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C-NITROSO COMPOUNDS.

PART IV. RESTRICTED ROTATION IN PHENYL NITROXIDES ').

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In the radical-anions derived from nitrosobenzene and azobenzene restricted rotation has been demonstrated by Geels et al.(1).For the neutral radical phenyl nitroxide (ØNHO•) the e.s.r.-spectrum did not indicate such an effect. Recently Ayscough et al.(2) found for this radical, that two of the three hydrogen atoms at ortho- and para-positions had identical hyperfine splitting (h.f.s.)constants, ascribed to equivalence of the ortho-hydrogen atoms.

We have found by comparison with para-substituted derivatives however,that in fact the para- and one ortho-hydrogen in the unsubstituted compound are magnetically equivalent, the second ortho-hydrogen having a different h.f.s. constant.

This is clearly shown in the e.s.r.-spectra of phenyl nitroxide (I) and p-fluoro-phenyl nitroxide (II).It demands restricted rotation around the Ø-N bond, the rotation frequency being less than 10^6 c/sec., the difference

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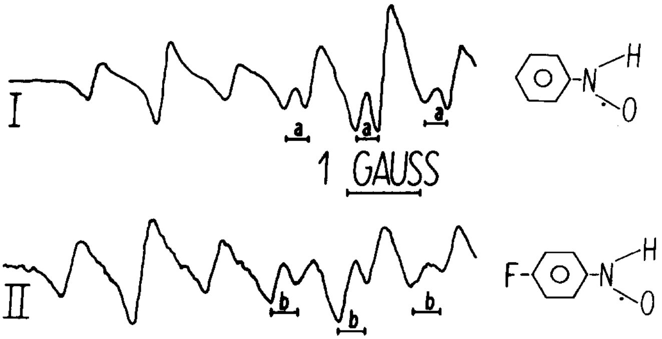
') Part III. A.Mackor, Th.A.J.W.Wajer, Th.J.de Boer and J.D.W.van Voorst, Tetrahedron Letters, 1967, 385.

in h.f.s.-constants of the ortho-hydrogen atoms (a and b in fig.1).

If the ortho- and para-hydrogen atoms were equivalent, they would give rise to a 1:3:3:1 pattern.However a 1:1:2:2:1:1 pattern is found.This means that one of the ortho- and para-hydrogen atoms has a h.f.s.-constant, different from that of the other two.The e.s.r.-spectrum of p-F-phenyl nitroxide (II) shows a 1:1:1:1 pattern for the ortho-hydrogen atoms, proving their non-equivalence. Each of the above-mentioned lines is further split into three lines (intensity ratio 1:2:1) by a smaller coupling with the equivalent meta-hydrogen atoms. In accordance with this the beginning of the low-field side of the e.s.r. spectra shows a 1:2:1:1:2:2:4:1:2 pattern for phenyl nitroxide and a 1:2:1:1:1:2:2:1:1 pattern for p-fluoro-phenyl nitroxide (fig.1).
In contrast to the ortho-hydrogen atoms no difference in h.f.s. for the meta-hydrogens is observed.

FIG.1

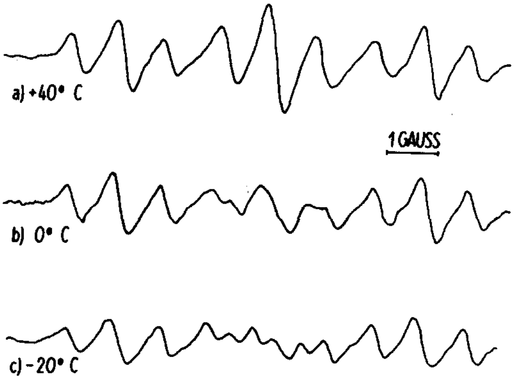


In p-t-butyl- and p-Br-phenyl nitroxide a difference in ortho-hydrogen atoms can be inferred from the intensity pattern.No separate lines are found in these cases, due to the linewidth-broadening, which may arise by unresolved hyperfine structure of the substituent or a more rapid rotation.
Also for p-trideutero-methoxy-phenyl nitroxide two different coupling

constants for the ortho-hydrogen atoms are found at -20°C (fig.2c).Increase in temperature, however, gives rise to a broadening and collapse of those lines, which are characterized by $m_I = +\frac{1}{2}$ and $-\frac{1}{2}$ for the two ortho-hydrogen nuclei respectively.On the other hand the lines for which both the ortho-hydrogen atoms have equal nuclear spin quantum number of either $m_I = +\frac{1}{2}$ or $-\frac{1}{2}$ remain sharp (fig.2b).A further increase in temperature results in a new set of sharp lines (fig.2a), the position of which is the average of the two lines which differ only in the m_I for the ortho-hydrogen nuclei.This temperature-effect, which is known as the linewidth-alternation effect (3), is due to an increase of the rotational frequency around the C-N-bond.

