cinimide with tetraphenylcyclopentadiene)[26] with zinc (20 equiv) in benzene at reflux for 24 hr gave **36** (21–34%):[26] mp 197–199°; spectral and melting point data agreed with the data presented for **36** obtained from **1** (see above).

Registry No.—**6**, 14935-22-9; **7**, 15071-25-7; **10**, 1749-36-6; **11**, 27192-88-7; **12**, 19968-81-1; **13**, 19968-82-2; **18**, 746-47-4; **19**, 27192-91-2; **22**, 16433-88-8; **23**, 1530-12-7; **24**, 27192-94-5; **26**, 27192-95-6; **32**, 26307-13-1; **36**, 26307-16-4; **46**, 27250-99-3.

Acknowledgment.—We are indebted to Professors Grace Borowitz, Maitland Jones, Jr., and Claibourne Griffin for stimulating discussions; Dr. Martin Grayson and Dr. J. Lancaster for ^{31}P nmr data; Dr. Jonathan Kurland, Mr. David Baugher, Dr. Karl Untch, Professors Carl Djerassi, and, Klaus Biemann, Varian Associates and Jeolco, Inc., for mass spectral data; and Dr. Paul Rusek and Mrs. Bernice Schiller for experimental aid. We wish to thank the National Science Foundation for grants toward the purchase of the Varian time-averaging computer (at Yeshiva) and a Varian A-60 nmr spectrometer (at Lehigh), and the National Institutes of Health for a grant used to purchase a Varian A-60A nmr spectrometer at Yeshiva.

Electron Spin Resonance Studies of Substituent Effects. IV.[1] Nitroxide Radicals from Bis(*N*-arylnaphthylamines)

ROBERT F. BRIDGER*[2a] AND E. THOMAS STROM[2b]

Mobil Research and Development Corporation, Central Research Division Laboratory, Princeton, New Jersey 08540, and Field Research Laboratory, Dallas, Texas 75221

Received July 8, 1970

Oxidation of bis(*N*-arylnaphthylamines) produces stable nitroxide radicals if the reactive naphthalene positions are blocked. Hyperfine splitting constants and substituent effects are reported and compared with analogous systems. The nitrogen hyperfine splitting in the β derivative is larger than that found in the α derivative. McLachlan molecular orbital calculations are carried out on *N*-phenyl-1-naphthyl nitroxide, *N*-phenyl-2-naphthyl nitroxide, and di-2-naphthyl nitroxide. The nitroxide radicals from these oxidative dimers may be responsible in part for electron spin resonance signals obtained during oxidation of aromatic amines such as *N*-phenyl-1- and *N*-phenyl-2-naphthylamine.

While various derivatives of phenyl nitroxides and diphenyl nitroxides have been studied in detail by electron spin resonance (esr),[3–6] no convincing spectra of *N*-arylnaphthyl nitroxides have appeared in the literature. Hoskins[7] reported spectra generated from aromatic amines added to base-catalyzed autoxidations of toluene–alcohol mixtures. Although the spectrum of diphenyl nitroxide was generated from diphenylamine, the spectrum produced from *N*-phenyl-2-naphthylamine did not exhibit the expected nitrogen hyperfine splitting constant (hfsc) and was quite narrow, suggesting a possible semiquinone radical arising from the oxidation products of *N*-phenyl-2-naphthylamine.[8]

Buchachenko[9] has reported spectra assigned to *N*-phenyl-1- and *N*-phenyl-2-naphthyl nitroxides. The 1-naphthyl derivative exhibited, in addition to a 10.8-G nitrogen hfs, a 2.4-G hfs characteristic of the ortho and para protons of the phenyl group, but no mention is made of the relatively large hfs expected of the 2- and 4-naphthyl protons. The 2-naphthyl derivative gave a gross triplet of 9.5 G with fine lines discernible on the main pattern. In their excellent review,[4] Forrester, Hay, and Thomson briefly refer to unpublished work on *tert*-butyl-1- and *tert*-butyl-2-naphthyl nitroxides, but no spectra are given. They note A^{N}'s for these nitroxides are 13.5 and 11.75 G, respectively, for the α- and β-naphthyl derivatives.

Several recent studies[8,10] of the *N*-phenyl-2-naphthylamino radical reveal that its chemistry is dominated by the high reactivity at the 1 carbon, resulting in coupling products when generated by oxidation of the amine or thermolysis of the tetrazene,[10] and mixtures of quinoid products when generated by reaction of the amine with peroxy radicals in the presence of hydroperoxide.[8,11] These results suggest that many routes to *N*-arylnaphthyl nitroxides will be diverted to other products. Since the oxidative dimers may be responsible in part for esr signals observed on oxidation of *N*-arylnaphthylamines, an investigation of the nitroxide radicals of these dimers should be instructive. The present paper deals with nitroxides derived from oxidation products of *N*-phenyl-1- and *N*-phenyl-2-naphthylamine.

