# ENDOR Spectra of Aminoxyls. Conformational Study of Alkyl and Aryl Spin Adducts of Deuterated α-Phenyl-*N*-*tert*-butylnitrone (PBN) Based on Proton and β-$^{13}$C Hyperfine Splittings

**Edward G. Janzen,* Uwe M. Oehler,† D. Larry Haire, and Yashige Kotake**

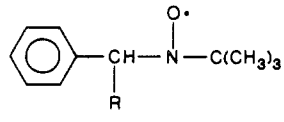
*Contribution from the Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph, Ontario, Canada N1G 2W1.* *Received October 30, 1985*

**Abstract**: Proton and nitrogen-14 ENDOR spectra of aminoxyls with a β hydrogen are presented and assigned. Long-range proton hyperfine splittings are detected in alkyl spin adducts of α-phenyl-*N*-*tert*-butylnitrone (PBN). From the changes in magnitude of these splittings, the preferred conformations of these aminoxyls is ascertained. Because of the additional resolution available in the deuterated aminoxyls, a number of α- and β-$^{13}$C hyperfine splittings could be resolved. The changes in the magnitude of these splittings as a function of group substitution and temperature indicate that in the preferred conformations the phenyl group eclipses the p orbital of the aminoxyl nitrogen atom. The signs of the proton hyperfine splitting constants obtained from CRISP or TRIPLE alternate throughout the carbon framework.

ENDOR spectra of a number of stable aminoxyls in liquid solution have been reported (see Table I for structures): TEMPO[1,2] (I), TEMPONE[1,2] (II), TEMPOL[1-3] (III), *N*-acetyl-TEMPAMINE[3] (IV), 4-carbomethoxy-TEMPO[4] (V), 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolidine-1-oxyl[2,3] (VI), di-*tert*-butylaminoxyl[2,5,6] (VII), Fremy's salt[7] (VIII), a doxyl cyclododecane[8] (IX), some spin-labeled crown ethers[9] (X-XII), bis(4-methoxyphenyl)aminoxyl[10] (XIII), phenyl-*tert*-butylaminoxyl[11] (XIV), Banfield and Kenyon radical[12] (XV), and 2,3-benzo-4-oxo-isoxazole-1-oxyl[13] (XVI).

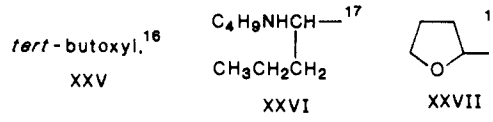
Some biradicals having the aminoxyl function as one component have also provided ENDOR spectra[4] (XVII-XIX) although experiments with three examples of diaminoxyl biradicals were unsuccessful.[14]

Some examples of less stable aminoxyl radicals have also been studied by ENDOR. Among these are spin adducts of α-phenyl-*N*-*tert*-butylnitrone (PBN) (XX-XXVII).



R = $CH_3$[15], $CD_3$[15], *n*-butyl[15], phenyl[15,16], benzoyloxyl[15,16]

XX XXI XXII XXIII XXIV



*tert*-butoxyl[16] XXV

XXVI XXVII

Radical adducts of 2-methyl-2-nitrosopropane produced from the autoxidation of methyl oleate, linoleate, or linolenate were investigated by ENDOR spectroscopy, but the structure of the aminoxyls could not be unambiguously ascertained.[18] A continuation of this work using various deuterated linoleic acids, however, gave results consistent with the spin trapping of radicals derived from the 9, 10, 12, or 13 positions.[19]

Aminoxyl N-14 ENDOR signals have been detected in the case of I,[1] II,[1] III,[1,3] IV,[3] V,[4], VI,[3] VII,[5] VIII,[7] XVI,[13] XVII,[4] XVIII,[4] XIX,[4] XXIII,[16] XXIV,[16], XXV,[16] and the aminoxyl(s) in ref 18 and 19. The optimum conditions for nitrogen ENDOR are somewhat different than for proton ENDOR. In general, higher temperatures (250-300 K) and higher rf power (300 W or ~10 G) are needed.[1,20] For neutral radicals the most popular solvent is toluene, although heptane, 3-methylpentane, decalin, *sec*-butylbenzene, methylene chloride, 1,2-dimethoxyethane, and tetrahydrofuran have also been used. Occassionally either 2-propanol, ethanol, or methanol is added to any of the above to increase the polarity of the solvent. Only one report of an ENDOR spectrum in water is available.[7]

A recent paper on the proton ENDOR of aminoxyls in frozen aqueous glycerol has appeared.[21] The study includes the stable aminoxyls I, II, III, VI, and VII. A crystalline clathrate comprised of the stable aminoxyl (I) and 2′-hydroxy-2,4,4,7,4′-pentamethylflavan has also been examined by proton ENDOR spectroscopy.[22]

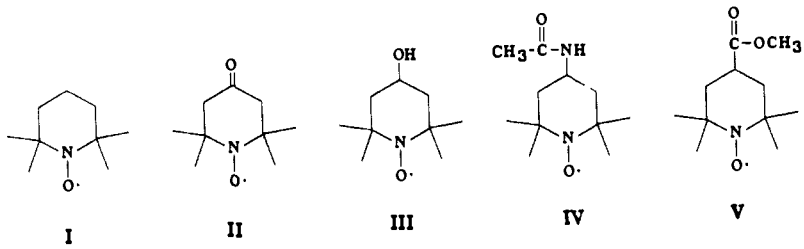
Our objective in this study was to investigate the possibility of obtaining additional hyperfine splittings (hfs's) to aid in the conformational assignments of spin adducts of PBN. The hfs's could come from γ or δ hydrogens or from the phenyl hydrogens via long-range interactions. In addition the relative signs of the hfs's were of interest. These can be determined by comparing the relative intensity changes within each of the nitrogen and proton doublets as different branches of the nitrogen triplet are saturated.[1,4,5,7] We have recently proposed the term CRISP (Cross

† NSERC postgraduate fellow.

