

# Characteristic Fragmentation Patterns of Some 4-(phenylazo)phenols Obtained by Electron Impact Mass Spectrometry

ANCA MOANTA\*

University of Craiova, Faculty of Chemistry, 1071 Calea Bucuresti Avenue, 200478 Craiova, Romania

*The mass spectra of fourteen substituted 4-(phenylazo)phenols have been recorded and compared. The most intense peaks have been used to characterize these spectra. The molecular ions are observed as highest intensity peaks. The influence of the substituents on the fragmentation is discussed.*

*Keywords: 4-phenylazo-phenols; azo dyes; mass spectra; electron impact ionization; molecular weight*

4-(phenylazo)phenols contain a conjugated chromophore azo group ( $-N=N-$ ), one hydroxyl group and two aromatic rings. They are intermediates in the synthesis of azo dyes. Azo dyes are an important class of organic colorants due to their relatively simple synthesis and almost unlimited number and types of substituents. The azo dyes are mainly used in dyeing natural textile fibres (cotton, wool, hemp, flax silk), artificial fibres (acetyl silk, viscose), synthetic fibres (polyamides, polyester, polyacrylonitriles), paper, leather and several kinds of plastic [1-4].

Hence, a simple, sensitive and reliable method of determining azo dyes in environment is required, making possible the identification of precursors, intermediates and by-products during the synthetic process. A variety of spectroscopic methods is employed for structure elucidation or confirmation of the identity of dyes. In addition to UV-Vis and IR spectroscopy, mass spectroscopy (MS) is suitable for this purpose. The first systematic survey regarding mass spectra of substituted azobenzenes was reported in 1967 [5]. It was found that, without exception, all azobenzene derivatives show skeletal rearrangement ions which arise from the loss of nitrogen together with the various substituents. Biphenyl is formed by loss of nitrogen from azobenzene and biphenylene radical is reported to be observed in all mass spectra and is often produced by the general process  $[M - (R + H + N_2)]^+$ , the relative decomposition order depending upon the nature of substituents. Detailed literature survey showed that a considerable amount of work has been done on the mass spectral studies of azoderivatives: azobenzene, substituted azobenzene, aromatic azoethers and commercial azo dyes [6-14].

We have recently reported mass spectrometric studies regarding azomonoethers, monoazobisethers, bisazobisethers and 4-phenylazo-phenoxyacetic acids [15-18]. This study concerns with the interpretation of mass spectra of fourteen 4-phenylazo-phenols.

## Experimental part

### Reagents

4-(Phenylazo)phenols analysed in this work were synthesized by coupling the corresponding diazonium salts with different phenols [19]. The azo compounds obtained were purified by recrystallization from ethanol and their

purity was examined by thin-layer chromatography and was checked by noting their melting points. Chemicals (phenol, 2,5-dichloro-phenol, *m*-cresol, *o*-cresol, 2-allyl-phenol, 2,3-dimethyl-phenol, 2-chloro-phenol, 2-bromo-phenol, 4-chloro-aniline, *o*-toluidine, aniline, *p*-toluidine, 4-nitro-aniline) used in all azophenols synthesis were purchased from Merck Company and were used without further purification.

### Apparatus

Mass spectra have been obtained using a HPGC-MS 5890 MD 5971 spectrometer at 70 eV, with carrier gas He at 2 mL/min.

## Results and discussions

The purpose of this study was to investigate the basic fragmentation processes for substituted 4-phenylazo-phenols, to ascertain whether the position of the substituents on the benzene rings may be determined by mass spectrometry, and to study the nature and genesis of any skeletal rearrangement ions. Thanks to these observations, the results obtained from mass spectrometry can be used in investigating the structure of these compounds. It is important to understand the relationship between the fragmentation behaviour and the structure of dye molecules, because it is essential for the interpretation of mass spectra of unknown azo dyes.

The molecular weight determination is the basic information, which results from the interpretation of mass spectra. If the ionization method used in mass spectrometry is electron impact ionization (EI) the molecular weight is determined from the presence of radical-cation  $M^+$ .

In this investigation we obtained and compared the mass spectra (table 1) of the 4-phenylazo-phenols (1-14), having general formula:

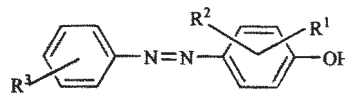


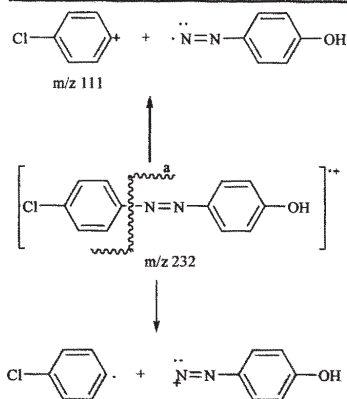
Fig. 1. The structure of 4-phenylazo-phenols

