Nitroxide Radicals. Part XIII.[1] Unpaired Electron Distribution in 1- and 2-Naphthyl t-Butyl Nitroxides

By **J. Lindsay Duncan**, **Alexander R. Forrester**,* **Gordon McConnachie**, and **Peter D. Mallinson**,
Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE

Nitrogen and proton coupling constants for a series of 1- and 2-naphthyl t-butyl nitroxides have been evaluated using both n.m.r. and e.s.r. techniques. McLachlan MO calculations on 2-naphthyl t-butyl nitroxide give values for the free spin densities on the ring positions which are in reasonably good agreement with those determined experimentally. Similar agreement for 1-naphthyl t-butyl nitroxide was not obtained.

INTEREST in the radical 2-naphthyl phenyl nitroxide stems from its ease of formation from the commercially useful antioxidant *N*-phenyl-2-naphthylamine.[2,3] Although the e.s.r. spectra of this and related 2-naphthyl nitroxides have been recorded previously, complete interpretation has not been achieved mainly because of the relatively large number of dissimilar splittings arising from coupling of the unpaired electron with the protons of the naphthyl ring. Indeed this is generally the case for radicals derived from 1- and 2-monosubstituted naphthalenes.[4] We now report on a series of 1- and 2-naphthyl t-butyl nitroxides which were suffi-

TABLE 1

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

$\left(\mathrm{ArN(O\cdot)Bu^t}\right)$

Ar	a_N	$a_H^{Bu^t}$	$a_{1\text{-}H}$	$a_{3\text{-}H}$	$a_{4\text{-}H}$	$a_{5\text{-}H}$	$a_{6\text{-}H}$	$a_{7\text{-}H}$	$a_{8\text{-}H}$	$a_{\text{other H}}$
2-Naphthyl	11·9	−0·064	2·9	−0·925	+0·865	+0·390	−0·714	+0·344	−0·714	
8-Methyl-2-naphthyl	11·9	−0·059	3·2	−1·084	+0·843	+0·423	−0·961	+0·347		$a_H^{Me} = +0{\cdot}489$
8-t-Butyl-2-naphthyl	12·2	−0·056	3·1	−1·214	+0·911	+0·412	−0·933	+0·343		$a_H^{8\text{-}Bu^t} = -0{\cdot}01$
4,5-Dimethyl-2-naphthyl	11·9	−0·055	3·4	−1·240			−0·915	+0·332	−0·714	$a_H^{4\text{-}Me} = -0{\cdot}595$; $a_H^{5\text{-}Me} = -0{\cdot}375$
6-Methoxy-2-naphthyl	12·1	−0·084	3·0	n.d.	+0·982	+0·314		+0·314	−0·646	$a_H^{OMe} = +0{\cdot}104$

* Values without signs obtained by e.s.r. measurements.

TABLE 2

Calculated hyperfine splittings (G) for 2-naphthyl t-butyl nitroxide

Parameters	a_N	$a_{1\text{-}H}$	$a_{3\text{-}H}$	$a_{4\text{-}H}$	$a_{5\text{-}H}$	$a_{6\text{-}H}$	$a_{7\text{-}H}$	$a_{8\text{-}H}$
i $k_{CN} = 0{\cdot}8$ $h_N = 1{\cdot}5$ $h_O = 1{\cdot}7$ $k_{NO} = 1{\cdot}6$ $\lambda = 1{\cdot}1$	12·0	−2·83	−0·998	+0·791	+0·502	−0·544	+0·406	−0·629
ii $k_{CN} = 0{\cdot}8$ $h_N = 1{\cdot}6$ $h_O = 1{\cdot}7$ $k_{NO} = 1{\cdot}7$ $\lambda = 1{\cdot}1$	11·3	−2·84	−0·924	+0·740	+0·468	−0·579	+0·396	−0·670
iii $k_{CN} = 0{\cdot}85$ $h_N = 1{\cdot}5$ $h_O = 1{\cdot}7$ $k_{NO} = 1{\cdot}6$ $\lambda = 1{\cdot}1$	11·8	−3·22	−1·08	+0·848	+0·542	−0·629	+0·444	−0·727
iv $k_{CN} = 0{\cdot}85$ $h_N = 1{\cdot}6$ $h_O = 1{\cdot}7$ $k_{NO} = 1{\cdot}7$ $\lambda = 1{\cdot}1$	11·0	−3·20	−1·01	+0·797	+0·507	−0·660	+0·439	−0·762

