The Protonation of Some 5-Substituted 3-Nitro- and 3-Substituted 5-Nitro-2-pyrrolidin-1-ylthiophenes

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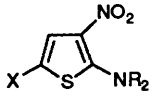
The protonation of some 5-substituted 3-nitro-2-pyrrolidin-1-ylthiophenes **1C** and 3-substituted 5-nitro-2-pyrrolidin-1-ylthiophenes **2C** in aqueous perchloric acid has been studied. The modified Hammett, Bunnett–Olsen and Marziano–Cox–Yates methods have been used to calculate pK_{BH^+} values, which have been correlated with substituent effects. Furthermore, the protonation of pyrrolidin-1-ylthiophenes **1C** and **2C** has been compared with that of the corresponding *N,N*-dimethylamino- (**1A** and **2A**) and piperidin-1-yl-thiophenes (**1B** and **2B**). The results have been interpreted on the grounds of the different interactions occurring between the amino group at C-2 and the nitro group or variable substituent at C-3.

In the framework of our researches[1] in the field of S_NAr reactions and of linear free energy (LFE) relationships in five-membered ring derivatives we have measured the pK_{BH^+} values of some 5-substituted 2-*N,N*-dimethylamino-3-nitrothiophenes[2] (**1A**) and 3-nitro-2-piperidin-1-ylthiophenes[3] (**1B**) to



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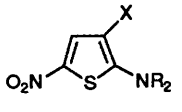


2

a X = Me
b X = H
c X = Br
d X = $CONH_2$
e X = $CONMe_2$
f X = CO_2Me
g X = Ac
h X = SO_2Me
i X = CN
j X = NO_2

A $NR_2 = NMe_2$
B $NR_2 = N(CH_2)_5$
C $NR_2 = N(CH_2)_4$

test the σ_p^- values proposed[1f] for thiophene S_NAr reactions. The good results obtained for the correlations between pK_{BH^+} values and thiophenic σ_p^- values have shown once more that *para* (or *para*-like) substituents affect both the acidity of aromatic (or heteroaromatic) protonated amines and the S_NAr reactivity in a similar way. The substituent effects measured for **1A** and **1B** were practically independent of the nature of the basic nitrogen atom (ρ_{1A} = *ca.* ρ_{1B} 4.2).

In contrast, amines **1A** and **1B** with the same substituent but with a different *N,N*-dialkyl structure showed significantly different pK_{BH^+} values (ΔpK_{BH^+} *ca.* 0.8) which were accounted for on the basis of the different proximity effects occurring between the nitro and the two different amino groups.[3]

Also the pK_{BH^+} data of isomers 3-substituted 2-*N,N*-dimethylamino-5-nitrothiophenes[3] (**2A**) and 5-nitro-2-piperidin-1-ylthiophenes[3] (**2B**) were interpreted on the grounds of the interactions occurring between the *ortho*-like variable substituent and the amino group, which affected both electronic and solvation effects. The balance of the two factors caused similar pK_{BH^+} values for corresponding compounds in the two series **2A** and **2B**.

In order to gain information about the role played by amino group structure in the proximity effects, we have determined the protonation constants of some 5-substituted 3-nitro-2-pyrrolidin-1-ylthiophenes (**1C**) and 3-substituted 5-nitro-2-pyrrolidin-1-ylthiophenes (**2C**) in aqueous perchloric acid. We chose the pyrrolidinyl group as a new amino moiety because piperidine and pyrrolidine are two secondary cyclic amines of comparable basic strength[4] but with different steric requirements. These, for example, are responsible for a greater reactivity of pyrrolidine with respect to piperidine in nucleophilic substitution reactions.[5]

Results and Discussion

The pK_{BH^+} values have been determined spectrophotometrically at 25 °C in aqueous perchloric acid. The protonation reaction of 3-bromo-5-nitro-2-pyrrolidin-1-ylthiophene (**2Cc**) has been carried out in aqueous sulphuric acid because perchloric acid caused a fast transformation of this amino compound. Also 3,5-dinitro-2-pyrrolidin-1-ylthiophene (**1Cj** = **2Cj**), because of its low basicity, has been studied in sulphuric acid. However, we have recently observed[3] that the pK_{BH^+} values of tertiary amines are much the same for the two acid solutions used, within experimental uncertainty, as required by the definition of pK_{BH^+}.

