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REACTION AND SUBSTITUENT CONSTANTS FOR PYRAMIDAL INVERSION

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We wish to show that from a Hammett ρ for the nitrogen inversion of 1-aryl-2,2-dimethylaziridines,¹ where the correlation is with σ_p^- of the p-substituent in the phenol,^{1,2} substituent constants for pyramidal inversion ($\sigma_{inv.}$) can be derived for substituents directly on the inverting atom.

In order to determine the Hammett ρ at 25°, the inversion rates of these 1-arylaziridines at 25° were determined from the experimental $\Delta G^\ddagger$ values¹ adjusted to 25° by assuming $\Delta S^\ddagger = 0$. A plot of these $\log k$ values vs σ_p^- gave a ρ of 2.5³ (Fig. 1). This value was used in Fig. 2 to determine $\sigma_{inv.}$ constants for the substituents on the nitrogen atom. The $\sigma_{inv.}$ constants so determined were used to determine ρ values for other series as shown in Fig. 3, using experimentally determined rate constants adjusted to 25°. From these ρ values, a number of $\sigma_{inv.}$ constants

Fig. 1. $\log k$ for N inversion vs σ_p^- ; solvent, CF_2Cl_2 .

Fig. 2. $\log k$ for nitrogen inversion in aziridines vs $\sigma_{inv.}$; see Table I for the data. The x's represent the points in Fig. 1 adjusted to solvent C, Table I; $\sigma_{inv.}$ for aryl = $\sigma_{inv.}$ for phenyl + σ_p^- for the p-substituent. Four substituents, which were present in the 2,2-dimethyl series, determined the ρ of the carbon unsubstituted aziridine series. The H substituent, which was present in this series, determined the position of the $\sigma_{inv.} = 0$.

were determined for substituents that were not present in the aziridine series. The data in Fig. 2 and 3 are summarized in Table 1. Substituents that were common to more than one series were $\text{Si}(\text{CH}_3)_3$, COCH_3 , $\text{SiH}(\text{CH}_3)_2$, SC_6H_5 , C_6H_5 , H, $\text{C}(\text{CH}_3)_3$, cyclohexyl, $\text{CH}(\text{CH}_3)_2$, CH_3 , NH_2 , Br, Cl, and OH. The other substituents occurred in only one series and those $\sigma_{inv.}$ constants are, therefore, subject to greater error.⁷ The $\sigma_{inv.}$ constants are many times larger in value than the Hammett σ constants. This can be attributed to the fact that the substituent is directly on the reacting center in inversion. There are three well-known factors evident in the order of the $\sigma_{inv.}$ constants: electronegativity, conjugative and steric effects.⁸

In the acyclic amine series, the $\sigma_{inv.}$ constants appear to be additive.⁹ N-Fluoro-N-methylformamide has a nitrogen atom with substituents of widely

Fig. 3. Log k for pyramidal inversion vs σ_{inv} constants. The points on the dashed lines are for the sum of σ_{inv} constants of the substituents on the inverting atom.

differing σ_{inv} constants, the sum of which is -4.9 . The log k corresponding to $\sigma_{\text{inv}} = -4.9$ determined from the $\text{H}_2\text{N}-$ line in Fig. 3 is 4.6, nearly the same as the 4.7 determined experimentally¹⁰ and adjusted to 25°.

From Fig. 3 can be seen that the cyclic amine series¹² converge to a point where $\log k = 12.8$ and $\sigma_{\text{inv}} = 4.9$. This indicates that a substituent with σ_{inv} of 4.9 would cause the amine to be effectively planar irrespective of ring constraints.¹³ The substituent, difluorophosphine, appears to have a σ_{inv} constant of 4.3 or greater, because it has been shown to give a planar amine.¹⁴

The difference in barrier between the cyclic amines and the oxaziridines at $\sigma_{\text{inv}} = 4.9$ is 6.5 kcal/mol, an increase due to the presence of the oxygen atom. Although there is only limited data for the 5 and 6 membered rings containing both O and N atoms as in the oxaziridines, the intersection of the line for the 6 membered ring with the oxaziridine line at $\sigma_{\text{inv}} = 4.9$ gives a ρ of 0.9 which is the same ρ as for the acyclic amines and homopiperidines. Also on this same line would be the acyclic hydroxylamine series assuming additive σ_{inv} constants. Therefore, it appears that the N-O ring series also converge at $\sigma_{\text{inv}} = 4.9$.

The data for acyclic phosphines and arsines are very limited for any one series. However, by plotting the $\log k$ vs the sum of the $\sigma_{\text{inv.}}$ constants, reasonably straight lines can be obtained.¹⁵ The ratio of the ρ values for the acyclic amines, phosphines, and arsines is 0.5: 1.0: 1.25 compared to the 0.34: 1.0: 1.4 ratio of sensitivities for calculated barriers.¹⁶

From the correlation of data reported here, predictions can be made for rates of inversion of many compounds not yet measured. As more experimental data becomes available, the values of the $\sigma_{\text{inv.}}$ constants reported here may need to be revised.

Table 1. Substituent Constants for Pyramidal Inversion.

