October 31, 2001

Lecture 4

EPR Course

NTU Fall 2001

Chan

Quenching of Orbital Angular Momentum in Molecules

In molecules, orbital angular momentum associated with unpaired electron is quenched, because the electrostatic forces acting on the electron is no longer spherical,

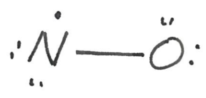
i.e., $V(\vec{r}) \neq V(|r|)$

according, $\langle \vec{L} \rangle = \langle \vec{l} \rangle = 0$, $\langle \vec{\mu}_L \rangle = 0$

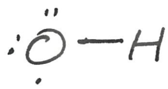
and $\langle \vec{\mu}_J \rangle = \langle \vec{\mu}_S \rangle$ or spin only!

Exceptions

There are a few exceptions!



,



nitric oxide

hydroxyl radical

Unpaired electron is in $2p$ orbital. But coulomb field on electron is axial, i.e., has cylindrical symmetry

$|\langle L_z \rangle| = |M_L| = 1$

$z \leftarrow N - O$

i.e., component of $\vec{L}$ along z-axis (symmetry axis of diatomic molecule) is quantized.

Expect $\langle J_z \rangle = \langle L_z \rangle + \langle S_z \rangle = \frac{3}{2}$ or $\frac{1}{2}$

These states are referred to as

$2S+1 \longrightarrow {}^{2}\Pi_{J_z} \longleftarrow L_z = 1$ Diatomics

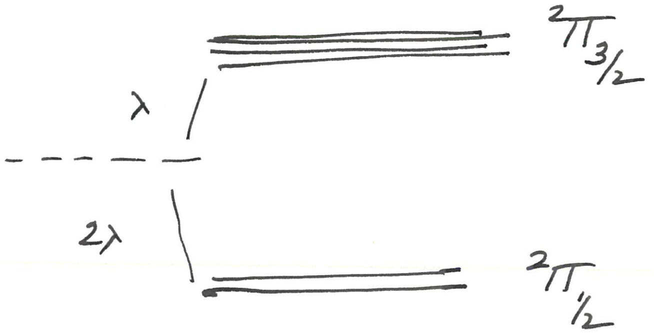
spin multiplicity

$L_z = 0 \rightarrow \Sigma$ state

$= 2 \rightarrow \Delta$ state

So for NO, we have

${}^{2}\Pi_{3/2}$ and ${}^{2}\Pi_{1/2}$ states



Spin-orbit splitting $\sim 100\ cm^{-1}$

But ${}^{2}\Pi_{1/2}$ state is diamagnetic!

$$\langle \mu_z \rangle = g_L \beta \langle L_z \rangle + g_s \beta \langle S_z \rangle$$

$$= g_L \beta M_L + g_s \beta \left(-\tfrac{1}{2}\right) = 1.000\beta(+1) + 2.0023\beta\left(-\tfrac{1}{2}\right)$$

$$\cong 0$$

However, large rotational magnetic moment for NO!

Nuclear Hyperfine Interaction

Simplest Case

H• (Hydrogen Atom)

$\boxed{^2S_{1/2} \text{ State}}$

Interaction of nuclear moment with magnetic field produced at the nucleus by electric currents

Unpaired electron is coupled to proton!

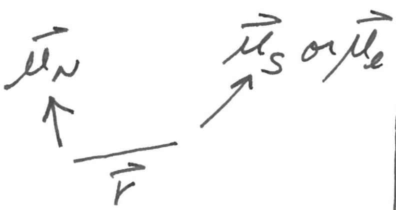
There are two types of nuclear hyperfine couplings:

(1) Dipolar Coupling

(2) Isotropic Hyperfine Coupling

Dipolar Coupling

This magnetic coupling between the magnetic moments of the electron and nucleus is entirely analogous to the classical dipolar coupling between two bar magnets



$$\boxed{\mathcal{H}_{Dipolar} = \frac{\vec{\mu}_e \cdot \vec{\mu}_N}{r^3} - \frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{r} \cdot \vec{\mu}_e)}{r^5}}$$