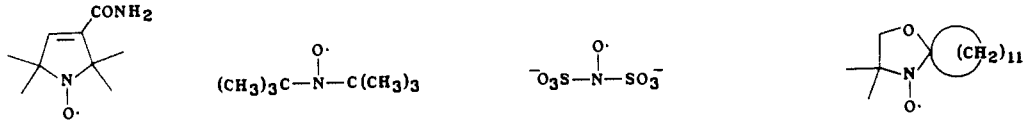
(1) Leniart, D. S.; Vedrine, J. C.; Hyde, J. S. *Chem. Phys. Lett.* **1970**, *6*, 637. Hyde, J. S. In *Magnetic Resonance in Biological Systems*; Ehrenberg, A., Malmström, B. G., Vänngard, T., Eds.; Pergamon Press: Oxford, 1967, p 63.
(2) Kotake, Y.; Kuwata, K. *Chem. Lett.* **1984**, 83.
(3) Dinse, K. P.; Möbius, K.; Plato, M.; Biehl, R; Haustein, H. *Chem. Phys. Lett.* **1972**, *14*, 196.
(4) Kirste, B.; Krüger, A.; Kurreck, H. *J. Am. Chem. Soc.* **1982**, *104*, 3850.
(5) Yamauchi, J.; Deguchi, Y. *Chem. Lett.* **1983**, 257.
(6) Yamauchi, J.; Deguchi, Y. *Chem. Lett.* **1985**, 111.
(7) Atherton, N. M.; Brustolon, M. *Mol. Phys.* **1976**, *32*, 23.
(8) Eaton, S. S.; van Willigen, H.; Heinig, M. J.; Eaton, G. R. *J. Magn. Reson.* **1980**, *38*, 325-330.
(9) Eastman, M. P.; Patterson, D. E.; Bartsch, R. A.; Liu, Y.; Eller, P. G. *J. Phys. Chem.* **1982**, *86*, 2052.
(10) Allendoerfer, R. D.; Engelmann, J. H. *Mol. Phys.* **1971**, *20*, 569.
(11) Ishizu, K.; Nagai, H.; Mukai, K.; Kohno, M.; Yamamoto, T. *Chem. Lett.* **1973**, 1261.
(12) Ishizu, K.; Yamamoto, T.; Kohno, M.; Nakajima, A.; Deguhi, Y. *Tetrahedron Lett.* **1974**, 1537.
(13) Janzen, E. G.; Oehler, U. M. *Tetrahedron Lett.* **1983**, 669.
(14) van Willigen, H.; Plato, M.; Möbius, K.; Dinse, K.-P.; Kurreck, H.; Reusch, J. *Mol. Phys.* **1975**, *30*, 1359.
(15) Kotake, Y.; Okazaki, M.; Kuwata, K. *J. Am. Chem. Soc.* **1977**, *99*, 5198.
(16) Janzen, E. G.; Oehler, U. M. *Chem. Lett.* **1984**, 1233.
(17) Kotake, Y.; Kuwata, K. *Can. J. Chem.* **1982**, *60*, 1610.
(18) Evans, J. C.; Jackson, S. K.; Rowlands, C. C.; Barratt, M. D. *Biochim. Biophys. Acta* **1984**, *792*, 239.
(19) Evans, J. C.; Jackson, S. K.; Rowlands, C. C.; Barratt, M. D. *Biochim. Biophys. Acta* **1985**, *835*, 421.
(20) Plato, W.; Lubitz, W.; Möbius, K. *J. Phys. Chem.* **1981**, *85*, 1202.
(21) Kotake, Y.; Tomita, Y.; Kuwata, K. *J. Phys. Chem.* **1985**, *89*, 207.
(22) Ohzeki, F.; Kispert, L. D. Arroyo, C.; Steffan, M. *J. Phys. Chem.* **1982**, *86*, 4011.

