Reactivity and Structure of *N*-Phenylnaphth-1-ylamines and Related Compounds. Part 2.† Unpaired Electron Distribution in Naphth-1-yl Phenyl Nitroxides

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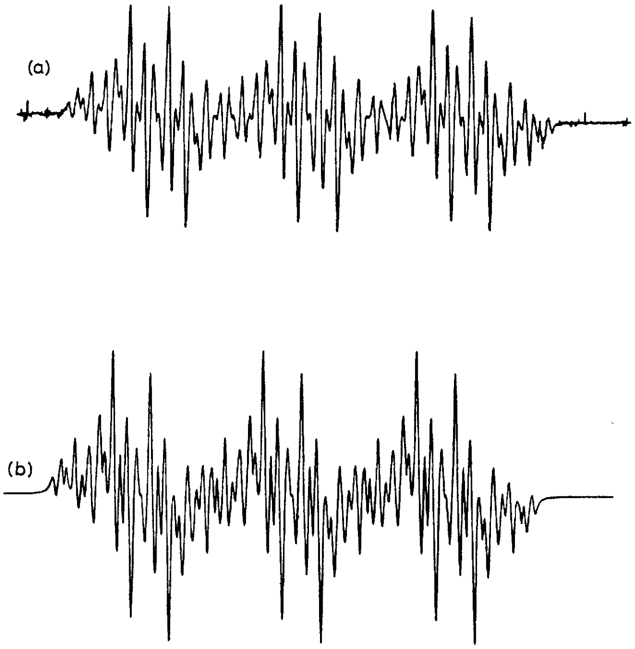
The e.s.r. spectra of a series of naphth-1-yl phenyl nitroxides have been interpreted with the aid of complementary n.m.r. measurements. McLachlan MO calculations on naphth-1-yl phenyl nitroxide gives values for the naphthyl proton coupling constants which are not in good agreement with the experimental ones.

There have been two previous measurements [1,2] of the e.s.r. spectrum of naphth-1-yl phenyl nitroxide (1a). In both cases the radical was generated in the cavity from the corresponding amine and a peroxy-oxidising agent but in neither case were proton coupling constants derived. The substituted naphth-1-yl phenyl nitroxide (2) has also been reported [3] but again full interpretation of the hyperfine splitting is lacking.

The series of nitroxides (1a—g) was generated from the corresponding hydroxylamines by oxidation with silver oxide or air. The derived values for the coupling constants are given in Table 1. In all cases there was good agreement between simulated and actual spectra (for an example see the Figure). The spectra have lines too broad (0.35 G) to allow resolution of the splittings due to the 5-, 6-, 7-, a nd 8-proton of the naphthyl ring. To evaluate these the n.m.r. spectra of two of the longest lived members of the series (1e and c) were measured. Such spectra provide both the magnitude and the sign of the coupling constants.[4] Concentrated solutions (*ca.* 3 mol l^{-1}) of the radicals in deuteriochloroform were used and shifts were measured relative to those of the corresponding protons in the parent amines. For the nitroxide (1e) two positive coupling constants were evaluated (0.06 and 0.04 G) both much smaller than the widths of the lines in the e.s.r. spectrum. After consideration of the predicted signs of the coupling constants of the 5-, 6-, 7-, and 8-proton [see (1)] these positive values are assigned to 6- and 8-H. For (1c) only one value (+0.11 G) was obtained; presumably the other signal is obscured by the signals of small amounts of a diamagnetic impurity. The signals from the 5- and 7-proton were also not detected. They would be shifted upfield and probably lie under the broad envelope of the resonances of the t-butyl protons.

The relative magnitudes of the coupling constants of the naphthyl ring protons $a_{2\text{-H}} > a_{3\text{-H}} > a_{4\text{-H}}$ and the very small values for $a_{5\text{-H}}$, $a_{6\text{-H}}$, $a_{7\text{-H}}$, and $a_{8\text{-H}}$ strongly suggest that the naphthyl ring is twisted out of conjugation with the N–O group to a greater extent than is the phenyl. This results in a_{N}, $a_{o\text{-H}}$, and $a_{p\text{-H}}$ values being larger than those of diphenyl nitroxide. The twisting is due to non-bonding interactions between 8-H and the oxygen of the nitroxide group (models). Unpaired-electron distribution in the naphthyl ring, as indicated by the proton coupling constants, is similar to that reported [5] for t-butyl naphth-1-yl nitroxide. In contrast the spectrum of naphth-1-oxyl [6] shows $a_{4\text{-H}} > a_{2\text{-H}} > a_{3\text{-H}}$ and that of the naphth-1-ylmethyl derivative [7] (3) $a_{4\text{-H}} \sim a_{2\text{-H}} > a_{3\text{-H}}$. Both are typical π-radicals.



