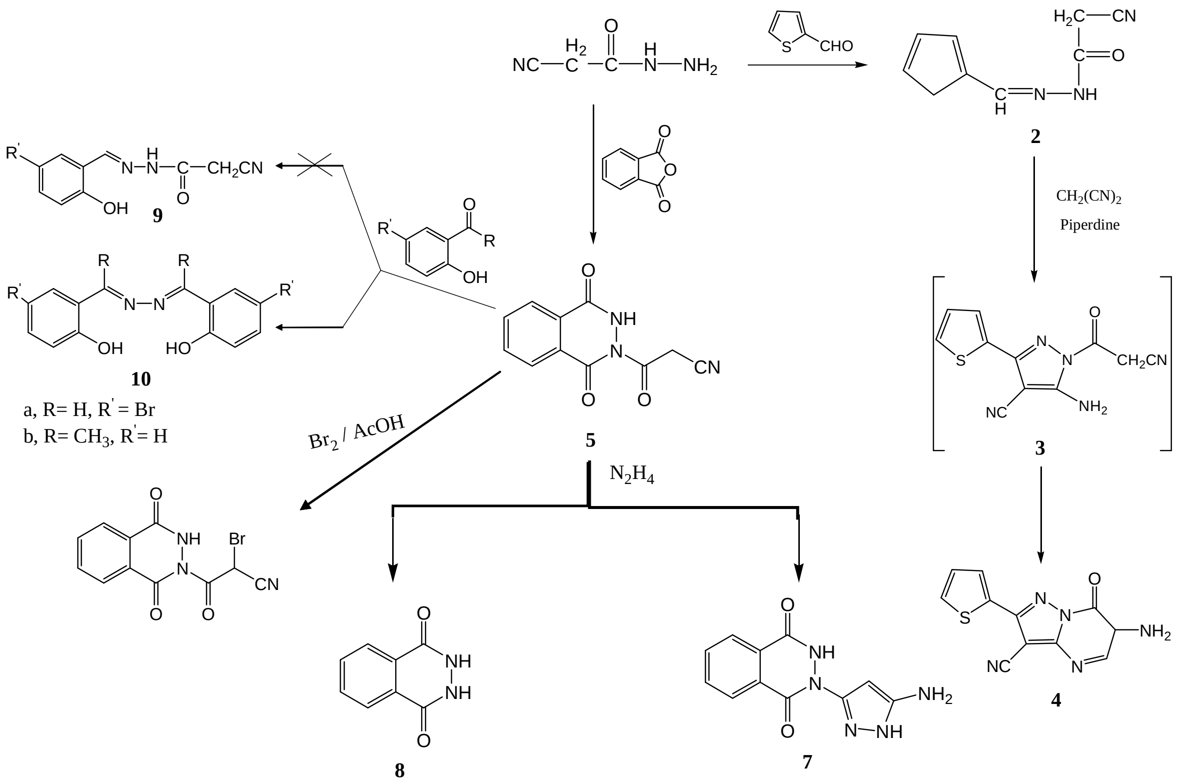
5- bromosaliayladazine (10_a)
Bis-1-(o-hydroxyphenylethylidene)amine (10_b)
A mixture of **2** (0.01 mole) and carbonyl compounds (such as 5- bromosalicylaldehyde and 2-hydroxyacetophenone, 0.01 mole) in methanol (50 ml) in presence of acetic acid (1 ml) was heated under reflux for 4hr. The solid formed after cooling was filtered off, dried and purified by recrystallization with ethanol to give to 10.
Compound 10_a as pale yellow crystals , yield 63%, m.p 288 °C, IR (KBr): 3430-2890(br. OH), 1632(C=N), 1605, 1583(C= C), 1225, 1085(C-O) cm^{-1}. ^{1}H.NMR (DMSO-d_6): δ 7.12-7.81 (m, 6H , Ar-H), 8.73 (s, 2H, 2x CH =N), 11.35 (br.s, 2H, 2xOH) ppm . Anal Calcd for $C_{14}H_{10}Br_2N_2O_2$: C, 42.42; H, 2.53; N, 7.07. Found: C, 42.18 ; H, 2.38; N, 6.98.
Compound 10_b as yellow crystals , yield 61%, m.p. 212 °C, IR (KBr); 3380-2700 (br.OH), 1635(C=N), 1063, 1587 (C=C), 1246, 1115(C-O) cm^{-1}. ^{1}H-NMR (DMSO-d_6); δ 2.53 (s, 6H, $2xCH_3$), 6.99-7.88 (m, 8H, Ar-H), 12.83 (s, 2H, 2xOH) ppm. Anal. Calcd for $C_{16}H_{16}N_2O_2$; C, 71.64; H, 5.97; N, 10.45. Found: C, 71.41; H, 5.68; N, 10.22.

RESULTS AND DISCUSSION

Chemistry
Condensation of cyanoacetic acid hydrazide (**1**) with thiophene-2-carboxaldehyde[12] in ethanol under reflux led to the formation of 1-(thiophene-2-carboxaldehyde)-cyanoacetic acid hydrazone (**2**). 2-Amino-6-(thinyl)-7-cyano-4-oxo-3-hydropyrazolo[5,1-a] pyrimidine (**4**) was prepared via the reaction of 4-(thiophene-2-carboxaldehyde)-cyanoacetic acid hydrazone (**2**) with malononitrile in methanol in presence of triethyl amine under reflux to give 1-(cyanomethyl)carbonyl-3-thinyl-4-cyano-5- amino pyrazole (**3**) as intermediate , followed by cyclization .

