

Nitroxide Radicals. Part XVI.¹ Unpaired Electron Distribution in *para*-Substituted Aryl *t*-Butyl Nitroxides and 2-Naphthyl Phenyl Nitroxides

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N.m.r. and e.s.r. measurements on a number of *p*-methoxy-, *p*-phenoxy-, *p*-alkyl-, and *p*-phenyl-phenyl *t*-butyl nitroxides are reported. The empirical relationship $a_{\text{H}}^{p\text{-OMe}}/G = 0.123a_{\text{H}}^{p\text{-H}}/G - 0.02$ between the $a_{\text{H}}^{\text{OMe}}$ value of *p*-methoxyaryl radicals and the $a_{p\text{-H}}$ value of the corresponding unsubstituted radicals has been established. The positive coupling constants of the β -protons of the *p*-*t*-butyl and -isopropyl groups of *p*-*t*-butyl-, *p*-isopropyl- and *p*-ethyl-phenyl *t*-butyl nitroxides are attributed to homohyperconjugative interaction between positive free spin on the *para*-carbon atom and the electrons of the β -C-H bond. E.s.r. and n.m.r. spectra of 2-naphthyl and 8-*t*-butyl-2-naphthyl phenyl nitroxides have been measured and interpreted.

IN this paper we report and account for the magnitudes and signs of the proton coupling constants of the *para*-substituents of the aryl *t*-butyl nitroxides whose stabilities and modes of decomposition have been described in preceding papers in this series. Spectra of two 2-naphthyl phenyl nitroxides have also been measured and interpreted.

a_{N} Values of *para*-substituted aryl nitroxides correlate well with the Hammett σ and/or σ^- values of their substituents.^{2,3} In all cases electron-donating groups increase and electron-withdrawing groups decrease the a_{N} values. Because the $a_{o\text{-H}}$ and $a_{m\text{-H}}$ values of these radicals vary little with the nature of the *para*-substituent it has been argued,³ correctly in our view, that

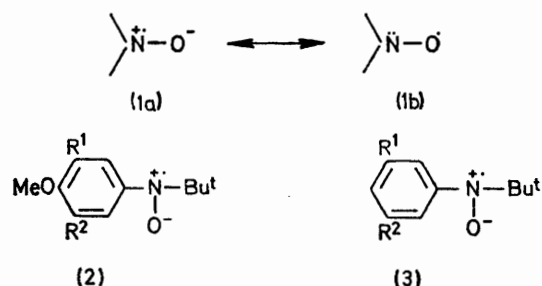
¹ Part XV, A. R. Forrester and S. P. Hepburn, preceding paper.

the principal effect of the substituent is not to alter unpaired electron delocalisation in the aromatic ring but to exert a polar effect on the electron distribution in the $>\text{N}-\text{O}\cdot$ group. Thus, electron-donating substituents, by favouring resonance structure (1a) over (1b), cause the a_{N} value to increase and electron-withdrawing groups have the opposite effect. The a_{N} value (12.8 G) of *p*-methoxyphenyl *t*-butyl nitroxide (2; $\text{R}^1 = \text{R}^2 = \text{H}$) (Table 1) is 0.5 G larger than that of phenyl *t*-butyl nitroxide (3; $\text{R}^1 = \text{R}^2 = \text{H}$) and so conforms to this pattern. Introduction of a *m*-methyl substituent predictably further increases the a_{N} value to 13.05 G, but a second *m*-methyl group significantly reduces it

² H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. chim. France*, 1965, 372.

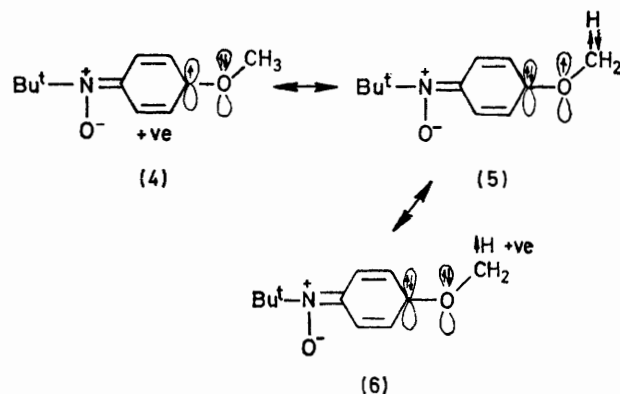
³ E. G. Janzen, *Accounts Chem. Res.*, 1969, 2, 279.

