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Kinetic Study of the Reactions of Some 2-L-3-Y-5-nitrothiophenes with Primary and Secondary Amines in Benzene

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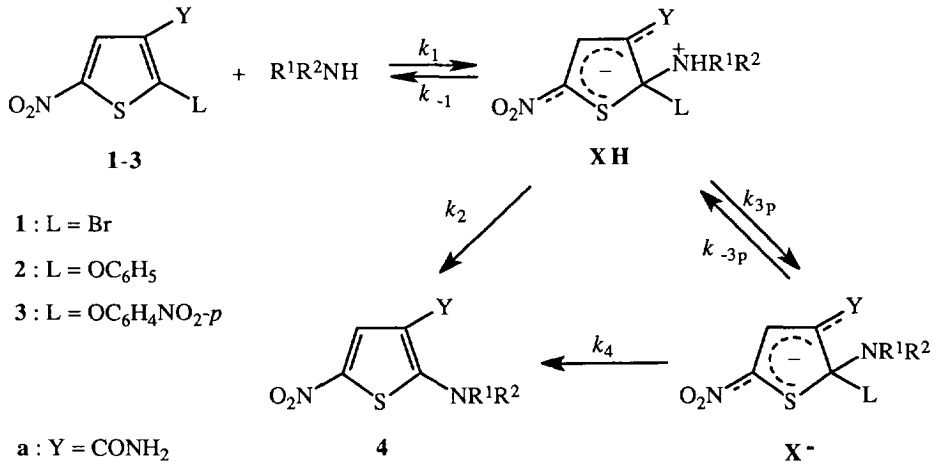
Abstract: The kinetics of the reactions of some 2-L-3-Y-5-nitrothiophenes (L = Br, OC_6H_5, $OC_6H_4NO_2$-*p*; Y = $CONH_2$, CO_2Me) with n-butylamine, benzylamine, pyrrolidine and piperidine in benzene at 293.15 K have been studied with the aim of obtaining an insight into the role played by the *ortho*-like substituent (Y) in determining the occurrence and the form of base catalysis. The results obtained have also allowed to gain important information about the interactions between the substituents, the thiophene ring and the reaction centre.

In previous publications[1] we have shown that S_NAr reactions of thiophene derivatives with amine nucleophiles can be catalysed. The observation of base catalysis and the form of the catalysis law depend on the nature of the aromatic substrate, the class of the amine, the nucleofugal group and the solvent.[2]

The apparent second-order kinetic constant, k_A, obtained by dividing the pseudo-first-order rate constant by amine concentration, can be expressed as a function of the catalysing base(s) by means of eqn. (1), which is obtained by applying the steady state approximation to the reaction intermediates of the attachment-detachment mechanism shown in the Scheme.



1-3

1 : L = Br

2 : L = OC_6H_5

3 : L = $OC_6H_4NO_2$-*p*

a : Y = $CONH_2$

b : Y = CO_2Me

R^1R^2NH = pyrrolidine, piperidine, *n*-butylamine, benzylamine

Scheme

$$k_A = [k_1k_2(k_{-3p} + k_4) + k_1k_{3p}k_4]/[(k_{-1} + k_2)(k_{-3p} + k_4) + k_{3p}k_4] \quad (1)$$

In the absence of bases added from the outside, the following equations apply

$$k_{3p} = k_{3p}^{Am}[Am] \quad (2)$$

$$k_{-3p} = k_{-3p}^{AmH}[AmH^+] \quad (3)$$

$$k_4 = k_4^{AmH}[AmH^+] \quad (4)$$

where k_{3p}^{Am} refers to deprotonation of XH by the amine (Am); k_{-3p}^{AmH} refers to the protonation of X^- by AmH^+ and k_4^{AmH} refers to general-acid catalysed leaving group detachment by the protonated amine.