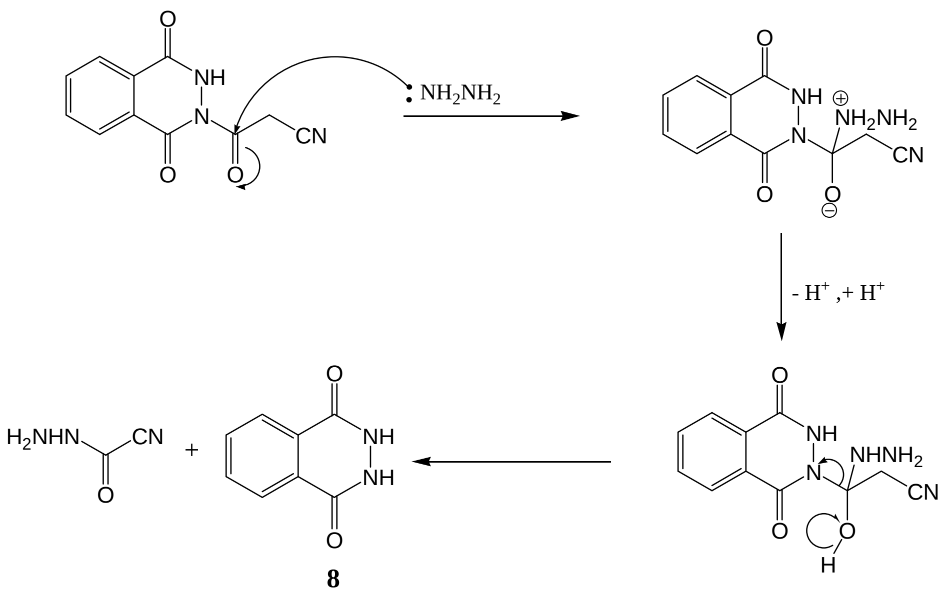
Treatment of cyanoacetic acid hydrazide (**1**) with phthalic anhydride in ethanol under reflux afforded the corresponding to 3-(cyanomethyl)carbonyl-phthantazin-1,4-dione (**5**) .

Bromination [16] of 2-(cyanomethyl)carbonyl-phthalazine-1,4-diane (**5**) with one mole from the bromine in glacial acetic acid at room temperature gave the corresponding 2-(bromocyanomethyl)carbonyl-phthalazin-1,4-diane (**6**), scheme (1).