0002-7863/86/1508-6858$01.50/0 

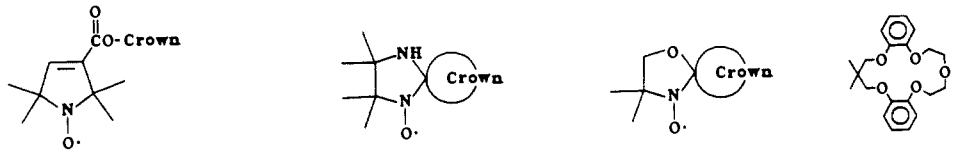
Table I



I II III IV V

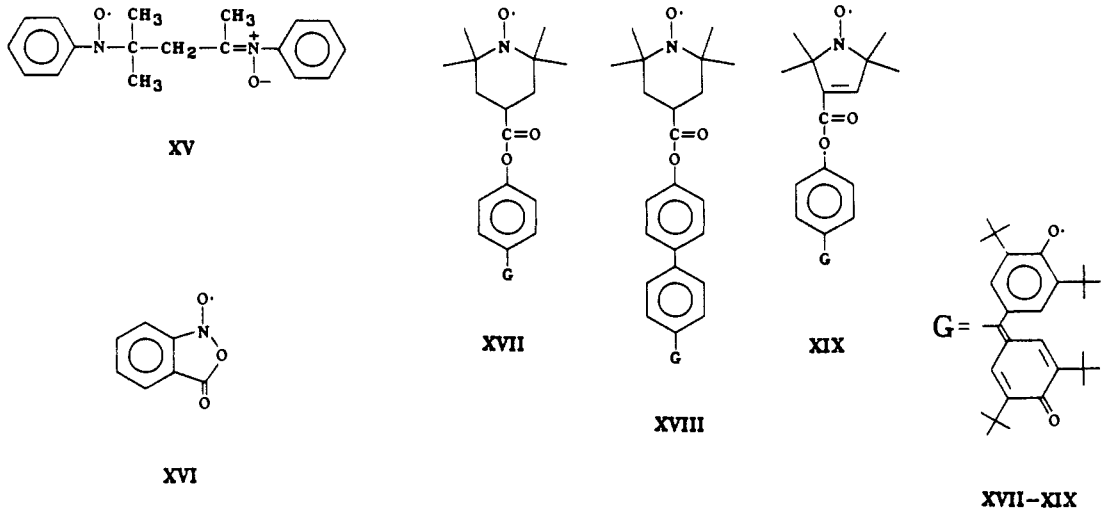


VI VII VIII IX



X XI XII X–XII

XIII XIV



XV XVI XVII XVIII XIX G=

XVII–XIX

Relaxation Intensity Sequence Pattern)[16] to describe this method of determining the relative signs of the hfs's. Spin adducts which exhibit strong ENDOR signals could also be investigated by the TRIPLE resonance technique,[23] and in all instances these results verified the correctness of the assignments made by the CRISP method.

## Experimental Section

The synthesis of the various deuterated and C-13 labeled versions of α-phenyl-*N*-*tert*-butylnitrone (PBN) will be described elsewhere.[24]

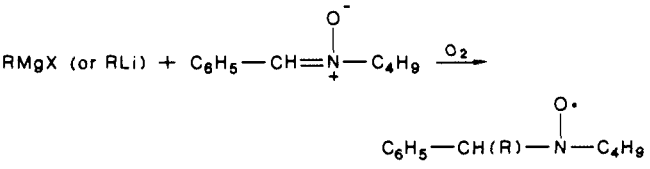
EPR and ENDOR spectra were recorded using a Bruker EPR ER-200D spectrometer with an ENDOR–TRIPLE accessory. Spectral accumulation was by use of the Bruker ER-140 (ASPECT 2000) data system. For long-term accumulations (i.e., several hours) a field frequency lock was used (with DPPH as the internal standard). All ENDOR spectra were obtained using 12.5-kHz radiofrequency modulation

(23) Dinse, K. P.; Biehl, R.; Möbius, K. *J. Chem. Phys.* **1974**, *61*, 4335. Möbius, K.; Biehl, R. In *Multiple Electron Resonance Spectroscopy*: Dorio, M. M., Freed, J. H., Eds.; Plenum Press: New York, 1979; p 475.

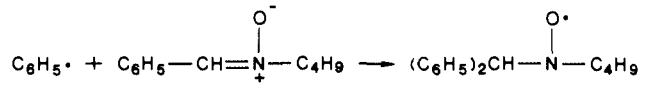
(24) Haire, D. L.; Janzen, E. G., manuscript in preparation.

and thus are presented as first derivative traces. In some of the weaker ENDOR spectra, some minor spikes at integral radiofrequency values (e.g., 12 and 16 MHz, Figure 1A) are due to instrumental limitations of the ENDOR unit.

The preparation of aminoxyl radicals was by organometallic addition followed by air oxidation:[25,26]



Spin trapping can also give high enough concentrations of spin adducts for ENDOR studies, for example, phenyl radicals from phenylazotriphenylmethane (PAT):

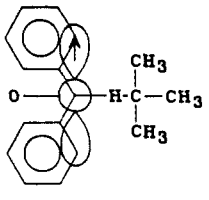


In the former case the solution of spin adduct was often diluted to reduce spin–spin broadening of lines. In the latter case the solution containing the initiator and PBN was sometimes slightly warmed to increase the radical flux for spin trapping.

EPR/ENDOR sample cells were deoxygenated by three freeze/pump/thaw cycles and sealed off on a vacuum line.

## Results and Discussion

**Phenyl Adduct.** The ESR spectrum of the phenyl adduct of PBN is well-known[25] and consists of a triplet of doublets due to the relatively large N-14 hfs and the smaller $\beta$-H hfs. The magnitudes of both the C-13 and $\beta$-H hfs's as a function of temperature[27] support the following conformation for this aminoxyl:



1

The first ENDOR spectrum of XXIII[15] obtained in toluene at 183–243 K consisted of one doublet centered about the free proton resonance ($\nu_H$) with a separation of 0.47 MHz and one line due to the $\beta$-H doublet. The smaller doublet was assigned to approximately equivalent hyperfine splittings from the *tert*-butyl and phenyl hydrogens.

