LETTER TO THE EDITOR

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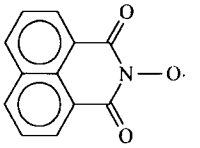
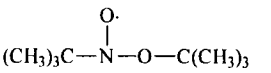
Dear Editor

A recent paper in *Free Radical Research*, Vol 20, No. 1, pp 1–10, 1994 by Pierre Lambelet, Francoise Saucy and Jürg Loliger entitled, "Radical Exchange Reactions between Vitamin E, Vitamin C and Phospholipids in Autoxidizing Polyunsaturated Lipids"[1] provided interesting data on indigenous radicals produced during or subsequent to lipid peroxidation. As perhaps expected, the transient presence of ascorbyl or tocopheroxyl radical was detected by EPR when phosphotidylcholine was used. However, a new free radical species assigned to an aminoxyl structure was observed when phosphotidylserine or phosphatidylethanolamine was used. These phospholipids have a primary amine function in contrast to phosphatidylcholine where the choline group is a quaternary amine. The EPR spectra published (Figure 3 and 5)[1] clearly indicate a pattern characteristic of an immobilized aminoxyl. However, the structure of this immobilized aminoxyl is difficult to determine from this type of EPR spectrum. Almost all the folk-lore on immobilized EPR spectra of aminoxyls comes from spin labels where the nitrogen hyperfine splitting (N-hfs) is about 15 Gauss (14–16 G depending slightly on type of spin label).[2] However, the N-hfs constants of alkyl and alicyclic aminoxyls can vary from 4 G for a bis-α-acyl aminoxyl radical (**I**) to 27 G for an alkoxyl aminoxyl radical (**II**) in mobile solvents.[3,4]

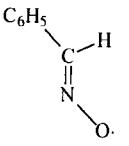


I

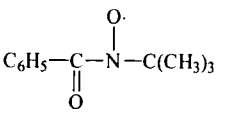


II

The EPR spectrum of an immobilized aminoxyl with a structure like I or II is difficult to predict. How the smaller or larger N-hfs would manifest itself as a function of preferred orientation in a partially immobilizing environment is not known. This situation is made even more complicated when iminoxyl radicals are considered. Iminoxyl radicals are a different *type* of radical as compared to aminoxyls and the N-hfs is quite large (about 30 G).[5] π-Type conjugation does not occur in iminoxyls because these radicals are σ-radicals; for example structure III.

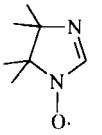


III

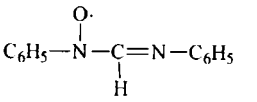


IV

In this paper[1] the immobilized aminoxyl radical EPR spectrum changes to a spectrum where the radical is more mobile when the sample is hydrated (Figure 4).[1] The N-hfs is reported as 8.2 G. The only aminoxyl function which has a N-hfs as small as 7–8 G is the acyl aminoxyl function,[6] for example structure IV,[7] although α-iminyl aminoxyls can have N-hfs constants between 7.5 G (cyclic, V)[8] and 9.8 G (open chain, VI):[9]

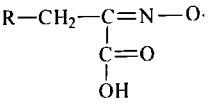


V

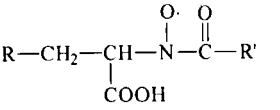


VI

The authors of this paper[1] tentatively ascribe the aminoxyl radical spectrum to VII.



VII



VIII

This structure is an iminoxyl radical and as such should have a N-hfs of about 30 G. No iminoxyl radicals with N-hfs values as low as 8 G are known, and are not likely to exist even with an α-carboxyl function attached. Since π-type conjugation does not occur in iminoxyl radicals this cannot be the reason why the N-hfs is so small.

The most likely structure for the aminoxyl with the EPR spectrum in Figure 4[1] is an α-acyl aminoxyl perhaps still as a derivative of phosphotidylserine (VIII). The oxidation of the primary amine of serine could produce a nitroso function which upon trapping an acyl radical would produce an α-acyl aminoxyl. The secondary hydrogen on the alkyl group attached to the nitroxyl function might have a β-H hfs smaller than the observed line width in Figure 4,[1] and the aminoxyl function could gain stability by intramolecular H-bonding with the contiguous carboxyl function.[10] Intramolecular H-bonding would also cause an increase in the N-hfs since the spin density on the nitrogen atom should increase in the chelated isomer.[11,12]

Acknowledgments

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References

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