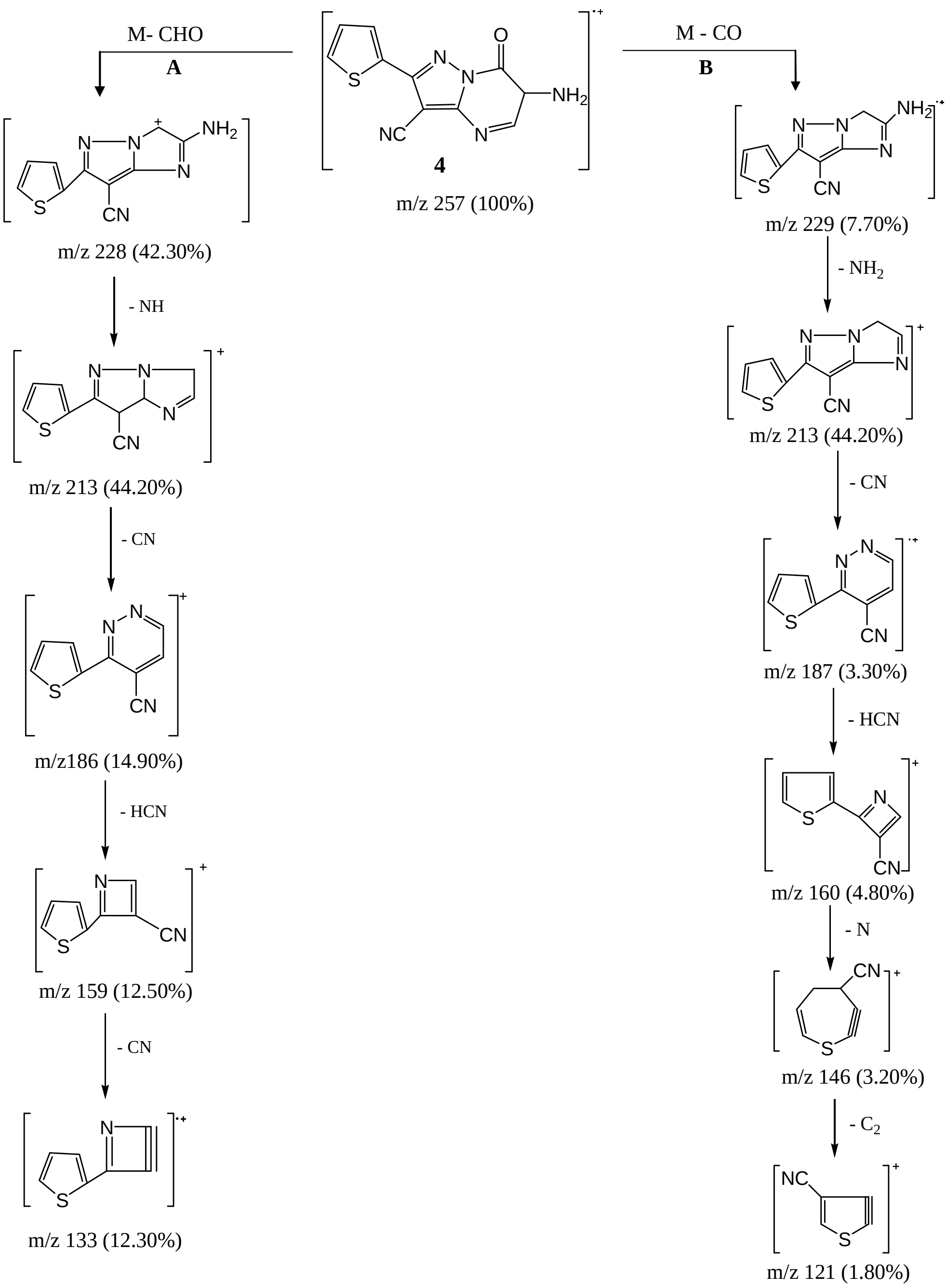
Scheme 1

Hydrazanylsis of **5** with hydrazine hydrate by fusion at 120°C, gave the corresponding to phthalazin-1,4-diane (**8**, known), which does not give the expected structure **7**(scheme 1). The formation of compound **8** takes place via the following mechanism as shown in scheme (2).



Scheme 2

The reaction of cyanoacetic acid hydrazide (**1**) with 5- bromosalicyladehyde and 2-hydroxyacetophenone in presence of acid catalyst in ethanol under reflux was expected to give structure **9**, but only 5- bromosalicylaldazine (**10**$_a$) and 1-(o-hydroxy-phenyl) ethylidene amine (**10**$_b$) were yielded.



Scheme 3: Main fragmentation pathway of compound 4

Mass spectrometry

The mass spectral decomposition[17-22] modes of various organic compounds such as hydrazone derivative, pyrazolopyrimidinone, 1,4-phthalazindione derivative and salicylaldazine derivatives have been suggested and investigated . Table (1) lists the *m/z* (relative abundance, %) values of the principle fragment of the prepared compounds.

The mass spectrum of compound **2** (Fig.1) shows a weak intense molecular ion peak at *m/z* 143, corresponding to the molecular formula $C_8H_7N_3OS$.

The molecular ion of compound **2** (*m/z* 193) underwent fragmentation via pathway *A* to produce a peak at *m/z* 125 by losing cyanoacetyl ($CNCH_2CO$) group. The lose of amino group (NH_2) from the ion with m/z 125 resulted in a stable fragment at *m/z* 109. The stable ion at *m/z* 109 underwent loss of cyano group and sulphur atom to give peaks at *m/z* 83 and *m/z* 51, respectively.

Also the ion at *m/z* 193 underwent loss of cyanoketene (CN-CH=C= O) via pathway B to give peak at *m/z* 126. The ion at *m/z* 126 underwent fragmentation to produce a peak at *m/z* 110, 96, and *m/z* 70 by losing amino group (NH_2), nitrogen atom and ethylene molecule, respectively.

The mass spectrum of compound 4 (Fig. 2) shows strong and intense molecular ion peak at *m/z* 257, corresponding to the molecular formula $C_{11}H_7N_5OS$. The molecular ion peak was found to be the base peak.

The molecular ion of compound **4** underwent fragmentation via pathway A to produce the peak at *m/z* 228 by losing formyl group (CHO), The ion of *m/z* 228 was broken to give ion of *m/z* 213 by losing imino group (NH). Ion of *m/z* 213 underwent loss of two molecules from the hydrogen cyanide to give peak at *m/z* 186 and *m/z* 159. This fragmentation led to the ions at *m/z* 133, 101, 76 and m/z 50, respectively.

Accordingly, the same molecular ion, of compound **4** (Scheme3) was found to undergo fragmentation via path way *B* to produce ion at *m/z* 229 by losing carbon monoxide (C=O). The ion of *m/z* 213 was obtained by loss of amino group (NH_2) from the ion of *m/z* 229. Ion of *m/z* 213 underwent loss of cyano group (CN), nitrogen atom and hydrogen cyanide (HCN) to give peaks at *m/z* 187, 173 and *m/z* 146, respectively. The loss of cyano group from the ion of *m/z* 146 gives peak at *m/z* 120. This fragmentation led to the ion of *m/z* 82 and *m/z* 58.