The pK_{BH^+} values reported in Tables 1 and 2 have been calculated by a modified Hammett method[6] (Hammett acidity functions method: HAFM, *i.e.* using H_0''' as the acidity function for tertiary aromatic amines), the Bunnett–Olsen method[7] (BOM) and the Marziano–Cox–Yates method[8] (excess acidity method: EAM). It must be observed that in some cases the three methods gave different results in accordance with what we have recently claimed.[9] Since HAFM often works better than EAM or BOM[10] the pK_{BH^+} values used in LFE correlations are those calculated by HAFM. The results obtained (Tables 1 and 2) show a large dependence on the basicity (some six and seven orders of magnitude in pK_{BH^+} for series **1C** and **2C**, respectively) on the substituent electronic effects.

The spectroscopic behaviour of **1Cg**† during the protonation,

† Compound **1Cg** shows two absorbance bands centred at 348 and 414 nm; the former decreases and the latter increases with increasing perchloric acid concentration. In contrast, the other compounds **1C** show a decrease of absorption bands with increasing perchloric acid concentration. It must be remembered that protonated 5-substituted 2-acetylthiophenes[11] show an absorption band at a longer wavelength than unprotonated ones, as observed for **1Cg**.

Table 1 pK_{BH^+} values of 5-substituted 3-nitro-2-pyrrolidin-1-ylthiophenes (**1C**) in aqueous perchloric acid

	HAFM[a]		EAM[a]		BOM[a]	
X	$-pK_{BH^+}$	m	$-pK_{BH^+}$	m^*	$-pK_{BH^+}$	$-\varphi$
Me	1.99 ± 0.14	0.92 ± 0.06	1.99 ± 0.08	1.25 ± 0.06	1.98 ± 0.05	0.48 ± 0.04
H	2.28 ± 0.04	0.89 ± 0.02	1.96 ± 0.02	1.12 ± 0.02	2.07 ± 0.06	0.44 ± 0.06
Br	3.15 ± 0.18	1.01 ± 0.06	2.77 ± 0.12	1.32 ± 0.08	2.63 ± 0.08	0.46 ± 0.08
$CONH_2$	3.30 ± 0.08	0.51 ± 0.01	3.90 ± 0.08	0.78 ± 0.02	3.73 ± 0.08	−0.22 ± 0.02
$CONMe_2$	5.68 ± 0.18	0.90 ± 0.03	6.40 ± 0.18	1.49 ± 0.05	5.99 ± 0.14	0.46 ± 0.04
CO_2Me	5.53 ± 0.29	0.99 ± 0.05	5.78 ± 0.17	1.50 ± 0.05	5.30 ± 0.20	0.45 ± 0.06
Ac	4.14 ± 0.16	0.97 ± 0.04	4.37 ± 0.17	1.46 ± 0.06	3.61 ± 0.11	0.30 ± 0.05
SO_2Me	6.42 ± 0.31	0.98 ± 0.05	6.64 ± 0.35	1.49 ± 0.09	6.44 ± 0.26	0.52 ± 0.07
CN	6.59 ± 0.18	0.98 ± 0.03	7.25 ± 0.19	1.62 ± 0.05	6.98 ± 0.23	0.63 ± 0.06
NO_2[b]	8.06 ± 0.35	0.92 ± 0.04	6.95 ± 0.22	1.07 ± 0.04	7.02 ± 0.18	0.04 ± 0.03

[a] The significance levels of the statistical parameters obtained in the calculation of $-pK_{BH^+}$ and m, m^* or $-\varphi$ are all better than 99.9%. [b] In aqueous sulphuric acid.