TABLE 3

Hyperfine coupling constants * (G) of 1-naphthyl t-butyl nitroxides

$\left(\mathrm{ArN(O\cdot)Bu^t}\right)$

Ar	a_N	$a_H^{Bu^t}$	$a_{2\text{-}H}$	$a_{3\text{-}H}$	$a_{4\text{-}H}$	$a_{5\text{-}H}$	$a_{6\text{-}H}$	$a_{7\text{-}H}$	$a_{8\text{-}H}$	$a_{\text{other H}}$
1-Naphthyl	13·5	−0·218	>1·2	+0·654	−0·430	−0·101	+0·074 or +0·040	−0·064	+0·040 or +0·074	
3,4-Dimethyl-1-naphthyl †	13·6	−0·218	>1·2			−0·188	+0·053	−0·042	+0·053	$a_H^{3\text{-}Me} = -0{\cdot}107$ $a_H^{4\text{-}Me} = +0{\cdot}112$
4,7-Dimethyl-1-naphthyl	13·6	−0·218	>1·2	+0·347		−0·136	+0·074 or +0·042		+0·042 or +0·074	$a_H^{4\text{-}Me} = +0{\cdot}073$ $a_H^{7\text{-}Me} = +0{\cdot}073$

* Values without signs determined by e.s.r. measurements. † N.m.r. spectrum measured in chloroform.

TABLE 4

Calculated hyperfine splitting constants (G) for 1-naphthyl t-butyl nitroxide

Parameters	$a_{2\text{-}H}$	$a_{3\text{-}H}$	$a_{4\text{-}H}$	$a_{5\text{-}H}$	$a_{6\text{-}H}$	$a_{7\text{-}H}$	$a_{8\text{-}H}$
$k_{CN} = 0{\cdot}8$ $h_N = 1{\cdot}7$ $h_O = 1{\cdot}6$ $k_{NO} = 1{\cdot}7$ $\lambda = 1{\cdot}1$	−2·73	+1·05	−2·50	−0·598	+0·450	−0·569	+0·577
$k_{CN} = 0{\cdot}6$ $h_N = 1{\cdot}7$ $h_O = 1{\cdot}6$ $k_{NO} = 1{\cdot}7$ $\lambda = 1{\cdot}1$	−1·53	+0·701	−1·34	−0·305	+0·309	−0·303	+0·418
$k_{CN} = 0{\cdot}5$ $h_N = 1{\cdot}7$ $h_O = 1{\cdot}6$ $k_{NO} = 1{\cdot}7$ $\lambda = 1{\cdot}1$	−1·03	+0·524	−0·889	−0·194	+0·234	−0·197	+0·324
$k_{CN} = 0{\cdot}4$ $h_N = 1{\cdot}7$ $h_O = 1{\cdot}6$ $k_{NO} = 1{\cdot}7$ $\lambda = 1{\cdot}1$	−0·637	+0·358	−0·530	−0·110	+0·162	−0·116	+0·228

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[1] Part XII, A. Calder, A. R. Forrester, and S. P. Hepburn, *J.C.S. Perkin I*, 1973, 456.

[2] A. L. Buchachenko, 'Stable Radicals,' Consultants Bureau, New York, 1965, p. 119.

[3] R. F. Bridger and E. T. Strom, *J. Org. Chem.*, 1971, **36**, 560 and earlier papers by these authors.

[4] *E.g.* see T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213; A. Rieker, N. Zeller, K. Schurr, and E. Müller, *Annalen*, 1966, **697**, 1; A. L. Buchachenko, Ya. S. Lebedev, and M. B. Neiman, *J. Struct. Chem.*, 1961, **2**, 516; R. E. Dessy, M. Kleiner, and S. C. Cohen, *J. Amer. Chem. Soc.*, 1969, **91**, 6800.

ciently stable to allow complementary n.m.r. and e.s.r. measurements to be made and hence for all naphthyl proton coupling constants to be evaluated.