---

[1] (a) Part III: E. T. Strom and J. R. Norton, *J. Amer. Chem. Soc.*, **92**, 2327 (1970); (b) presented in part at the Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970.

[2] (a) Author to whom inquiries should be addressed at the Central Research Laboratory; (b) Field Research Laboratory.

[3] E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, **32**, 3853 (1967).

[4] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 5.

[5] (a) A. Calder and A. R. Forrester, *J. Chem. Soc. C*, 1459 (1969); (b) *Chem. Commun.*, 682 (1967).

[6] (a) H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. Fr.*, 372 (1965); (b) G. Barbarella and A. Rassat, *ibid.*, 2378 (1969); (c) A. J. W. Wajer, A. Mackor, and Th. J. deBoer, *Tetrahedron Lett.*, 1941 (1967); (d) A. B. Sullivan, *J. Org. Chem.*, **31**, 2811 (1966); (e) O. Kikuchi and K. Someno, *Bull. Chem. Soc. Jap.*, **40**, 2549 (1967); (f) J. Yamauchi, H. Nishiguchi, K. Mukai, Y. Deguchi, and H. Takaki, *ibid.*, **40**, 2512 (1967); (g) P. H. H. Fischer and F. A. Neugebauer, *Z. Naturforsch. A*, **19**, 1514 (1964); (h) F. A. Neugebauer and P. H. H. Fischer, *ibid. B*, **21**, 1036 (1966); (i) J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961).

[7] R. Hoskins, *ibid.*, **25**, 788 (1956).

[8] D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, **34**, 3456 (1969).

[9] (a) A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965, p 119; (b) A. L. Buchachenko, *Opt. Spectrosk.*, **13**, 795 (1962).

[10] (a) R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton, and K. U. Ingold, *J. Org. Chem.*, **33**, 4329 (1968); (b) R. F. Bridger, *ibid.*, **35**, 1746 (1970).

[11] K. Adamic and K. U. Ingold, *Can. J. Chem.*, **47**, 295 (1969).

TABLE I

NITROXIDE RADICALS FROM BIS(N-ARYLNAPHTHYLAMINES)

Radical	Amine	A^{N}	$A^{H\,a}$ Ortho	Meta	Para	Naphthyl
1b	1,1′-Bis(*N*-phenyl-2-naphthylamine)[b]	10.26 ± 0.08	2.52	0.82	2.52	0.82 (2 protons)
3b	4,4′-Bis(*N*-phenyl-1-naphthylamine)[c]	9.93 ± 0.07	2.48	0.83	2.48	0.83 (2 protons)
2b	1,1′-Bis(di-2-naphthylamine)[d]	10.3 ± 0.2				4.2 ± 0.2 (α-naphthyl)

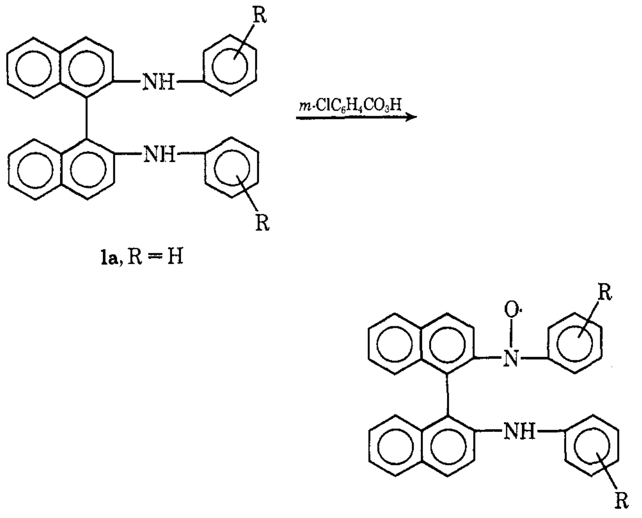
[a] ±0.05 G. [b] Line width, 0.6 G. [c] Line width, 0.4 G. [d] Line width, 3.3 G.

Experimental Section

Radicals were generated by mixing a 20-fold excess of amine $(1.25 \times 10^{-2}\ M)$ with *m*-chloroperbenzoic acid $(6.25 \times 10^{-4}\ M)$ at room temperature in benzene. Solutions were outgassed by two freeze–thaw cycles, and sample tubes were sealed. Within 30 min after mixing, esr signals were well developed. All nitroxide radicals were stable at room temperature. The spectrum of **1b** was slightly diminished after standing 48 hr at room temperature. Spectra were measured with a Varian V-4500-10 esr spectrometer equipped with a 12-in. magnet and 100-kc/sec field modulation. Simulated spectra were computed using the program of Snowden and Strom.[12] The preparation of the amines has been described.[10] The reactions of *m*-chloroperbenzoic acid with *N*-phenyl-1-naphthylamine, *N*-phenyl-2-naphthylamine, and *N*-(2-naphthyl)-*N*,*N*′-diphenyl-1,2-naphthylenediamine[10] produced only very weak esr signals which were ill-defined and which exhibited no hydrogen hyperfine splitting.