According to eqn. 1, when $k_2 >> k_{-1}$ the reaction shows absence of base catalysis; the overall reaction rate is controlled by the formation of the reaction intermediate and $k_A = k_1$. On the other hand, when $k_2 < k_{-1}$, the reaction needs base catalysis. The mechanism of the base catalysed step implies the removal of the ammonium proton from the intermediate **XH**: for this two main possibilities are currently accepted:[3] one is a rate-limiting proton abstraction by the base to form deprotonated intermediate, followed by rapid leaving-group expulsion ($k_4 >> k_{-3p}$); the other involves a rapid equilibrium deprotonation followed by rate-limiting general acid-catalysed detachment of the nucleofuge ($k_4 << k_{-3p}$, SB-GA mechanism).

It can be shown that, in both cases, there is the same formal dependence of k_A on the amine concentration [(eqn. (5)] and thus the two mechanisms of base catalysis cannot be distinguished experimentally.

$$k_A = (k_1k_2 + k_1k_3^{Am}[Am])/(k_{-1} + k_2 + k_3^{Am}[Am]) \quad (5)$$

In this paper we report on the results of a kinetic study of the reactions of some 2-L-3-Y-5-nitrothiophenes (**1-3**) with two primary amines [*n*-butylamine (BuA) and benzylamine (BzA)] and two secondary amines [pyrrolidine (PYR) and piperidine (PIP)] in benzene, at 293.15 K.

The aim of this work was to obtain information about the role of the *ortho*-like substituent (Y) in determining the occurrence and the form of base catalysis and to gain a deeper knowledge of the substituent-ring-reaction centre interactions along the reaction pathway.

RESULTS AND DISCUSSION

Kinetic Data

The apparent second-order kinetic constants, k_A, for the amino substitutions of compounds **1-3**, at various nucleophile concentrations, are reported in Tables 1-3.

An examination of kinetic data in Table 1 shows that for the reactions of compounds **1** with pyrrolidine or piperidine k_A is almost independent of the initial amine concentration. Thus, these reactions are second-order overall, first-order both in substrate and in nucleophile. This corresponds to the situation where $k_A = k_1$.

The apparent second-order kinetic constants, k_A, for the reactions of the same substrates with *n*-butylamine or benzylamine increases linearly with increasing amine concentration obeying eqn. (6) and showing k_{Am}/k_0 ratios (Table 4) which are not representative of genuine base catalysis according to Bunnett's classification.[4]

$$k_A = k_0 + k_{Am}[Am] \quad (6)$$

Kinetic data in Table 2 for the reactions of compounds **2** with *n*-butylamine or benzylamine give a similar linear correlation between k_A and amine concentration. The relevant k_{Am}/k_0 ratios are also shown in Table 4.

The curved concave downwards plots (not shown) of k_A values for the reactions of compounds **2** with pyrrolidine or piperidine (Table 2) as a function of amine concentration show that k_A is a hyperbolical function of the base.

An analysis of kinetic data for the reactions of compounds **3** with primary amines (Table 3) shows that k_A is independent of [Am] or increases linearly with increasing amine concentration. On the other hand, k_A is a curvilinear function of amine concentration for secondary amines.

In the case of linear relationships the kinetic data have been treated by a least-squares method and the k_{Am}/k_0 ratios obtained are reported in Table 4. In the case of curvilinear (hyperbolic) relationships, since the curves cross the origin of the axes, that is, k_A extrapolates to zero for [Am] = 0, equation (5), which is representative

of this situation can be simplified to equation (7), which, in turn, can be 'inverted' and give equation (8).

$$k_A = k_1 k_3^{Am}[Am]/(k_{-1} + k_3^{Am}[Am]) \quad (7)$$

$$1/k_A = 1/k_1 + k_{-1}/k_1 k_3^{Am}[Am] \quad (8)$$

Table 1. Apparent Kinetic Constants[a] for the Reactions of 2-Bromo-3-Y-5-nitrothiophenes (1) with some Amines in Benzene at 293.15 K

