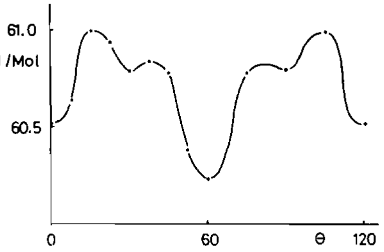
two origins, the crystal packing and the rigidity of the ligand systems. The former is difficult to estimate. The latter however can be calculated using the Consistent Force Field [2] method.

Calculations of this type have been carried out for several ligands such as tacn (1,4,7-triaminocyclononane), tame (1,1,1-trisaminomethyl-ethane) and tach (1,3,5-*cis*, *cis*-triaminocyclohexane) changing the Cu–N reference bond length along the circular path given by the mexican-hat potential. Figure 1 shows the result obtained for Cu(tacn)$_2^{2+}$ in the more stable optical active configuration. The relative energies obtained are a measure for the ease of the ligand, to adapt to the new geometry imposed by the Jahn–Teller distortion, defined by the angle θ [3]. The surprising result of these calculations is, that all three ligands stabilize a compressed tetragonal coordination (θ = 60°) by energies in the order of 1 kJ/mol. The lack of any experimental evidence for tetragonal compressed systems, indicate that for Cu^{2+} this preference of the ligand systems is overridden by other effects.



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Vibrational Hydrogen Tunnelling in Free Base Porphines

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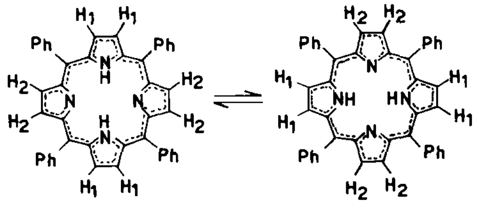
The kinetics of the hydrogen and the deuterium migration in *meso*-tetraphenylporphines (TPP) has been studied by a combination of NMR-lineshape analysis and selective $T_{1\rho}$ relaxation time measurements [1]. The anomalous Arrhenius-curves of the migration in TPP–H$_2$, TPP–HD, and TPP–D$_2$ proves that the reaction proceeds by resonance tunnelling between quantized vibrational NH-stretching states. The rate constants are independent of the choice of the solvent which indicates the absence of specific interactions between the inner porphine cavity and the solvent.



The experimental tunnel rates are used to calculate in quasiclassical one-dimensional WKB-approximation the distances over which each hydrogen atom is transported during the reaction [2]. These distances are in good agreement with the crystallographic data for the case of synchronous hydrogen tunnelling.

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^{1}H-NMR Spectroscopic Study of the Thermodynamics of Hydrogen Bonding and the Kinetics of Proton Exchange Between Acetic Acid and Methanol in Tetrahydrofuran-d$_8$

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The ^{1}H-NMR spectra of the systems acetic acid/methanol/tetrahydrofuran-d$_8$ (THF), acetic acid/THF, and methanol/THF have been measured as a function of the temperature and the concentrations. The kinetics of proton exchange between acetic acid and methanol in THF were determined [1] by NMR-lineshape analysis using the quantum mechanical density matrix formalism [2]. The proton chemical shifts provide the thermodynamic data of the following association reactions between hydrogen bonded species (S = THF):