Results

The reaction of 1,1′-bis(*N*-phenyl-2-naphthylamine) (**1a**) with *m*-chloroperbenzoic acid at room temperature produced a stable nitroxide radical, resulting in the esr spectrum shown in Figure 1. Because of the extreme steric requirements of **1b**, the contribution of the first, as well as the second, naphthyl group to the hyperfine splitting was expected to be negligible. Inspection of the spectrum of **1b** suggested hfsc of A^{N} (1 N) = 10.26, $A^{H}_{o,p}$ (3 H) = 2.52, and A^{H}_{m} (2 H) = 0.82 G. This predicts a spectrum of 36 lines. The observed spectrum consists of 38 distinct lines, however, and the observed intensities do not agree with those predicted using only the phenyl hydrogen hfsc. It was necessary to include two small naphthyl hfs of A^{H} = 0.82 G. The computed spectrum using these hfsc with the experimental line width of 0.6 G is shown in Figure 1 and agrees well with the experimental spectrum.



1a, R = H

1b, R = H

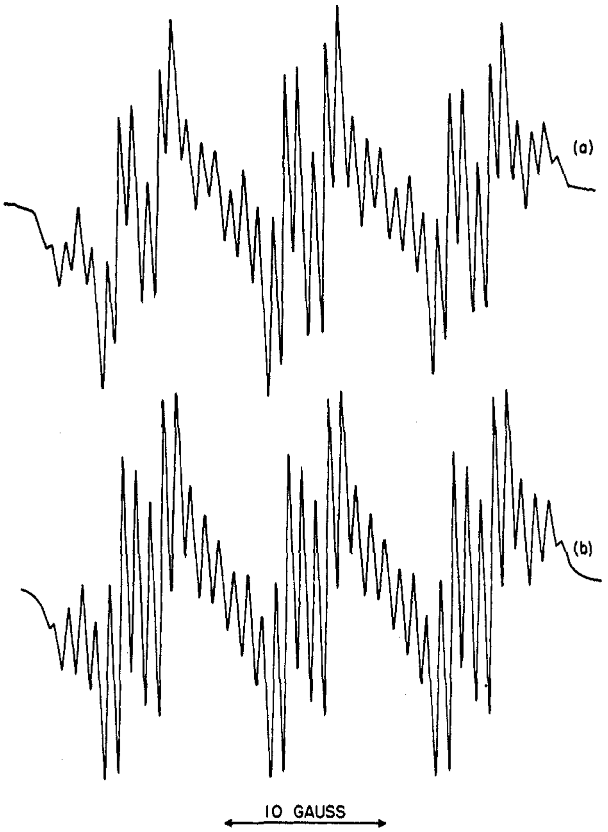
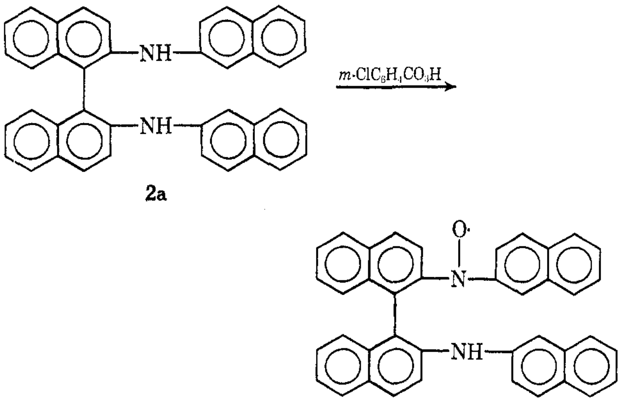


Figure 1.—Nitroxide radical from 1,1′-bis(*N*-phenyl-2-naphthylamine): (a) experimental, (b) simulated.

Oxidation of 1,1′-bis(di-2-naphthylamine) (**2a**) produced nitroxide radical **2b**. The radical concentration was quite low, possibly because of extensive disproportionation[5,13] *via* the reactive α-naphthyl carbon. Because of the high gain and modulation amplitude required for detection, the line width was quite broad (3.3 G) and much of the hyperfine splitting was lost. It was possible, however, to resolve A^{N} (1 N) of 10.3



2a

2b

---

(12) B. S. Snowden, Jr., and E. T. Strom, QCPE Program No. 160.

(13) A. R. Forrester and R. H. Thomson, *Nature*, **203**, 74 (1964).

