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HINDERED ROTATION IN SEVERAL DIARYLAMIDINES

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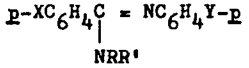
During our study of the substitution of diarylimidoyl chlorides by amines,[1] we prepared the diarylamidines Ia-Ig and found that Ia-If showed temperature-dependent



$$\underline{p}\text{-}XC_6H_4\underset{\displaystyle NRR'}{\underset{|}{C}} = NC_6H_4Y\text{-}\underline{p}$$

Ia : X=Y=H , R=R'=CHMe$_2$ Ie : X=H , Y=NO$_2$, RR' =(CH$_2$)$_5$

Ib : X=H , Y=NO$_2$, R=R'=CHMe$_2$ If : X=H , Y=MeO , RR' =(CH$_2$)$_5$

Ic : X=Y=H , RR' = (CH$_2$)$_5$ Ig : X=Y=H , R=Ph , R'=Me

Id : X=MeO , Y=H , RR'= (CH$_2$)$_5$

nmr spectra in CDCl$_3$. At room temperature, only one doublet and one septet were observed for the two isopropyl groups of Ia and Ib. On cooling, the doublet first broadens, then separates into two singlets below the coalescence temperature, and then gives two sharp doublets. The corresponding changes in the septet were not followed closely due to its low intensity and multiplicity.

The broad singlet of the α-methylene protons of the piperidine groups of Ic-If broadens at room temperature and separates into two broad singlets on cooling. The Table gives the chemical shifts in the range of slow and fast exchange, the separation of the peaks in Hz ($\Delta\nu$), and the coalescence temperature T_c with the corresponding $\Delta G^{\ddagger}$. The $\Delta H^{\ddagger}$ and the $\Delta S^{\ddagger}$ values which were derived from the temperature-dependence of the rate coefficients, using the peak separation or the peak widths[2] should be regarded only as approximate.[2]

Table

Compound	δ (T, °C) [a]	$\Delta\nu$ Hz	T_c, °C	$\Delta G^{\ddagger}$ Kcal/m	$\Delta H^{\ddagger}$ Kcal/m	$\Delta S^{\ddagger}$ e.u.
Ia	1.14 , 1.67(-71) ; 1.42(32)[b]	54	-13.9	12.6	12.6±0.8	ca. 0
Ib	1.13 , 1.61(-26) ; 1.39(55)	48	+10.1	13.9	13.3±1.0	ca. 0
Ic	3.05 , 3.70(-69) ; 3.41(49)	65	-21.9	12.1	12.3±1.2	ca. 0
Id	3.06 , 3.68(-63) ; 3.40(55)	62	-30.4	11.7	8.9±0.6	11±2
Ie	3.14 , 3.70(-59) ; 3.44(30)	55.5	-4.8	13.1	17.7±1.7	17±6
If	2.99 , 3.65(-59) ; 3.33(30)	66	-17.0	12.3	16.2±1.2	15±5
Ig	3.58(30)					

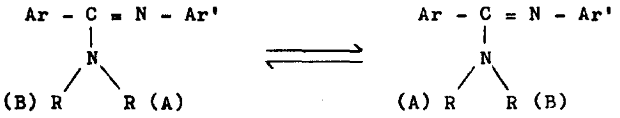
[a] Data are for the sharp signals (δ_{Me} for Ia,Ib , $\delta_{\alpha\text{-}CH_2}$ for Ic-If and $\delta_{N\text{-}Me}$ for Ig) in δ units downfield from TMS at the highest and the lowest temperatures studied.

[b] The width of the lines of the sharp doublet was unchanged from 30° to 155° in 1,2-dichlorobenzene.

In trifluoroacetic and pentafluoropropionic acids at 30° , Ia shows a pair of methyl doublets with $\Delta\nu$=51 Hz and two methine septets with $\Delta\nu$=31 Hz. No spectral change was observed up to 65° in trifluoroacetic acid, but in pentafluoropropionic acid at 105° , $\Delta\nu$(Me) = 49 Hz and $\Delta\nu$ (CH) = 32 Hz and the signals are slightly broader than at 30°.