FIG.2

Low-field side of the e.s.r.-spectrum of p-CD$_3$O-phenyl nitroxide in toluene at different temperatures.



This effect is only found for the electron-releasing methoxy-substituent, indicating that the NHO• group has an electron-donating effect, which is counteracted by the methoxy-group.In all other radicals investigated, electron-release from the NHO• group to the aryl-group is apparently more effective and consequently rotational barriers round the Ar-N-bond are still sufficiently high at 40°C (the limit of thermal stability) to cause a measurable non-equivalence of ortho-hydrogens.

The h.f.s.-constants of the measured p-substituted phenyl nitroxides are listed in Table 1 together with some o-substituted radicals.

TABLE 1

H.f.s.-constants of phenyl nitroxides, measured at -20°C in toluene.

Radical p-$XC_6H_4NHO\cdot$ X=	Splitting Constants (in gauss) a_{H-N}	a_N	a_{H_o}	$a_{H_{o'}}$	a_{H_p}	a_{X_p}	a_{H_m}
$-OCD_3$	12,55	9,64	3,14	2,73	-	0,38 (3H)'	0,92
$-C(Me)_3$	12,50	9,48	2,98	2,98	-	-	1,00
$-CH_3$	12,68	9,28	3,09	2,80	-	3,32 (3H)	1,00
-H	12,12	9,13	3,07	2,74	3,07	-	0,98
-F	12,34	9,38	3,27	2,86	-	7,37 (F)	1,00
-Cl''	12,12	9,06	-	-	-	-	-
-Br	12,26	9,14	2,99	2,99	-	-	1,03
$-\underset{O}{\underset{\|}{C}}-Me$	11,32	8,22	2,80	3,10	-	-	1,02
o-$XC_6H_4NHO\cdot$ X=	a_{H-N}	a_N	a_{H_o}	a_{X_o}	a_{H_p}		a_{H_m}
$-C(Me)_3$	12,79	9,73	3,17	-	3,17		1,01
$-C_6H_5$	12,62	9,46	3,15	-	3,15		1,01
-F	12,31	9,10	3,20	4,16	3,20		0,98
-J	12,14	9,00	3,14	-	3,14		1,02

') for the undeuterated compound.

'') splittings due to aromatic hydrogen atoms could not be assigned with certainty in this case.

By substituting one *ortho*-position in the phenyl nitroxide by F,J,Ø and t-Bt only one of the two possible conformations, in which the *ortho*- and *para*-hydrogen atoms are equivalent, is observed.Molecular models make it very probable, that in this conformation the O-atom is furthest removed from the *ortho*-substituent.It is therefore very likely to assign the larger *ortho*-splitting in the unsubstituted phenyl nitroxide, which has the same value as the *para*-splitting, to the hydrogen atom that is closest to oxygen.
The phenyl nitroxides were generated by mixing toluene solutions of a nitrosobenzene with either the corresponding phenylhydroxylamine or cyclohexylhydroxylamine, or from a phenylhydroxylamine and t-nitrosobutane.
The aromatic nitroso compounds were synthesized by oxidation of the corresponding amines with Caro's acid (4) or by reduction of the nitro compound to the hydroxylamine with Zn/NH_4Cl followed by oxidation with potassium dichromate (5).p-Trideuteromethoxy-nitrosobenzene was prepared from p-nitrosophenol and deuterated methanol (6).
The e.s.r.-spectra were measured using a Varian V4502 e-s-r-spectrometer with 100 kc/sec. modulation along with a Varian V4531 multipurpose cavity and a variable temperature accessory, financed by the Stichting voor Scheikundig Onderzoek in Nederland (S.O.N.).

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