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Note

Dynamic ^{1}H NMR study of rotational energy barrier around the aryl-nitrogen single bond in γ-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 γ-spiroiminolactones such as dimethyl-5-(2,6-dimethylphenylimino)-6'-oxo-5*H*,6*H*'-spiro[furan-2,5'-[1,10]phenanthroline]-3,4-dicarboxylate and di-*tert*-butyl-5-(2,6-dimethylphenylimino)-6'-oxo-5*H*, 6*H*'-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 γ-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, γ-spiroiminolactones, isocyanides, acetylenic esters

One of the most important reactions for the preparation of the heterocyclic systems is the multi-component reaction[1,2]. Earlier literature revealed the preparation of spiroiminolactones and derivatives[3-7].

The alkyl or aryl-nitrogen single bonds and the polarized carbon-carbon double bonds are reported[8-11]. The isomerism of C=N double bonds is importance in oximes, imines, hydrazones, and so on[12]. The question that arises in *cis-trans* isomerization about a C=N bond is whether the process is a true rotation or an inversion (flipping) of the nitrogen substituent *via* an *sp*-hybridized transition state[12,13].

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 spectroscopy[14]. Thus, herein the free-energy of activation ($\Delta G^{\neq}$) for restricted rotation around the aryl-nitrogen single bonds of γ-spiroiminolactones **4a** and **4b** (**Scheme I**) is described..

Results and Discussion

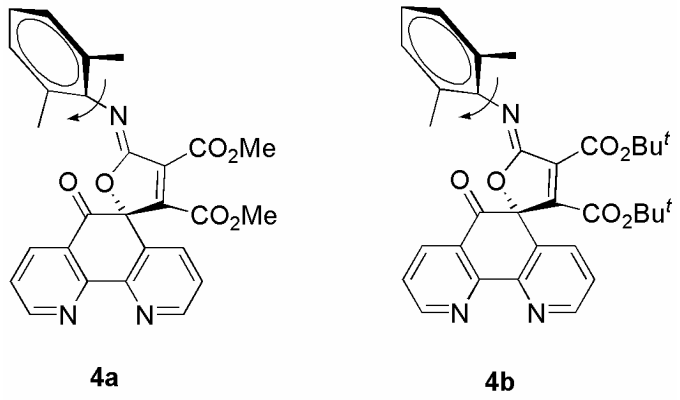
Implication is that the two processes (*cis-trans* isomerization and racemization) occur *via* the same transition stat, as shown in **Scheme II**, this transition state must involve nitrogen inversion. To eliminate the (unlikely) possibility that two separate processes, C-N single bond rotation around 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 yields[15].

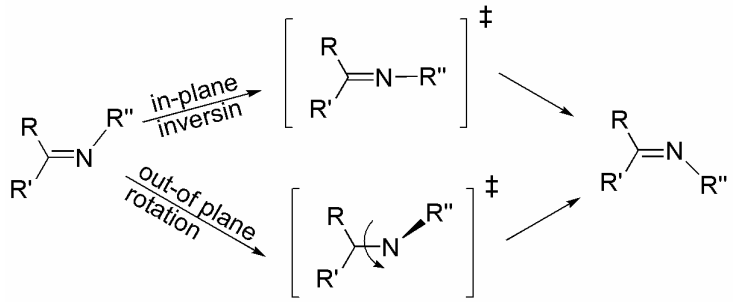
The ^{1}H NMR spectrum of **4a** in $CDCl_3$ at ambient temperature displayed three single resonances due to the C-Me (δ 2.20) and methoxy (δ 3.51 and 4.03) protons. At about -10ºC, the resonances arising from the C-Me protons were appreciably broadened when compared to the corresponding signals at room 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 rotation[16] in **4a** (**Scheme IV**).

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

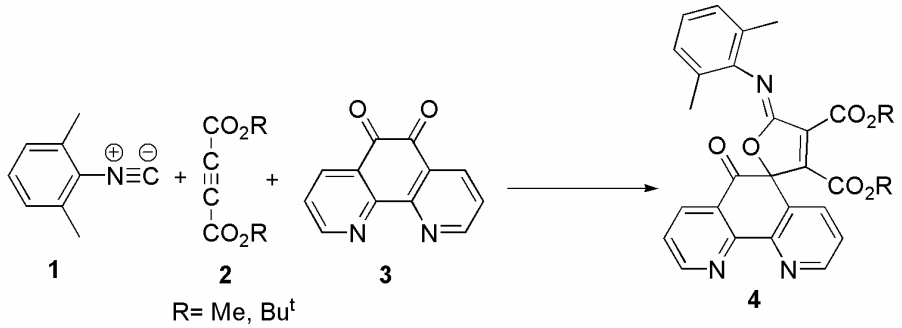
Application of the absolute rate theory with a transmission coefficient of **4a** gave free-energy activation ($\Delta G^{\neq}$) of 44.4 kJ.mol^{-1}, where all known sources of errors were estimated and included [17]. The experimental data available were not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ were not large[18]. It is