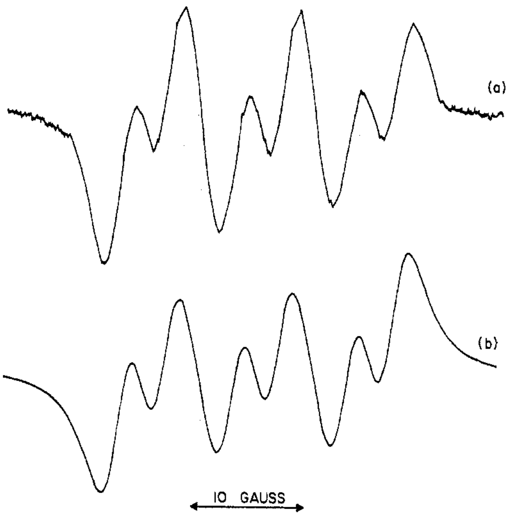
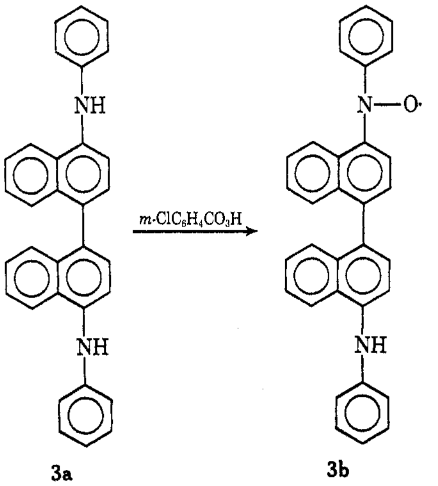


Figure 2.—Nitroxide radical from 1,1′-bis(di-2-naphthylamine): (a) experimental, (b) simulated.

and A^H (1 H) of 4.2 G. The hydrogen hfsc is of the magnitude expected for the α-naphthyl proton (*vide infra*). The experimental and simulated spectra are shown in Figure 2.

4,4′-Bis(*N*-phenyl-1-naphthylamine) (**3a**) produced upon oxidation with *m*-chloroperbenzoic acid radical **3b**. Analysis produced the computed spectrum which is compared with the experimental spectrum in Figure 3. The splittings used were A^N (1 N) = 9.93, $A^H_{o,p}$ (3 H) = 2.48, and $A^H_{m,\mathrm{naph}}$ (4 H) = 0.83 G. These values are very similar to those found for **1b**. Results for **1b**, **2b**, and **3b** are summarized in Table I.



3a **3b**

Finally, the effect of substituents in the benzene ring of **1b** on the nitrogen hfs was measured by oxidizing a series of substituted 1,1′-bis(*N*-aryl-2-naphthylamines). The nitrogen hfsc are shown in Table II. A plot of $A^H_{\mathrm{subst}}/A^H_{p\text{-H}}$ *vs.* σ yielded a slope of −0.100 (Figure 4).

Discussion

The experimental results for **1b** and **3b** indicate little delocalization of the spin into the naphthyl group. This is expected for **1b** because of the severe steric requirements of the 1,1′-binaphthyl system. Forrester, *et al.*,[4] reason from their and Buchachenko's[9] data that nitroxides substituted at the α position of naphthalene will have larger nitrogen hfs than the corresponding β derivatives because of steric interaction between the nitroxide oxygen and the peri hydrogen. In **3b** this factor could reduce delocalization into the naphthyl group. The net result is that radicals **1b** and **3b** have larger values of A^N and A^H_{phenyl} than diphenyl nitroxide, in which the unpaired electron can be delocalized over two rings. The splittings for diphenyl nitroxide in xylene are A^N = 9.66, $A^H_{o,p}$ = 1.83, and A^H_m = 0.79 G.[6h] The observed hfsc of the ortho and para hydrogens of **1b** and **3b** are intermediate in value between those of phenyl nitroxide (A^H_o = 2.74, 3.07, A^H_p = 3.07 G[6c]) and phenyl-*tert*-butyl nitroxide ($A^H_{o,p}$ = 2.05 G[5]).

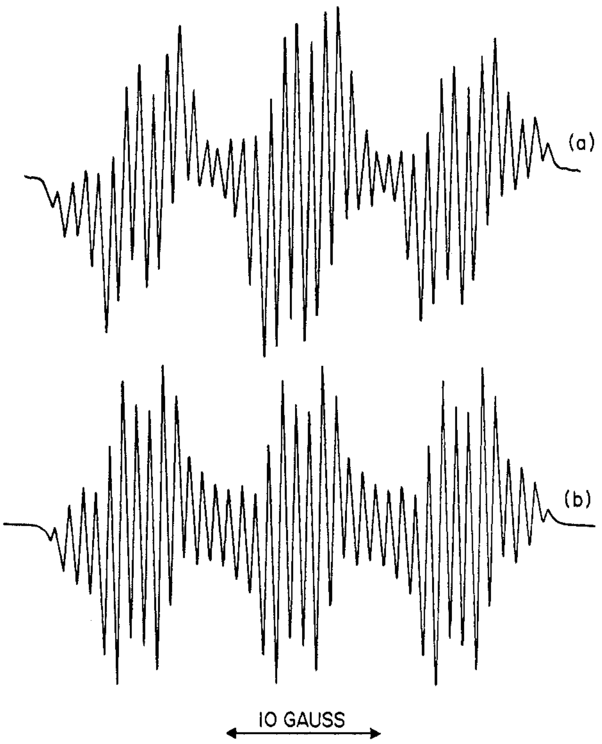


Figure 3.—Nitroxide radical from 4,4′-bis(*N*-phenyl-1-naphthylamine): (a) experimental, (b) simulated.