$r \equiv$ distance between the two magnetic moments

For $H_\bullet$, $\quad \vec{\mu}_e = \vec{\mu}_S = -g_S \beta \vec{S}$

$$\vec{\mu}_N = +g_N \beta_N \vec{I}$$

β_N = Nuclear Magneton $= \dfrac{e\hbar}{2M_pc}$

so that

$$\boxed{\mathcal{H}_{Dipolar} = -g_S g_N \beta \beta_N \left\{ \frac{\vec{I}\cdot\vec{S}}{r^3} - \frac{3(\vec{I}\cdot\vec{r})(\vec{S}\cdot\vec{r})}{r^5} \right\}}$$

<u>Expand</u>

$$\mathcal{H}_{Dipolar} = -g_S g_N \beta \beta_N \cdot$$

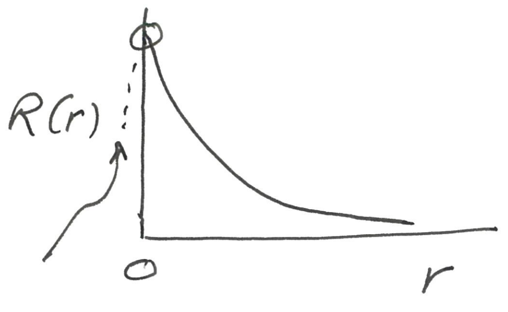
$$[I_x, I_y, I_z] \begin{bmatrix} \frac{(r^2-3x^2)}{r^5} & -\frac{3xy}{r^5} & -\frac{3xz}{r^5} \\ -\frac{3xy}{r^5} & \frac{(r^2-3y^2)}{r^5} & -\frac{3yz}{r^5} \\ -\frac{3xz}{r^5} & -\frac{3yz}{r^5} & \frac{(r^2-3z^2)}{r^5} \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

For s-electron, or S-state, or for spherical charge distribution 

$\langle r^2-3x^2\rangle = 0$, $\langle r^2-3y^2\rangle = 0$, $\langle r^2-3z^2\rangle = 0$, $\langle xy\rangle = 0$, $\langle xz\rangle = 0$, $\langle yz\rangle = 0$

So $\langle \mathcal{H}_{Dipolar}\rangle = 0$

Actually, for s-electrons, Radial wave function has an anti-node at $r=0$, or at the nucleus!



$$R(r) = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

$$a_0 = \text{Bohr radius} = \frac{\hbar^2}{m_e e^2}$$

So need to be more careful in evaluating

$\left\langle \frac{r^2-3x^2}{r^5} \right\rangle$, $\left\langle \frac{xy}{r^5} \right\rangle$ etc.

because of divergence of r^{-5} near $r=0$

So, unless $|R(r)|^2 \longrightarrow 0$ as $r \to 0$, I wasn't doing it right!

Earlier result is OK for "p" and "d" electrons, because $|R(r)|^2 \longrightarrow 0$ as $r \to 0$ for these electrons.

As a matter of fact, all orbitals, except the s-orbital, have NODES at $r=0$.

Fermi did it correctly for "s" electrons, and this leads to the "Isotropic Hyperfine Interaction" or the "Fermi Contact Interaction".

(2) Isotropic Nuclear Hyperfine Coupling

For s-electrons, Fermi showed that we need to add the term

$$\mathcal{H}_C = a\,\vec{I}\cdot\vec{S} = a\left(I_x S_x + I_y S_y + I_z S_z\right)$$

x, y, z arbitrary set of orthogonal axes

where $a = \frac{8\pi}{3} g_S g_N \beta \beta_N \left|\psi(0)\right|^2 \qquad (a>0)$

For the hydrogen atom, $(a/h) = 1422.74$ MHz

ESR of atomic hydrogen

So the more complete Hamiltonian for atomic hydrogen is

$$\mathcal{H}_Z = \underbrace{g_S \beta \vec{S}\cdot\vec{H}}_{\text{Zeeman}} + a\,\vec{I}\cdot\vec{S} - \underbrace{g_N \beta_N \vec{I}\cdot\vec{H}}_{\text{nuclear Zeeman}}$$

For the proton, $I = 1/2$

Expand $\mathcal{H}_Z$ using the same coordinate system for Zeeman interaction and nuclear hyperfine interaction

also define Z axis along magnetic field

$$\mathcal{H}_Z = g_S \beta S_Z H_0 + a\left(I_X S_X + I_Y S_Y + I_Z S_Z\right) - g_N \beta_N I_Z H_0$$