The transformation of the two magnetically non-equivalent alkyl groups at low temperature to two equivalent groups at higher temperature may be due either to (a)syn-anti isomerization (eqn. 1)[3,4] or (b)to restricted rotation around the carbon-nitrogen single bond (eqn. 2) which creates a barrier for the IIa $\rightleftharpoons$ IIb transformation. This results from the partial double bond character of the C-N bond (see IIc).

syn anti (1)



(IIa) (IIb) (2)

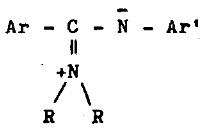
Identification of the only one barrier observed as that shown in eqn. 2 is based on the following:

(a)In all our systems the two magnetically different species observed at low temperatures are in a 1 : 1 ratio. This is a corollary of eqn. 2, but it is highly improbable that for all our compounds the syn and the anti isomers have equal energies.

(b)No change in the methoxyl signal of Id and If was observed on cooling, as expected by eqn. 2. Such change was observed for the syn-anti isomerization of N-arylketimines.[5]

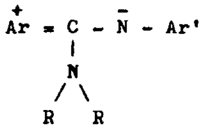
(c)Our $\Delta G^{\ddagger}$ values (12-14 Kcal/mole) are similar to the $\Delta G^{\ddagger}$ values which were observed for the rotation around the C-N single bond of $Me_2NCH{:}NC_6H_4NO_2$-p (14.1 Kcal/mole in chloroform)[6a] or for $Me_2NCH{:}NBu$-t (12 Kcal/mole in toluene).[6b] We did not find $\Delta G^{\ddagger}$ values for the syn-anti isomerization of amidines. From data on the $PhC{:}CX_2$ series where X=OMe,SMe and NR_2,[7] and if steric and electronic effects in other related systems are taken into account,[5,8] $\Delta G^{\ddagger}$ for the syn-anti isomerization is in the range observed for Ia-If.

(d)Since structure IIc is responsible for the barrier for rotation,[6a] the barrier height should be raised for electron-attracting Ar'. It should be lowered for electron-donating Ar due to the contribution of (IId), as found in other systems.[4] On the other hand, both the lateral shift (inversion) and the rotation mechanisms[3] for the syn-anti isomerization show a positive ρ value (1.5-2.2)[9] for the substituents on the nitrogen and a positive but much lower ρ value (0.1-0.35)[3] for the substituents on carbon. The increase in $\Delta G^{\ddagger}$ on changing the N-phenyl to N-p-nitrophenyl ("ρ"= -3.5 for the pair Ia,Ib at 30° and -2.4 for the pair Ic,Ie at -5°) and the C-phenyl to C-p-methoxyphenyl ("ρ"= -3.1 for the pair Ic,Id at 30°) fits only eqn. 2. The increase of $\Delta G^{\ddagger}$ by 0.5 Kcal/mole when the NR_2 group becomes larger has a precedent,[10] and an explanation in terms of higher steric hindrance in the transition state compared with the ground state is possible.[4] However, this is contrary to the syn-anti isomerization



$Ar-C(=\overset{+}{N}R_2)-\bar{N}-Ar'$

(IIc)



$\overset{+}{Ar}=C(-NR_2)-\bar{N}-Ar'$

(IId)

(by inversion)[4] since an increase in the ground state energy of both isomers is expected on increasing the bulk of the NR$_2$ group.

The barrier for internal rotation in the acidic solvents, where coalescence was not achieved, is apparently much higher than in CDCl$_3$. This behaviour is anticipated by our mechanism if the amidine is protonated by the strong acids, and when the site of protonation is the negatively charged nitrogen of IIc.

Only Ig however, did not show any temperature-dependent spectra down to -70°. This may be due to either a greater free energy difference than 2 Kcal/mole between the two conformers (enabling only the thermodynamically more stable conformer to be observed), or a rotation barrier either too high or too low to be measured by the nmr technique.[11]

In view of the similar $\Delta G^{\ddagger}$ values expected for both syn-anti isomerization and the restricted rotation, the fact that syn-anti isomerization was not observed is probably due to the sufficient ground state energy difference between the syn and the anti isomers.

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