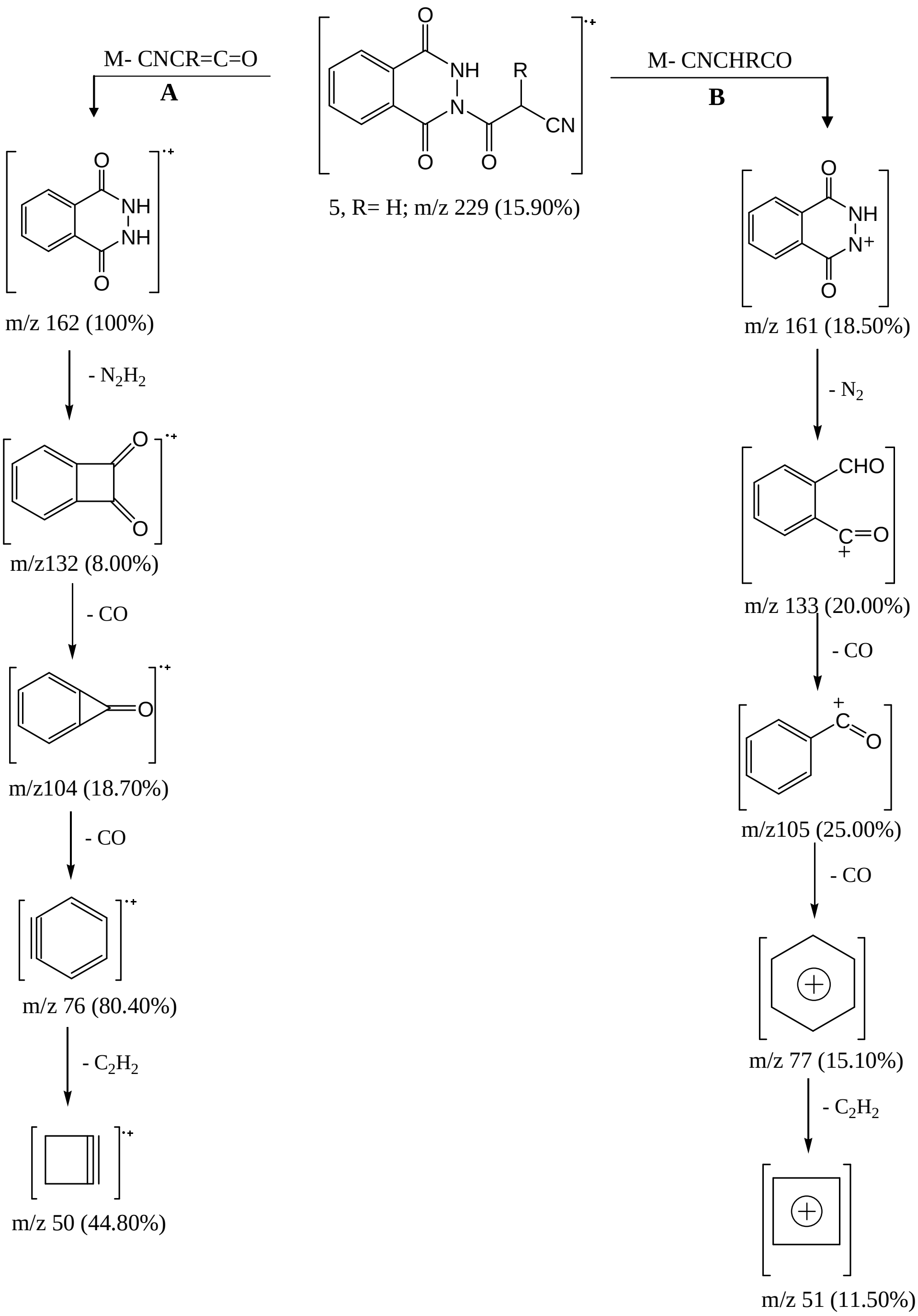
Table (1) EI Mass Spectra (70 eV) of Compounds 2, 4,5,6,8 and 10

Compd	M^+	Pathway A		Pathway B		Other ions
		-M	m/z	-M	m/z	
2	$[C_8H_7N_3OS]^+$ 193 (24.60)	$COCH_2CN$	$[C_5H_5N_2S]^+$ 125 (15.50)	NC – CH= = O	$[C_5H_6N_2S]^+$ 126(4.00)	194 (M^++l, 3.4), 142 (M^+-1, 2.60), 153 (2. 60), 124 (2.70), 112 (5.10), 111 (10.30), 105 (1.40), 99 (6.90), 98 (34.90), 97 (11.00), 95 (10.50), 94 (4.80), 84 (6.20), 82 (6.20), 81 (12.10), 71 (9.30), 69 (15.00), 68 (14.60), 63 (9.60), 62 (4.00), 58 (10.40), 57 (6.50), 54 (12.01), 53 (10.20), 52 (12.00), 50 (7.90)
		NH_2	$[C_5H_3NS]^+$ 109 (100)	NH_2	$[C_5H_4NS]^+$ 110(64.30)	
		CN	$[C_4H_3S]^+$ 83 (7.60)	N	$[C_5H_4S]^+$ 96(16.90)	
		S	$[C_4H_3]^+$ 51 (11.50)	C_2H_2	$[C_3H_2S]^+$ 70 (22.40)	
4	$[C_{11}H_7N_5OS]^+$ 257 (100)	CHO	$[C_{10}H_6N_5S]^+$ 228 (42.20)	CO	$[C_{10}H_7N_5S]^+$ 229 (7.70)	258 (M^++l, 20.30), 256 (M^+-1, 8.00), 242 (3.30), 241 (1.40), 227 (7.50), 214 (4.20), 200 (4.10), 199 (3.30). 197 (4.50), 192 (2.70), 192 (13.30), 185(7.90), 174(3.40), 171 (6.20), 169 (4.00), 160 (4.80), 158 I (3.90), 145(3.20), 135(3.30), 134 (8.90), 132(1.00), 121 (1.80), 118 (2.70), 1 15 (2.50), 1 14 (3.10), 108 (1.80) 107(2.70), 106(2.20), 100 (5.00), 99(3.60), 95(2.80). 94(6.60), 93(3.30), 90(5.00), 89(5.20), 88(7.30), 87(5.30), 84(3.70)
		NH	$[C_{10}H_5N_4S]^+$ 213 (44.20)	NH_2	$[C_{10}H_5N_4S]^+$ 213 (44.20)	
		HCN	$[C_9H_4N_3S]^+$ 186 (14.90)	CN	$[C_9H_5N_3S]^+$ 187 (3.30)	
		HCN	$[C_8H_3N_2S]^+$ 159 (12.50)	N	$[C_9H_5N_2S]^+$ 173 (4.20)	
		CN	$[C_7H_3NS]^+$ 133 (12.30)	HCN	$[C_8H_4NS]^+$ 146 (5.10)	