to 12.8 G. This change may be attributed to steric inhibition of mesomerism, the two methyl groups causing the methoxy-group to be twisted out of conjugation with the ring and the $\text{>N-O}\cdot$ group. The similarity



in the a_N values of the nitroxides (2; $R^1 = R^2 = \text{Me}$) and (3; $R^1 = R^2 = \text{Me}$) implies that there is residual mesomeric interaction between the methoxyl and $\text{>N-O}\cdot$ groups, otherwise the $-I$ effect of the oxygen atom would have caused the a_N value to be reduced below that of the dimethylphenyl nitroxide (3; $R^1 = R^2 = \text{Me}$) (cf. *p*-chlorophenyl *t*-butyl nitroxide,⁴ which has a_N 12.0 G). Although there are several apparent analogies to the aforementioned results, e.g. bromination of methoxydurene occurs only *ca.* 10^5 times as fast as that of durene but anisole is brominated *ca.* 10^{10} times as fast as benzene,⁵ when comparing the relative magnitudes of

G, respectively, for *p*-methoxyphenyl and 3-methyl-4-methoxyphenyl *t*-butyl nitroxides (2; $R^1 = R^2 = \text{H}$; $R^1 = \text{Me}$, $R^2 = \text{H}$). The positive sign of these couplings is most simply accounted for in terms of the structures (4) \leftrightarrow (5) \leftrightarrow (6), which imply transfer of positive spin from the *para*-carbon atom to the hydrogen of the methoxy-group by a combination of mesomeric and hyperconjugative interactions.⁷ From the similarity in



the a_N and $a_{\text{H}^{\text{OMe}}}$ values of the nitroxides (2; $R^1 = \text{Me}$, $R^2 = \text{H}$; $R^1 = \text{Bu}^t$, $R^2 = \text{H}$) (Table 1) it is evident that conjugation of the methoxyl with the $\text{>N-O}\cdot$ group is little affected by one relatively bulky adjacent group.

TABLE 1
Hyperfine coupling constants (G) of aryl *t*-butyl nitroxides $[\text{ArN}(\text{O})\text{Bu}^t]^*$

Ar	a_N	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{\text{H}^{\text{OMe}}}$	a (other H)	$a_{\text{H}^{\text{Bu}^t}}$
<i>p</i> -MeO·C ₆ H ₄	12.8	1.8	0.9	+0.19		-0.102
3-Me-4-MeO·C ₆ H ₃	13.05	2.0	+0.8	+0.18	$a_{\text{H}^{\text{m-Me}}} = -0.52$	-0.10
3,5-Me ₂ -4-MeO·C ₆ H ₂	12.8	2.4	+0.71	+0.006	$a_{\text{H}^{\text{m-Me}}} = 0.6$ -0.5	-0.11
3-Bu ^t -4-MeO·C ₆ H ₃	12.85	1.7	0.8	+0.19	$a_{\text{H}^{\text{Bu}^t}} = -0.005$	-0.10
4-PhO·C ₆ H ₄	12.60	2.0	+0.71			
4-(<i>p</i> -BrC ₆ H ₄ ·O)C ₆ H ₄	12.6	1.9	1.0			
4-PhC ₆ H ₄	11.9	2.5	0.9		$a_{\text{H}^{\text{m-H}}} = +0.12$ $a_{\text{H}^{\text{o,p-H}}} = -0.28$	-0.07
4-Bu ^t C ₆ H ₄	12.4	2.2	1.1		$a_{\text{H}^{\text{Bu}^t}} = +0.059$	-0.069
4-Pr ¹ C ₆ H ₄	12.5	1.9	+0.83		$a_{\text{H}^{\text{Me}}} = +0.052$	-0.075
4-EtC ₆ H ₄	12.45	1.95	1.0		$a_{\text{H}^{\text{Me}}} = +0.106$	-0.073

* E.s.r. and n.m.r. spectra measured in carbon tetrachloride solution. Values with signs determined by n.m.r. spectroscopy.

these effects it is important to remember the caution⁶ that 'steric effects on mesomerism as revealed by different criteria should be compared judiciously.' E.s.r., like u.v. measurements reflect only electronic strains, whereas rates of chemical reactions are affected by both electronic and steric strains.

The reduction in conjugation of the methoxy-group in (2; $R^1 = R^2 = \text{Me}$) with the $\text{>N-O}\cdot$ group is further exemplified by the small $a_{\text{H}^{\text{OMe}}}$ value of +0.006 G (measured by n.m.r. spectroscopy); cf. +0.19 and +0.18

⁴ A. Calder, A. R. Forrester, and S. P. Hepburn, *J.C.S. Perkin I*, 1973, 456.

