Electron Paramagnetic and Nuclear Magnetic Resonance Spectra of Di-*tert*-butyliminoxy and Di(1-adamantyl)iminoxy[1]

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Abstract: The NMR spectrum of di-*tert*-butyliminoxy shows that all 18 protons are magnetically equivalent and yields +0.61 G for the electron–proton hyperfine coupling, a^H. Positive spin density at the *tert*-butyl protons contrasts with the negative spin density found in di-*tert*-butyl nitroxide. The EPR spectrum of the iminoxy at temperatures of −50° and below can be analyzed in terms of two groups of nine protons having a^H = +0.481 (probably the anti *tert*-butyl protons) and +0.772 G (probably the syn protons). At a temperature of 70°, the EPR spectrum can be analyzed in terms of 18 equivalent protons. At intermediate temperatures, theoretical EPR spectra calculated for mutual exchange of syn and anti *tert*-butyl groups did not fit the experimental spectra. The EPR and NMR spectra of di-(1-adamantyl)iminoxy are also reported.

^{1}H NMR spectroscopy of concentrated solutions of organic free radicals provides a simple method for determining the sign and magnitude of the electron–proton hyperfine coupling constants. This technique has been applied to a variety of π radicals such as aromatic radical ions,[2,3] phenoxys,[4,5] and nitroxides.[4,6-9] We wish to report the first application of the technique to σ radicals, using two of our recently prepared di-*tert*-alkyliminoxys.

Experimental Section

Di-*tert*-butyliminoxy[10,11] and di-(1-adamantyl)iminoxy[12] were prepared as previously described.[10-12] EPR spectra were recorded on a Varian E-4 spectrometer having a Varian temperature controller. The temperature of the EPR sample was measured with a copper–constantan thermocouple. The NMR spectra were recorded on a Varian HA-100D spectrometer at room temperature.

Results and Discussion

Di-*tert*-butyliminoxy [$(t\text{-Bu})_2C$=NO·] in dilute solution has a temperature-dependent EPR spectrum consisting of a triplet (a^N = 31.32 G in benzene at 23°)[11] of multiplets. A 100-MHz NMR spectrum of neat (but somewhat impure) $(t\text{-Bu})_2C$=NO· at room temperature has a *single* broad peak ($\Delta H \sim 1600$ Hz) shifted to *low* field. The average spin density on the *tert*-butyl protons is therefore *positive* in sign.[2-9] The paramagnetic shift is −45.7 ppm relative to $(t\text{-Bu})_2C$=NOH[13] which yields a^H (av) = +0.61 G. This contrasts with the π radical $(t\text{-Bu})_2$NO· where the spin density on the t-Bu groups is negative[4,6] and a^H (av) $\approx$ −0.11 G.

Syn-anti isomerization was described in the first report on iminoxy radicals.[14] The multiplet structure in the limiting low-temperature spectrum (Figure 1A) may be simulated[15] by two groups of nine protons each, with a^H values of 0.481 and 0.772 G, average +0.627 G. That is, both syn and anti protons have *positive* spin density. The larger splitting can almost certainly be assigned to the syn protons.[16] These syn splittings are somewhat smaller than the values found for two bisected syn methyls both in cyclic iminoxys with the general structure

$$\overline{|}\text{-- (C=NO·)}CMe_2$$
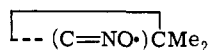
viz.,[16a,16e,17] a^H (6 H) = 1.2 ± 0.1 G, and in t-Bu-(C=NO·)CHMe₂, viz.,[11,18] a^H (6 H) = 1.0 G.

Some EPR spectra at different temperatures are shown in Figure 1 together with theoretical spectra calculated[15] on the assumption that mutual exchange between the syn and anti t-Bu groups occurs at the rate shown for each theoretical spectrum.[19] There is excellent agreement between experimental and theoretical spectra at slow and rapid exchange rates but not in the intermediate region. This suggests that the actual exchange process is more complicated than the assumed one. Whatever the mechanism of exchange, the rate is much greater than that estimated using a radical trapping procedure for inversion at nitrogen in phenyl-*p*-tolyliminoxy, viz.,[20] $k \sim$ 10 sec^{-1} at 144°, while the syn and anti forms of CH_3COC(=NO·)CF_3 are reported not to be in thermodynamic equilibrium.[21]