Compd	M^+	Pathway A -M	Pathway A m/z	Pathway B -M	Pathway B m/z	Other ions
5	$[C_{11}H_7N_3O_3]^+$ 229 (15.90)	CNCH=C=O	$[C_8H_6N_2O_2]^+$ 162 (73.80)	CH_2	$[C_4H_5N_2O_3]^+$ 184(6.40)	164(0.80), 163(7.30), 160(1.50), 134(1.00), 131(13.60), 118(1.50), 117(1.70), 116(0.90), 106(2.00), 105(21.50), 102(2.40), 101(1.30), 91(4.50), 102(2.40), 101(1.30), 91(4.50), 90(6.10), 89(5.40), 78(3.30), 77(26.90), 74(38.70), 73(30.30), 72(6.40), 68(46.60), 67(46.30), 66(5.10), 65(2.80), 64(6.20), 53(6.90), 52(10.40)
		NH	$[C_8H_5NO_2]^+$ 147 (1.20)	CO	$[C_8H_4N_2O_2]^+$ 161(75.50)	
		NH	$[C_8H_4O_2]^+$ 123 (15.10)	N_2	$[C_8H_5O_2]^+$ 133(6.90)	
		CO	$[C_7H_4O]^+$ 104(70.70)	CH_2O	$[C_7H_3O]^+$ 103 (75.90)	
		CO	$[C_6H_4]^+$ 76(38.70)	CO	$[C_6H_3]^+$ 75(88.60)	
		CH=C	$[C_4H_3]^+$ 51(35.30)	CH≡C	$[C_4H_2]^+$ 500(100)	
6	$[C_{11}H_6N_3BrO_3]^+$ 307(2.60)	Br	$[C_4H_6N_3O_3]^+$ 228 (2.60)	BrCHCN	$[C_9H_5N_2O_2]^+$ 184(79.50)	309 (M^++2, 2.60), 292(0.80), 29190.70), 200(2.50), 191(0.80), 190(1.00), 188(1.10), 173(3.30), 164(1.90), 163(8..60), 148(1.70), 146(1.20), 45(5.60), 134(2.70), 130(1.60), 121(1.80), 120(7.40), 119(1.50), 118(8.40), 117(2.80), 103(2.70), 102(2.90), 94(1.90), 92(1.60), 88(1.30), 78(1.80), 75(11.50), 74(7.90), 67(5.10), 66(2.00), 64(2.40), 63(1.80), 52(3.70),
		C=C=O	$[C_8H_6N_2O_2]^+$ 162 (100)	CO	$[C_8H_5N_2O_2]^+$ 16(18.50)	
		NH	$[C_8H_5NO_2]^+$ 147 (0.70)	N_2	$[C_8H_5O_2]^+$ 133(20.00)	
		NH	$[C_8H_4O_2]^+$ 132 (2.10)	CO	$[C_7H_5O]^+$ 105(25.00)	
		CO	$[C_7H_4O]^+$ 104(71.20)	CO	$[C_6H_5]^+$ 77(15.10)	
		CO	$[C_6H_4]^+$ 76(76.50)	C_2H_2	$[C_4H_3]^+$ 51(11.50)	
		C_2H_2	$[C_4H_2]^+$ 50 (56.10)			