TABLE II

NITROXIDE RADICALS FROM PHENYL-SUBSTITUTED 1,1′-BIS(*N*-ARYL-2-NAPHTHYLAMINES)

Substituent on 1b	A^N
p-OCH_3[a]	10.59 ± 0.09
p-CH_3	10.45 ± 0.05
m-CH_3	10.33 ± 0.05
H	10.26 ± 0.08
m-OCH_3	10.24 ± 0.05
m-Cl[b]	9.89 ± 0.08

[a] Also resolved was A^H_o of 2.69 G. [b] $A^H_{o,p}$ 2.55 and A^H_m 0.73 G were observed.

Recently, extensive data have become available concerning substituent effects on hfsc in free radicals,[1a,3,6b,14] and a review on the subject has appeared.[15] The nitroxide function, with its high spin density, was found by Strom, *et al.*,[3] to be less sensitive to substituents than certain anion radical functions. The slope of −0.100 found for **1b** derivatives is very close to the slopes found for phenyl nitroxides and phenyl-*tert*-

---

[14] E. T. Strom, *J. Amer. Chem. Soc.*, **88**, 2065 (1966).

[15] E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).

butyl nitroxides. (The data for the latter series are for a protonic solvent with a concomitant reduction in slope.) Data taken from the compilation in ref 3 are shown in Table III. The magnitude of the slope for radicals of structure **1b** and monophenyl nitroxides appears to be less than that found in symmetrically disubstituted diphenyl nitroxides. Although the difference is small, it appears to be real and probably reflects the presence of the second substituent. In all systems of Table III, the correlations reflect (in valence bond language) the stabilization of resonance structure II by electron-donating substituents.[15]

TABLE III

SUBSTITUENT EFFECTS OF NITROXIDE RADICALS

Radical	Solvent	Ref	ρ^a
$\mathrm{Ar\underset{+}{\dot{N}}(O^{-})H}$	$\mathrm{PhCH_3}$	6c	−0.0930
$\mathrm{Ar\underset{+}{\dot{N}}(O^{-})C(CH_3)_3}$	$\mathrm{(CH_2OH)_2}$	6a	−0.0659
$\mathrm{Ar\underset{+}{\dot{N}}(O^{-})Ar}$	PhH and xylene	3, 6h	−0.1160
1b	PhH	This work	−0.100

[a] Slope of A^N_{subst}/A^N *vs.* σ.

$$>\ddot{N}-\dot{O} \qquad >\underset{+}{\dot{N}}-O^{-}$$
$$\mathrm{I} \qquad\qquad \mathrm{II}$$

In order to gain some insight into the possible sites producing the naphthyl splittings in **1b** and **3b** and to better assess the literature data for *N*-phenylnaphthyl nitroxides, we undertook theoretical calculations on *N*-phenyl-1-naphthyl nitroxide (III), *N*-phenyl-2-naphthyl nitroxide (IV), and di-2-naphthyl nitroxide (V). The method chosen was McLachlan's modification of simple Hückel molecular orbital theory.[16] In applying an approximate method to complex systems like these, one should look only for broad trends rather than quantitative correspondence of theoretical spin densities with experimental values. For calculations on the model nitroxides to have any pertinence to radicals **1b**–**3b**, the extra attached naphthyl group must be regarded as an inert substituent. We submit that this is a basically correct assumption, as models of the radicals show that the naphthyl groups must be approximately perpendicular. A possible complication would be increasing σ character of the molecular orbital containing the unpaired electron due to steric perturbations. This has been found to occur in ortho-substituted phenyl-*tert*-butyl nitroxides.[17] In such cases, however, the ratio of ortho,para to meta splitting is abnormal. The normal phenyl proton splittings found in **1b** and **3b** indicate that the unpaired electron is in a π molecular orbital.