(Phenylazo)phenols fragments are well defined and characteristic features in electron impact ionization. By mass measurement and comparison between different

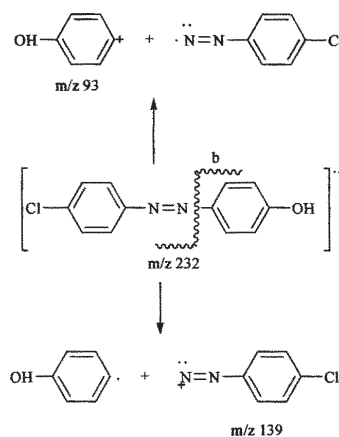
\* email address: moantaanca@yahoo.com; Tel.: +40251-597048

Compound	Name	m/z (Relative abundance [%])
1	4-(4-chlorophenylazo)phenol	232 (73.4%), 139 (13.9%), 121 (51.9%), 111 (50.6%), 93 (100%), 65 (34.2%), 39 (12.7%)
2	3,6-dichloro-4-(4-chlorophenylazo)phenol	300 (67.6%), 198 (44.3%), 161 (46.2%), 139 (38.6%), 133 (21.4%), 111 (100%), 107 (0.02%)
3	3-methyl-4-(4-chlorophenylazo)phenol	246 (100%), 139 (22.2%), 135 (55.5%), 111 (77.8%), 107 (86.1%), 79 (30.5%), 63 (11.1%)
4	2-methyl-4-(4-chlorophenylazo)phenol	246 (66.3%), 139 (6.4%), 135 (29.2%), 111 (40.6%), 107 (100%), 79 (16.8%), 63 (3.5%)
5	2-allyl-4-(4-chlorophenylazo)phenol	272 (57.1%), 161 (14.8%), 139 (3.8%), 133 (100%), 111 (40.5%), 105 (4.3%), 79 (16.2%)
6	4-(2-methyl-phenylazo)phenol	212 (98.6%), 121 (42.5%), 119 (0.05%), 93 (100%), 91 (97.3%), 65 (58.9%), 39 (16.4%)
7	3-methyl-4-phenylazo-phenol	212 (100%), 135 (27.6%), 107 (92.1%), 105 (3.9%), 79 (9.2%), 77 (65.8%), 53 (5.3%)
8	4-(4-methyl-phenylazo)phenol	212 (100%), 121 (26.2%), 119 (3.9%), 93 (55.2%), 91 (55.2%), 65 (27.6%), 39 (9.2%)
9	2,3-dimethyl-4-phenylazo-phenol	226 (98.7%), 149 (15.7%), 121 (100%), 105 (2.6%), 93 (6.5%), 79 (0.01%), 77 (52.2%), 67 (0.02%), 53 (0.04%)
10	2-methyl-4-(4-methyl-phenylazo)phenol	226 (94.4%), 135 (29.2%), 119 (9.7%), 107 (100%), 105 (0.01%), 91 (91.7%), 79 (15.3%), 65 (23.6%), 39 (9.7%)
11	2-allyl-4-(4-methyl-phenylazo)phenol	252 (92.1%), 161 (37.9%), 133 (100%), 119 (13.6%), 91 (99.3%), 65 (19.3%), 39 (12.4%)
12	4-(4-nitro-phenylazo)phenol	243 (37.6%), 213 (11.4%), 150 (1.2%), 122 (11.4%), 121 (48.6%), 93(100%), 65 (47.6%), 39 (15.2%)
13	2-chloro-4-(4-nitro-phenylazo)phenol	277 (43.6%), 247 (6.4%), 155 (55.1%), 150 (3.8%), 127 (100%), 122 (15.4%), 99 (42.3%), 73 (19.2%)
14	2-bromo-4-phenylazo-phenol	276 (72.4%), 248 (0.01%), 199 (38.1%), 171 (63.3%), 143 (16.7%), 115 (5.7%), 105 (20.5%), 77 (100%)

Table 1  
MASS SPECTRAL DATA



Scheme 1.  
Fragmentation of 4-(4-chlorophenylazo)phenol by process a

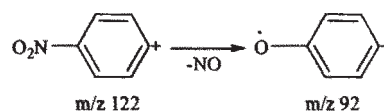


Scheme 2. Fragmentation of 4-(4-chlorophenylazo)phenol by process b

spectra, we have found that the spectra of azophenols are characterized by peaks due to molecular ions and fragment ions. They are formed by cleavage of one of the carbon-nitrogen bonds adjacent to the azo group with the positive charge remaining with the azo or aromatic fragment. 4-(4-Chlorophenylazo)phenol (1) is an example of a typical azophenols and the fragmentation under electron impact is characteristic for other compounds analyzed during this work. The molecular ion peak at m/z 232 (73.4%, table 1) is intense and the molecule tends to undergo cleavage of the C-N bonds to give fragments at m/z 93 (base peak), m/z 111, m/z 121 and m/z 139, respectively (schemes 1 and 2). The ion at m/z 93 produced by C-N bond cleavage loses CO and acetylene, leading to the cyclopropenilium ion, m/z 39.