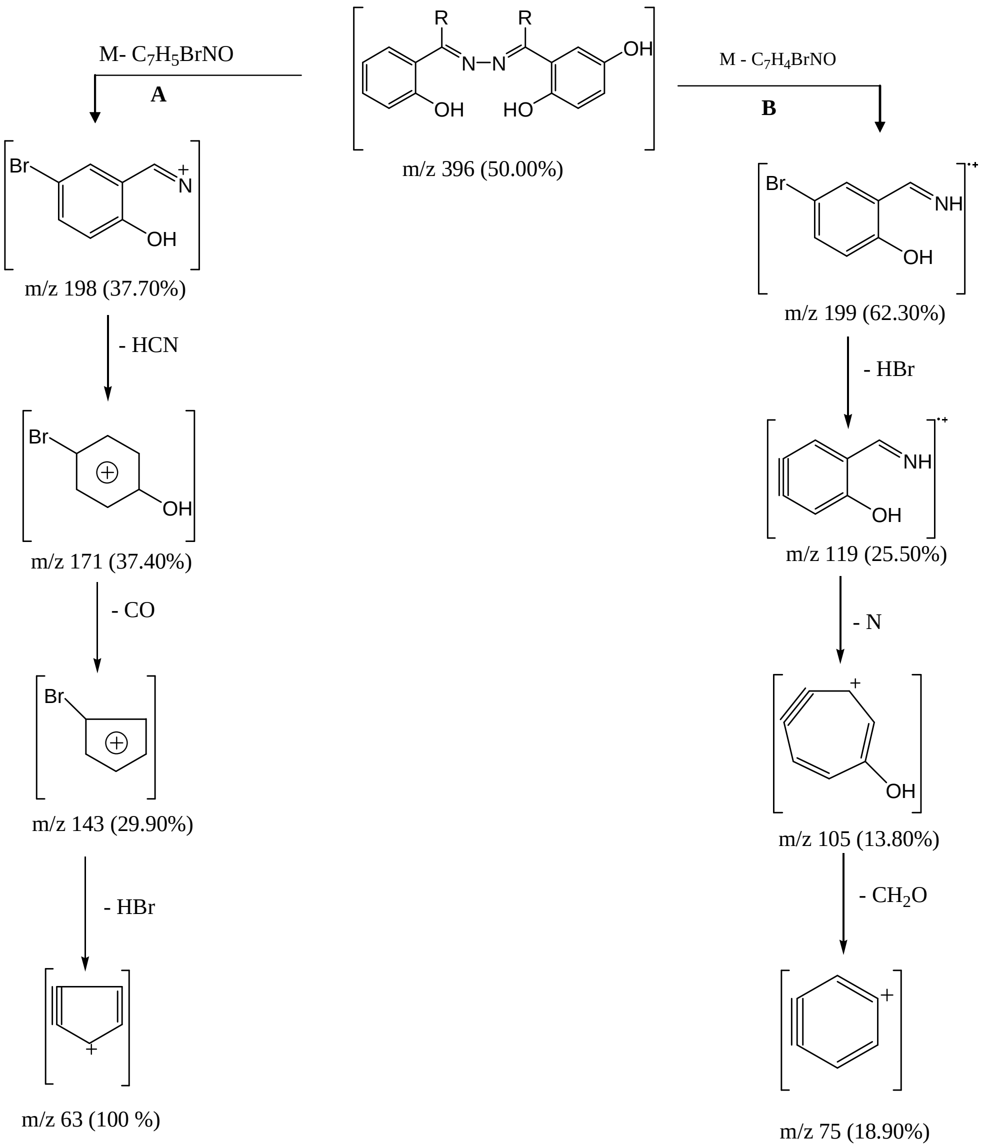
Compd	M^+	Pathway A -M	Pathway A m/z	Pathway B -M	Pathway B m/z	Other ions
8	$[C_8H_6N_2O_2]^+$ 162(80.10)	N_2H_2	$[C_8H_4O_2]^+$ 132(18.00)	N_2H_2	$[C_8H_5O_2]^+$ 133(4.60)	163(M^++1,5.50), 161(M^+-1,3.40), 131(2.10), 128(4.40),128(4.40), 118(2.90), 106(2.50), 103(6.30), 101(2.30), 91(5.30), 90(1.60), 81(2.50), 79(1.70), 78(4.10), 75(12.20), 74(11.20), 73(5.70), 66(3.30), 65(1.30), 64(3.80), 63(4.70), 62(4.60), 61(3.80), 58(12.50), 5315.20), 52(8.60).
		CO	$[C_7H_4O]^+$ 104(100)	CO	$[C_7H_5O]^+$ 105(22.80)	
		CO	$[C_6H_4]^+$ 76(29.50)	CO	$[C_6H_5]^+$ 77(29.50)	
		C_2H_2	$[C_4H_2]^+$ 50 (32.90)	C_2H_2	$[C_4H_3]^+$ 51(28.10)	
10a	$[C_{14}H_{10}N_2Br_2O_2]^+$ 396(37.50)	C_7H_5NBrO	$[C_7H_5NBrO]^+$ 198(37.70)	C_7H_4NBrO	$[C_7H_6NBrO]^+$ 119(62.30)	400(M^++4, 4.40), 398(M^++3, 72.90), 396(M^+, 37.30), 383(16.30), 38(3.70), 379(15.00), 320(20.30), 318(20.10), 303(11 .7O), 301(12.00), 300(11.50), 227(16.20), 226(5.20), 225(16.00), 201(58.30), 200(30.30), 197(13.80), 173(27.60), 172(10.20), 169(13,10), 146(13,50), 145(26.90), 144(13.60), 121(16.10), 120(13.10), 118(8,30), 106(4.30), 93(19.00), 92(24.80), 90(18.50), 77(29.30), 76(18.40), 74(13.10), 66(17.20), 65(47.90), 64(42.20), 62(28.90), 61(13.30), 53(37.50)
		HCN	$[C_6H_4BrO]^+$ 171(37.90)	HBr	$[C_7H_5NO]^+$ 199(25.50)	
		CO	$[C_5H_4Br]^+$ 143(28.90)	N	$[C_7H_5O]^+$ 105(13.80)	
		HBr	$[C_5H_3]^+$ 63(100)	CH_2	$[C_6H_3O]^+$ 91(24.20)	
				O	$[C_6H_3]^+$ 75(12.20)	
				C_2	$[C_4H_3]^+$ 51(49.90)	
10b	$[C_{16}H_{16}N_2O_2]^+$ 268(100)	CH_3	$[C_{15}H_{13}N_2O_2]^+$ 253.(91.70)	OH	$[C_{16}H_{15}N_2O]^+$ 251(93.60)	269(M^+ +1, 21 .0), 254(34.90), 252(33,90)., 227(11.00), 211(9.20), 210(19.30), 180(7.30), 179(15.60), 175(7.30), 173(3.70), 159(12.80), 127(8.30), 125(11.00), 124(11.00), 123(6.40), 97(7.30), 72(4.60).
		C_7H_5O	$[C_8H_8N_2O]^+$ 148(24.80)	C_3H_3	$[C_{13}H_{12}N_2O]^+$ 212(26.60)	
		C_4H_4	$[C_4H_4N_2O]^+$ 96(7.10)	OH	$[C_{13}H_{11}N_2]^+$ 195(11.90)	
		C_2H	$[C_2H_3N_2O]^+$ 71(21.10)	C_3H	$[C_{10}H_{10}N_2]^+$ 158(11.90)	
		CH_2	$[CHN_2O]^+$ 57(13.80)	C_5H_2	$[C_5H_8N_2]^+$ 96(7.30)	

The mass spectra of compound **5** (Fig.3) showed intense molecular ion peak at *m/z* 229, corresponding to the molecular formula $C_{11}H_7N_3O_3$. The molecular ion of *m/z* 229 fragmented via pathway *A* to give peak at *m/z* 162 by losing cyanoketene (CNCHCO) molecule. The peak at *m/z* 162 underwent fragmentation to produce a peak at *m/z* 147, corresponding to the molecular ion of phthalaimide by losing group (NH). It further under went loss of imino group (NH), two carbon monoxide molecules and acetylene molecule to give peaks at m/z 132, 104, 76 and m/z 50, respectively.