Heteroatom parameters suitable for use with the nitroxide function have been developed by Ayscough and Sargent,[18] who studied solvent effects on the esr spectra of mono- and diphenyl nitroxide. Their parameters were $h_N = 1.5$, $k_{NO} = 1.6$, $k_{CN} = 1.05$[19] with h_O allowed to vary with solvent. From their table it appeared that $h_O = 1.2$ was suitable for use with a benzene solvent. It also seemed likely that, in radicals **1b**–**3b**, the aromatic moieties would be more twisted than in the model radicals. Accordingly, calculations were also carried out in which the parameter k_{CN} for the nitrogen–naphthyl carbon bond was decreased. Ayscough and Sargent evaluated spin densities using the McConnell[20] equation and a $Q^H{}_{CH}$ of 23.7 G. McLachlan[16] found a $Q^H{}_{CH}$ of 24.2 G to be suitable for condensed aromatic systems. We calculated theoretical proton hfsc's using $Q^H{}_{CH} = 24.0$ G. Semiempirical parameters have been developed to calculate nitrogen hfsc in systems in which the nitrogen is attached to an oxygen and two carbons,[18,21,22] but in view of the unavoidable arbitrariness of such parameters[23] we prefer to tabulate only the nitrogen spin densities. The numbering system is shown in Chart I, and the results of the calculations are given in Tables IV–VI.

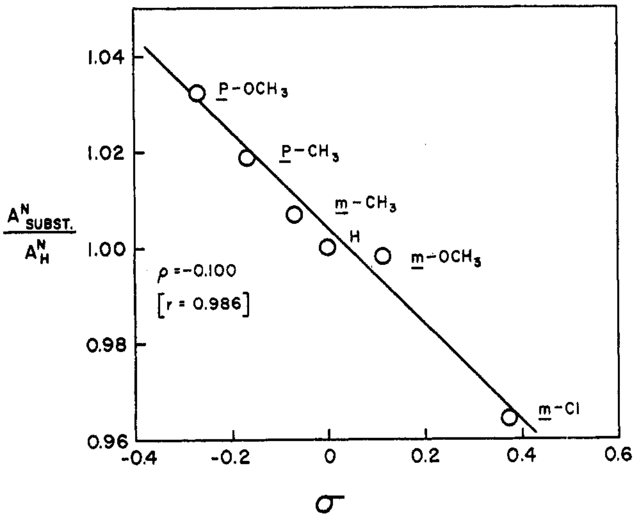
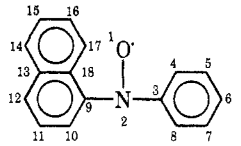


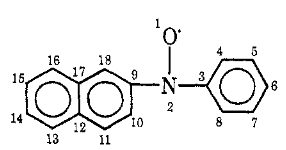
Figure 4.—Substituent effects on A^N of nitroxide radicals from 1,1′-bis(*N*-aryl-2-naphthylamines).

CHART I

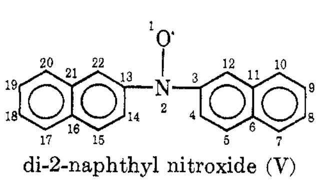
NUMBERING OF MODEL NITROXIDES



N-phenyl-1-naphthyl nitroxide (III)



N-phenyl-2-naphthyl nitroxide (IV)



di-2-naphthyl nitroxide (V)

---

[16] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[17] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *ibid.*, **18**, 481 (1970).

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

[19] Defined in the usual manner: $\alpha_X = \alpha_C + h_X\beta_{CC}$, $\beta_{XY} = k_{XY}\beta_{CC}$.

[20] H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

[21] T. Kubota, K. Nishikida, H. Miyazaki, K. Iwatani, and Y. Oishi, *J. Amer. Chem. Soc.*, **90**, 5080 (1968).

[22] E. G. Janzen and J. W. Happ, *J. Phys. Chem.*, **73**, 2335 (1969).

[23] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

TABLE IV

CALCULATED SPIN DENSITIES AND HYPERFINE SPLITTINGS IN N-PHENYL-1-NAPHTHYL NITROXIDE[a]

	$k_{2,9}$ = 1.05		$k_{2,9}$ = 0.9		$k_{2,9}$ = 0.7		$k_{2,9}$ = 0.5	
Position	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|
O	0.428		0.466		0.514		0.553	
N	0.244		0.270		0.307		0.337	
4	0.075	1.80	0.082	1.97	0.090	2.16	0.098	2.35
5	−0.030	0.72	−0.033	0.79	−0.036	0.86	−0.041	0.98
6	0.069	1.66	0.076	1.82	0.083	1.99	0.088	2.11
10	0.137	3.29	0.103	2.47	0.060	1.44	0.025	0.60
11	−0.046	1.10	−0.039	0.94	−0.029	0.70	−0.019	0.46
12	0.133	3.19	0.098	2.35	0.051	1.22	0.017	0.41
14	0.033	0.79	0.023	0.55	0.009	0.22	−0.003	0.07
15	−0.019	0.46	−0.016	0.38	−0.012	0.29	−0.009	0.22
16	0.028	0.67	0.020	0.48	0.010	0.24	0.002	0.05
17	−0.020	0.48	−0.019	0.46	−0.018	0.43	−0.017	0.41

[a] $\lambda = 1.2$.