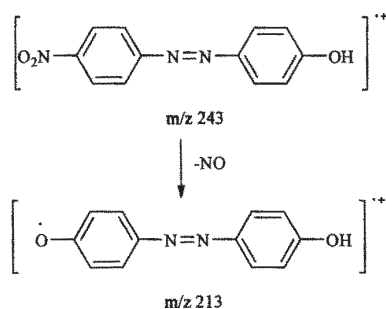
All compounds are non-symmetrically substituted and the spectra are complex because C-N fission by process "a" (scheme 1) and "b" (scheme 2) produces different ions according to the nature of the substituent.

For nitro-compounds, we observed that  $O_2N-C_6H_4^+$  can lose NO and can generate m/z 92:



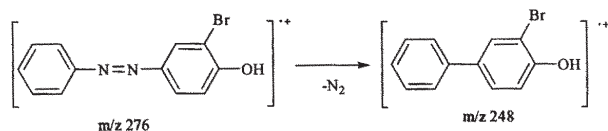
Scheme 3. Fragmentation of nitrophenyl cation

A typical peak observed for nitro-azobenzene compounds results from the loss of NO from the molecular ion. This loss is characteristic for an aromatic nitro group. This peak is usually weak, but nevertheless it is always present. For 4-(4-nitro-phenylazo)-phenol, Scheme 4 shows the fragmentation process specific to nitro-compounds by NO elimination.



Scheme 4. The fragmentation of 4-(4-nitro-phenylazo)-phenol

The mass spectrum of 2-bromo-4-phenylazo-phenol shows a peak at  $m/z$  248, corresponding to the molecular formula  $\text{C}_{12}\text{H}_9\text{OBr}$ . Under electron impact this ion loses a  $\text{N}_2$  molecule (scheme 5).



Scheme 5. The fragmentation of 2-bromo-4-phenylazo-phenol

The chlorine and bromine atoms have characteristic patterns of isotopic peaks ( $^{35}\text{Cl}:$  $^{37}\text{Cl}=3:1$  for chlorine and  $^{79}\text{Br}:$  $^{81}\text{Br}=1:1$  for bromine). These patterns can be used for an easy identification of the presence and number of chlorine and bromine atoms in analysed molecules. When more chlorine or bromine atoms are present, their isotopic ratio can be calculated by binomial equation  $(3a+b)^n$  for chlorine or  $(a+b)^n$  for bromine, where  $n$  is the number of chlorine or bromine atoms. When both chlorine and bromine atoms are present, the equation is  $(3a+b)^{n1}(a+b)^{n2}$ , where  $n1$  is the number of chlorine atoms and  $n2$  is the number of bromine atom [20]. The presence of a chlorine atom in the molecular ion of 4-(4-chlorophenylazo)phenol is reflected in EI mass spectrum by the pair of peaks  $M$  ( $m/z$  232) and  $M+2$  with isotopic intensities 3:1 respectively. The absence of chlorine after fragmentation is reflected by the absence of abundant  $M+2$  isotopic peak.

The tropylium ion,  $m/z$  91, obtained by skeletal rearrangement, characteristic for monoalkyl aromatic compounds, could eliminate acetylene, and forms the fragment  $m/z$  65 (cyclopentadienilium). At its turn, the latter can lose acetylene and generate the cyclopropenilium ion ( $m/z$  39).

Previously published mass spectrometric works on monosubstituted or simple disubstituted azobenzenes show the presence of the biphenylene ion, because of skeletal rearrangement [5,15]. However, our work deals more with complex compounds having a hydroxyl group in the 4 position of azobenzene it is probably because of this fact that the presence of biphenylene ion is not detected in the

mass spectra.

The mass spectrum of 3-methyl-4-(4-chlorophenylazo)phenol is similar to the spectrum of its isomer 2-methyl-4-(4-chlorophenylazo)phenol (table 1). The spectra of the isomeric compounds 4-(2-methyl-phenylazo)phenol and 4-(4-methyl-phenylazo)phenol are similar. 3-methyl-4-phenylazo-phenol is an isomer with compounds (6) and (8) from table 1, but its spectra is different because the position of one methyl group. The mass spectra of 2,3-dimethyl-4-phenylazo-phenol and 2-methyl-4-(4-methyl-phenylazo)phenol are also different because of the position of the two methyl groups.

## Conclusions

Electron impact mass spectra of some 4-phenylazo-phenols have been reported and discussed. In conclusion, azo compounds have been shown to be a very interesting class of organic compounds for mass spectrometric analysis. This study shows that 4-hydroxy-azobenzene derivatives exhibit fragmentations, which are dependent in a consistent manner on the types and the position of substituents. The results of this study have confirmed the structure of all compounds using mass spectra under electron impact. This work provides a basis for a systematic approach to the identification of these compounds.

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