Figure 1A shows the ENDOR spectrum of XXIII in the 11.0–18.0-MHz region in toluene at 230 K. The two doublets are due to the $\beta$-H hfs and the *tert*-butyl/phenyl hydrogen hfs's. In Figure 1B is shown the same spectrum with the *tert*-butyl group deuterated (from PBN-$d_9$). A small doublet centered about the free proton resonance remains and must be assigned to the phenyl protons since all remaining protons are accounted for. On further inspection (see insert Figure 1B), this doublet can be resolved into two doublets which are attributable to hyperfine splitting from phenyl hydrogens. The relative signs of the hfs's, assuming that the $\beta$-H hfs is positive, can be obtained from a TRIPLE spectrum of the phenyl adduct of PBN-$d_9$. It is concluded that the sign of the phenyl hydrogen hfs's is the same as the sign of the $\beta$-H hfs, namely, positive. The $\gamma$-H hfs is opposite in sign to the $\beta$-H hfs, namely, negative. Thus:

| | $\beta$-H | $\gamma$-H | phenyl-H |
|---|---|---|---|
| hfs's for the phenyl adduct of PBN (in MHz) | +5.60 | −0.3 | +0.46, +0.3 |

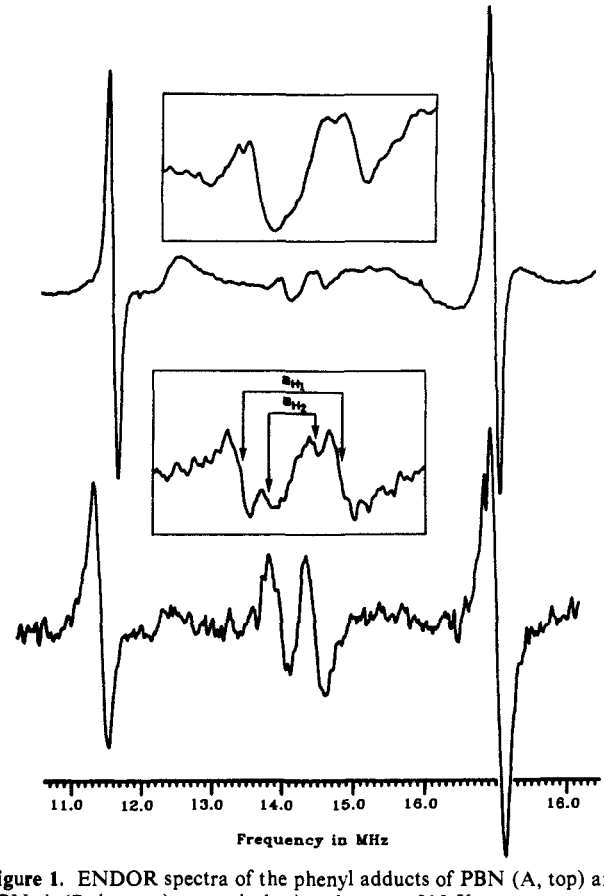



**Figure 1.** ENDOR spectra of the phenyl adducts of PBN (A, top) and PBN-$d_9$ (B, bottom), repectively, in toluene at 230 K.

In benzene at 290 K the ENDOR spectrum shows the nitrogen doublet in addition to the $\beta$- and $\gamma$-proton doublets at near room temperature.[16] Although the conditions are not optimum for resolving the $\beta$-H doublet, benzene seems to be an excellent solvent for detecting N-14 ENDOR doublets. In toluene the ENDOR spectrum also shows the N-14 doublet at higher temperatures, but under these conditions the proton ENDOR signals are very weak.

All the ESR and ENDOR data for the phenyl adduct of PBN are given in Table II.

**Methyl Adduct.** The ESR spectrum of the methyl adduct of PBN (XX) consists of six broad lines (Figure 2A). When either the *tert*-butyl or phenyl group is fully deuterated (i.e., PBN-$d_9$ and PBN-$d_5$), the hyperfine splitting from the $\gamma$ hydrogens of the methyl group can be resolved ($a_{\gamma\text{-H}}^{CH_3}$ = 0.47 G). The methyl adduct of the former (i.e., PBN-$d_9$) is shown in Figure 2B. When both the phenyl and the *tert*-butyl groups in PBN are detuerated, resolution becomes much better (Figure 2C).

The first reported ENDOR spectrum of the methyl adduct of PBN showed two small doublets close to the free proton resonance.[15] The larger of the two doublets (1.41 MHz) was assigned to the $\gamma$-H hfs of the hydrogens in the added methyl group based on the spectrum obtained from methyl-$d_3$-lithium.[15] The smaller doublet (0.40 MHz) was attributed to *tert*-butyl and phenyl hydrogens.

In Figure 3A is shown the ENDOR spectrum of the methyl adduct of PBN-$d_9$ at 200 K in toluene. The assignments are marked. The insert shows that the inner doublet can be separated into two doublets. Since the *tert*-butyl group is deuterated, these hfs's must be assigned to two kinds of phenyl hydrogens. The signs of the hfs's can be obtained from TRIPLE. Thus:

| | $\beta$-H | $\gamma$-H (*t*-Bu) | $\gamma$-H (Me) | phenyl-H |
|---|---|---|---|---|
| hfs's for the methyl adduct of PBN (in MHz) | +10.20 | −0.28 | −1.33 | +0.56, +0.32 |

In Figure 3B the ENDOR spectrum of the methyl adduct at slightly higher temperature shows the N-14 doublet with the

(25) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481.
(26) Janzen, E. G.; Weber, J. R.; Haire, D. L.; Fung, D. M. *Anal. Lett.* **1985**, *18A*, 1749.
(27) Janzen, E. G. *Can. J. Chem.* **1984**, *62*, 1653.