Substituent	$\sigma_{\text{inv.}}$	$\log k^a$ (25°)	Substituent	$\sigma_{\text{inv.}}$	$\log k^a$ (25°)
-Si(CH ₃) ₃	+ 4.4	-1.2B ^{b,c} , -5.9D ^{b,c}	-C(CH ₃) ₃	0	8.5V ^z , -0.6N ^{aa,n} , -6.3T ^{bb}
-COCH ₃	+ 3.8	>8.7V ^d , -1.6D ^e , 4.1 ^f	-cyclohexyl	- 0.2	-11.3D ^{t,u} , -12.2N ^{l,n}
-SiH(CH ₃) ₂	+ 3.5	3.9R ^{b,g} , -0.2 ^{b,g}	-CH(CH ₃) ₂	- 0.3	-0.1C ^l , -13.6D ^{t,u}
-COH	+ 3.5	12.0N ^h			3.7M ^{cc} , 1.9M ^{cc} , -0.3C ^r
-CO ₂ CH ₃	+ 3.1	7.8V ^d			-10.1T ^{dd}
-PO(C ₆ H ₅) ₂	+ 2.7	6.9M ⁱ	-CH ₂ C ₆ H ₅	- 0.3	-0.3C ^l
-CN	+ 2.6	11.3N ^j	-CH ₃	- 0.6	9.3N ^{ee} , 8.5V ^z , 8.2V ^{ff}
-CON(CH ₃) ₂	+ 2.3	5.7V ^d			8.0C ^{gg} , 7.6C ^o , 6.8C ^{gg}
-SCCl ₃	+ 2.3	6.3M ^k			6.3R ^{p,n} , 5.5C ^{gg} , 2.8M ^{hh}
-NO ₂	+ 2.1	10.8N ^j			1.3C ^{hh} , -1.0C ^r , -2.2C ^{r,n}
-As(CH ₃) ₂	+ 1.9	5.4M ^l	-NH ₂	- 1.6	-10.9T ^{bb,ii}
-SO ₂ C ₆ H ₅	+ 1.6	3.8C ⁱ			7.3N ^{jj} , 7.0C ^{kk} , 6.8C ^o
-SO ₂ CH ₃	+ 1.5	3.5C ^d			5.2R ^{l,n}
-SC ₆ H ₅	+ 1.4	4.2M ^k , 3.3C ⁱ	-Br	- 2.2	6.4R ^{o,n} , 4.5M ^p
-C ₆ H ₅	+ 1.3	4.4R ^{m,n} , 3.2S ^{d,n} , -4.4R ^s	-Cl	- 2.5	6.3M ^{ll} , 5.8C ^{mm} , 6.2C ^{gg}
		-9.6D ^{t,u} , -10.8D ^{t,u,v}			6.0C ^o , 4.9A ^{nn,n} , 5.1R ^{oo,n}
		-18.8D ^{w,u}			4.2M ^p , 3.0C ^{gg} , -5.6B ^{pp,n}
-SOC ₆ H ₅	+ 1.2	2.8C ⁱ			-7.2R ^{qq,n}
-SCH ₃	+ 0.9	2.9C ^k	-OCH ₃	- 2.5	5.2A ^{nn,n}
-H	0	8.5N ^x , -0.5R ^{y,n}	-OCOCH ₃	- 4.9	4.0C ^{rr}
			-OH	- 5.5	3.5C ^{rr} , 3.4C ^o , 3.3A ^{nn,n}
			-F	- 7.8	1.7R ^{ss,n}

^a Calculated from the Eyring equation assuming a transmission coefficient of unity; $\Delta G^\ddagger_{25^\circ}$ was calculated from $\Delta G^\ddagger_{25^\circ} = \Delta G^\ddagger_T + RT - RT_{25^\circ}$, assuming $\Delta S^\ddagger = 0$. $\log k = \log k_0 + \rho \sigma_{\text{inv.}}$ where $\log k_0$ is for the H substituent. Solvents: A, (CD₃)₂CO; B, C₆H₆; C, DCD₃, CHClF₂, CHFCl₂; D, decalin, toluene, bromonaphthalene; M, CH₂Cl₂; N, no solvent; R, CCl₄, CF₂Cl₂, CFC₃; S, CS₂; T, C₂Cl₄; V, CD₂ = CDCl. ^b R.D. Baechler, J.P. Casey, R.J. Cook, G. Senkler and K. Mislow, J. Amer. Chem. Soc., 94, 2859 (1972). ^c Sum of $\sigma_{\text{inv.}}$ for (C₆H₅)((CH₃)₂CH)(Si(CH₃)₃) = 5.4. ^d F.A.L. Anet and J.M. Osyany, J. Amer. Chem. Soc., 89, 352 (1967). ^e W. Egan and K. Mislow, *ibid.*, 93, 1805 (1971); sum of $\sigma_{\text{inv.}}$ for (C₆H₅)(CH(CH₃)₂)(COCH₃) = 4.8. ^f G. Senkler in K. Mislow, Trans. N.Y. Acad. Sci., 35, 227 (1973); sum of $\sigma_{\text{inv.}}$ for (C₆H₅)(COCH(CH₃)₂)₂ = 8.9. ^g Sum of $\sigma_{\text{inv.}}$ for (C₆H₅)(SiH(CH₃)₂)₂ = 8.3.

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