THE ANILINE RADICAL CATION

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The aniline radical cation IIa, which has not yet been identified by esr, is an interesting link in the radical cation series

$$\overset{\bullet}{N}H_3{}^+ \qquad\qquad C_6H_5\overset{\bullet}{N}H_2{}^+ \qquad\qquad (C_6H_5)_2\overset{\bullet}{N}H^+ \qquad\qquad (C_6H_5)_3\overset{\bullet}{N}{}^+$$

$$\text{Ia}^{[1,2]} \qquad\qquad\qquad \text{IIa} \qquad\qquad\qquad\qquad \text{IIIa}^{[3]} \qquad\qquad\qquad \text{IVa}^{[4]}$$

This series is isoelectronic with the $\overset{\bullet}{C}H_3 \longrightarrow (C_6H_5)_3\overset{\bullet}{C}$ series.

Esr studies during the oxidation of aromatic amines by ceric sulphate in a flow system showed that distinct esr spectra could only be obtained in the case of some arylamines having electron withdrawing substituents [5,6]. We have now found that if a methylene chloride solution of aniline (ca. 0.2 M) and a solution of lead tetraacetate (ca. 0.03 M) in methylene chloride/trifluoroacetic acid (9 : 1) are allowed to mix in a flow system, a defined esr spectrum of IIa can be observed. The p-toluidine (IIb) and the 3,5-di-tert-butyl-aniline (IIc) radical cations can be studied under the same conditions. The 2,4,6-trimethyl-aniline radical cation (IId) can even be observed in trifluoroacetic acid under stationary conditions. Satisfactory computer simulations have been obtained for all esr spectra. The assignments of the hyperfine splittings can be made unequivocally from the spectra and are in agreement with the already known data of arylamine radical cations [5,6,7].

The a^N/a^{HNH} ratio should be quite sensitive to the configuration of these radical cations and should increase with increasing deviation from planarity. The reasonably constant a^N/a^{HNH} ratio of 0.80 ± 0.04 for Ia, IIa and IIIa indicates that the aminium moieties of these molecules are planar, as in the case of $\overset{\bullet}{N}H_3{}^+$ [1,2,8]. A consistent picture of the spin density distribution in IIa, IIIa and IVa can be obtained by considering $a^H = -23.7\, \rho_C$ [9], $a^N = 28.6\, \rho_N$ [10] and $a^{HNH} = -33.7\, \rho_N$ [11]. In all three species two-thirds of the unpaired electron are delocalized into the phenyl substituents. Going from IIa to IVa the increasing delocalization of the unpaired electron into the phenyl substituents is compensated by the increasing average twist of the phenyl substituents. This behaviour has also been found in the isoelectronic benzyl $\longrightarrow$ triphenylmethyl series.

Hyperfine Splitting Constants in Gauss

Substituents	a^N	$a^H{}_{NH}$	$a^H{}_o$	$a^H{}_m$	$a^H{}_p$
Ia[1,2]	19.5	25.9			
IIa	7.68	9.58	5.82	1.52	9.58
IIb 4-CH_3	7.19	9.03	5.31	0.87	12.40 (CH_3)
IIc 3,5-$[C(CH_3)_3]_2$	7.12	8.94	5.50	0.18 $[C(CH_3)_3]$	10.30
IId 2,4,6-$(CH_3)_3$	7.39	8.02	4.62 (CH_3)	0.88	11.74 (CH_3)
IIIa[3]	9.03	10.98	3.46	1.31	4.86
IVa[4]	10.16		2.28	1.22	3.32

References

1) T.Cole, J.Chem.Phys. 35, 1169 (1961); J.S. Hydet and E.S. Freeman, J.Phys.Chem. 65, 1636 (1961).

2) K.V.S.Rao and M.C.R.Symons, J.Chem.Soc. A, 1971, 2163.

3) F.A.Neugebauer and S.Bamberger, Angew.Chem. 83, 48 (1971); Angew.Chem.internat. Ed. Engl. 10, 71 (1971).

4) H.van Willigen, J.Amer.Chem.Soc. 89, 2229 (1967).

5) T.J.Stone and W.A.Waters, Proc.Chem.Soc. 1962, 253.

6) W.M.Fox and W.A.Waters, J.Chem.Soc. 1964, 6010.

7) G.Cauquis and M.Geniès, C.R.Acad.Sci.Ser.C. 265, 1340 (1967).

8) W.A.Lathan, W.J.Hehre, L.A.Curtiss and J.A.Pople, J.Amer.Chem.Soc. 93, 6377 (1971).

9) H.M.McConnell, J.Chem.Phys. 24, 632 (1956); M.Karplus and G.K.Fraenkel, ibid. 35, 1312 (1961).

10) E.W.Stone and A.H.Maki, J.Chem.Phys. 39, 1635 (1963).

11) B.L.Barton and G.K.Fraenkel, J.Chem.Phys. 41, 1455 (1964).