Scheme 4: Main fragmentation pathway of compounds 5, 6 and 8

Also, the same molecular ion m/z 229 fragmented via the pathway B by cleavage of cyanomethyl ($CNCH_2$) to give a peak at *m/z* 189, which lost carbon monoxide to give a peak at *m/z* 161. Then it lost nitrogen molecule to give a peak at *m/z* 133. It further underwent loss of formaldehyde, carbon monoxide molecules and acetylene cation (C_2H) to give peaks at *m/z* 103, *m/z* 75 and a base peak at *m/z* 50, respectively.



Scheme 5: Main fragmentation pathway of compound 10_a

The molecular ion peak of compound **6** (Fig4) was observed at *m/z* 307/309, corresponding to the molecular formula $C_{11}H_6N_3BrO_3$. The M+2 was observed along with the molecular ion peak due to the presence of isotopes of bromine atom in the compound.

The molecular ion of *m/z* 307 fragmented via the pathway *A* to give peak at *m/z* 228 by losing bromine atom, which lost (CNC=C=O) to give peak at *m/z* 162. The ion of *m/z* 162 underwent fragmentation via pathway *A* in the same fragmentation processes which was observed for compound **5**.

Also, the same ion of *m/z* 307 fragmented via pathway *B* by a cleavage of bromocyanomethyl (CNCHBr) to give a peak at *m/z* 189, which lost carbon monoxide to give a peak at *m/z* 161. The ion of *m/z* 161 underwent broken via pathway *B* in the same fragmentation processes which was observed for compound **5**.

The molecular ion of compound **8** (Fig. 5) at *m/z* 162 fragments via pathway *A* to give peak at *m/z* 132 by losing N_2H_2 molecule. The loss of carbon monoxide from the ion of *m/z* 132 gave the stable ion of *m/z* 104. This fragmentation led to ions of *m/z* 76 and *m/z* 50. The same ion of *m/z* 162 fragmented to ion *m/z* 133 via pathway *B*. Ion of *m/z* 133 underwent fragmentation to produce a peak at m/z 105 and *m/z* 77 by losing two carbon monoxide molecules. The ion of *m/z* 77 was broken to give an ion of *m/z* 51.

The mass fragmentation pattern of compounds **5**, **6** and **8** are summarized in scheme (4).

The mass spectrum of compounds $\mathbf{10}_a$ and $\mathbf{10}_b$ (Fig. 6 and 7) are fully consistent with the assigned structures. In most cases, intense molecular ion peaks were observed. Thus, compound $\mathbf{10}_a$ and $\mathbf{10}_b$ showed strong intense molecular ion peaks at *m/z* 396 and *m/z* 268, consistent with the molecular formula $C_{14}H_{10}N_2Br_2O_2$ and $C_{16}H_{16}N_2O_2$, respectively.

The molecular ion of compound $\mathbf{10}_a$ (Scheme 5) underwent fragmentation via pathway *A* to produce peak at *m/z* 198, corresponding to 5-bromo-2-hydroxy phenylmethylamion radical cation. It further underwent loss of hydrogen cyanide (HCN), carbon monoxide and hydrogen bromide to give peaks at *m/z* 171, 143 and stable fragmentation at *m/z* 63, respectively .

The molecular ion of compound $\mathbf{10}_a$ was also found to undergo fragmentation via pathway *B* to produce the ion of *m/z* 199, which further broke to give an ion at *m/z* 119.

The ion of m/z 119 broke to give an ion at *m/z* 105 which lost nitrogen atom. It further underwent loss of methylene group, oxygen atom and two carbon atoms to give peaks at *m/z* 91, 75 and *m/z* 51, respectively. The mass fragmentation pattern of compound 10_b was summarized in Table 1.