Energy levels are given by

$$W = g_s \beta m_s H_0 - g_N \beta_N m_I H_0 + a m_s m_I$$

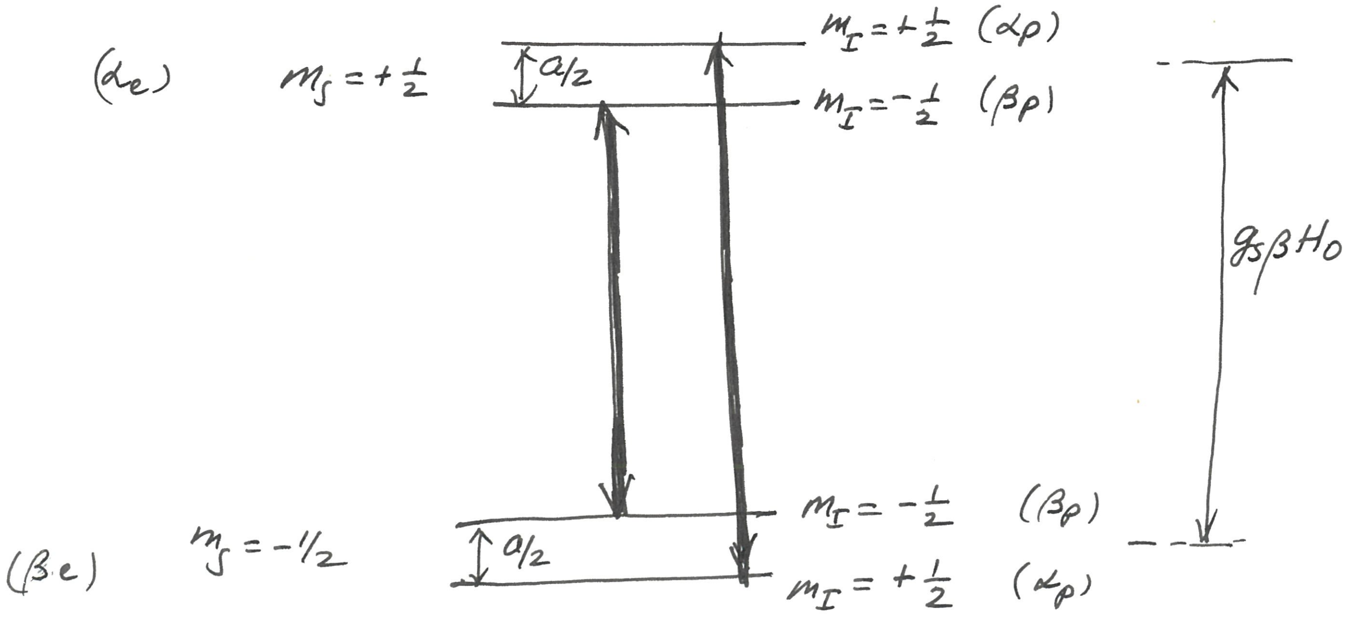
Result correct for strong magnetic fields!

Nuclear Zeeman is very small (NMR frequencies)
∴ Ignore.

$$\boxed{W \doteq g_s \beta m_s H_0 + a m_s m_I}$$

$m_s = \pm \frac{1}{2}$
$m_I = \pm \frac{1}{2}$

So at constant H_0, we have the following energy level diagram



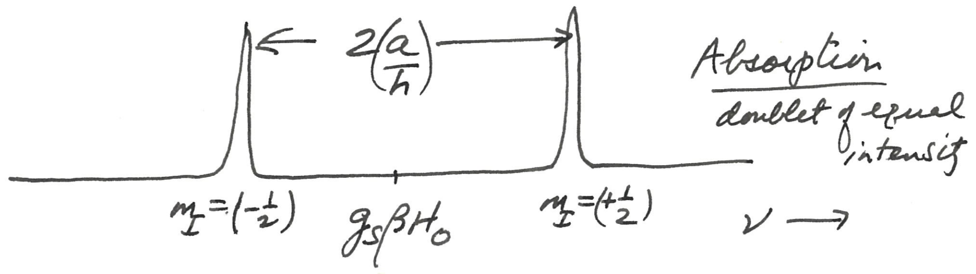
EPR: Selection rules $\Delta m_s = \pm 1$ EPR transitions
$\Delta m_I = 0$