Di-(1-adamantyl)iminoxy [$(1\text{-Ad})_2C$=NO·] has a simple EPR spectrum consisting of three fairly broad lines (peak-to-peak width 1.8 G, overall width ca. 6 G) and no resolvable proton splittings, a^N = 31.14 G in benzene at 23°. Because these lines are reasonably sharp, it is possible to detect splitting by two different ^{13}C nuclei (a = 8.0 and 13.6 G)[22] and by ^{15}N (a = 43.3 G)[23] in natural abundance. The NMR spectrum of a 0.8 M solution in C_6D_6 at 23° shows *three* peaks, all at low field. The paramagnetic shifts[25] are −1.6 (width ~120 Hz), −14.2 (~650 Hz) and ca. −41 ppm (very broad). The intensity ratio of the first two lines is approximately 1:1, but the third line was too broad to integrate. The shifts yield a^H values of +0.02, +0.19, and +0.55 ± 0.04 G, respectively. By analogy with $(t\text{-Bu})_2C$=NO·, the largest a^H value is assigned to the six CH_2 protons in the 2 positions of the adamantane skeleton. The 0.19 G value is tentatively assigned to the six CH protons in the 3 positions and the +0.02 G value to the six axial (with respect to the 1 position) protons in the 4 positions. For comparison, in $(1\text{-Ad})_2$NO·, the proton couplings are both positive and negative,[8] viz., −0.405 (2 CH_2), +0.54 (3 CH), and −0.035 and −0.015 G (axial and equatorial 4 CH_2).

Iminoxys derived from anthraquinone monoxime and fluorenone oxime show splitting from the unique proton, which is the syn 1 proton. From the anisotropic EPR spectra of these radicals, Fox and Symons[16d] have concluded that the spin density on this proton is positive. The *tert*-butyl protons in $(t\text{-Bu})_2C$=NO· and the 2-methylene protons in $(1\text{-Ad})_2C$=NO· are removed from the C=NO· group by an equal number of bonds and so the positive spin density of these protons in the syn position is not entirely unexpected. It is also reasonable to expect positive spin on the corresponding anti protons.[16d,16j] The positive spin on the more remote protons in $(1\text{-Ad})_2C$=NO· is more surprising since theoretical calculations on aryliminoxys[16j] suggest that at least some more remote protons may have negative spin.
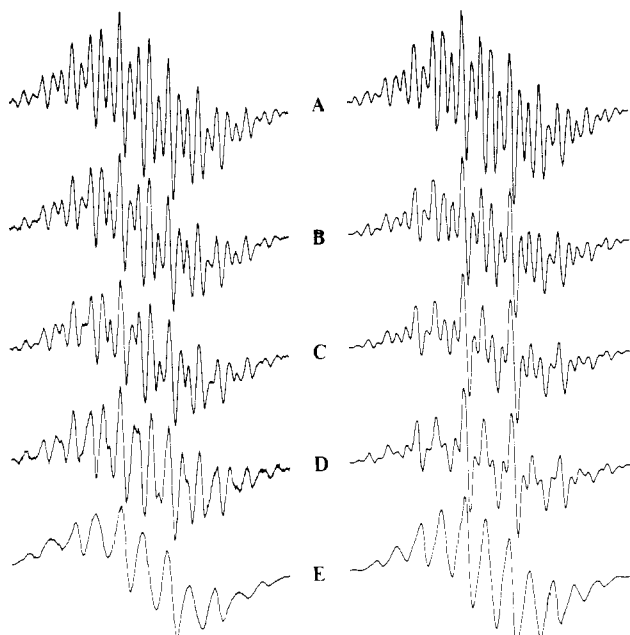
Figure 1. Experimental (left) and simulated (right) EPR spectra of the highest field multiplet of $(t\text{-Bu})_2C=NO\cdot$ in isopentane: (A) $-50°$, $k = 0$; (B) $-37°$, $k = 2.1 \times 10^5$ sec^{-1}; (C) $-27°$, $k = 4.2 \times 10^5$ sec^{-1}; (D) $14°$, $k = 6.3 \times 10^5$ sec^{-1}; (E) $72°$, $k = 1.3 \times 10^6$ sec^{-1}.

Unfortunately, the lifetimes of most aryliminoxys appear to be too short[17] to permit their study by NMR.