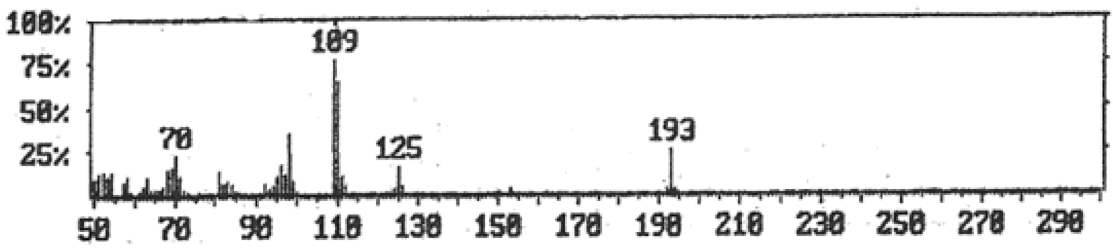


Fig. 1: mass spectra of compound 2

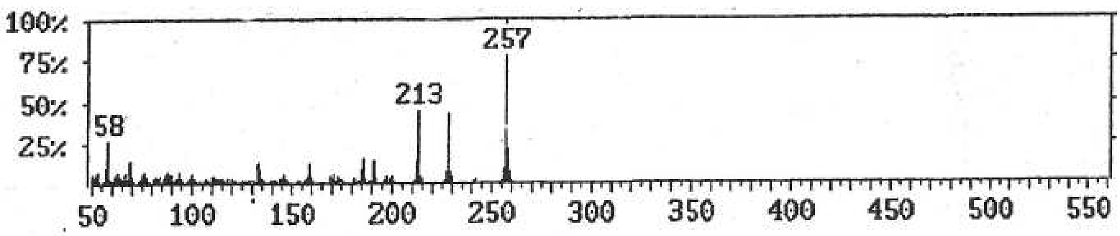


Fig. 2: mass spectra of compound 4

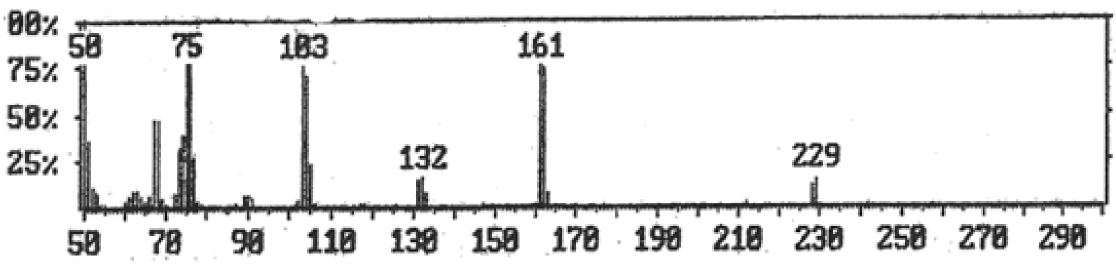


Fig. 3: mass spectra of compound 5

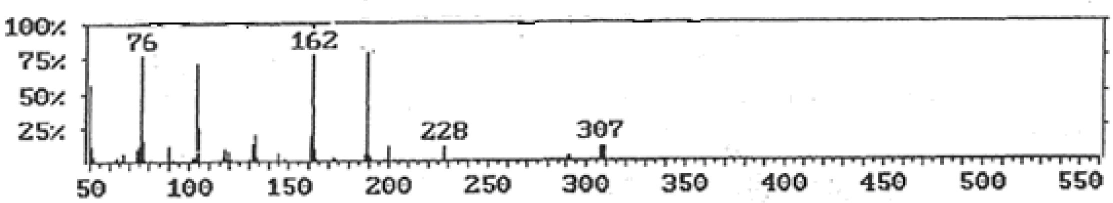


Fig. 4: mass spectra of compound 6

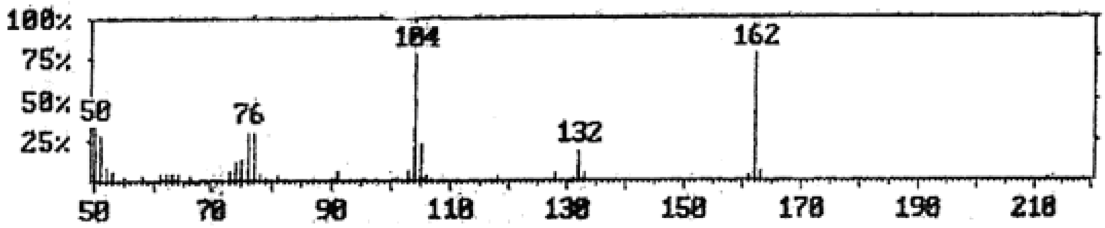


Fig. 5: mass spectra of compound 8

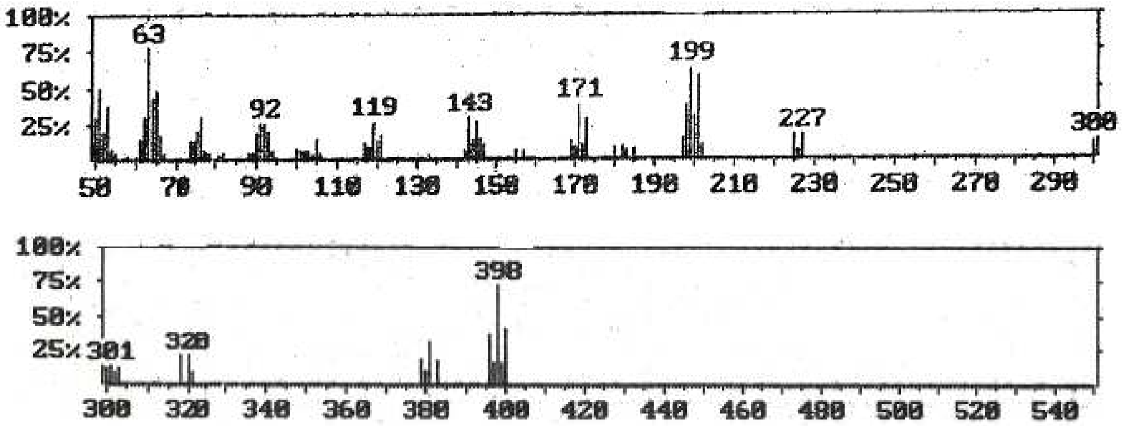


Fig. 6: mass spectra of compound 10_a

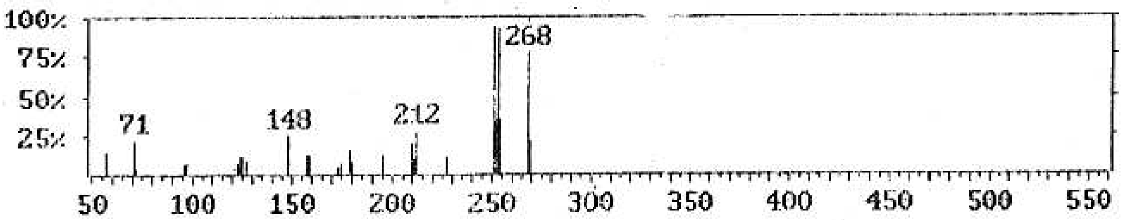


Fig. 6: mass spectra of compound 10_b

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