Resonances (EPR) occur at the following frequencies

$m_I = -\frac{1}{2}$ $\qquad h\nu = g_s\beta H_0 - a$

$m_I = +\frac{1}{2}$ $\qquad h\nu = g_s\beta H_0 + a$

Frequency swept spectrum (constant H_0)

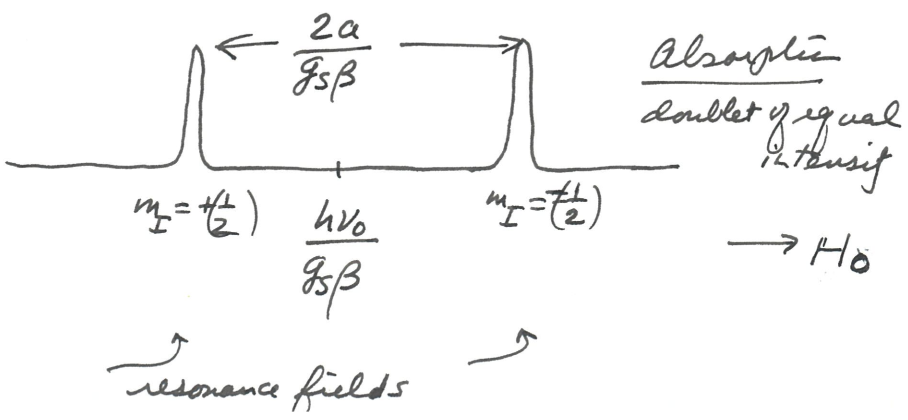


or Resonances (EPR) occur at the following resonance fields for microwave frequency ν_0

$m_I = -\frac{1}{2}$: $\qquad h\nu_0 + a = g_s\beta H_{resonance}$

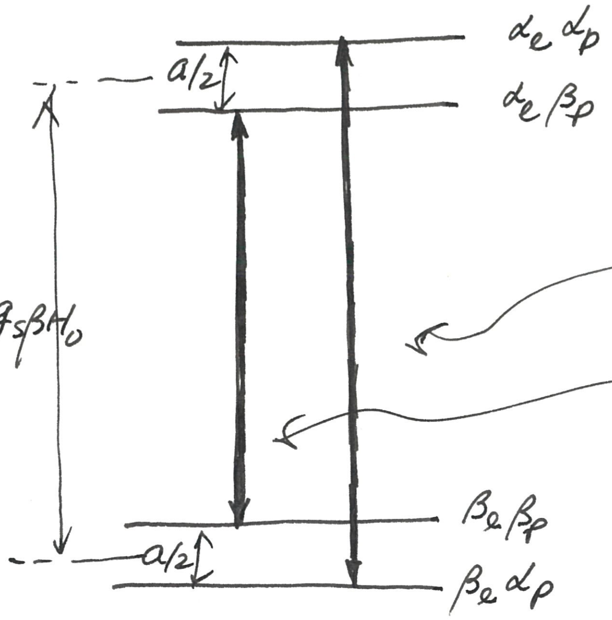
$m_I = +\frac{1}{2}$: $\qquad h\nu_0 - a = g_s\beta H_{resonance}$

Field swept spectrum (constant ν_0)



Strong fields

$g_s\beta H_0 >> a$



EPR transitions

$\Delta m_S = \pm 1$

$\Delta m_I = 0$

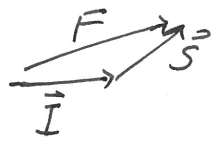
wavefunctions

Zero-field levels of Atomic Hydrogen

$H_0 = 0$

$\mathcal{H} = a \vec{I} \cdot \vec{S}$

Define $\vec{F} = \vec{I} + \vec{S}$



$I = 1/2$

$S = 1/2$

$F = 1, 0$

$m_F = \pm 1, 0$ $\quad m_F = 0$

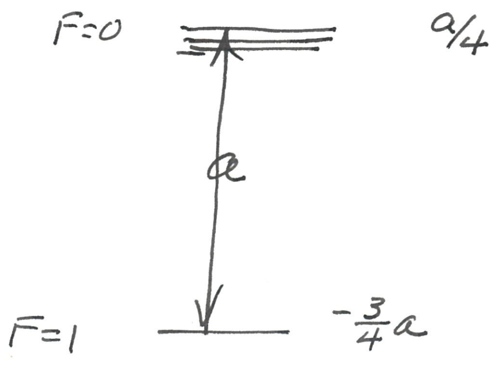
Since $\langle F^2 \rangle = \langle I^2 + S^2 + 2\vec{I}\cdot\vec{S} \rangle$

