

FRAGMENTATION PATTERN OF POLYFUNCTION ANTHRAQUINONES UNDER ELECTRON IMPACT

Y.A.M. Marghlany and S.A.M. Metwally*

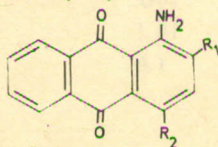
Chemistry Department, Faculty of Education, Mecca, Saudi Arabia

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The mass spectra of some anthraquinone derivatives having functional groups as substituents were examined. The pathway of fragmentation was found to be different from the known pattern of anthraquinone compounds. A mechanism for such fragmentation was suggested.

The mass spectra of anthraquinone compounds have been the subject of many investigations [1-5]. Among the compounds investigated were the parent anthraquinone and derivatives such as amino, hydroxy, alkoxy, alkyl and aryl compounds. The fragmentation of these compounds under electron impact was characterised by the loss of two neutral carbon monoxide molecules from the molecular ion, successively. Recently, we have covered the mass spectra of (hydroxymethyl) anthraquinone [6].

During a survey of mass spectral data of polyfunctional anthraquinone compounds, it was found that in the presence of functional groups especially the aldehyde group, several analogous regularities were observed. The explanation of these additional fragmentation patterns form the subject of this paper. For this study, we have selected some polyfunctional anthraquinone derivatives having more than one functional groups especially in the 1, 2 and 4-positions. Our study includes the following derivatives: 1-aminoanthraquinone-2-carbaldehyde (I), 1, 4-diaminoanthraquinone-2-carbaldehyde (III), 1-amino-4-bromoanthraquinone-2-carbaldehyde (V) and 1-amino-4-chloro-2-(chloromethyl) anthraquinone (VI). The spectra were compared with those spectra of compounds without functional groups in the 2-position, i.e. 1-aminoanthraquinone (II), 1, 4-diaminoanthraquinone (IV) and 1-amino-4-chloro-anthraquinone (VII).



	R ₁	R ₂
I	CHO	H
II	H	H
III	CHO	NH ₂
IV	H	NH ₂
V	CHO	Br
VI	CH ₂ Cl	Cl
VII	H	Cl

The mass spectra of these anthraquinone derivatives were determined on an AEI MS 12 mass spectrometer operating with an electron energy of 70 eV. The direct insertion technique was used, with a probe temperature range between 150 - 250°. Accurate mass measurements [7] were used to determine the formula of various peaks in the spectra. Details of the spectra are summarised in Table 1; in the Table all ions having an abundance greater than 5% of that of the base peak (arbitrary taken as 100%) are recorded.

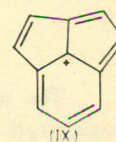
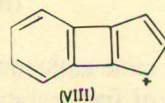
The mass spectra of the anthraquinone derivatives having an aldehydic group in the 2-position are characterised by a molecular ion which is not the base peak. The later is found at m/e values of M-CO.

1-Aminoanthraquinone-2-carbaldehyde is characterised by a molecular ion at m/e 251 which represents 63.1% of the relative abundance of the base peak at M-CO. Loss of the aldehyde hydrogen from the molecular ion is not indicated. This represents a difference between this aromatic aldehyde and the other simple analogues [8]. Direct loss of the CHO substituent [9] occurs only to a small extent, as does the expulsion of CO from the molecular ion to give the base peak at m/e 223. The direct loss of the amino group from the molecular ion is not indicated and this shows the effect of hydrogen bonding on such elimination [1]. The mass 28 was proved to be due to the ejection of a neutral carbon monoxide fragment and was accompanied by a metastable peak at m/e 198.1. This ejection was found to be from the side-chain and this was verified by the fact that 1-aminoanthraquinone-2-O¹⁸-aldehyde loses a mass unit of 30 from the molecular ion to give the base peak at m/e 223. Below mass 223, the mass spectra of the two compounds are identical with that of 1-aminoanthraquinone [1]. The ion at m/e value of 223 loses a CO neutral fragment to give the amino biphenylene molecular ion at an m/e value of 195 which is considered to have the structure of an aminofluorenone molecular

* Author to whom all correspondence should be addressed.

ion. The presence of a metastable peak at 170.5 verifies such a transition. The aminofluorenone molecular ion ejects another CO neutral fragment to give the aminobiphenylene molecular ion at m/e 167 as shown by the presence of a metastable peak at 143. The mechanism of the loss of neutral CO fragments from carbonyl compounds was fully studied by Beynon and his collaborators [10]. The aminobiphenylene molecular ion at m/e 167 loses HCN followed by the loss of a hydrogen radical to give the stable ion at m/e 139. This was supported by the metastable peaks at m/e 117.4 and 138 which proves these transitions and excludes the expulsion of H_2CN in one process. The mechanism for the fragmentation of the aminofluorenone molecular ion to the ion at m/e 139 is complicated by the fact that two structures have been put forward for this species. Structure (VIII) for this ionic species was suggested by Beynon and Williams [1] who observed it in the mass spectra of both 1- and 2-hydroxyanthraquinone. These authors inferred, from the relatively large intensities (7%) of the ion peaks corresponding to the doubly charged species at m/e 69.5, that the

ion at m/e 139 possessed exceptional stability. An examination of the data in Table 1 shows that the intensities of the peaks at m/e 69.5 found in these experiments are of the same order of intensity as those recorded by Beynon and Williams. Later McLafferty [11] put forward the structure (IX) for the m/e 139 ion species. An ion of this mass occurs widely in the mass spectra of aromatic hydrocarbons.



