

THE MASS SPECTRA OF p- AND m-AMINO-n-BUTYLBENZENES.
THE ELECTRONIC STATE OF THE MOLECULAR ION.

Hisao Nakata

Department of Chemistry, Aichi Kyoiku University, Higashi-ku, Nagoya
and

Akira Tatematsu

Faculty of Pharmacy, Meijo University, Showa-ku, Nagoya, Japan

(Received in Japan 19 August 1969; received in UK for publication 15 September 1969)

In recent years, the localized positive charge and the localized unpaired electron are considered to be a driving force for mass spectral fragmentation reactions (1,2). The concept of this localized radical ion in mass spectrometry (3) has been used by a number of workers to rationalize many specific fragmentation patterns of various organic compounds (2,4). Although several experimental examinations and theoretical arguments have been reported (5,6,7,8,9), the evidence for the exact electronic state of the molecular ion is still limited. It is usually assumed that the molecular ion has the structure in which an electron is removed from a hetero atom or a multiple bond of the molecule, and this implies the localization of both a positive charge and a radical electron on the highest occupied orbital of the resulting molecular ion. Because an electron may be abstracted from any part of a given molecule by electron impact under ordinary conditions, the above assumption requires the primary ionization process of the molecule as shown in Fig. 1 (10), which involves a demotion step (11) of an electron from the higher energy level to the lower vacant, half-occupied orbital before fragmentation reactions. We now wish to present an evidence that supports the electronic state of the molecular ion as illustrated in Fig. 1.

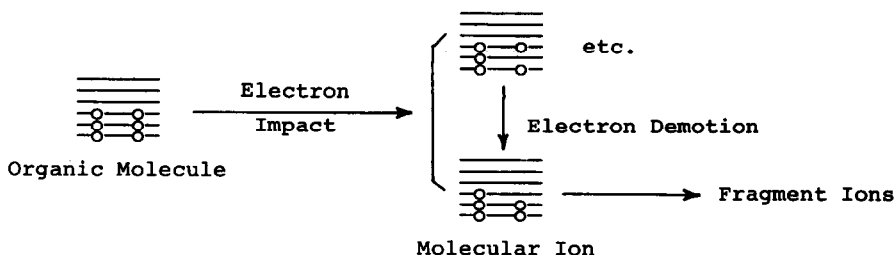


Fig. 1. A Schematic Diagram of Ionization Process.

The mass spectrum of *n*-butylbenzene (I) at 20 eV showed only two fragment ion peaks at m/e 92 (M-42) and m/e 91 (M-43). The fragmentation mechanism is depicted in Fig. 2, where the ionization of a benzene double bond is formulated in two different directions. The two molecular ions A and B afford the M-43 and M-42 peaks, respectively. For the sake of simplicity, we do not specify whether the structure of the M-43 ion is benzylic or tropylium-like (12), nor the scheme indicate the exact timing (stepwise or concerted fashion) of the McLafferty cleavage of the side chain (13).

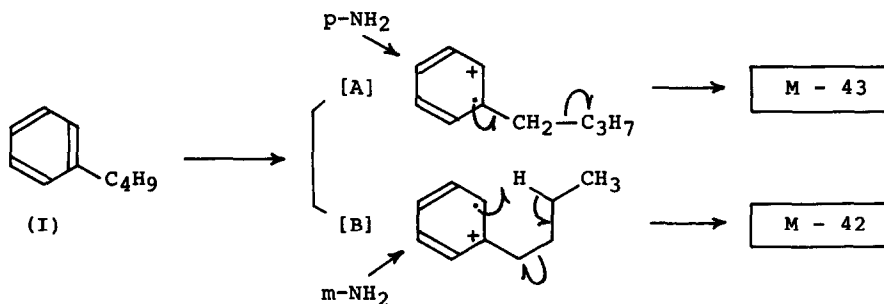


Fig. 2. Fragmentations of *n*-Butylbenzene (I).

Introduction of an amino group in *p*- and *m*-positions do not alter the fragmentation, but exhibited a dramatic change of intensity ratios of the corresponding fragment ions. Thus, *p*-amino-*n*-butylbenzene (II) showed a very intense M-43 peak and essentially no M-42 peak, whereas *m*-amino-*n*-butylbenzene (III) gave a strong M-42 and a negligibly small M-43 peaks (14). The relative ratios of these two peaks are summarized in Table 1 after the correction of isotopic abundances of adjacent peaks. The high-energy impact (70 eV) also displayed the same trend.

Table 1. Intensity Ratios of Fragment Ions (20 eV).