$$\vec{I}\cdot\vec{S} = \frac{1}{2}\left[F(F+1) - I(I+1) - S(S+1)\right]$$

$$W = \frac{a}{2}\left[(F)(F+1) - I(I+1) - S(S+1)\right]$$

$W_{F=0} = -\frac{3}{4}a$

$W_{F=1} = +\frac{a}{4}$



$a > 0$

$$+\frac{a}{4} \quad \left\{ \begin{array}{l} \alpha_e \alpha_p \\ \frac{1}{\sqrt{2}}[\alpha_e\beta_p + \beta_e\alpha_p] \\ \beta_e \beta_p \end{array} \right.$$

$$-\frac{3a}{4} \quad \frac{1}{\sqrt{2}}[\alpha_e\beta_p - \beta_e\alpha_p]$$

Emission from atomic hydrogen in interstellar dust

— a single line at 1420 MHz, (a/h)

$\boxed{\text{Radio astronomy}}$

Intensity of microwave from different parts of the sky

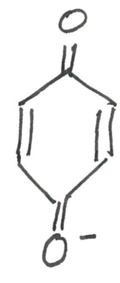
$\Rightarrow$ anisotropy of universe!

Organic Radicals in Solution

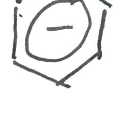
$\boxed{\text{Coupling of unpaired } e^- \text{ to protons}}$

$\cdot CH_3$, $\cdot CH_2-CH_3$,

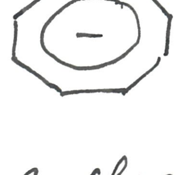
methyl (3) ethyl (2, 3)



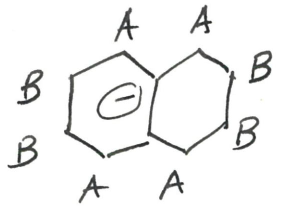
p-benzosemiquinone (4)



benzene anion (6)

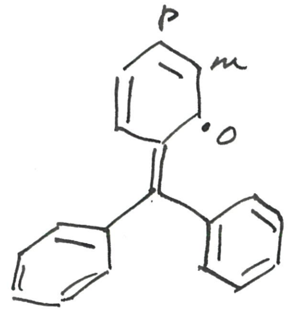


cyclooctatetraene anion (8)



Naphthalene negative ion

(two sets 4A's, 4B's)

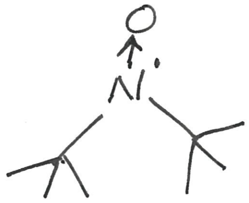


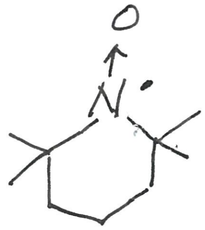
Triphenylmethyl

(three sets: 3p's, 6m's, 6o's)

Hyperfine coupling with other nuclei

$\cdot{}^{13}CH_3$ $\quad$ (1 ^{13}C + 3 H's)





(1 ^{14}N)

$I = 1$

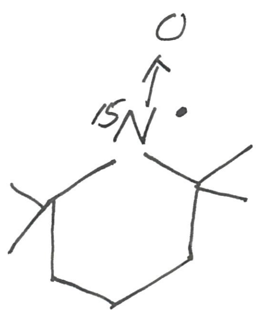
DTBN

TEMPO

Di tert-butyl nitroxide

2,2,6,6-Tetramethyl-1-piperidine N-oxide

(^{14}N + ^1H's)