			Y = $CONH_2$			
10^2[PYR]/M	0.202	0.303	0.404	0.505		
k_A	0.189	0.197	0.200	0.207		
10^2[PIP]/M	0.505	1.01	2.02			
10 k_A	0.693	0.725	0.757			
[BuA]/M	0.102	0.203	0.305	0.406	0.508	
10^4 k_A	4.05	4.69	5.42	6.12	6.82	
[BzA]/M	0.505	0.606	0.707	0.808	0.909	1.01
10^4 k_A	1.82	1.98	2.17	2.29	2.46	2.71
			Y = CO_2CH_3			
10^2[PYR]/M	0.249	0.498	0.996			
k_A	0.147	0.149	0.147			
10^2[PIP]/M	0.505	1.01	1.50			
k_A	0.432	0.437	0.439			
[BuA]/M	0.102	0.203	0.305	0.406	0.508	
10^4 k_A	2.82	3.69	4.54	5.42	6.28	
[BzA]/M	0.5	0.6	0.7	0.8	0.9	1
10^4 k_A	1.19	1.37	1.54	1.66	1.83	2.14

[a] $dm^{-1}mol^{-1}s^{-1}$; the kinetic constants were reproducible within ± 3%.

Table 2. Apparent Kinetic Constants[a] for the Reactions of 2-Phenoxy-3-Y-5-nitrothiophenes (2) with some Amines in Benzene at 293.15 K

$Y = CONH_2$

10^3[PYR]/M	0.205	0.256	0.307	0.358	0.505	0.606	0.708	0.808	1.01	1.49	2.02	2.49	3.03
$10\,k_A$	0.175	0.195	0.218	0.248	0.268	0.288	0.298	0.306	0.330	0.356	0.366	0.379	0.390
10^3[PYR]/M	4.04	4.98	6.06	8.19	10.1								
$10\,k_A$	0.398	0.396	0.410	0.424	0.422								
10^2[PIP]/M	0.205	0.307	0.410	0.614	0.819	1.02	2.04	3.06	4.10	5.12			
$10^2\,k_A$	0.962	1.23	1.42	1.68	1.92	2.00	2.41	2.66	2.77	2.98			
[BuA]/M	0.102	0.204	0.306	0.408	0.510	0.765							
$10^4\,k_A$	2.32	2.67	3.10	3.72	4.00	5.18							
[BzA]/M	0.693	0.792	0.891	0.990									
$10^4\,k_A$	1.18	1.30	1.39	1.50									

$Y = CO_2CH_3$

10^2[PYR]/M	0.104	0.130	0.156	0.182	0.208	0.260	0.312	0.364	0.416	0.520	0.624	0.832	1.04
k_A	0.117	0.131	0.148	0.155	0.170	0.191	0.201	0.215	0.212	0.232	0.252	0.256	0.261
10^2[PIP]/M	0.204	0.255	0.306	0.357	0.408	0.510	0.612	0.714	0.816	0.918	1.02	1.28	1.53
$10\,k_A$	0.195	0.235	0.277	0.316	0.347	0.411	0.467	0.512	0.564	0.634	0.659	0.732	0.825
[BuA]/M	0.1	0.2	0.3	0.4	0.5	0.6							
$10^3\,k_A$	1.34	1.60	1.88	2.14	2.35	2.71							
[BzA]/M	0.4	0.5	0.6	0.7	0.8	0.9	1						
$10^4\,k_A$	4.34	4.72	5.47	5.99	6.57	7.09	7.71						

[a] As in Table 1.

Table 3. Apparent Kinetic Constants[a] for the Reactions of 2-*p*-Nitrophenoxy-3-Y-5-nitrothiophenes (3) with some Amines in Benzene at 293.15 K