⁵ G. Illuminati, *J. Amer. Chem. Soc.*, 1958, **80**, 4945.

⁶ B. M. Wepster, in 'Progress in Stereochemistry,' vol. 2, ed. W. Klyne and P. B. D. de la Mare, Butterworths, London, 1958, p. 99.

Calculations and spectral measurements on methoxybenzo- and methoxynaphtho-quinone radical-anions led Rabold *et al.*⁸ to derive an expression (i) (in which $Q_{\text{OMe}} = 5.6$ G) relating the unpaired spin density on the oxygen atom of a methoxy-group (ρ_0) to the coupling constant of the methoxy-protons ($a_{\text{H}^{\text{OMe}}}$). Equation (i) is

$$a_{\text{H}^{\text{OMe}}} = Q_{\text{OMe}} \cdot \rho_0 \quad (\text{i})$$

analogous to other, more familiar expressions relating the unpaired π -electron density on an aromatic carbon atom to the coupling constant of an adjacent proton⁹

⁷ H. J. Jakobsen and K. Torrsell, *Tetrahedron Letters*, 1970, 5003.

⁸ G. P. Rabold, R. T. Ogata, M. Okamaru, L. H. Piette, R. E. Moore, and P. J. Scheuer, *J. Chem. Phys.*, 1967, **46**, 1161.

⁹ H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 746.

[equation (ii)] and to the coupling constant of the protons

$$a_{\text{Cl-H}} = Q_{\text{Cl-H}} \cdot \rho_{\text{Cl}} \quad (\text{ii})$$

$$a_{\text{H}^{\text{Me}}} = Q_{\text{Cl-Me}} \cdot \rho_{\text{Cl}} \quad (\text{iii})$$

of an adjacent methyl group¹⁰ [equation (iii)]. Since the unpaired spin density on the oxygen atom of a *para*-methoxy-group should be proportional to that on the adjacent aromatic carbon atom, then (i) can be modified to give (iv). Unfortunately ρ_{Cl} in equation (iv) cannot

$$a_{\text{H}^{\text{OMe}}} = Q_{\text{Cl-OMe}} \cdot \rho_{\text{Cl}} \quad (\text{iv})$$

be measured easily, but by adhering to our previous contention that the introduction of a *p*-methoxy-group into an aromatic nitroxide does not significantly alter the unpaired electron distribution in the ring, and then equating ρ_{Cl} in equations (ii) and (iv), we obtain equation (v). This predicts that the coupling constant of the *p*-proton in an aromatic nitroxide should be proportional

$$a_{\text{H}^{\text{OMe}}} = (Q_{\text{Cl-OMe}}/Q_{\text{Cl-H}})a_{\text{Cl-H}} \quad (\text{v})$$

to that of the methoxy-protons in the corresponding *p*-methoxy-aromatic nitroxide. Figure 1 shows that when

TABLE 2
Coupling constants of *p*-protons and *p*-methoxy protons in aromatic π -radicals

No.*		$a_{p\text{-H}}$	$a_{\text{H}^{\text{OMe}}}$	Ref.
1	Phenyl nitroxide	3.07	—	11
	<i>p</i> -Methoxyphenyl nitroxide		0.38	
2	Diphenyl nitroxide	1.84		12
	Bis- <i>p</i> -methoxyphenyl nitroxide		0.21	
3	Phenyl <i>t</i> -butyl nitroxide	2.0		This work
	<i>p</i> -Methoxyphenyl <i>t</i> -butyl nitroxide		0.19	
4	Diphenylaminyl	4.34		13
	Bis- <i>p</i> -methoxyphenylaminyl		0.59	
5	Phenyl- <i>t</i> -butylaminyl	7.09		14
	<i>p</i> -Methoxyphenyl- <i>t</i> -butylaminyl		0.91	
6	Benzyl	6.17		15
	<i>p</i> -Methoxybenzyl		0.63	
7	Triphenylmethyl	2.78		16
	Tris- <i>p</i> -methoxyphenylmethyl		0.34	
8	Phenoxy	10.1		17
	<i>p</i> -Methoxyphenoxy		1.7	
9	2,6-Di- <i>t</i> -butylphenoxy	9.6		18
	2,6-Di- <i>t</i> -butyl-4-methoxyphenoxy		1.6	
	Radical-cations			
10	Triphenylammoniumyl	3.32		19
	Tris- <i>p</i> -methoxyphenylammoniumyl		0.61	
11	Diphenylammoniumyl	4.88		20
	Bis- <i>p</i> -methoxyphenylammoniumyl		1.60	
12	Dimethyl(phenyl)ammoniumyl	8.18		21
	<i>p</i> -Methoxyphenylammoniumyl		1.85	
	Radical-anions			
13	Nitrobenzene	3.97		22
	<i>p</i> -Methoxynitrobenzene		0.3	
14	Benzophenone	3.53		23
	4,4'-Dimethoxybenzophenone		0.25	
15	Thiobenzophenone	2.75		23
	4,4'-Dimethoxythiobenzophenone		0.25	

* Numbers as in Figure 1.