**Table II.** Magnitudes and Signs of the Hyperfine Splittings (hfs's) of the Various Spin Adducts of α-phenyl-*N*-*tert*-butylnitrone (PBN)[a-c]

| radical | H• | $CH_3$• | $C_2H_5$• | *n*-$C_4H_9$• | $C_6H_5$•[d] |
|---|---|---|---|---|---|
| $a_N$ | +41.6[e] | +41.97 | +40.97 | +40.94 | +40.13 |
| $a_\beta^H$ | +20.4[e] | +10.20 | +9.16 | +9.05 | +5.56 (ESR)<br>+5.60 (ENDOR) |
| $a_{\text{radical addend-H}}$ | see $a_\beta^{He}$ | −1.33 | −1.38 | −1.41 | see $a_{\text{phenyl-H}}$ |
| $a_{\text{tert-butyl-H}}$ | (−)(0.4)[e] | −0.28 | −0.27 | −0.28 | (−)(0.3) |
| $a_{\text{phenyl-H}}$ | (+)(0.4)[e] | +0.56, +0.32 | +0.53, +0.26 | +0.73, +0.23 | +0.46, (+)(0.3) |
| $a_{\text{benzyl-}\alpha\text{-C-13}}$[f] | (−)15.12 | (−)14.86 (ESR)<br>(−)14.42 (ENDOR)[g] | (−)15.26 | (−)(15.12) | (−)15.54 |
| $a_{\text{radical addend-C-13}}$[h] | | (+)9.13[i] | | | see $a_{\text{phenyl-C-13}}$ |
| $a_{\text{tert-butyl-C-13}}$ | (±)(12.93−13.77)[j] | *j* | *j* | *j* | *j* |
| $a_{\text{phenyl-C-13}}$[h] | (+)27.6 | (+)29.5 | (+)31.47 | (+)13.75 | (+)20.75 |

[a] All the ENDOR spectra were recorded in toluene at approximately 200 K unless otherwise noted. [b] All the hyperfine splittings (hfs's) are given in MHz. Note the conversion factor from megahertz to gauss is division by 2.81. [c] Entries in parentheses indicate estimated values. [d] See ref 27 for further ESR/ENDOR information on this spin adduct. [e] These values were obtained at 270 K. [f] These values were obtained by ESR in benzene at 298 K using PBN in which the nitronyl carbon is C-13 enriched (PBN-nitronyl-C-13).[24] [g] It is noteworthy that the optimum temperature for C-13 ENDOR for the methyl adduct of PBN-nitronyl-C-13 in toluene was approximately 160 K. [h] These values were obtained by ESR in toluene at 298 K. [i] See the ESR data in the private communication in ref 28. [j] This range of values for the α and β carbons of the *tert*-butyl group of the various PBN spin adducts is estimated from ESR data of structurally related aminoxyls.[27,29]

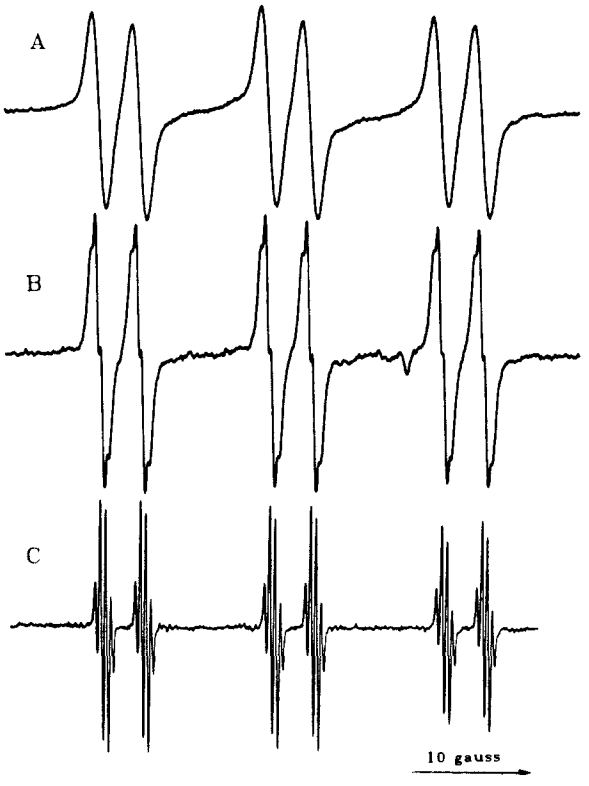
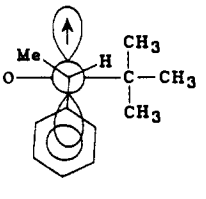



**Figure 2.** ESR spectra of the methyl adducts of PBN (A), PBN-$d_9$ (B), and PBN-$d_{14}$ (C) in toluene at 298 K.

low-frequency line overlapping the high-frequency line of the β-H doublet.

It is of interest to note that the hfs's of the phenyl hydrogens are larger in the methyl adduct than in the phenyl adduct of PBN. If the conformation of the phenyl adduct is as shown in **1**, the time average dihedral angle to the phenyl group must be 30°. If the magnitude of the phenyl hydrogen hfs's follows a $(\cos\theta)^2$ dependence, the dihedral angle to the first carbon of the phenyl group in the methyl adduct must be smaller than in the phenyl adduct:




**2**

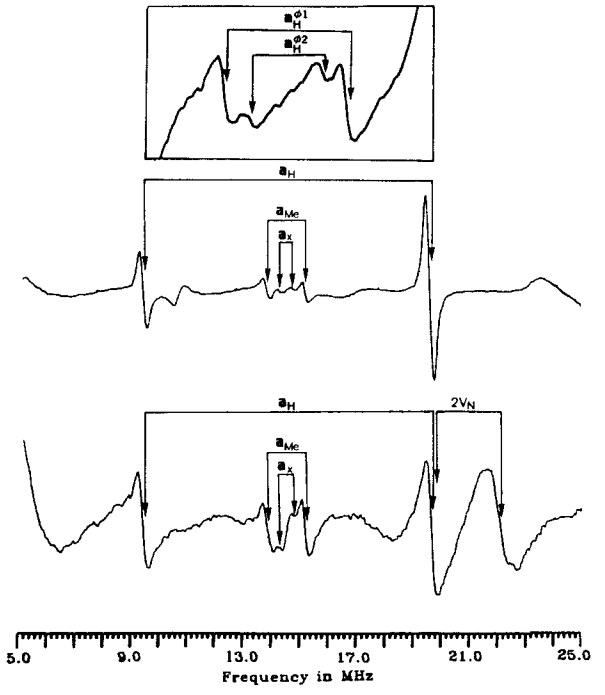



**Figure 3.** ENDOR spectra of the methyl adduct of PBN-$d_9$ in toluene at 200 (A, top) and 290 K (B, bottom), respectively.

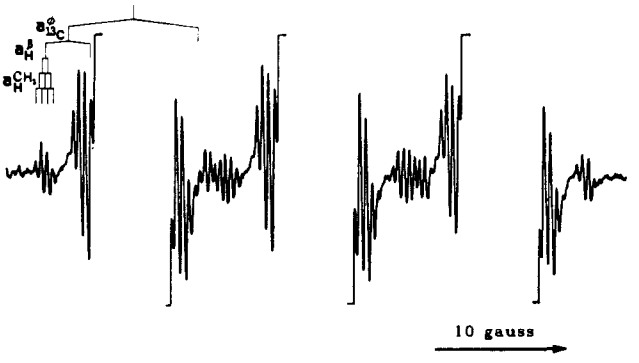



**Figure 4.** ESR spectrum of methyl adduct of PBN-$d_{14}$ in toluene at 298 K at high gain showing the naturally abundant C-13 hyperfine splittings.

This description of the preferred conformation is supported by the C-13 hfs from the added methyl group and the first carbon of the phenyl group. Figure 4 shows C-13 satellites of the ESR spectrum of the methyl adduct of PBN-$d_{14}$ in toluene at high gain at 297 K. The largest C-13 doublet can be assigned to the first carbon of the phenyl group[27] on the basis of data provided for the

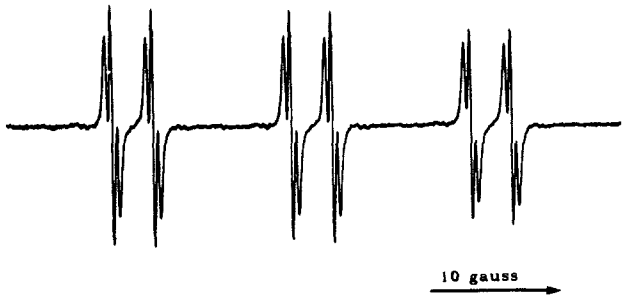



**Figure 5.** ESR spectrum of the ethyl adduct of PBN-$d_{14}$ in toluene at 298 K.

methyl adduct of PBN (private communication in ref 28). Thus the C-13 hfs of the added methyl group is smaller than the C-13 hfs of the first carbon of the phenyl group:

| | phenyl | methyl addend | *tert*-butyl ($\alpha$ and $\beta$ carbons) |
|---|---|---|---|
| C-13 hfs's of $\alpha$ and $\beta$ carbons for the methyl adduct of PBN (in G) | 10.5 | 3.25 | 4.6–4.9[27,29] |

In toluene the N hfs increases slightly with increase in temperature ($\sim 1 \times 10^{-4}$ G/deg) in the range of 210–360 K. This trend has been observed in the phenyl adduct.[27]

The C-13 hfs of the first carbon of the phenyl group increases significantly with *decrease* in temperature ($\sim 5.0 \times 10^{-3}$ G/deg) indicating that the most stable conformation has an even smaller dihedral angle to the phenyl group at lower temperatures. The $\beta$-H hfs also *increases* slightly with *decrease* in temperature ($\sim 3 \times 10^{-4}$ G/deg) over the same temperature range.

All the hyperfine splitting constants of the methyl adduct of PBN are given in Table II.

**Ethyl and *n*-Butyl Adduct.** Using PBN-$d_{14}$ the ESR spectrum of the ethyl adduct clearly shows the 1:2:1 methylene $\gamma$-H hfs pattern (Figure 5). Proof of this assignment was provided by the 1,1-dideuterioethyl adduct of PBN-$d_{14}$ which caused the ESR triplet pattern to collapse to one peak. Additionally, the ENDOR spectrum of the 1,1-dideuterioethyl adduct of PBN-$d_{14}$ gives only a very weak doublet near the free proton resonance assignable to the residual (<6.5%) undeuterated *tert*-butyl hydrogens. The relative signs for the HFS were obtained from TRIPLE. Thus:

| | $\beta$-H | $\gamma$-H ($-CH_2-$) | $\gamma$-H (*t*-Bu) | phenyl-H |
|---|---|---|---|---|
| hfs's for the ethyl adduct of PBN (in MHz) | +9.16 | −1.38 | −0.27 | +0.53, +0.26 |

The ENDOR spectrum of the *n*-butyl adduct (XXII) has been reported before.[15] Better resolution was obtained with PBN-$d_9$ so that two small splittings could be detected and these are assigned to protons on the phenyl group.

| | $\beta$-H | $\gamma$-H ($-CH_2-$) | $\gamma$-H (*t*-Bu) | phenyl-H |
|---|---|---|---|---|
| hfs's for the *n*-butyl adduct of PBN (in MHz) | +9.05 | −1.41 | −0.28 | +0.73, +0.23 |

The phenyl C-13 hfs's for the first carbon of the phenyl group of the ethyl and *n*-butyl adducts are 11.2 and 11.3 G, respectively, indicating that the preferred conformations of these adducts are similar to that of the methyl adduct.