Compound	M - 43	M - 42
I H	31.9 %	68.1 %
II p-NH ₂	99.1	0.9
III m-NH ₂	3.6	96.4

The remarkable spectral difference between II and III indicates that the electron distribution of the molecular ion is distinctly affected by the p- and m-amino substituents. It should be noted that the positive charge in the molecular ion is not only on one carbon atom as shown in Fig. 2, but distributes over three alternating carbon atoms of the benzene ring through π -electron conjugation. The radical electron is also located in three other carbon atoms. Since the amino group stabilizes the positive charge better than the radical electron, the type A electron distribution (Fig. 2) is preferable for the molecular ion of the p-amino derivative (II) and, therefore, only the M-43 ion was produced. On the other hand, the type B ion predominates in the m-amino compound (III) and the exclusive formation of the M-42 ion resulted. In both cases, the radical electron that causes the two major fragmentation reactions clearly localizes on a carbon atom para (and presumably ortho) to the amino group, and not on the meta carbon atoms.

In order to examine the more detailed nature of the electronic state of the molecular ion, the above results are compared with simple LCAO-MO calculations of the aniline-like ion (15). If D_p , D_m , and D_o are taken as radical densities of p-, m-, and o-carbon atoms, respectively, the experimental results require the radical density ratio, $[D_p + 2D_o]/2D_m$, to be very large. As is seen from Table 2, however, the ratios are in the range of about 1 to 2, if an electron is removed from any one of the low-lying, stable molecular orbitals. This is incompatible with the experiments. On the other hand, when the electron is removed from the highest occupied orbital ψ_4 , the selective localization of the remaining radical electron on para and ortho carbon atoms (and, of course, on the nitrogen atom) is expected, which explains the experiments. Changes in Coulomb and resonance integral parameters, H and K, do not alter the conclusion. Thus, the observed,

Table 2. Radical Densities of Aniline Molecular Ion.*

Removal of an Electron from	D_p	D_m	D_o	$[D_p + 2D_o]/2D_m$
ψ_1	0.0670	0.0819	0.1396	2.1
ψ_2	0.2719	0.1539	0.0047	0.9
ψ_3	0.0000	0.2500	0.2500	1.0
ψ_4	0.1968	0.0125	0.1500	19.9

* Calculated by LCAO-MO. Integral parameters $K=1.0000$, $H=1.0000$. Orbital energies are in the following order of decreasing stability: $\psi_1 > \psi_2 > \psi_3 > \psi_4$.

clear-cut preference of the fragmentation pathways in p- and m-amino-n-butylbenzenes can be accounted for only by assuming that the molecular ion of these compounds has the radical electron in their highest occupied molecular orbitals.

The formation of such a molecular ion is satisfactorily described by the primary ionization process shown in Fig. 1. However, it is still uncertain whether or not the ionization would first afford species of various electronic states and then the electron demotion follows. From the present data, we could not exclude a possibility that most of the molecular ion might be directly formed even when the energy of the impact electron is much higher than the ionization potentials. It is hoped that further studies currently in progress in our laboratory will shed light on the more precise feature of these processes.

References

- 1) F. W. McLafferty, *Chem. Communications*, 1966, 78.
- 2) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco (1967).
- 3) F. W. McLafferty, in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips ed., Academic Press, New York (1962), p. 93.
- 4) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Holden-Day, San Francisco (1964), Vol. 1 and 2.
- 5) T. Wachs and F. W. McLafferty, *J. Am. Chem. Soc.*, 89, 5044 (1967).
- 6) H. Bruderer, W. Richter, and W. Vetter, *Helv. Chim. Acta*, 50, 1917 (1967).
- 7) A. Mandelbaum and K. Biemann, *J. Am. Chem. Soc.*, 90, 2975 (1968).
- 8) I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, 90, 5461 (1968).
- 9) T. H. Kinstle and W. R. Oliver, *J. Am. Chem. Soc.*, 91, 1864 (1969).
- 10) H. Nakata, A. Tatematsu, H. Tsuyama, and H. Doi, *Mass Spectroscopy*, 13, 99 (1965).
- 11) The term "cascading" or "healing" is also used. See, Ref. 4), and G. G. Hall, *Bull. Soc. Chim. Belges*, 73, 305 (1964).
- 12) See, for example, P. Brown, *J. Am. Chem. Soc.*, 90, 4459, 4461 (1968).
- 13) See, for example, F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Am. Chem. Soc.*, 90, 7239 (1968).
- 14) The spectra of p- and m-amino-n-butylbenzenes have been reported: R. Nicoletti and D. A. Lightner, *J. Am. Chem. Soc.*, 90, 2997 (1968); *Tetrahedron Letters*, 1968, 4553.
- 15) C. A. Coulson, and A. Streitwieser, Jr., "Dictionary of π -Electron Calculations," Pergamon Press, Oxford (1965), p. 263 - 272.