The relative stabilities and modes of decomposition of the 1- and 2-naphthyl t-butyl nitroxides listed in Tables 3 and 1, respectively, will be described subsequently.[5] Suffice it to say here that *ca.* 3M solutions in carbon tetrachloride of these nitroxides deteriorated sufficiently slowly for their n.m.r. spectra to be conveniently measured using a conventional 100 MHz spectrometer. We have found that the largest coupling constants which may be determined in this way are *ca.* 1·2 G. Protons with larger coupling constants give very broad n.m.r. bands which are difficult to detect and measure. As seen from Figure 1 the computerised reconstruction of the e.s.r. spectrum of t-butyl 8-t-butyl-2-naphthyl nitroxide using the coupling constants obtained from n.m.r. and e.s.r. spectra was in excellent agreement with that observed experimentally. Agreement between the actual and synthetic spectra for 8-methyl-2-naphthyl and 2-naphthyl t-butyl nitroxides was only slightly worse and we did not attempt to reconstruct the spectra of the 6-methoxy-2-naphthyl and 4,5-dimethyl-2-naphthyl t-butyl nitroxides because the fine structure in these spectra was inadequately resolved. Signs of the coupling constants of the ring protons of both the 1- and 2-naphthyl nitroxides are those expected from a conjugated π radical. Those of the coupling constants of protons of the substituents may be satisfactorily accounted for in terms of either hyperconjugation (methyl) or a combination of mesomeric interaction and hyperconjugation (methoxy) as indicated in the Scheme.

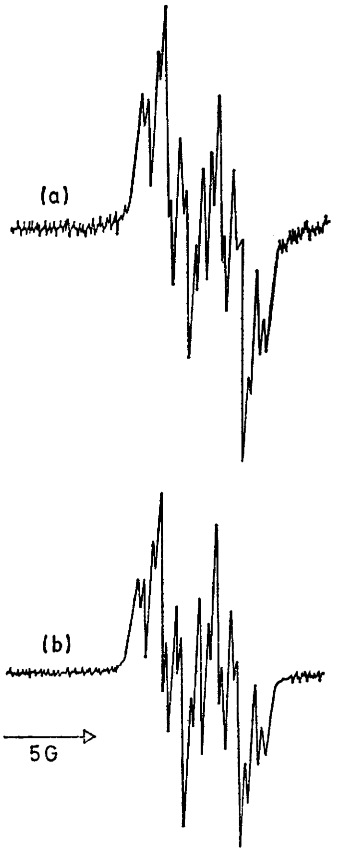
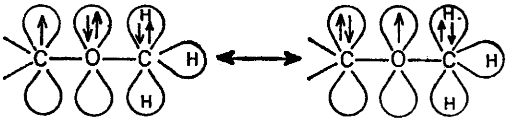


FIGURE 1 (a) Actual and (b) reconstructed e.s.r. spectra of 8-t-butyl-2-naphthyl nitroxide



SCHEME

Significantly the coupling constants of the 6-, 7-, and 8-protons of 4,5-dimethyl-2-naphthyl t-butyl nitroxide were little different from the corresponding values in the other 2-naphthyl nitroxides although the carbon skeleton in this radical would be expected to be slightly buckled due to steric compression by the *peri*-methyl groups (*cf.* 2-bromo-4,5-dimethylnaphthalene [6]).