(a) Actual and (b) simulated spectrum of naphth-1-yl phenyl nitroxide

Molecular orbital calculations were made using the McLachlan modification [8] of the Hückel MO method, of the unpaired electron spin densities and hence the proton coupling constants for phenyl naphth-1-yl and naphth-2-yl nitroxides. In such calculations on aryl nitroxides a wide variety of values for the semi-empirical parameters h_N, h_O, k_{NO}, and k_{CN} have been used. Representative values from the literature are given in Table 2. For phenyl naphth-2-yl nitroxide h_N, h_O, k_{NO}, and λ were set and k_{CN} (naphthyl) and k_{CN} (phenyl) were varied. Only a few of the many variations used are given in Table 3. Correlation between experimental and calculated values was best with k_{CN} (phenyl) 1.0 and k_{CN} (naphthyl) 0.9. Hence the phenyl group cannot be twisted significantly out of conjugation with the nitroxide group and the naphth-2-yl only slightly if at all. The largest difference was for $a_{1\text{-H}}$.

Use of a similar set of parameters for phenyl naphth-1-yl nitroxide and varying k_{CN} (naphthyl) between 0.55 and 1.05 gave best results with k_{CN} (naphthyl) 0.55. However, a major discrepancy was the high calculated value for $a_{4\text{-H}}$ (Table 4) which was about twice the observed value. The low k_{CN} (naphthyl) supports our previous contention that the naphthyl, but not the phenyl, is twisted out of conjugation with the

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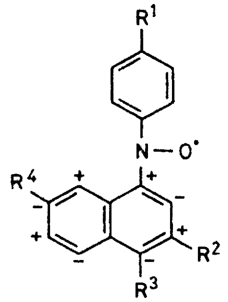
† Part 1, J. E. Bennett, G. Brunton, A. R. Forrester, and J. D. Fullerton, preceding paper.

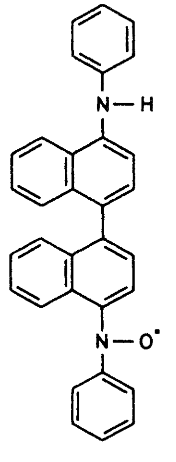
Table 1. Hyperfine coupling constants (±0.05 G) * of phenyl naphth-1-yl nitroxides (1)

Naphth-1-yl nitroxide	^{a} N	^{a} 2′, 4′, 6′-H	^{a} 5′, 3′-H	^{a} 2-H	^{a} 3-H	^{a} 4-H	Linewidth
(1b)	10.00	2.55 †	0.85	1.00	0.60	0.60	0.35
(1e)	10.00	2.55 †	0.85	1.00		0.65	0.35
(1c)	10.00	2.55 †	0.85	1.05	0.70		0.35
(1a)	10.00	2.55	0.85	1.00	0.55	0.55	0.25
(1d)	9.90	2.60	0.95	1.05		0.70	0.35
(1f)	9.93	2.60	0.95	0.95	0.60		0.20
(1g)	10.00	2.55 †	0.85	1.00	0.55		0.35

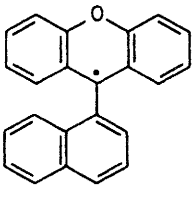
* 1 gauss (G) = 0.1 mT. † Refers to 2′ and 6′-H only.



(1) a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = Bu^t, R^2 = R^3 = R^4 = H$
c; $R^1 = R^3 = Bu^t, R^2 = R^4 = H$
d; $R^1 = R^3 = H, R^2 = R^4 = Bu^t$
e; $R^1 = R^2 = R^4 = Bu^t, R^3 = H$
f; $R^1 = R^2 = R^4 = H, R^3 = Bu^t$
g; $R^1 = Bu^t, R^2 = R^4 = H, R^3 = OMe$



(2)



(3)

Table 2. Coulomb and bond integral parameters used for McLachlan MO calculations on aryl nitroxides

h_N	k_{NO}	k_{CN}	h_O	λ	Reference
1.5	1.6	1.05—1.00	2.0—1.0	1.2	9
1.5	0.7	1.0	1.0		10
1.4—1.5	1.6		1.2	1.2	11
1.5	1.6	1.05—0.5	1.2		3
1.5—1.6	1.6—1.7	0.85—0.8	1.7	1.1	5

nitroxide group to a significant extent. In such 'twisted radicals' the extent to which the free spin is transmitted through the σ-bond framework is important and the MO calculations used here do not take sufficient account of this.

Similar MO calculations on both naphth-1-yl and naphth-2-yl phenyl nitroxides have been reported previously by Bridger and Strom[3] and our results for the naphth-2-yl radical approximate to theirs. However, our results for the naphth-1-yl radical are significantly different (Table 4) especially for $a_{4\text{-H}}$. We cannot account for this difference but affirm that our calculations on diphenyl[9] and phenoxazinyl[10] nitroxides gave results identical with those published.