							Y = $CONH_2$							
10^3[PYR]/M	0.153	0.204	0.255	0.306	0.357	0.408	0.510	0.612	0.816	1.02	1.53	2.04	2.55	3.06
k_A	0.435	0.495	0.537	0.533	0.532	0.583	0.616	0.606	0.681	0.673	0.716	0.739	0.757	0.790
10^2[PIP]/M	0.202	0.252	0.303	0.354	0.404	0.505								
k_A	0.213	0.240	0.257	0.281	0.294	0.312								
[BuA]/M	0.402	0.603	0.804	1.00	2.00	3.00								
$10^3\ k_A$	2.81	2.89	2.80	2.63	2.71	2.83								
[BzA]/M	0.100	0.151	0.201	0.301	0.402	0.502	0.602							
$10^3\ k_A$	0.870	0.887	0.999	1.13	1.31	1.43	1.65							
							Y = CO_2CH_3							
10^3[PYR]/M	0.596	0.794	0.992	1.19	1.49	1.98	2.48							
k_A	0.835	0.947	1.07	1.16	1.30	1.44	1.46							
10^2[PIP]/M	0.202	0.252	0.303	0.354	0.404	0.454	0.505							
k_A	0.202	0.236	0.272	0.302	0.331	0.358	0.383							
10 [BuA]/M	0.202	0.303	0.404	0.505	0.606	0.707	0.808	0.909						
$10^3\ k_A$	6.58	6.75	7.18	7.27	7.66	7.99	8.20	8.31						
10 [BzA]/M	0.502	1.00	1.51	2.01	3.01	4.02								
$10^3\ k_A$	1.57	1.70	2.10	2.22	2.65	2.99								

[a] As in Table 1.

Table 4. Linear Regression Analysis[a] of Apparent Second Order Kinetic Constants, k_A, for the Reactions of 2-L-3-Y-5-nitrothiophenes (1-3) with some Amines in Benzene, at 293.15 K, according to the Equation $k_A = k_0 + k_{Am}[Am]$

Y	L	R^1R^2NH	$k_0 \pm s_0$	$k_{Am} \pm s_{Am}$	n	r	k_{Am}/k_0
$CONH_2$	Br	PYR	0.195 ± 0.05	—	4	—	–
$CONH_2$	Br	PIP	0.0725 ± 0.032	—	3	—	–
$CONH_2$	Br	BuA	$(3.33 \pm 0.02)10^{-4}$	$(6.87 \pm 0.07)10^{-4}$	5	1.000	2.1
$CONH_2$	Br	BzA	$(9.50 \pm 0.63)10^{-5}$	$(1.70 \pm 0.08)10^{-4}$	6	0.995	1.8
CO_2CH_3	Br	PYR	0.145 ± 0.01	—	3	—	–
CO_2CH_3	Br	PIP	0.0436 ± 0.003	—	3	—	–
CO_2CH_3	Br	BuA	$(1.95 \pm 0.01)10^{-4}$	$(8.52 \pm 0.03)10^{-4}$	5	1.000	4.4
CO_2CH_3	Br	BzA	$(3.90 \pm 0.26)10^{-5}$	$(1.60 \pm 0.04)10^{-4}$	6	0.999	4.1
$CONH_2$	OC_6H_5	BuA	$(1.83 \pm 0.06)10^{-4}$	$(4.37 \pm 0.15)10^{-4}$	6	0.998	2.4
$CONH_2$	OC_6H_5	BzA	$(4.50 \pm 0.33)10^{-4}$	$(1.06 \pm 0.04)10^{-4}$	4	0.999	2.4
CO_2CH_3	OC_6H_5	BuA	$(1.07 \pm 0.03)10^{-3}$	$(2.67 \pm 0.08)10^{-3}$	6	0.998	2.5
CO_2CH_3	OC_6H_5	BzA	$(2.00 \pm 0.10)10^{-4}$	$(5.70 \pm 0.13)10^{-4}$	7	0.999	2.8
$CONH_2$	$OC_6H_4NO_2$-*p*	BuA	$(2.78 \pm 0.07)10^{-3}$	—	6	—	–
$CONH_2$	$OC_6H_4NO_2$-*p*	BzA	$(6.79 \pm 0.24)10^{-4}$	$(1.56 \pm 0.06)10^{-3}$	7	0.996	2.3
CO_2CH_3	$OC_6H_4NO_2$-*p*	BuA	$(6.04 \pm 0.08)10^{-3}$	$(2.61 \pm 0.14)10^{-2}$	8	0.992	4.3
CO_2CH_3	$OC_6H_4NO_2$-*p*	BzA	$(1.38 \pm 0.06)10^{-3}$	$(4.13 \pm 0.25)10^{-3}$	6	0.993	3.0

[a] s_0 and s_{Am} are the standard deviations of the regression parameters k_0 and k_{Am}, respectively; r is the correlation coefficient; n is the number of experimental points. The confidence levels for significance of regression are all better than 99.9%.