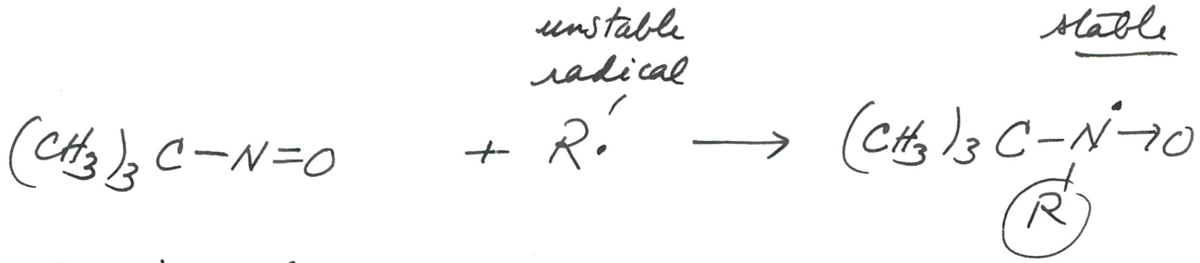


(1 ^{15}N)

$I = \frac{1}{2}$

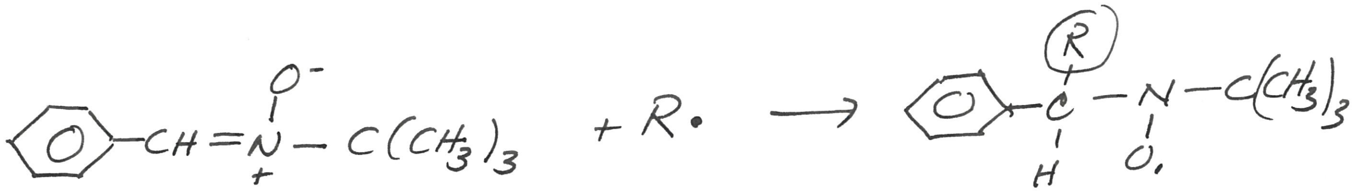
^{15}N - TEMPO

Spin Traps



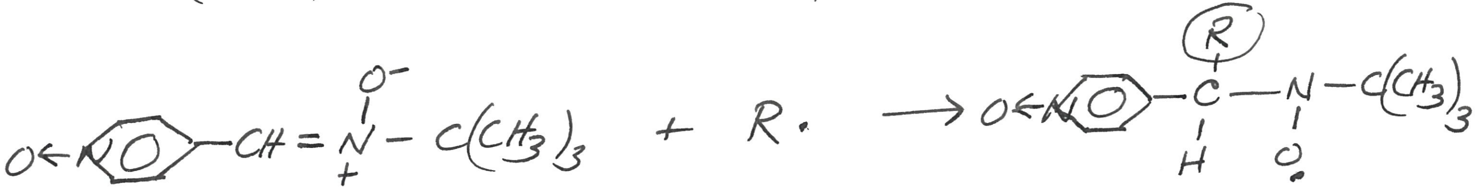
tert-nitrosobutane

or 2-methyl-2-nitrosopropane



phenyl-tert-butylnitrone

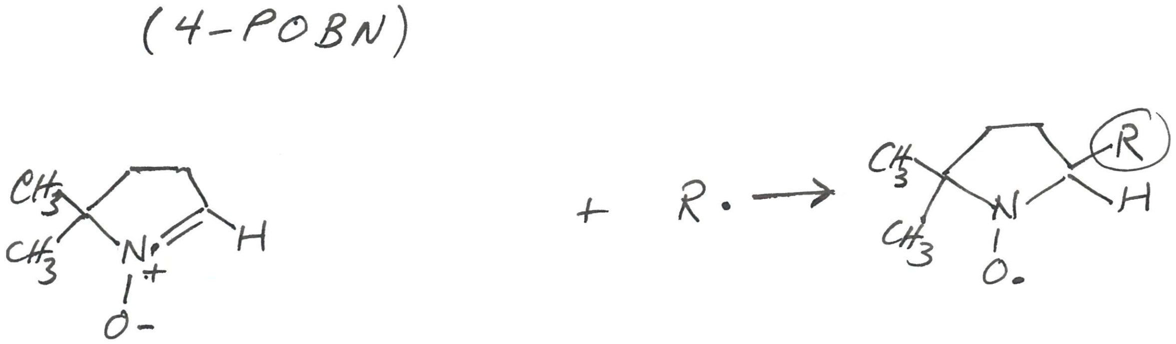
(PBN)



α-4-Pyridyl-1-oxide

N-tert-butylnitrone

(4-POBN)



5,5-dimethylpyrroline

N-oxide

(DMPO)