NMR STUDIES OF INTERNAL ROTATION

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ABSTRACT

Density matrix theory has been used to develop a computer program for the solution of a four-nuclear spin system. A description of the theory used to develop this program is given in Chapter Three.

This theory has been used to study a range of p-substituted nitrosobenzenes. The activation parameters have been determined and for N,N-dimethyl-p-nitrosoaniline, a comparison has been made with previous studies which have used more approximate methods.

The solvent dependency of the barrier to rotation has been investigated in the N,N-dialkyl-p-nitrosoanilines and no significant solvent dependence found.

In the early stages of this thesis, attempts were made to find a tetrahedral cobalt (II) complex involving ligand exchange, but no such complex suitable for a detailed NMR investigation was found. The investigation, though unsuccessful, has been briefly reported. These findings may aid further work in this area.

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B_o	external magnetic field in the + z direction
B_1	radiofrequency magnetic field
$\hbar$	Planck's constant divided by 2π
$\mathcal{H}$	Hamiltonian, or Spin Hamiltonian
I^+, I^-	raising and lowering operators
I_x, I_y, I_z	angular momentum operators in units of $h/2\pi$
i	$\sqrt{-1}$
J'_{ij}	Isotropic spin-spin coupling constant between nuclei i and j in terms of linear frequency. It is related to J_{ij} by the following expression, $J'_{ij} = \frac{2\pi J_{ij}}{\hbar}$
Tr	Trace
α β	spin functions
σ	sheilding constant
ρ	density matrix
ρ_{ij}	the ijth element of the density matrix
τ, τ'	mean lifetime of the nucleus in a given environment in units of s rad^{-1} and Hz^{-1} respectively.
T_2, T'_2	Transverse relaxation time in units of s rad^{-1} and Hz^{-1} respectively.
T_1, T'_1	Longitudinal relaxation time in units of s rad^{-1} and Hz^{-1} respectively.
Ψ ψ, Φ, ϕ	wave functions
ω_o, ω	angular frequencies

γ	Magnetogyric ratio
f	$\gamma B_1/4\pi$
ω_r	γB_1
$\otimes$	tensor product
k_B	Boltzmann constant
k	specific rotational rate
$K^{\neq}$	equilibrium constant
χ	transmission coefficient
ω_A	angular frequency of proton at site A
ω_B	angular frequency of proton at site B
$\langle I_{yT} \rangle$	total angular momentum in the y direction