

## Supporting Information to Accompany

### EPR Line Shifts and Line Shape Changes Due to Spin Exchange between Nitroxide Free Radicals in Liquids 3. Extension to Five Hyperfine Lines. Additional line shifts due to re-encounters.

Barney L Bales, Miroslav Peric, and Ileana Dragutan

**Second order terms in hyperfine spacing in the absence of spin exchange.** The separation between the five hyperfine lines differs by small second order terms that have their origin in both static and dynamic effects.<sup>1-3</sup> These effects, which were discussed in detail for free radicals possessing two equivalent  $^{14}\text{N}$  nuclei by Faber and Fraenkel<sup>3</sup> are not of consequence in this work, having a negligible effect on the sums giving  $b_{M_I}$ , eq 11. Here, we give a brief summary of the second order effects.

According to eq 2.10 of ref<sup>3</sup>, in the absence of appreciable instantaneous variations in the isotropic hyperfine splittings, static shifts of the hyperfine lines are given by  $\epsilon(\pm 2) = -2\delta$ ;  $\epsilon(\pm 1) = -3\delta$ ; and  $\epsilon(0) = -8\delta/3$ , where the characteristic shift  $\delta$  is defined to be  $\delta = A^2/2H(0)_0$ . For  $A \approx 8.1$  G in a field of  $H(0)_0 \approx 3323$  G,  $\delta \approx 9.8$  mG. These shifts alter the spacing between the hyperfine components as follows:

$$\begin{aligned} S(+2) &= [H(0)_{+2} - H(0)_{+1}] = A - \delta, \\ S(+1) &= [H(0)_{+1} - H(0)_0] = A + \delta/3, \\ S(-1) &= [H(0)_0 - H(0)_{-1}] = A - \delta/3, \\ S(-2) &= [H(0)_{-1} - H(0)_{-2}] = A + \delta. \end{aligned} \quad (\text{S1})$$

When dynamic effects are present, the observed second order shifts are different from eq S1 not only because dynamic shifts occur but also because the static shifts are different than those given in eq S1.<sup>3</sup> We

summarize the experimental results in terms of the departures of the shifts given by eq S1 normalized to  $\delta$  as follows:

$$\begin{aligned}\Delta S(+2)/\delta &= [A - \delta - S_{\text{exp}(+2)}]/\delta \\ \Delta S(+1)/\delta &= [A + \delta/3 - S_{\text{exp}(+1)}]/\delta \\ \Delta S(-1)/\delta &= [A - \delta/3 - S_{\text{exp}(-1)}]/\delta \\ \Delta S(-2)/\delta &= [A + \delta - S_{\text{exp}(-2)}]/\delta,\end{aligned}\quad (\text{S2})$$

where the subscript *exp* denotes the experimentally measured spacing between the hyperfine components. The departures given by eq S1 are seen to be the difference in the spacing predicted from static shifts alone to those measured, normalized to the characteristic shift  $\delta$ . Shifts dominated by static effects would lead to zero for the departures given by eq S2. The results are given in Table S1.

Table S1. Departures of second order shifts from theoretical static shifts<sup>a</sup>.

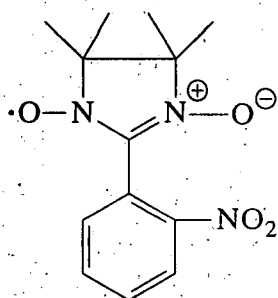
T, °C	$\Delta S(+2)/\delta$	$\Delta S(+1)/\delta$	$\Delta S(-1)/\delta$	$\Delta S(-2)/\delta$
$-7.2 \pm 0.2$	$-1.08 \pm 0.1$	$-0.73 \pm 0.11$	$0.86 \pm 0.18$	$0.95 \pm 0.31$
$24.8 \pm 0.2$	$-0.68 \pm 0.14$	$-1.23 \pm 0.04$	$0.57 \pm 0.09$	$1.34 \pm 0.15$
$44.8 \pm 0.4$	$-0.50 \pm 0.14$	$-1.26 \pm 0.04$	$0.35 \pm 0.10$	$1.40 \pm 0.13$
$84.8 \pm 0.7$	$-0.12 \pm 0.19$	$-1.47 \pm 0.20$	$0.16 \pm 0.22$	$1.43 \pm 0.46$
$105 \pm 1$	$-0.36 \pm 0.33$	$-0.82 \pm 0.44$	$0.16 \pm 0.25$	$1.01 \pm 0.17$

<sup>a</sup>Equation S2.