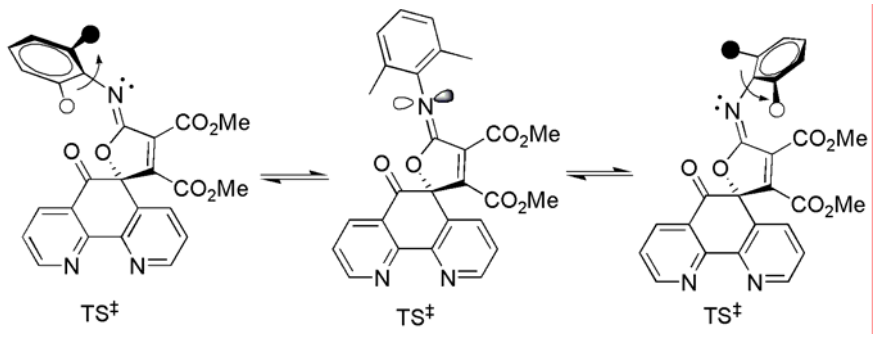
Scheme I — Rotation around aryl-nitrogen single bond.



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



Scheme III — Iminolactone synthesis



Scheme IV — Mechanism of *cis-trans* (*E-Z*) interchange

Table I — Selected proton chemical shift (at 500.1 MHz, in ppm, Me_4Si) and calculated activation parameters (kJ mol^{-1}) for **4a** and **4b** in $CDCl_3$ solvent.

Compd	Temp (°C)	Resonance *C*-Me	Δν (Hz)	k (s^{-1})	T_C (K)	$\Delta G^{\neq}$ (kJ. mol^{-1})
4a	25	2.20	—	—	—	—
	-60	2.21 2.14	35	109.9	218	44.4±2
4b	25	1.90	—	—	—	—
	-70	1.91 1.81	50	111.0	223	45.3±2

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 $CDCl_3$ 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 $\Delta G^{\neq}$ for interconversion of these compounds are about (44.4 and 45.3)±2 kJ.mol^{-1}.

Acknowledgements

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References

1 Ugi I, *Angew Chem Int Edn, Eng*, 21, **1982**, 810.
2 Ugi I, Lohberer S, Karl R & Introst B M, *Comprehensive Organic Synthesis*, Edited by Fleming I, Vol. 2, (Pergamon, Oxford), **1991**, pp. 1083-1106.
3 Maghsoodlou M T, Hazeri N, Habibi-Khorassani S M, Heydari R, Marandi G & Nassiri M, *Synth Commun*, 35, **2005**, 2569.
4 Maghsoodlou M T, Hazeri N, Habibi-Khorassani S M, Marandi G & Nassiri M, *Synth Commun*, 35, **2005**, 2771.
5 Esmaeili A A & Darbaniani M, *Tetrahedron*, 59, **2003**, 5545.
6 Nair V, Vinod A U, Somarajan-Nair J, Sreekanth A R & Rath N P, *Tetrahedron Lett*, 41, **2000**, 6675.
7 Nair V, Vinod A U, Abhilash N, Menon R S, Santhi V, Varma, R L, Viji S, Mathew S & Srinivas R, *Tetrahedron*, 59, **2003**, 10279.
8 Maghsoodlou M T, Yavari I, Nassiri F, Djahaniani H & Razmjoo Z, *Monatsh Chem*, 134, **2003**, 1585.
9 Yavari I, Hazeri N, Maghsoodlou M T & Zabarjad-Shiraz N, *Monatsh Chem*, 132, **2001**, 683.
10 Maghsoodlou M T, Habibi-Khorassani S M, Hazeri N, Marandi G & Bijanzadeh H R, *J Chem Res*, **2006**, 73.
11 Hazeri N, Habibi-Khorassani S M, Maghsoodlou M T, Marandi G, Nassiri M & Ghulame-Shahzadeh A, *J Chem Res*, **2006**, 185.
12 Kalinowski H O & Kessler H, *Top Streo Chem*, 7, **1972**, 295.
13 Eliel E L, Wilen S H & Mander L N, *Stereochemistry of Organic Compounds*, (John Wiley & Sons, New York), **1994**, Chapter 9, pp. 551-553.
14 Oki M, *Application of Dynamic NMR Spectroscopy to Organic Chemistry*, Edited by VCH publishers, **1985**.
15 Maghsoodlou M T, Habibi-Khorassani S M, Hazeri N, Heydari R, Marandi G & Nassiri M, *J Chem Res*, **2006**, 225.
16 Cervinka O, *The Chemistry of Enamines*, Edited by Roppoport Z (Wiley, New York) **1994**, Part.1, p. 219.
17 Gunther H, *NMR Spectroscopy*, 2nd edn (Wiley, New York), **1995**, Capter 9.
18 Anet F A L & Anet R, *Dynamic Nuclear Maghnetic Resonance Spectroscopy*, Edited by Cotton F A, Jackman L M (Academic Press, New York), **1975**, Chapter 8.