Experimental

The nitroxides were generated from the corresponding hydroxylamines in solution in carbon tetrachloride by oxidation with silver oxide. The preparation and characterisation of the hydroxylamines will be described subsequently.

E.s.r. measurements were recorded on a Varian E104A spectrometer using dilute solutions of the nitroxide in benzene (*ca.* 10^{-5} mol l^{-1}) at room temperature. N.m.r. spectra were measured on a Varian HA100D spectrometer using 10—15 KHz modulation. Peaks shifted upfield were measured on the upper sideband and those shifted downfield were measured on the lower sideband. This procedure minimised the risk of overlap of peaks from the main band.

Table 3. Calculated hyperfine splittings ^{a} (G) for phenyl naphth-2-yl nitroxide, $h_O = 1.2$, $k_{NO} = 1.6$, $h_N = 1.5$, $\lambda = 1.2$

Position	$k_{CN}(Ph) = 1.0$ $k_{CN}(Nph) = 1.0$	$k_{CN}(Ph) = 1.0$ $k_{CN}(Nph) = 1.05$	$k_{CN}(Ph) = 1.0$ $k_{CN}(Nph) = 0.9$	$k_{CN}(Ph) = 0.9$ $k_{CN}(Nph) = 1.05$	Ref. 3 ^{b}	Observed
2′	1.80	1.76	1.87	1.46	1.92	1.78
3′	0.74	0.72	0.77	0.61	0.79	0.79
4′	1.78	1.74	1.86	1.45	1.78	1.78
3	0.79	0.85	0.66	0.87	1.13	1.14
4	0.64	0.68	0.55	0.70	0.62	0.79
5	0.42	0.46	0.36	0.47	0.48	0.42
6	0.84	0.91	0.71	0.95	0.72	0.96
7	0.44	0.47	0.38	0.49	0.46	0.36
8	0.98	1.05	0.82	1.10	0.89	0.75
1	3.47	3.76	2.90	3.89	3.46	2.87

^{a} $Q_{CH}^H = 24.0$ G used. ^{b} $k_{CN(Ph)} = 1.0$, $k_{CN(Nph)} = 1.05$.

Table 4. Calculated hyperfine splittings [a] (G) in *N*-phenyl naphth-1-yl nitroxide (1a), $h_O = 1.5$, $k_{NO} = 1.6$, $h_N = 1.5$, $\lambda = 1.2$

Position	$k_{CN(Ph)} = 1.1$ $k_{CN(Nph)} = 0.55$	$k_{CN(Ph)} = 1.05$ $k_{CN(Nph)} = 0.55$	$k_{CN(Ph)} = 1.0$ $k_{CN(Nph)} = 0.85$	$k_{CN(Ph)} = 1.0$ $k_{CN(Nph)} = 0.75$	Ref. 3 [b]	Actual [c]
2′, 6′	2.75	2.55	2.10	2.19	2.35	2.55
3′, 5′	1.10	1.04	0.82	0.87	0.98	0.85
4′	2.59	2.39	1.99	2.06	2.11	2.50
2	1.11	1.13	2.61	2.08	0.60	1.00
3	0.44	0.45	0.92	0.77	0.46	0.55
4	1.07	1.09	2.54	2.02	0.41	0.55

[a] $Q_{CH}^{H} = 24.0$ G used. [b] $k_{CN(Ph)} = 1.0$, $k_{CN(Nph)} = 0.5$. [c] ±0.05 G.

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References

1 A. L. Buchachenko, ‘ Stable Radicals,’ Consultants Bureau, New York, 1965, p. 119.
2 J. Pannell, *Mol. Phys.*, 1964, **7**, 317.
3 R. F. Bridger and E. T. Strom, *J. Org. Chem.*, 1971, **36**, 560.
4 D. B. Chesnut and H. M. McConnell, *J. Chem. Phys.*, 1958, **28** 107.
5 J. L. Duncan, A. R. Forrester, G. McConnachie, and P. D. Mallinson, *J. Chem. Soc., Perkin Trans. 2*, 1973, 718.
6 T. J. Stone and W. Waters, *J. Chem. Soc.*, 1964, 213; W. T. Dixon, W. E. J. Forster, and D. Murphy, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2124; 1978, 77; D. Murphy, *J. Chem. Res.* (S), 1980, 321.
7 K. Murayama and S. Arakawa, *Bull. Chem. Soc. Jpn.*, 1974, **78**, 2512.
8 A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
9 P. B. Ayscough and F. B. Sargent, *J. Chem. Soc. B*, 1966, 907.
10 M. F. Chiu, B. C. Gilbert, and P. Hansen, *J. Chem. Soc. B*, 1970, 1700.
11 H. G. Aurich, E. Deuschle, and I. Lotz, *J. Chem. Res.* (S), 1977, 248.

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