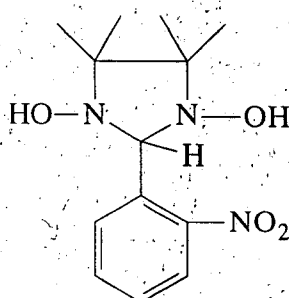
## References

- (1) Fraenkel, G. K. *J. Chem. Phys.* **1965**, *42*, 4275.
- (2) Fraenkel, G. K. *J. Phys. Chem.* **1967**, *71*, 139.
- (3) Faber, R. J.; Fraenkel, G. K. *J. Chem. Phys.* **1967**, *47*, 2462.

## Further details on the synthesis of NN-NP



1



2

1-H-Imidazol-1-yloxy-4,5-dihydro-4,4,5,5-tetramethyl-2-(o-nitrophenyl)-3-oxide (1)

Nitroxide **1** was prepared by the Ullman procedure,<sup>1-3</sup> essentially as previously described<sup>4</sup> with the exception that pure 2,3-dimethyl-2,3-dihydroxylaminobutane<sup>5</sup> (7.3 g; 41.5 mM) and 2-nitrobenzaldehyde (7.0 g; 46.3 mM)(Aldrich) were reacted in ethanol for 8 hrs., at room temperature. The precipitated dihydroxylamine **2** was filtered in *vacuo*, washed on filter with 50 ml of n-hexane, dried overnight under reduced pressure, then suspended in acetone and lead dioxide (60 g) added. After stirring for 3 hrs. lead dioxide was filtered off under reduced pressure through a thin layer of sand deposited on a frit and the filtrate concentrated in *vacuo*. The residue (10.2 g) was purified by two-fold crystallization from acetone/n-hexane (1/6, v/v), at  $-35^{\circ}\text{C}$ , to give dark-brown crystals (5.3 g; 46%), m.p.  $145-147^{\circ}\text{C}$  (lit.<sup>6</sup> m.p.  $145-147^{\circ}\text{C}$  for **1**, resulting from nitration of 1-H-imidazol-1-yloxy-4,5-dihydro-4,4,5,5-tetramethyl-2-phenyl-3-oxide). Anal. *Calcd.* for  $\text{C}_{13}\text{H}_{16}\text{N}_3\text{O}_4$ : C, 56.09; H, 5.80; N, 15.10 %. *Found*: C, 55.98; H, 5.78; N, 14.93 %. EI-MS (70 eV):  $m/z$  84.2 (100%), 278.2 ( $\text{M}^+$ )(23%). IR( $\text{CCl}_4$ ): 1370 (vs, NO<sub>2</sub>), 1410 (vs), 1445 (s), 1545 (m)(vNO<sub>2</sub>), 1580 (w) (vC=C), 2860 (w), 2925 (m) and 2990 (m)  $\text{cm}^{-1}$  (vC-H). UV  $\lambda_{\text{max}}$  (nm), [lg  $\epsilon$ ]: 285 (s), 300 (s), 313 [4.190], 513 (s); 540.3 [3.202] (in water); 292 [3.991], 323 [4.041], 556 [2.948] (ethanol); 582 [2.812] (toluene).

ESR:  $a_{\text{N}}$ .....

## References

- (1) Osiecki, J.H.; Ullman, E.F. *J. Am. Chem. Soc.* **1968**, *90*, 1078.
- (2) Boocock, D.G.B.; Darcy, R.; Ullman, E.F. *J. Am. Chem. Soc.* **1968**, *90*, 5945, 6873.
- (3) Ullman, E.F.; Osiecki, J.H.; Boocock, D.G.B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.
- (4) Dragutan, I.; Dragutan, V.; Caragheorghopol, A.; Zarkadis, A.K.; Fischer, H.; Hoffmann, H. *Colloids Surf. A* **2001**, *183-185*, 767.
- (5) a) Ovcharenko, V.I.; Fokin, S.V.; Rey, P. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 109.  
b) Ovcharenko, V. I.; Fokin, S.V.; Romanenko, G.V.; Korobkov, I.V.; Rey, P. *Russ. Chem. Bull.* **1999**, *48*, 1519.
- (6) Kálai, T.; Jekő, J.; Szabó, Z.; Párkányi, L.; Hideg, K. *Synthesis* **1997**, 1049.