All the data for the ethyl and *n*-butyl adducts are given in Table II.

**Hydrogen Adduct.** The hydrogen adduct of PBN is benzyl-*tert*-butylaminoxyl. The ESR spectrum shown in Figure 6A,

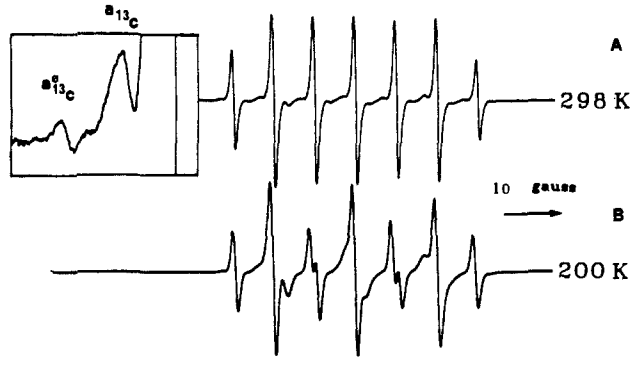
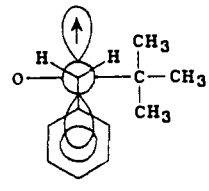



**Figure 6.** ESR spectra of the hydrogen atom adduct of PBN in toluene at 298 (A) and 200 K (B), respectively.

consists of three 1:2:1 triplets which arise from the two equivalent $\beta$ hydrogens. Even at low temperatures (200 K in toluene, Figure 6B), these hydrogens remain magnetically equivalent, indicating that in the two equivalent preferred conformations for this aminoxyl the two hydrogens are placed symmetrically about the nitrogen p orbital (i.e., with the phenyl group eclipsing the upper or the lower lobe of the p orbital):



**3**

The $\beta$-H hfs *increases* with *increases* in temperature: 6.86 G at 200 K and 7.41 G at 290 K. This observation is consistent with the above conformation since as the temperature is increased rocking will alternately increase the dihedral angle to one hydrogen while decreasing the dihedral angle to the other hydrogen. However, because the $\beta$-H hfs is related to the dihedral angle by a $(\cos \theta)^2$ relationship, the increase in the $\beta$-H hfs with the smaller dihedral angle is larger than the decrease in the HFS of the other hydrogen with a larger dihedral angle.[27]

The $\beta$-$^{13}$C hfs of the first carbon of the phenyl group *decreases* with *increase* in temperature: 10.47 G at 200 K; 9.82 G at 290 K. Since any movement away from the preferred conformation shown in **3** would increase the dihedral angle, the temperature dependence of the $\beta$-$^{13}$C hfs of the first carbon of the phenyl group is also consistent with this assignment of conformation.

The ENDOR spectrum of benzyl-*tert*-butylaminoxyl could only be obtained in toluene near 270 K. At higher temperatures the ENDOR signal is vanishingly small while at lower temperatures where the proton ENDOR response is expected to be better the radical concentration decreases sharply. The $\beta$-H doublet, a combined *tert*-butyl-/phenyl-H doublet, and the aminoxyl nitrogen doublet were visible in the ENDOR spectrum. Thus:

| | N-14 | $\beta$-H | $\gamma$-H (*t*-Bu) | phenyl-H |
|---|---|---|---|---|
| hfs's for the H atom adduct of PBN (in MHz) | +41.6 | +20.4 | −0.4 | +0.4 |

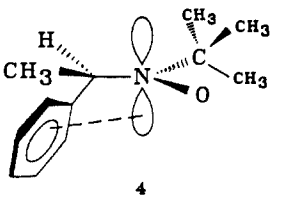
All the data for the hydrogen adduct of PBN can be found in Table II.

## Summary

In summary, the most stable conformations of the alkyl and aryl adducts of PBN place the phenyl ring in positions that are as close as possible to the p orbital of the nitrogen atom of the aminoxyl function in spite of the fact that more steric hindrance should be experienced between the phenyl and *tert*-butyl groups in these conformations. Thus we conclude that there is some attraction between the p orbital on the nitrogen atom (i.e., $\pi$ orbital

(28) Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 2493.

of the aminoxyl function) and the $\pi$ orbital of the phenyl ring in these aminoxyls:



4

The complexing of aromatic molecules with aminoxyls has been reported before, based on a chromatographic experiment.[30] This appears to be the first example of an intramolecular interaction between the aminoxyl function and an aromatic ring. Whether the attraction has electron-transfer character so that the aminoxyl function is reduced or oxidized is not known. An analogous intramolecular orbital interaction (albeit at one bond more distant) has recently been suggested for the carbon centered radical (3-methyl-3-phenylbut-1-yl).[31]

**Acknowledgment.** This work has been supported by the Natural Sciences and Engineering Research Council of Canada. Continuing support and a grant for the purchase of the ENDOR spectrometer is gratefully acknowledged.