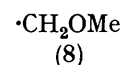
¹⁰ A. D. McLachlan, *Mol. Phys.*, 1958, **1**, 233.

¹¹ T. A. J. Wajer, A. Mackor, T. J. de Boer, and J. O. W. Van Voorst, *Tetrahedron Letters*, 1967, 1941.

¹² P. H. H. Fischer and F. A. Neugebauer, *Z. Naturforsch.*, 1964, **19a**, 1514.

¹³ F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, 1965, **98**, 944.

the appropriate values (taken from this and other work¹¹⁻²³ summarised in Table 2) are plotted such a proportionality does exist not only for aromatic nitroxides but also for arylaminyls and arylmethyls. This corresponds to the relationship $a_{\text{H}^{\text{OMe}}}/G = 0.123a_{\text{H}^{\text{H}}}/G - 0.02$. Hence, a useful estimate of *p*-methoxy-proton coupling constants (which are frequently too small to be resolved easily) can be obtained readily, in a completely empirical way, from a knowledge of the coupling constant of the *p*-proton in the unsubstituted radical. The relationship may also hold for methoxy-groups in other positions (*cf.* ref. 24) (but not presumably for *o*-methoxy-groups) but suitable examples to test this in a general way are scarce. It is also significant that a_{H} and $a_{\text{H}^{\text{OMe}}}$ for the radicals (7) ($a_{\text{H}} = 23.0$ G) and (8) ($a_{\text{H}^{\text{OMe}}} = 2.1$ G),



respectively,²⁵ are similarly related although, because of their relatively large values, this result has not been included in Figure 1. We have preferred to omit the *p*-methoxyphenoxy radicals when deriving the above relationship since it has been emphasised elsewhere³ that substituents which resemble too closely the main functional group should not be considered as valid substituents since they perturb the unpaired electron distribution to too great an extent, *e.g.* the *p*-dinitrobenzene radical-anion should not be regarded as a nitrobenzene radical-anion with a *p*-nitro-substituent (when the phenoxy radicals are included, the relationship becomes $a_{\text{H}^{\text{OMe}}} = 0.175a_{\text{H}^{\text{H}}} - 0.187$, the standard deviation on the slope of the line being 0.015).

The coupling constants of *p*-methoxy-protons in substituted aromatic radical-cations (relative to the *p*-protons of the corresponding unsubstituted radical-cations) are much larger than and those of substituted radical-anions are much smaller than those of neutral aromatic π -radicals and neither falls close to the plot for the neutral radicals (Figure 1). Intuitively this is the result expected and is one which can be rationalised most

¹⁴ S. F. Nelson, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, 1972, **94**, 1610.

¹⁵ P. Neta and R. H. Schuler, *J. Phys. Chem.*, 1973, **77**, 1367.

¹⁶ H. Judeikis and D. Kivelson, *J. Amer. Chem. Soc.*, 1962, **84**, 1132.

¹⁷ T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213; W. G. B. Huysmans and W. A. Waters, *J. Chem. Soc. (B)*, 1966, 1047.

¹⁸ E. Müller, K. Ley, K. Scheffler, and R. Meyer, *Chem. Ber.*, 1958, **91**, 2682.

¹⁹ E. T. Seo, R. F. Nelsen, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, 1966, **88**, 3498; H. Van Willigen, *ibid.*, 1967, **89**, 2229.

²⁰ F. A. Neugebauer and S. Bamberger, *Angew. Chem. Internat. Edn.*, 1971, **10**, 71.

²¹ B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, 1967, **89**, 5172.

²² A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

²³ L. Lunazzi, G. Maccagnani, G. Mazzanti, and G. Placucci, *J. Chem. Soc. (B)*, 1971, 162.

²⁴ J. L. Duncan, A. R. Forrester, G. McConnachie, and P. D. Mallinson, *J.C.S. Perkin II*, 1973, 718.

