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A MARKED DIFFERENCE BETWEEN THE DECOMPOSING $(M-H)^+$ IONS FROM BENZYL AMINE AND *P*-AMINOTOLUENE, IN THE LIGHT OF BENZYL VERSUS TROPYLIUM ION STRUCTURES

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In our efforts to get information about the structure of $(XC_7H_6)^+$ ions [1], we have generated the $(NH_2C_7H_6)^+$ ion from two different sources, *viz*. benzyl amine and *p*-aminotoluene.

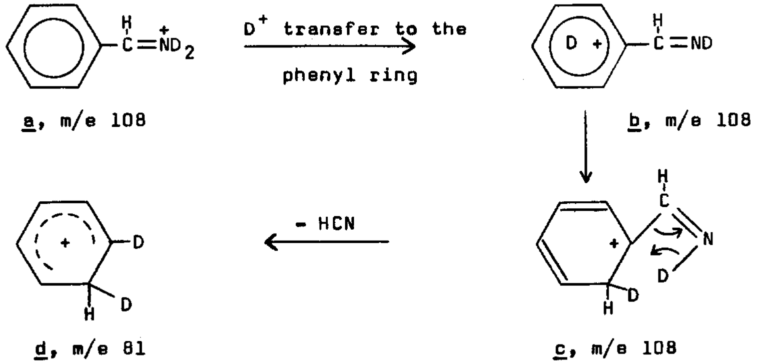
The mass spectra of these isomers at 70 eV are very simple and similar: both molecular ions m/e 107 lose a hydrogen atom and HCN subsequently, thus giving rise to m/e 106 and m/e 79, while the frequently occurring peaks in spectra of aromatic compounds at m/e 91, 77, 65, 51 etc. complete the set of most abundant ions. Fragment m/e 30 only originates from benzyl amine.

Deuterium labelling [2] in each amino group revealed an almost complete retention (> 98%) of the original amino hydrogen atoms in the $(M-H)^+$ i.c. $(ND_2C_7H_6)^+$ ion, so that the earlier proposed aminotropylium ion [3] cannot be rejected.

The $(ND_2C_7H_6)^+$ ions however appear to decompose quite differently in the second field free region: the ion from benzyl amine loses exclusively HCN, thus producing $(C_6H_5D_2)^+$, with complete retention of the original amino hydrogens, whereas that from *p*-aminotoluene not only ejects HCN, but also DCN, in the ratio 1 : 0.7.

It is therefore highly improbable that the decomposing $(M-H)^+$ ions from the compounds studied, have the same structure.

The observation that in aniline [4] the amino hydrogens are mostly retained (~70%) in the expelled HCN (or HNC), fits well with the behaviour of the $(ND_2C_7H_6)^+$ ion from *p*-aminotoluene, so we may conclude that the amino group in this ion is still attached to an aromatic ring, be it 6- or 7-membered. This also suggests an unrearranged carbon skeleton for the $(ND_2C_7H_6)^+$ ion from benzyl amine, which can easily account for the complete retention of the amino hydrogens in the $(C_6H_5D_2)^+$ ion, as rationalized below through sequence a→b→c→d .



This again demonstrates, that in the question of benzyl versus tropylium ion structures, ions with a 6-membered ring do frequently intervene, as noted earlier [1].

References

1. T.A.Molenaar-Langeveld and N.M.M.Nibbering, Tetrahedron 28, 1043 (1972) and references therein.
2. From the ratio (M-H)/(M-D) in the spectra of α-d_2, ortho-d_2 and p-d benzyl amines we calculated $p_\alpha : p_{ring} = 2.1 : 1$ and $i = 1.9$. From the same ratio in the spectra of CD_3, ortho-d_2, meta-d_2 and ring-d_4-p-aminotoluenes we found $i = 1.5$ and $p_{methyl} : p_{ortho} : p_{meta} = 2.5 : 1 : 0.9$. Cf. R.Neeter, N.M.M.Nibbering and Th.J.de Boer, Org. Mass Spectrom. 3, 597 (1970) and references therein. Labelled benzyl amines were prepared from (un)labelled benzamides via reduction with $LiAlH_4$ or $LiAlD_4$. Ring labelled p-aminotoluenes were precursors for the compounds described in ref. 1. p-CD_3-C_6H_4-NH_2 (2.8 g) was obtained by exchange (3 times, 150°, 48 hours) of p-nitrotoluene (5.6 g) in a mixture of 13 ml D_2O and 50 ml DMF, containing 0.0003 mole NaOD, followed by reduction.
3. H.Budzikiewicz, C.Djerassi and D.H.Williams, Mass Spectrometry of Organic compounds, Holden Day Inc., San Fransisco 1967, p.323
4. P.N.Rylander, S.Meyerson, E.I.Eliel and J.D.McCollum, J.Amer.Chem.Soc. 85, 2723 (1963)