Restricted Rotation in Azobenzene and Nitrosobenzene Radical-anions

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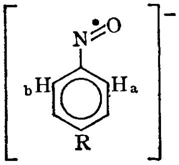
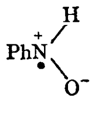
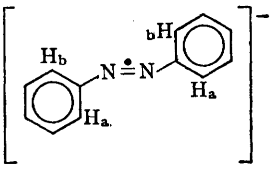
ONE-ELECTRON reduction of nitrosobenzene or one-electron oxidation of phenylhydroxylamine has been shown to yield (I; R = H) or (II) depending on pH.[1,2] We have also observed (I; R = H) or (II) as intermediates in the condensation of nitrosobenzene and phenylhydroxylamine to give azoxybenzene while (III) has been formed from equivalent amounts of azobenzene and hydrazobenzene in the presence of an excess of potassium t-butoxide in dimethyl sulphoxide (80%)–t-butyl alcohol (20%) solution (K_e obtained when $[B^-] \rightarrow \infty$).



(I)



(II)



(III)

$$ArN{=}NAr + (ArN{\cdot}NAr)^{2-} \overset{K_e = 2{\cdot}7}{\rightleftharpoons} 2(ArN^{\bullet}{=}NAr)^-$$

$$ArNO + ArNH{\cdot}OH \xrightarrow{OR^-} 2\,ArNO^{\bullet -} \xrightarrow{H^+} ArN(O){=}NAr + OH^-$$

$$ArNO + ArNH{\cdot}OH \longrightarrow 2\,ArNHO^{\bullet} \longrightarrow ArN(O){=}NAr + H_2O$$

Preparation of (I; R = D, Cl) as well as a variety of deuterated analogues of (III) has shown that the *ortho*-hydrogen atoms in (I) and (III) are not magnetically equivalent in e.s.r. spectroscopy at 23°. This demands restricted rotation around the Ar–N bond in planar (I) and (III) in terms of the spectrometer frequency [~9,500 Mc./sec.]. In both (I; R = H) and (III) one *ortho*-hydrogen and the *para*-hydrogen fortuitously have identical hyperfine splitting constants (hfsc) so that the magnetic non-equivalence of *ortho*-hydrogen atoms becomes apparent only upon *para*-substitution. Restricted rotation cannot be detected in substituted phenyl nitroxides (II; *p*-Cl) but may exist in unsubstituted nitrobenzene radical-anions where the symmetry of the nitro-group would prevent its experimental observation. The Table lists pertinent hyperfine splitting constants observed in dimethyl sulphoxide (80%)–t-butyl alcohol (20%) at 23 ± 1°. Restricted rotation was also detected for (I; R = D, Cl) in t-butyl and ethyl alcohol solutions.

(*Received, November 23rd, 1964.*)

Splitting constants (oersted)

Radical-anion	a_N	a_{H-o_1}	a_{H-o_2}	a_{H-p}	a_{H-m}	a_{H-N}
[*ooo'o'pp'*-$^2H_6$]Azobenzene	4·84					
[*ooo'o'mmm'm'*-$^2H_6$]Azobenzene	4·84			2·81		
[*mmm'm'*-$^2H_4$]Azobenzene	4·84	2·81	2·03	2·81		
Azobenzene	4·84	2·81	2·03	2·81	0·78	
[*oop*-$^2H_3$]Nitrosobenzene	7·90					
p-Deuteronitrosobenzene	8·00	3·90	2·90	*a*	1·00	
p-Chloronitrosobenzene	7·57	3·82	2·78		1·18	
Nitrosobenzene	7·90	3·90	2·83	3·90	1·01	
Nitrobenzene	10·21	3·34	3·34	3·84	1·07	
[*oop*-$^2H_3$]Phenyl nitroxide	8·90					11·70
p-Chlorophenyl nitroxide	8·95	3·00	3·00		1·00	11·75
Phenyl nitroxide	9·10	3·00	3·00	3·00	1·14	11·90

$^a a_{D-p} = 0{\cdot}59$.

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