²⁵ I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, 1972, **28**, 867.

easily by reference to the simplified structures (9)—(11). Delocalisation of the unpaired electron onto the methoxy-group in the radical-anion (11) as represented by (11c)

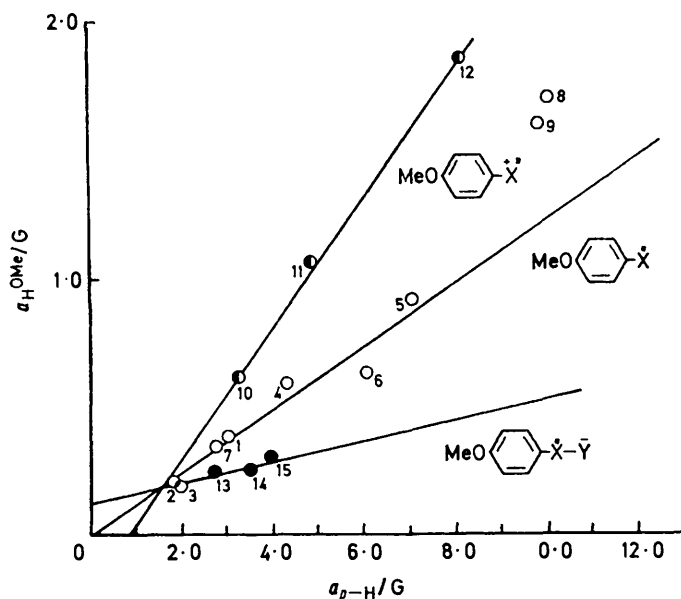
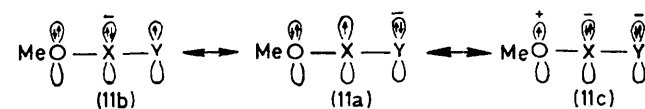


FIGURE 1 Plot of a_{p-H} for unsubstituted radicals and radical-ions vs. $a_{H^{OMe}}$ for *p*-methoxy-substituted radicals and radical-ions (slope for neutral radicals = 0.123; standard devn. 0.0134)

will be much less favoured because of charge separation than in the neutral radical (9a) \leftrightarrow (9b). Conversely, in the cation (10) unpaired electron delocalisation should be more favoured than in (9). Expressions similar to (v) but with different proportionality constants may well hold for cation- and anion-radicals but insufficient data are presently available to establish this (see Figure 1).

The a_N values of *p*-phenyl- and *p*-phenoxy-phenyl *t*-butyl nitroxides (Table 1) are commensurate with the Hammett σ values of their *para*-substituents. However,



evidence (from n.m.r. measurements) for the transmission of free spin onto these substituents could only be

obtained for the former radical (Figure 2). The relatively small coupling constants for the protons in the substituent ring (about 10% of those of the adjacent ring) indicate that there is considerable deviation from coplanarity in the aromatic part of this radical. The *p*-phenoxyphenyl nitroxide decomposed too rapidly in concentrated solution for meaningful n.m.r. measurements to be made.

The coupling constants of the protons of the *t*-butyl group in aryl *t*-butyl nitroxides are invariably small and negative (Table 1). The sign of the coupling constant can be considered to arise by spin polarisation of the bonds linking the nitrogen and the hydrogen atoms by the positive spin on the nitrogen and/or by hyperconjugative interaction of the unpaired electron on nitrogen

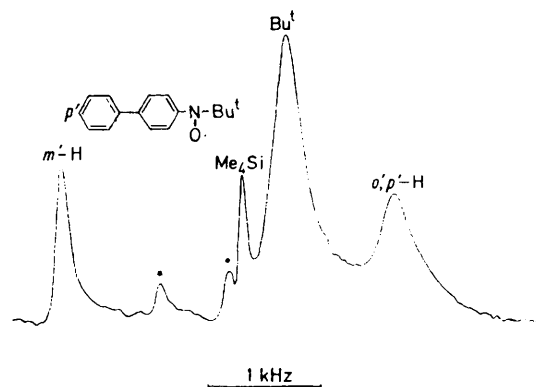
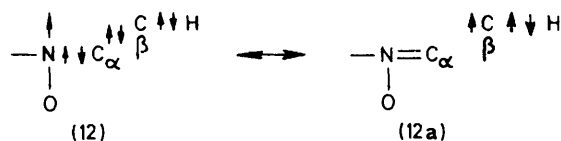


FIGURE 2 N.m.r. spectra of biphenyl-4-yl *t*-butyl nitroxide (asterisks denote peaks due to diamagnetic impurity)

with the electrons of the C_α - C_β bond, the resulting spin on C_β being transmitted to the adjacent hydrogen atom by spin polarisation.²⁶ As indicated in (12) and (12a)

