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NMR STUDIES OF INTERNAL ROTATION

A thesis presented in partial fulfilment
of the requirements for the degree of
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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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List of Symbols

| | |
|--------------------------|--|
| B_0 | 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 $\hbar/2\pi$ |
| 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 | shielding constant |
| ρ | density matrix |
| ρ_{ij} | the ij th element of the density matrix |
| τ, τ' | mean lifetime of the nucleus in a given environment in units of $s \text{ rad}^{-1}$ and Hz^{-1} respectively. |
| T_2, T_2' | Transverse relaxation time in units of $s \text{ rad}^{-1}$ and Hz^{-1} respectively. |
| T_1, T_1' | Longitudinal relaxation time in units of $s \text{ rad}^{-1}$ and Hz^{-1} respectively. |
| Ψ, ψ, Φ, ϕ | wave functions |
| ω_0, 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^\ddagger | 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 |