TABLE V

CALCULATED SPIN DENSITIES AND HYPERFINE SPLITTINGS IN N-PHENYL-2-NAPHTHYL NITROXIDE[a]

	$k_{2,9}$ = 1.05		$k_{2,9}$ = 0.9		$k_{2,9}$ = 0.7		$k_{2,9}$ = 0.5	
Position	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|
O	0.457		0.488		0.526		0.556	
N	0.258		0.282		0.312		0.338	
4	0.080	1.92	0.085	2.04	0.091	2.18	0.095	2.28
5	−0.033	0.79	−0.035	0.84	−0.039	0.94	−0.042	1.01
6	0.074	1.78	0.079	1.90	0.083	1.99	0.084	2.02
10	0.047	1.13	0.038	0.91	0.026	0.62	0.013	0.31
11	−0.026	0.62	−0.023	0.55	−0.020	0.48	−0.016	0.38
13	−0.020	0.48	−0.017	0.41	−0.014	0.34	−0.011	0.26
14	0.030	0.72	0.020	0.48	0.009	0.22	0.000	0.00
15	−0.019	0.46	−0.015	0.36	−0.010	0.24	0.006	0.14
16	0.037	0.89	0.025	0.60	0.010	0.24	−0.001	0.02
18	0.144	3.46	0.104	2.50	0.056	1.34	0.019	0.46

[a] $\lambda = 1.2$.

TABLE VI

CALCULATED SPIN DENSITIES AND HYPERFINE SPLITTINGS IN DI-2-NAPHTHYL NITROXIDE[a]

	$k_{2,13}$ = 1.05		$k_{2,13}$ = 0.9		$k_{2,13}$ = 0.7		$k_{2,13}$ = 0.5	
Position	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|	Calcd ρ	Calcd |hfs|
O	0.449		0.476		0.510		0.536	
N	0.257		0.277		0.303		0.324	
4	0.036	0.86	0.039	0.94	0.042	1.01	0.046	1.10
5	−0.028	0.67	−0.028	0.67	−0.031	0.74	−0.032	0.77
7	−0.019	0.46	−0.020	0.48	−0.022	0.53	−0.024	0.58
8	0.030	0.72	0.031	0.74	0.032	0.77	0.030	0.72
9	−0.018	0.43	−0.020	0.48	−0.021	0.50	−0.023	0.55
10	0.036	0.86	0.038	0.91	0.039	0.94	0.039	0.94
12	0.145	3.48	0.152	3.65	0.164	3.94	0.168	4.03
14	Identical		0.030	0.72	0.021	0.50	0.013	0.31
15	for		−0.024	0.58	−0.018	0.43	−0.012	0.29
17	symmetrical		−0.016	0.38	−0.012	0.29	−0.008	0.19
18	positions		0.020	0.48	0.010	0.24	0.002	0.05
19			−0.014	0.34	−0.010	0.24	−0.006	0.14
20			0.025	0.60	0.011	0.26	0.000	0.00
22			0.104	2.52	0.057	1.37	0.019	0.46

[a] $\lambda = 1.2$.

The similarity of the phenyl splittings in **1b** and **3b** is mirrored in the calculations. The differences in calculated values of $A^{H}{}_{\text{phenyl}}$ in III and IV for identical values of $k_{2,9}$ are indeed small. The calculations also predict that, for identical values of $k_{2,9}$, ρ_N (and presumably A^N) is larger in the β-naphthyl derivative than in the α-naphthyl derivative. We find experimentally that **1b** does have a larger value of A^N than **3b**. It appears that the twist angles relating the naphthyl moiety with the phenyl nitroxide function are similar in **1b** and **3b**. The absolute magnitude of the calculated phenyl splitting is low when compared to the experimental value, which indicates that the parameters of Ayscough and Sargent are not completely suitable for the phenylnaphthyl nitroxide system. Assigning the ~0.8-G splitting to given naphthyl positions is risky, but the trends with decreasing $k_{2,9}$ would suggest that in both **1b** and **3b** the ~0.8-G naphthyl splittings arise from the 10 and 11 positions, as numbered in Chart I.

The calculations on V demonstrate quite clearly that the 4.2-G splitting in **2b** comes from the α-naphthyl proton (position 12 in Chart I). The calculations also predict that ρ_N in V is extremely close to ρ_N in IV, for identical values of k_{CN}. The A^N values for **1b** and **2b** are very close.

In view of our experimental results and the calculations shown above, Buchachenko's results for *N*-phenyl-2-naphthyl nitroxide are surprising. The nitroxide was made by heating H_2O_2 and the amine together with a trace of cobalt salt to 50–80° in an unspecified hydrocarbon solvent and then cooling the solution and recording the spectrum.[9b] Our results would indicate that a doublet splitting of ~4.0 G from the α-naphthyl proton ought to be readily resolvable. Thus, the possibility that Buchachenko's spectra partly involve radicals from these oxidative dimers must be considered. A complete answer to this question will have to entail unambiguous syntheses of *N*-phenyl-1- and *N*-phenyl-2-naphthyl nitroxides in larger amounts than heretofore possible.