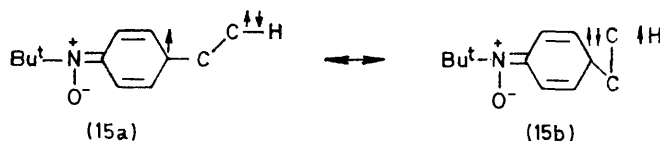


these models predict that negative spin will be induced on the β -hydrogen atom and positive spin on the β -carbon atom. ¹³C N.m.r. measurements²⁷ on di-*t*-butyl nitroxide have indeed confirmed these signs. Since the coupling constant of the *para*-carbon atom of aryl *t*-butyl nitroxides is also positive [see (13)] we were surprised to find that the values for the *t*-butyl protons of (14; R = Bu^t) and the methyl protons of (14; R = Prⁱ or Et) were also positive. Although this observation has

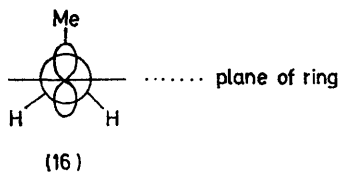
²⁶ A. Rassat and P. Rey, *Tetrahedron*, 1973, **29**, 2845.

²⁷ G. F. Hatch and R. W. Kreilick, *J. Chem. Phys.*, 1972, **57**, 3696.

been independently made by Torrsell *et al.*,²⁸ and Kreilick²⁹ has shown that the *ortho*- and *para*-*t*-butyl protons of several hindered phenoxyls have positive coupling constants, no explanation of this effect has yet been offered. The simplest way to account for this result is to consider that the unpaired electron on the *para*-carbon atom polarises directly the electrons in the C_β-H bond as illustrated in (15a) ↔ (15b) and that this is the



dominant mechanism for spin transfer.³⁰ Such a mechanism, termed 'homohyperconjugation,' has been used to account for the signs of the β-hydrogen coupling constants of some cyclic semidione radical-anions³¹ and bicyclic nitroxides.²⁶ However, these radicals, unlike the nitroxides under discussion here, were of fixed geometry and were thought to be held rigidly in conformations especially suited for such an interaction; hence it is surprising that this mechanism should operate in systems in which the barriers to rotation about the C_{Ar}-C_α bond are so small. The relatively large a_{H}^{Me} value for the *p*-ethylphenyl nitroxide (14; R = Et) for which the preferred conformation (16) has the half-filled orbital on *para*-carbon coplanar with the C_α-C_β bond, strongly supports the notion that spin delocalisation occurs in this



way. The smaller values of a_{H}^{Me} for the *p*-*t*-butyl- and *p*-isopropyl-phenyl nitroxides reflect the smaller weighting of conformations of these groups in which the methyls are suitably disposed for homohyperconjugative interaction, *i.e.*, conformations analogous to (16). Attempts to obtain further information about the conformational preferences of the *p*-ethyl and -isopropyl groups by variable-temperature n.m.r. measurements in the range 40° to -40° were unavailing. Although the a_{H}^{Me} values for the two radicals increased from 0.106 to 0.175 G and from 0.052 to 0.081 G, respectively, as the temperature was decreased from 40° to -40°, suggesting that conformations in which the methyl groups had smaller torsion angles were becoming increasingly important, this result is equivocal since the coupling constants of the *meta* ring protons also increased as the

* The spectra of 2-naphthyl and 1-naphthyl phenyl nitroxides have been confused in ref. 32. This we assume to be merely a typographical error.

²⁸ K. Torrsell, J. Goldman, and T. E. Petersen, *Annalen*, 1973, 231.

²⁹ R. W. Kreilick, *Mol. Phys.*, 1968, 14, 495.

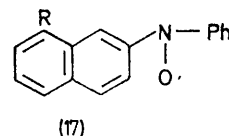
³⁰ G. R. Underwood and V. L. Vogel, *J. Amer. Chem. Soc.*, 1971, 93, 1058.

temperature was decreased. For example, the value for the *p*-isopropyl radical changed from 0.962 to 1.256 G. Clearly the average conformation of the nitroxide grouping also changes under these conditions and the extent to which this affects the coupling constants of the protons in the *para*-substituent cannot be separated from that caused by conformational changes in the substituent itself. In this respect variable-temperature n.m.r. studies on *p*-alkylphenoxyls would be more profitable.