The mass spectra of the other 2-carbaldehyde anthraquinone derivatives which had been studied do not give any evidence for the operation of bond cleavages other than those noted for 1-aminoanthraquinone-2-carbaldehyde. In the mass spectrum of 1,4-diaminoanthraquinone-2-carbaldehyde (III), the base peak is at M-CO. The spectrum from 238 to the low mass end is identical with that of 1,4-diaminoanthraquinone (IV) (cf. Table 1). The mass spectrum of 1-amino-4-bromoanthraquinone-2-carbalde-

Table 1. Mass spectra of some polyfunction anthraquinone derivatives

	m/e	Rel.int.	m/e	Rel.int.	m/e	Rel.int.
<i>1-Aminoanthraquinone-2-carbaldehyde (I)</i>	28	25.1	139	19	222	8.6
	32	4.2		11	223	100
	63	5.1	150	5.5	224	16.6
	69.5	7.1	166	10.8	225	1.6
	70.5	3.1	167	23.1	251(M)	65.1
	75	4.4	168	12.1	252	11
	76	5.2	194	6	253	1.7
	77	4.3	195	15.88	—	—
	83.5	9.2	196	5.8		
125.5	3.7	205	3.3			
<i>1-Aminoanthraquinone (II)</i>	28	23.1	195	21.8		
	32	4.1	196	3.5		
	69.5	4	222	11.2		
	70.5	4.1	223(M)	100		
	83.5	9.7	224	16.1		
	139	15.6	225	1.6		
	140	8.6				
	166	10.8				
	167	19				
168	8.3					
<i>1, 4-Diaminoanthraquinone-2-carbaldehyde (III)</i>	28	35.9	127	6.7	210	8.2
	32	7.5	133	5.7	237	27
	43	4.3	138	4.8	238	100
	57	5.7	139	3	239	17.4
	69	4	154	7	265	2.1

Table 1 – continued

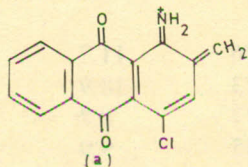
	77	10.7	164	8.1	266	89
	91	6.4	165	5.4	267	15
	91.5	3.9	181	5.5	268	2.1
	105	4.5	182	9.5		
	119	4.4	193	4.6		
<i>1,4-Diaminoanthraquinone (IV)</i>						
	28	39.6	127	8.6	210	5.3
	32	8.9	133	6.5	237	27.3
	43	12.7	138	5.1	238(M)	100
	57	5.7	139	2.3	239	16.1
	69	5	154	8.8	240	1.2
	77	11.6	164	5.3		
	91	7.4	165	6.2		
	91.5	2.2	181	7.3		
	105	6.1	182	10.2		
	119	5.7	193	6.4		
<i>1-Amino-4-bromoanthraquinone-2-carbaldehyde (V)</i>						
	28	21.9	76	11.7	113	5.6
	165	11.4	223	18.9	301	100
	44	18.7	77	8.7	137	11.1
	165.5	3.3	245	9.9	302	20.9
	50	6.8	82.5	15.2	138	17.4
	166	29	246	6.4	303	99.9
	51	4.9	83	14.9	139	47.5
	167	26.7	247	9.8	304	15.1
	62	6.1	87	5.5	140	16.9
	168	4.6	248	4.9	329	97.5
	63	10.2	88	6.1	144	5.2
	175	6.1	251	10.2	330	18.5
	69	4.6	89	8.6	149	6.7
	194	19.3	273	11	331	97.9
	69.5	15.5	97	9.1	150	5.6
	195	5.2	274	7.1	332	16
	74	5.4	105	6.9	164	13.4
	221	7.1	275	10.8	333	2.3
	75	8.2	111	17.7	164.5	3.5
	222	27.7	300	5.3		
<i>1-Amino-4-chloro-2-(chloromethyl)anthraquinone (VI)</i>						
	28	5.8	153	4.6	273	8.4
	75	10.3	177	8.3	305	54.2
	75.5	3.2	178	7.3	306	9.9
	76	15.7	236	17	307	35.2
	77	7.5	242	41.7	308	6.3
	88	3.3	243	7.1	309	6
	89	7.5	244	13.3		
	150	9.5	270	100		
	151	16.2	271	26.5		
	152	20.6	272	35.7		
<i>1-Amino-4-chloroanthraquinone (VII)</i>						
	28	20.3	153	3.9		
	75	9.6	177	5.7		
	75.5	7.8	178	8.5		
	76	14.4	236	5.7		

Table 1 Continued

77	8.2	242	100
88	2.3	243	10.7
89	8.2	244	35.2
150	10.3	245	4.1
151	18.4	246	1.2
152	19.1		

hyde (V) shows the characteristic abundance of two bromine isotopes (Br^{79} Br^{81} 1:1). As usual the base peak is represented by the M-CO ion (m/e 301, 100% and 303, 99.89%).

The other halogenated anthraquinone derivatives studied in this series was 1-amino-4-chloro-2-(chloromethyl) anthraquinone (VI). The molecular ion is not the base peak and the latter is represented by M-Cl. It is supposed that a chlorine radical is ejected from the side-chain to give the stable ion (a).



The formation of ion (a) is favoured by stabilisation due to the o -quinonoid structure [12]. Ion (a) can lose H_2CN , to give the ion at the m/e value of 242 which fragments in the same way as does 1-chloroanthraquinone (VII). This fact can be used as an evidence for ring expansion and hydrogen rearrangement.

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