Registry No.—**1b** (R = p-OCH$_3$), 27067-21-6; **1b** (R = p-CH$_3$), 27067-22-7; **1b** (R = m-CH$_3$), 27067-23-8; **1b** (R = H), 27067-24-9; **1b** (R = m-OCH$_3$), 27067-25-0; **1b** (R = m-Cl), 27067-26-1; **2b,** 27067-27-2; **3b,** 27067-28-3; **4b,** 27067-24-9; III, 27067-30-7; IV, 27067-31-8; V, 27067-32-9.

Acknowledgment.—The authors are grateful to O. M. Epifanio for technical assistance in measuring the spectra.

Restricted Rotation of Aryl Rings in *cis*-1,2-Diarylcyclopentanes and Diarylmethylcyclobutanes[1,2]

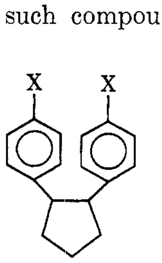
DAVID Y. CURTIN,* PAUL E. BENDER,[3] AND DONALD S. HETZEL

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

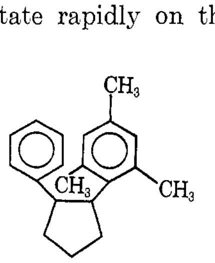
Received June 8, 1970

cis-1-Mesityl-2-phenylcyclopentane (*cis*-I) has been found to undergo rotation of the mesityl ring slowly enough to permit detection by a change in nmr line shape at low temperatures. At the coalescence temperature (−44°), the rate of rotation is approximately 160 sec^{-1}. Cyclobutylmesitylphenylmethane (IX), 3-bromomesitylcyclobutylphenylmethane (X), isopropylmesitylphenylmethane (XI), and β,β'-dimesityladipic acid (XIII) and its ester XII show restriction of rotation of the mesityl rings at room temperature or below; results of the studies of these compounds are compared with related examples which have been described previously. In the course of the synthetic work it has been found that, although cyclobutyldiphenylcarbinol and cyclobutyl(2,4-dimethylphenyl)phenylcarbinol (V) undergo dehydration with ring expansion on treatment with hot formic acid, cyclobutylmesitylphenylcarbinol (II), 9-anthrylcyclobutylphenylcarbinol (XIV), and cyclobutyl(2,3-dimethyl-9-anthryl)phenylcarbinol undergo dehydration under the same conditions without skeletal rearrangement. All of these dehydrations occur without skeletal rearrangement when the reaction is catalyzed by iodine. Mesitylphenylmethylenecyclobutane (IV) can be converted to 1-mesityl-2-phenylcyclopentene by treatment with hot trifluoroacetic acid.

In a search for isomerism due to restriction of rotation of adjacent aromatic rings, several *cis*-1,2-di(p-substituted phenyl)cyclopentanes (A) were previously investigated.[4] Nmr studies showed that the phenyl rings in such compounds rotate rapidly on the nmr time scale at room temperature around the single bonds joining them to the cyclopentane ring. The objective of the present work was to decrease the rate of rotation by placing substituents on the phenyl rings in such a way as to increase the energy barrier to rotation.



A



cis-I

The preparation of *cis*-1-mesityl-2-phenylcyclopentane was undertaken as a point of departure. A possible synthetic route seemed to be through cyclobutylmesitylphenylcarbinol (II). It was anticipated that conversion of carbinol II to olefin III would occur with the desired carbon skeletal rearrangement, since the analogous cyclobutyldiphenylcarbinol had been reported[5] to undergo such a Wagner–Meerwein rearrangement when treated with hot formic acid. Instead, the reaction of carbinol II with formic acid under the conditions reported previously for the diphenylcarbinol gave only the unrearranged methylenecyclobutane IV. The structure of IV was established by a comparison of its nmr, uv, and ir spectra with those of related compounds and by oxidation to mesityl phenyl ketone. This difference in behavior led to a reinvestigation of the dehydration reactions of the parent cyclobutyldiphenylcarbinol to be described later in this paper.

The conversion of the methylenecyclobutane IV to the desired cyclopentene III was accomplished by treatment with trifluoracetic acid. Catalytic hydrogenation of III gave the desired *cis*-cyclopentane *cis*-I. A similar series of reactions was employed to prepare the related 2,4-dimethylphenylcyclopentane *cis*-VII.

---

[1] Taken from the Ph.D. Theses, University of Illinois, of D. S. H. (1968) and P. E. B. (1969).

[2] We are indebted to the Army Research Office, Durham, and to the National Science Foundation for grants supporting this work.

[3] U. S. Public Health Service Trainee, 1966–1969.

[4] D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42**, 867 (1964).

[5] R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955).