The plots of $1/k_A$ values as a function of the reciprocals of amine concentration are linear and henceforth it is possible to obtain k_1 values and k_3^{Am}/k_{-1} ratios, by a least-squares treatment of kinetic data. The results of the correlations are reported in Table 5.

Table 5. k_1 and k_3^{Am}/k_{-1} Values for the Reactions of 2-Phenoxy- (2) and 2-*p*-Nitrophenoxy-3-Y-5-nitrothiophenes (3) with some Amines in Benzene at 293.15 K

Y	L	R^1R^2NH	k_1[a]	k_3^{Am}/k_{-1}[b]
$CONH_2$	OC_6H_5	PYR	0.0427	3400
$CONH_2$	OC_6H_5	PIP	0.0298	228
CO_2CH_3	OC_6H_5	PYR	0.312	571
CO_2CH_3	OC_6H_5	PIP	0.170	66.4
$CONH_2$	$OC_6H_4NO_2$-*p*	PYR	0.767	8280
$CONH_2$	$OC_6H_4NO_2$-*p*	PIP	0.462	425
CO_2CH_3	$OC_6H_4NO_2$-*p*	PYR	2.01	1170
CO_2CH_3	$OC_6H_4NO_2$-*p*	PIP	0.944	134

[a] $dm^3mol^{-1}s^{-1}$. [b] $dm^6mol^{-2}s^{-2}$.

k_{Am}/k_0 ratios

According to Bunnett's classification,[4] the k_{Am}/k_0 ratios of Table 4 are not representative of base catalysis. Apart from the low value of these ratios, there are some other considerations which allow us to support this interpretation. The reactions of compounds **1** (L = Br) with secondary amines are second-order overall, that is, $k_2/k_{-1} >> 1$ and $k_A = k_1$. On going from secondary to primary amines, k_2/k_{-1} should increase[5] and therefore the reactions should not need catalysis, *a fortiori*.

The observed increase of k_A with increasing amine concentration for primary amines can be safely abscribed to an increase of the medium polarity; in fact, on account of the low rates of these reactions, relatively high amine concentrations have to be used and thus this phenomenon becomes observable.

The catalysis observed (Table 5) in the reactions of compounds **2** (L = OC_6H_5) or **3** (L = $OC_6H_4NO_2$-*p*) depends on the circumstance that in these cases L is a sluggish leaving group and the nucleophile is a secondary amine. This causes such very low k_2/k_{-1} ratios that, from a statistical point of view, they are undistinguishable from zero.

On going from secondary to primary amines there is a change to the situation where $k_2/k_{-1} >> 1$, that is, the reactions are not catalysed. As a matter of fact, either k_A does not change with increasing amine concentration or the k_{Am}/k_0 ratios, when observed, can be attributed, as above, to a medium effect caused by the high amine concentrations used. Moreover, the k_{Am}/k_0 ratios of Table 4 show no correlation with the basic power of the amines involved; they probably bear some relation with the range of concentrations used.

Relative reactivities for the intermediate formation

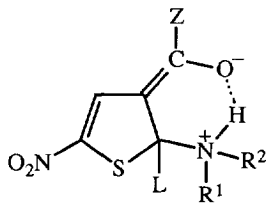
As k_0 values can be considered equivalent to k_1 values (see above), they can be used together with those in Table 5 to establish the relative nucleophilicity of the four amines with each substrate. The reactivity order of the four nucleophiles parallels the relative basicity of the amines. The plots (not shown) of log k_1 values against the logarithms of the constants of ion-pair formation of the amines with 2,4-dinitrophenol in benzene[6] are linear and show slopes in the range 1.2–1.4.

