Dynamic $^1$H NMR study of rotational energy barrier around the aryl-nitrogen single bond in $\gamma$-spiroiminolactones derived from reaction between 2,6-dimethylphenyl isocyanide and dialkyl acetylenedicarboxylates in the presence of phendione

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The Dynamic effects are observed in $^1$H NMR spectra of highly functional $\gamma$-spiroiminolactones such as dimethyl-5-(2,6-dimethylphenyliminol),-6'-oxo-5H-spiro[furan-2,5'-[1,10]phenanthroline]-3,4-dicarboxylate and di-tert-butyl-5-(2,6-dimethylphenyliminol)-6'-oxo-5H, 6H-spiro[furan-2, 5'-[1,10]phenanthroline]-3,4-dicarboxylate. The calculated free-energy of activation ($\Delta G^\neq$) for restricted rotation around the aryl-nitrogen single bonds in $\gamma$-spiroiminolactones 4a and 4b amounts to (44.4 and 45.3)±2 kJ.mol$^{-1}$ with first order rate constant (k=109.9 and 111.0 s$^{-1}$) at appropriate temperature respectively.

Keywords: Dynamic NMR, $\gamma$-spiroiminolactones, isocyanides, acetylenic esters

One of the most important reactions for the preparation of the heterocyclic systems is the multi-component reaction1,2. Earlier literature revealed the preparation of spiroiminolactones and derivatives3-7.

The alkyl or aryl-nitrogen single bonds and the polarized carbon-carbon double bonds are reported8-11. The isomerism of C=N double bonds is importance in preparation of spiroiminolactones and derivatives3-7. The isomerism of C=N double bonds is whether the process is a true rotation or an inversion (flipping) of the nitrogen substituent via an sp-hybridized transition state12,13.

Dynamic NMR affords good information in this matter on a dynamic process and provides important kinetic data; it is useful tool when discussing the barrier separating two states that are observable by NMR spectroscopy14. Thus, herein the free-energy of activation ($\Delta G^\neq$) for restricted rotation around the aryl-nitrogen single bonds of $\gamma$-spiroiminolactones 4a and 4b (Scheme I) is described..

Results and Discussion

Implication is that the two processes (cis-trans isomerization and racemization) occur via the same transition stat, as shown in Scheme II, this transition state must involve nitrogen inversion. To eliminate the (unlikely) possibility that two separate processes, C-N single bond rotation around the Ar-N bond (leading to racemization) and purported C=N double bond rotation (leading to cis-trans isomerization) might fortuitously occur with the same low activation energy and the activation energy of racemization higher than the activation energy of (cis-trans isomerization)13 see Scheme III and IV.

The reaction of aryl isocyanides 1 with electron-deficient acetylenic esters 2 in the presence of carbonyl compounds 3 led to spiroiminolactones 4 in fairly high yields15.

The $^1$H NMR spectrum of 4a in CDCl$_3$ at ambient temperature displayed three single resonances due to the C-Me ($\delta$ 2.20) and methoxy ($\delta$ 3.51 and 4.03) protons. At about -10°C, the resonances arising from the C-Me protons were appreciably broadened when compared to the corresponding signals at room temperature, whereas the methoxy groups resonances remained unchanged. The C-Me protons coalescences near -55°C and appeared as a fairly symmetrical line at -60°C. The variable temperature spectra allowed calculating the free-energy barrier for the N-aryl bond rotation16 in 4a (Scheme IV).

Using the expression $k=\pi\Delta\nu/\sqrt{2}$, first order rate constant (k=109.9 s$^{-1}$) was calculated for the N-aryl bond rotation in 4a at -55°C (Table I).

Application of the absolute rate theory with a transmission coefficient of 4a gave free-energy activation ($\Delta G^\neq$) of 44.4 kJ.mol$^{-1}$, where all known sources of errors were estimated and included17. The experimental data available were not suitable for obtaining meaningful values of $AH^\neq$ and $AS^\neq$, even though the errors in $\Delta G^\neq$ were not large18. It is
Scheme I — Rotation around aryl-nitrogen single bond.

Scheme II — Rotation and inversion mechanism in C=N compounds

Scheme III — Iminolactone synthesis

Scheme IV — Mechanism of cis-trans (E-Z) interchange
necessary to mention that, measurement of different chemical shift in a series of low variable spectra was too less so that changes in first order rate constant and also the free-energy of activation are negligible in comparison with the results have been previously mentioned for -60°C (ref.14).

Experimental Section
The dynamic ¹H NMR spectrum was measured on a BRUKER DRX-500 AVANCE instrument with CDCl₃ as a solvent at 500.1 MHz.

Conclusion
In conclusion, dynamic NMR effects were observed in the ¹H NMR spectra of products 4a and 4b and were attributed to restricted rotation around the aryl-nitrogen bonds and amounts of ΔG⁻ for interconversion of these compounds are about (44.4 and 45.3)±2 kJ.mol⁻¹.

Acknowledgements
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References

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<th>Resonance C-Me</th>
<th>Δν (Hz)</th>
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<th>Tc (K)</th>
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