**Registry No.** XX, 21894-27-9; XXII, 21999-41-7; XXIII, 21572-75-8; PBN, 24293-08-1; PhCH(Et)N(O•)-*t*-Bu, 21984-28-0.

(29) Briere, R.; Chapelet-Letourneux, G.; Lemaire, H.; Rassat, A. *Mol. Phys.* **1971**, *20*, 211.
(30) Batt, L.; Burnett, G. M.; Cameron, G. G.; Cameron, J. *J. Chem. Soc., Chem. Commun.* **1971**, *29*. Burnett, G. M.; Cameron, G. G.; Cameron, J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 864.
(31) Ingold, K. U.; Nonhebel, D. C.; Wildman, T. A. *J. Phys. Chem.* **1984**, *88*, 1675.

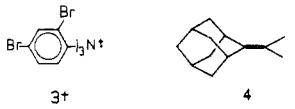
# A Cyclic Voltammetry Study of the Cation Radical Catalyzed Oxygenation of Tetraalkyl Olefins to Dioxetanes

**Stephen F. Nelsen,* Daniel L. Kapp, Ryoichi Akaba, and Dennis H. Evans**

*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.* *Received January 21, 1986*

**Abstract:** Cyclic voltammetry studies allow estimation of the rate constant for addition of $O_2$ to biadamantylidene cation radical ($\mathbf{1}^{\bullet+}$) to be 5600 $M^{-1}$ $s^{-1}$ at room temperature and for the cleavage of biadamantylidene dioxetane cation radical to oxygen and $\mathbf{1}^{\bullet+}$ >800 $s^{-1}$. Chlorination of the adamantane skeleton slows the overall rate of oxygen addition, and the face selectivity for oxygenation of **5**(Cl) is 25:1 in favor of attack from the olefin face syn to the chlorine. The implications of these findings for the mechanism of the reaction are discussed.

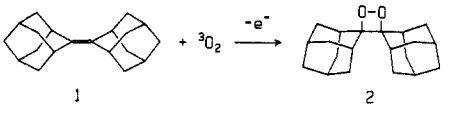
The groups of Nelsen[1] and Clennan[2] simultaneously reported the oxygenation of biadamantylidene (**1**) to its dioxetane **2** by a radical cation chain reaction with ground state. $^3O_2$, which could be initiated by chemical or electrochemical oxidation (Scheme I). Various acidic[3] and oxidizing reagents cause formation of **2**, the epoxide of **1**, and their decomposition products, but it was argued that the cation radical chain mechanism gives essentially only **2**.[1,2] Ando and co-workers[4] have contrasted the stereochemistry of dioxetane formation for analogues of **1** in the electrochemically initiated reaction with those of photogenerated $^1O_2$ and by photolysis with reducible sensitizers like 9,10-dicyanoanthracene, which initially generates pairs of olefin cations and $O_2^{-}$.[5] The use of $\mathbf{3}^{\bullet+}$,[6] a powerful enough oxidant to form tetraalkylolefin cation radicals rapidly at low temperature, makes the cation radical chain oxygenation reaction preparatively useful.[7] Conversion of isopropylideneadamantane (**4**) to dioxetane under



3+ 4

these conditions without formation of the allylic hydroperoxide, which is the sole product both with $^1O_2$ and easily reduced photosensitizers, showed that the chemistry of the cation radical chain oxygenation reaction is effectively separate from that of the other reaction conditions.[7] Dioxetane cation radicals have been demonstrated to build up at −78 °C in the absence of reductants,[8] and the oxidation of **1** by $\mathbf{2}^{\bullet+}$ has been shown to be quite exothermic at −78 °C, providing the driving force for an effective chain reaction. MNDO-level calculations[9] suggest that oxygen adds to olefin cations one C–O bond at a time, and evidence for C–C bond rotation of an open $O_2$, olefin cation radical adduct, has been provided by product studies on an analogue of **1**.[10]

**Scheme I**



1 2

This paper gives a full report on the contribution of cyclic voltammetry (CV) studies to the elucidation of the mechanism of cation radical chain oxygenation of monoolefins of dioxetanes, including an investigation of the effect of heteroatom substituents on **1** on both electron loss and oxygen addition.

## Results

**One-Electron Oxidation of 1 Analogues.** **1** gives chemically reversible CV curves at 0.05 V/s in acetonitrile (0.1 M in *n*-$Bu_4NClO_4$, $E^{\circ\prime}$ 1.44 V vs. SCE[11]) and methylene chloride (0.1 M in *n*-$Bu_4NClO_4$, $E^{\circ\prime}$ 1.53 V[1]), showing that $\mathbf{1}^{\bullet+}$ lasts at least

(1) Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 2096.
(2) Clennan, E. L.; Simmons, W.; Almgren, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 2098.
(3) Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1984**, *25*, 665.
(4) (a) Ando, W.; Kabe, Y.; Takata, T. *J. Am. Chem. Soc.* **1982**, *104*, 7314. (b) Kabe, Y.; Takata, T.; Ueno, K.; Ando, W. *Ibid.* **1984**, *106*, 8174.
(5) Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, L. W.-M. *J. Am. Chem. Soc.* **1980**, *102*, 389.
(6) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.
(7) Nelsen, S. F.; Kapp, D. L.; Teasley, M. F. *J. Org. Chem.* **1984**, *49*, 579.
(8) Nelsen, S. F.; Kapp, D. L.; Gerson, F.; Lopez, J. *J. Am. Chem. Soc.* **1986**, *108*, 1027.
(9) Chen, C.-C.; Fox, M. A. *J. Comput. Chem.* **1983**, *4*, 488.
(10) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 1265.
(11) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503.

0002-7863/86/1508-6863$01.50/0 