The amine being equal, the reactivity order, as determined by the Y variation (Table 6), is a function of the leaving group. In particular, $k_1^{CO_2Me}/k_1^{CONH_2} > 1$ for the oxygenated leaving groups (compounds **2** and **3**) whereas $k_1^{CO_2Me}/k_1^{CONH_2} < 1$ for bromine leaving group (compounds **1**). Since the relative electron-withdrawing effect of the two COZ groups (Z = NH_2, OMe) with respect to the aromatic ring should be independent of the leaving group, the reactivity order observed must involve some 'proximity' interaction between the activating COZ group with both the nucleophile and the leaving group.

Table 6. Substituent Reactivity Ratios for the Reactions of 2-L-3-Y-5-nitrothiophenes (1-3) with some Amines in Benzene at 293.15 K

L	R^1R^2NH	$k_1^{CO_2CH_3}/k_1^{CONH_2}$
Br	PYR	0.76
	PIP	0.60
	BuA	0.59
	BzA	0.41
OC_6H_5	PYR	7.3
	PIP	5.7
	BuA	5.8
	BzA	4.4
$OC_6H_4NO_2$-*p*	PYR	2.6
	PIP	2.0
	BuA	2.2
	BzA	2.0

It is evident that the conjugation of COZ group with the aromatic ring, as represented in **5**, is possible only when this group is coplanar with the ring. In contrast, the 'internal' conjugation, shown in **6**, is possible,



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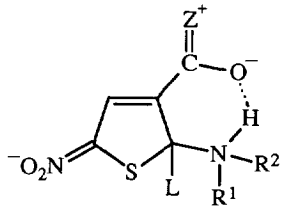


6

whatever the dihedral angle between the plane of the COZ group and that of the thiophene ring is. In the case of bromine, which is a bulky and 'compact' leaving group, there is probably a steric hindrance to the coplanarity whereas when L = OC_6H_5 or L = $OC_6H_4NO_2$-*p*, the coplanarity is still possible.

As a matter of fact, the competition between the internal and the external conjugation renders the $CONH_2$ group less activating than CO_2Me group. However, when only the internal conjugation can occur [**6**, L = Br], the negative charge on the carbonyl oxygen is greater for Z = NH_2 than for Z = OMe. As a consequence, there is a greater stabilization by hydrogen-bonding of both the reaction intermediate **6** and the transition state leading to it when Y = $CONH_2$ and the relevant substrate turns out more reactive.

The Y substituent being equal, the reactivity order in all cases is $OC_6H_4NO_2$-*p* > OC_6H_5 and the reactivity ratio $k_1^{OC_6H_4NO_2\text{-}p}/k_1^{OC_6H_5}$ is almost independent of the nucleophile (Table 7). The variation of the leaving group from OC_6H_5 to $OC_6H_4NO_2$-*p* causes an increase in the 'efficient electronegativity'[7] of the group at C–2 without involving a serious change in the steric hindrance to the approach of the nucleophile; as a consequence, for the compounds where L = $OC_6H_4NO_2$-*p*, k_1 is higher and k_{-1} lower, respectively, with respect to the case where L = OC_6H_5 and henceforth the first transition state of the attachment-detachment mechanism is earlier for L = $OC_6H_4NO_2$-*p* than for L = OC_6H_5.

This difference of positioning of the rate-determining transition state along the reaction co-ordinate is more marked with Y = $CONH_2$ than with Y = CO_2Me, in obedience to the reactivity-selectivity principle.[8]

As we pointed out above, the regression parameters obtained for eqn. (7) (Table 5) do not allow us to make a choice between the mechanisms proposed for the base catalysed step. However, an aprotic solvent like benzene is not able to assist by solvation the leaving group expulsion and, moreover, there is a significant p*K* difference between leaving group and protonated amine; thus, the SB-GA mechanism is most favoured.

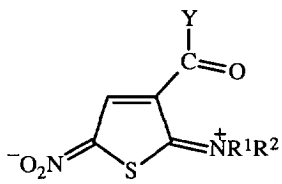
Y substituent and leaving group being equal, the k_3^{Am}/k_{-1} ratios calculated for pyrrolidine are greater than those calculated for piperidine. Assuming $k_{-1}^{PYR} = k_{-1}^{PIP}$ one obtains k_3^{PYR}/k_3^{PIP} 20 for Y = $CONH_2$ and 10 for Y = CO_2Me. These results suggest that the base catalysed product-forming step (k_3^{Am}) is controlled by the ring size of the cyclic amine.