MO Calculations of electron spin densities have been carried out on 2-naphthyl t-butyl nitroxide. Initially, simple Hückel calculations revealed that reasonable reproduction of the observed data was achieved when the Coulomb and bond integral parameters h_O, h_N, k_{NO}, and k_{CN} had values close to 1·6, 1·5, 1·6, and 0·95. Refinement of these values, using the McLachlan method[7] and Q^H_{CH} and Q^N_N 24·0 [8,9] and 25·0,[9] respectively, enabled the observed values for the proton couplings to be fairly closely reproduced (Tables 1 and 2). Of the several sets of parameters listed, those given in entries ii and iii (Table 2) are probably the most appropriate. The h_O value of 1·7 is somewhat higher than that used by others [3,10] in calculations on related molecules, but is more in keeping with the expected value based on atomic electronegativities.[11] (Undoubtedly, this parameter will be influenced to some extent by the nature of the solvent used.) Values of h_N and k_{NO} in the region of 1·5 and 1·6 are close to those reported previously for similar molecules,[3,10] the high value for k_{NO} being essential for reasonable reproduction of the observed data. Insofar as these calculations have physical significance, the value of k_{CN} found implies that the nitroxide group in 2-naphthyl t-butyl nitroxide is to some extent twisted out of conjugation with the naphthyl π-system. If the normal value of k_{CN} is accepted as 1·0—1·1,[3,10-12] the deviation from co-planarity is estimated to be some 30—40°.

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[5] A. R. Forrester and G. McConnachie, unpublished work.

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[8] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 632.

[9] J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance,' McGraw-Hill, New York, 1972.

[10] P. B. Ayscough and F. B. Sargent, *J. Chem. Soc.* (*B*), 1966, 907.

[11] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

[12] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.

E.s.r. spectra of 1-naphthyl t-butyl nitroxides (*e.g.*, see Figure 2) were characterised by larger a_N values and much smaller proton hyperfine splittings (Table 3). The difference in unpaired electron distribution between 1- and 2-naphthyl t-butyl nitroxides is similar to that between *o*-tolyl and phenyl t-butyl nitroxides already described.[10] Interaction between the hydrogen of the 8-position and the oxygen twists the nitroxide group of 1-naphthyl t-butyl nitroxide out of the plane of the naphthyl ring to a large extent and so reduces the free spin density at the ring positions. The positions which are most affected are those which are furthest from the nitroxide group. Moreover, the pattern of unpaired electron distribution is altered by this twisting so that it no longer resembles that in a typical π radical. Clearly the 1-naphthyl nitroxides have more σ character than their 2-naphthyl isomers. Not unexpectedly, McLachlan calculations using the parameters successfully employed for the 2-naphthyl radical gave an unpaired electron distribution inherently different from that observed. Reducing the values of k_{CN} to account for the greater degree of twisting did not fundamentally alter this order (Table 4). Hence, in such ' twisted radicals ' the extent to which the free spin is transmitted through the σ bond framework is relatively important and MO calculations, such as those used here, which take no account of this, are inapplicable.

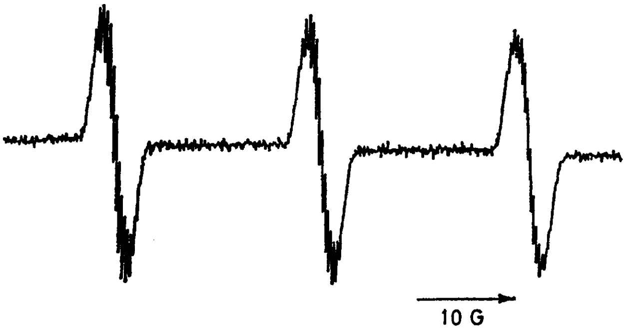

FIGURE 2 E.s.r. spectrum of 1-naphthyl t-butyl nitroxide

We anticipate that the coupling constants given (especially for the 2-naphthyl radicals) in Tables 1 and 3 will provide a useful aid in the interpretation of e.s.r. spectra of other naphthyl radicals whose instability makes measurement of their n.m.r. spectra impracticable.

EXPERIMENTAL

The nitroxides were obtained by oxidation of the corresponding hydroxylamines, the preparation and characterisation of which will be reported elsewhere.

E.s.r. measurements were recorded on a Varian E3 spectrometer. N.m.r. spectra were measured on a Varian HA100D spectrometer using 10—15 kHz modulation. MO Calculations were carried out on the University of Aberdeen I.C.L. 4/50 computer.

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