2-Naphthyl Phenyl Nitroxides.—The only published spectrum of the nitroxide (17; R = H) is that of Buchachenko.³² * This was obtained from measurements on a mixture of *N*-phenyl-2-naphthylamine, hydrogen peroxide, and a cobalt catalyst. The assignment of this spectrum to the nitroxide (17; R = H) has been questioned by Bridger and Strom³³ because it does not exhibit an easily discernible proton splitting of *ca.* 4.0 G which they consider, on the basis of MO calculations and measurements on related radicals, to be the value expected for the coupling constant of the 1-naphthyl proton.

In view of the potential importance of this nitroxide, since it is thought³⁴ to be formed during inhibition of autoxidation by the commercial antioxidant *N*-phenyl-2-naphthylamine, and our previous experience with 2-naphthyl *t*-butyl nitroxides,²⁴ we have sought to clarify the position by preparing the radical and measuring its e.s.r. and n.m.r. spectra.

2-Naphthyl phenyl nitroxide (17; R = H) was prepared as a red crystalline solid by the reaction of 2-naphthylmagnesium bromide with nitrosobenzene followed by oxidation of the product with silver oxide. Crystals of this radical were stable for months below 0°, but on dissolution decomposition began almost immediately. Phenyl 8-*t*-butyl-2-naphthyl nitroxide (17; R = Bu^t) was similarly prepared (44%) as a red viscous oil.



Our spectra (Figures 3 and 4), obtained after prolonged deoxygenation of very dilute solutions of the nitroxides (17; R = H or Bu^t) in carbon tetrachloride, corroborate Buchachenko's ascription although his spectrum of the nitroxide (17; R = H) is not so well resolved as ours and there are minor differences between the two. Interpretation of such spectra (which are derived from the unpaired electron coupling with ten and nine sets, respectively, of magnetically nonequivalent nuclei) was greatly aided by n.m.r. measurements on concentrated solutions

³¹ G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Letters*, 1967, 1955.

³² A. L. Buchachenko, 'Stable Radicals,' Consultants Bureau, New York, 1965, p. 119.

³³ R. F. Bridger and E. T. Strom, *J. Org. Chem.*, 1971, 36, 560.

³⁴ K. Adamic, M. Dunn, and K. U. Ingold, *Canad. J. Chem.*, 1969, 47, 287.

(ca. 3M) of the radicals in carbon tetrachloride. Values of a_{3-H} , a_{4-H} , a_{5-H} , a_{6-H} , a_{7-H} , a_{8-H} , and $a_{3'-H}$ were obtained in this way and the remaining coupling constants were deduced from the e.s.r. spectra. Simulations using these

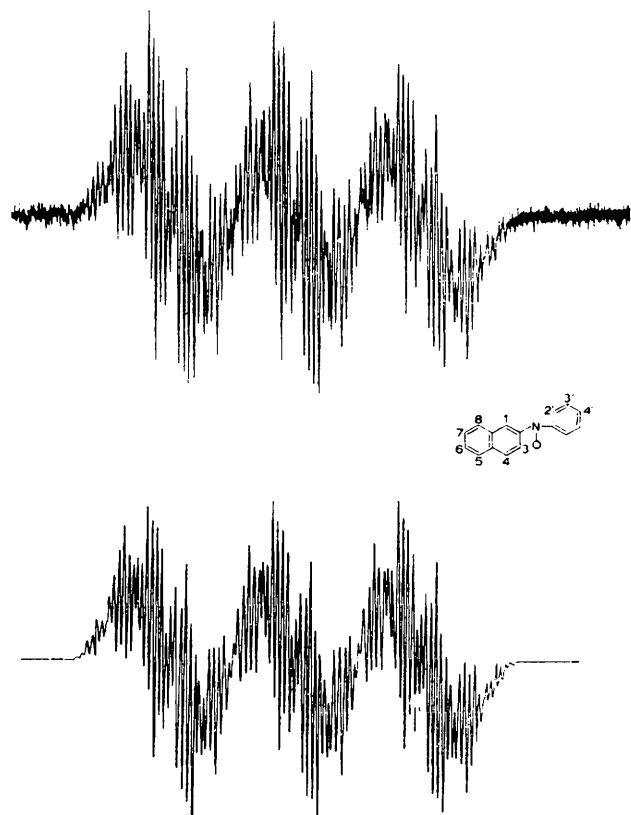


FIGURE 3 Actual (upper) and simulated (lower) e.s.r. spectra of 2-naphthyl phenyl nitroxide

values (Table 3) were in excellent agreement with the actual spectra (Figures 3 and 4). Also included in the

TABLE 3

Hyperfine coupling constants * (G) of 2-naphthyl phenyl nitroxides

	Nitroxide (17; R = H)		Nitroxide
	Actual	Calc. ³³	(17; R = Bu ^t)
a_N	9.48		9.48
a_{1-H}	2.87	3.46	2.91
a_{3-H}	-1.138	1.13	-1.152
a_{4-H}	+0.791	0.62	+0.779
a_{6-H}	+0.424	0.48	+0.413
a_{6-H}	-0.957	0.72	-0.963
a_{7-H}	+0.359	0.46	+0.343
a_{8-H}	-0.746	0.89	-0.009 †
$a_{2'-H}$	1.775	1.92	1.75
$a_{3'-H}$	+0.791	0.79	+0.779
$a_{4'-H}$	1.775	1.78	1.75

* Values with signs determined by n.m.r. measurements.