Table 7. Leaving Group Reactivity Ratios for the Reactions of 2-Phenoxy- (2) and 2-*p*-Nitrophenoxy-3-Y-5-nitrothiophenes (3) with some Amines in Benzene at 293.15 K

Y	R^1R^2NH	$k_1^{OC_6H_5NO_2\text{-}p}/k_1^{OC_6H_5}$
$CONH_2$	PYR	18
	PIP	16
	BuA	15
	BzA	15
CO_2CH_3	PYR	6.4
	PIP	5.6
	BuA	5.6
	BzA	6.9

In the SB-GA mechanism k_3^{Am} represents the product of the equilibrium constant between **XH** and each base Am by the specific rate constant for the general acid-catalysed detachment of the nucleofuge (i. e., $k_3^{Am} = K_{3p}^{Am}k_4^{AmH}$). K_{3p}^{Am} constant for the reaction between **XH** and the corresponding amine is expected to be independent of the nature of the amine, because $K_{3p}^{Am} = K_a^{XH}/K_a^{AmH}$ and both electronic and steric effects are much the same for each **XH** intermediate: therefore, the difference in k_3^{Am} parameter must stem from a difference in k_4^{AmH} values.

In principle, this difference might involve only the amino moiety of the σ adduct $\mathbf{X}^-$. In fact, the resonance (structures **7** and **8**) developing in the transition state leading to **4** is sterically hindered by Y



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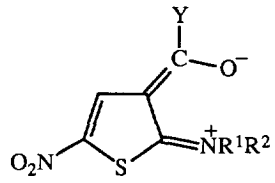

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substituent to an extent which depends on the amine ring size. However, it is probable that the bulkiness of the amine plays also a role in determining a different steric hindrance to the approach of the amine conjugate acid to the carbon bound amino moiety with changing amine ring size.

EXPERIMENTAL SECTION

Synthesis and Purification of Compounds

Compounds **1a, b**,[9] pyrrolidine,[1b] piperidine[10] and benzene[11] were prepared and/or purified as previously reported. *n*-Butylamine and benzylamine were purified by the same procedure used for piperidine.[10]

Ethers **2a, b** and **3a, b** were prepared according to the general methods of ref. 7 and ref. 12, respectively. The relevant physical data are reported in Table 8. Amino derivatives **4** were prepared according to the general method of ref. 10. The relevant physical data are reported in Table 8. All the new compounds gave correct analyses.

Kinetic Measurements

The kinetics were followed spectrophotometrically as previously described. The concentrations used were 2×10^{-4} mol dm^{-3} for substrates and those indicated in Tables 1-3 for the amines. The wavelength and lg ε values for UV spectral measurements are reported in Table 8.

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Table 8. Physical and Spectroscopic Data for Ethers 2a,b and 3a,b and for Amino Derivatives 4

Compound	$NR^1(R^2)$	Crystallization solvent	M. p. (°C)	λ_{max}/[a] nm	log ε[a]
2a		methanol	176		
2b		methanol	96		
3a		dioxan-methanol	210		
3b		methanol-dioxan	166-7		
4a	NC_4H_8	dioxan-methanol	248-9	430	4.41
4b	NC_4H_8	methanol	118	420	4.37
4a	NC_5H_{10}[b]	methanol	154-5	420	3.88
4b	NC_5H_{10}[b]	methanol	71	414	4.21
4a	$NH[(CH_2)_3CH_3]$	methanol-dioxan	208-9	420	4.35
4b	$NH[(CH_2)_3CH_3]$	light petroleum-benzene	66	410	4.33
4a	$NH(CH_2C_6H_5)$	methanol-dioxan	227-8	420	4.34
4b	$NH(CH_2C_6H_5)$	methanol	134-5	400	4.31

[a] In benzene. [b] Ref. 9.

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