References and Notes

(1) Issued as N.R.C.C. No. 14534.
(2) E. de Boer and C. MacLean, *Mol. Phys.*, **9**, 191 (1965); *J. Chem. Phys.*, **44**, 1334 (1966); E. de Boer and J. P. Colpa, *J. Phys. Chem.*, **71**, 21 (1967).
(3) T. Takeshita and N. Hirota, *J. Chem. Phys.*, **58**, 3745 (1973).
(4) K. H. Hausser, H. Brunner, and J. C. Jockims, *Mol. Phys.*, **10**, 253 (1966).
(5) R. W. Kreilick, *Mol. Phys.*, **14**, 495 (1968); *J. Am. Chem. Soc.*, **90**, 2711, 5991 (1968).
(6) R. W. Kreilick, *J. Chem. Phys.*, **45**, 1922 (1966); **46**, 4260 (1967).
(7) R. Brière, H. Lemaire, A. Rassat, P. Rey, and A. Rousseau, *Bull. Soc. Chim. Fr.*, 4479 (1967); H. Lemaire, A. Rassat, and P. Rey, *Chem. Phys. Lett.*, **2**, 573 (1968); R. Brière, H. Lemaire, A. Rassat, and J. J. Dunand, *Bull. Soc. Chim. Fr.*, 4220 (1970); P. Michon and A. Rassat, ibid., 3561 (1971); A. Rassat and J. Ronzaud, *J. Am. Chem. Soc.*, **93**, 5041 (1971); A. Rassat and P. Rey, *Tetrahedron*, **29**, 1599, 2845 (1973).
(8) C. Morat and A. Rassat, *Bull. Soc. Chim. Fr.*, 893 (1971).
(9) A. Calder, A. R. Forrester, J. W. Elmsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, **18**, 481 (1970).
(10) J. L. Brokenshire, G. D. Mendenhall, and K. U. Ingold, *J. Am. Chem. Soc.*, **93**, 5278 (1971).
(11) G. D. Mendenhall and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 2963 (1973).
(12) D. Lindsay, E. C. Horswill, D. W. Davidson, and K. U. Ingold, *Can. J. Chem.*, **52**, 3554 (1974).
(13) In C_6D_6 at room temperature, the two t-Bu groups occur at 1.15 and 1.42 ppm downfield from Me_4Si. The hydroxylic proton is at 9.94 ppm.
(14) J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 1446 (1964).
(15) J. Heinzer, Quantum Chemistry Program Exchange, Indiana University, Program 209.
(16) See, e.g., (a) M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1985 (1964); (b) B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc., London*, 234 (1964); (c) W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965); (d) W. M. Fox and M. C. R. Symons, *J. Chem. Soc. A*, 1503 (1966); (e) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 86 (1966); (f) ibid., 722 (1966); (g) ibid., 981 (1967); (h) ibid., 123 (1968); (i) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); (j) M. F. Chiu, B. C. Gilbert, and B. T. Sutcliffe, ibid., **76**, 553 (1972).
(17) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 7040 (1972).
(18) In this radical, neither alkyl group rotates freely.[11]
(19) The mechanism for such a mutual exchange (which could be either an inversion at nitrogen or a rotation about the C=N bond) is not required for calculating the theoretical spectra.
(20) T. S. Dobashi and E. J. Grubbs, *J. Am. Chem. Soc.*, **95**, 5070 (1973).
(21) W. H. Woldarsky and J. K. S. Wan, *Spectrosc. Lett.*, **6**, 429 (1973).
(22) Compare ref 16e.
(23) A doublet splitting with almost the expected[24] value of 1.4 for a^{15N}/a^{14N}.
(24) See, e.g., J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York, N.Y., 1972.
(25) These are relative to $(1\text{-Ad})_2C=NOCH_3$ in C_6D_6, the adamantyl protons of which appear in the range 1.54–2.46 ppm downfield from Me_4Si.

Nitroxides. LXX. Electron Spin Resonance Study of Cyclodextrin Inclusion Compounds

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Abstract: Complexation of nitroxide radicals with cyclodextrins has been studied by electron spin resonance spectroscopy (esr). There is evidence for a complexation equilibrium between 2,2,6,6-tetramethylpiperidine-1-oxy (**1**) and β-cyclodextrin, but not with α-cyclodextrin. Substituted tetramethylpiperidine-*N*-oxy radicals **2** and **3** are not complexed by α- or β-cyclodextrins. On the other hand, oxazolidine-*N*-oxy derivatives are complexed either by α- and β-cyclodextrins or by β-cyclodextrin only, depending on the size of the radicals. Hyperfine splittings are consistent with a nonpolar environment of the complexed nitroxide group. These results are interpreted as evidence for inclusion of the nitroxide radical in the cyclodextrin cavity. This is in agreement with an independent ultraviolet spectroscopy study on 5-nitro-1,1,3,3-tetraethylisoindoline-2-oxy (**9**). Different models of inclusion are discussed. Quantitative information on cyclodextrin-guest equilibrium can easily be obtained using the biradical **10** [dispiro(2,2,6,6-tetramethylpiperidine-1-oxy)-4,4'-(oxazolidine-3'-oxy)-2',1''-cyclohexane] for which the following thermodynamic data on its association equilibrium with β-cyclodextrin can be measured: $\Delta H_{assoc} = -12 \pm 2$ kcal/mol; $\Delta S_{assoc} = -30 \pm 3$ cal/(deg mol).

Cyclodextrins are known to give noncovalent inclusion complexes with various organic molecules in aqueous solution.[1,2] For this reason, they have been used as models for enzymes[3,4] or proteins.[5]

The structure of cyclodextrins has been established by chemical studies.[6-8] The structures of some cyclodextrin inclusion complexes have been determined by X-ray diffraction:[9-11] α-cyclodextrin (β-cyclodextrin) is a cyclic molecule consisting of six (seven) α $-1 \rightarrow 4$ linked D-glucopyranose units. The principal difference between α- and β-