† $a_{H^{Bu^t}}$ Value.

Table are the hyperfine coupling constants, calculated by Bridger and Strom,³³ which most closely fit the experimental data. These were obtained using the McLachlan

modification of the Hückel MO theory and parameters $h_N = 1.5$, $k_{NO} = 1.6$, $k_{ON} = 1.05$ (nitrogen-naphthyl carbon bond) and $h_0 = 1.2$. Similar calculations on 2-naphthyl t-butyl nitroxide gave coupling constant values which most closely resembled the experimental ones for $k_{ON} = 0.8$ or 0.85. This result implies that the nitrogen atom is twisted out of conjugation with the 2-naphthyl ring to a greater extent when it is flanked by a t-butyl group than it is when it is flanked by a phenyl group. The relatively large difference (2.4 G) between the a_N values of t-butyl and phenyl 2-naphthyl nitroxides compared

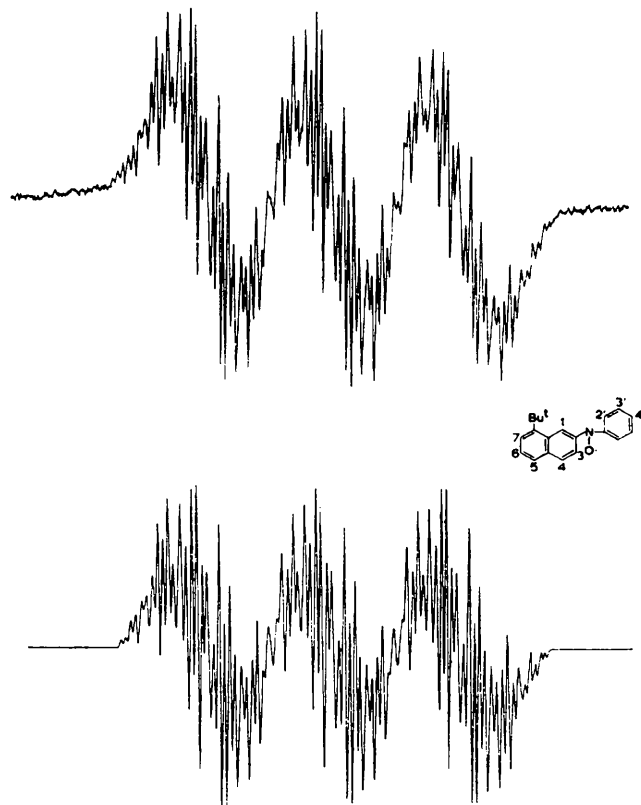


FIGURE 4 Actual (upper) and simulated (lower) e.s.r. spectra of phenyl 8-t-butyl-2-naphthyl nitroxide

with that (1.4 G) between t-butyl phenyl and diphenyl nitroxides supports this view.

EXPERIMENTAL

The nitroxides were prepared by treatment of the corresponding 2-naphthylmagnesium bromides in tetrahydrofuran with nitrosobenzene followed by oxidation of the resulting product mixture with silver oxide as previously described.¹ Purification was achieved by separation on silica (t.l.c.) with chloroform.

2-Naphthyl phenyl nitroxide (77%) formed red plates, m.p. 74–75° (decomp.) (Found: C, 82.0; H, 5.4; N, 5.8. $C_{16}H_{12}NO$ requires C, 82.0; H, 5.2; N, 6.0%), λ_{max} (EtOH) 272, 277sh, 317, 364, 546, and 584sh nm (log ϵ 4.11, 4.10, 4.08, 3.72, 2.50, 3.27), ν_{max} 1375 cm^{-1} (N–O).

Phenyl 8-t-butyl-2-naphthyl nitroxide (44%) formed a red viscous oil, ν_{max} 1375 cm^{-1} (N-O).

E.s.r. and n.m.r. measurements were recorded with Varian E3 and HA-100 (with 10—15 kHz modulation) spectrometers, respectively.

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