Table 2 pK_{BH^+} values of 3-substituted 5-nitro-2-pyrrolidin-1-ylthiophenes (**2C**) in aqueous perchloric acid

	HAFM[a]		EAM[a]		BOM[a]	
X	$-pK_{BH^+}$	m	$-pK_{BH^+}$	m^*	$-pK_{BH^+}$	$-\varphi$
Me	0.96 ± 0.04	0.94 ± 0.03	0.77 ± 0.04	1.53 ± 0.07	0.73 ± 0.04	0.49 ± 0.09
H	1.74 ± 0.08	0.63 ± 0.03	1.76 ± 0.03	0.84 ± 0.02	1.77 ± 0.06	−0.14 ± 0.04
Br	2.51 ± 0.08	0.72 ± 0.02	2.52 ± 0.08	1.03 ± 0.04	2.46 ± 0.08	0.00 ± 0.04
$CONH_2$	2.19 ± 0.08	0.94 ± 0.03	1.70 ± 0.05	1.08 ± 0.04	1.78 ± 0.08	0.33 ± 0.07
CO_2Me	4.76 ± 0.26	0.98 ± 0.05	4.78 ± 0.06	1.42 ± 0.02	4.41 ± 0.16	0.40 ± 0.06
Ac	3.40 ± 0.21	0.84 ± 0.05	3.54 ± 0.15	1.20 ± 0.06	3.01 ± 0.25	0.11 ± 0.12
SO_2Me	6.46 ± 0.17	0.90 ± 0.02	7.12 ± 0.17	1.48 ± 0.04	6.50 ± 0.28	0.40 ± 0.07
CN	6.96 ± 0.60	0.93 ± 0.08	6.91 ± 0.41	1.38 ± 0.09	6.32 ± 0.35	0.30 ± 0.08
NO_2[b]	8.06 ± 0.35	0.92 ± 0.04	6.95 ± 0.22	1.07 ± 0.04	7.02 ± 0.18	0.04 ± 0.03

[a] The significance levels of the statistical parameters obtained in the calculation of $-pK_{BH^+}$ and m, m^* or $-\varphi$ are all better than 99.9%. [b] In aqueous sulphuric acid.

as well as the pK_{BH^+} value calculated for this compound, are indicative of protonation of the carbonyl group. In the case of **1Cd**, the low m value obtained (see Table 1) also seems to indicate protonation of the carbonyl group.

The pK_{BH^+} values of 5-substituted 3-nitro-2-pyrrolidin-1-ylthiophenes (**1C**) give, provided that the points relative to 5-Ac (**1Cg**), 5-$CONH_2$ (**1Cd**) and 5-$CONMe_2$ (**1Ce**) are excluded, an excellent LFE correlation with the thiophenic σ_p^- values [1f] [eqn. (1)].

$$(-pK_{BH^+})_{1C} = (4.66 \pm 0.21)\sigma_p^- + (2.20 \pm 0.28) \quad (1)$$

$$(r = 0.991, n = 7, \text{C.L.} > 99.9\%)$$

The pK_{BH^+} values measured for the pyrrolidinyl derivatives **1C** showed that these compounds are in general weaker bases than the corresponding *N,N*-dimethylamino derivatives **1A** (ΔpK_{BH^+} 0.8) and piperidino derivatives **1B** (ΔpK_{BH^+} 1.5) when the protonation occurs at the tertiary nitrogen atom. Considering the fact that pyrrolidine and piperidine have much the same basicity and that the pK_{BH^+} value[4] of dimethylamine is different by only 0.4 pK units, one can suppose that the differences observed depend on all of the interactions occurring between thiophene ring, amino and nitro groups.

The differences observed could depend on external factors (for example, different solute–solvent interactions in the three series) or could be due to a different extent of conjugation between thiophene ring and amino group. This would be larger in compounds **1C** than in **1A** and **1B**, according to the observation that the nitrogen atom of the pyrrolidine ring has a greater ability to give rise to a double bond by conjugation than the nitrogen atoms of the other two amino moieties.[12] On the other hand, since the conjugation between the amino group and the thiophene ring depends on the geometry of the amino group with respect to the ring, the behaviour observed could also be a consequence of the different proximity effects between nitro and amino groups in the three series **1A–C**. The bulkier piperidinyl group causes larger steric interactions (and consequently smaller electronic interactions) between amino and nitro groups than *N,N*-dimethylamino and pyrrolidinyl groups, therefore the 3-nitro group affects (lowers) the basicity of **1B** less than that of **1A** and **1C**. The very similar m^* values (1.47 ± 0.10, 1.49 ± 0.21 and 1.36 ± 0.17 for **1A**, **1B** and **1C**, respectively) calculated for the three classes of compound seem to exclude significant differences in the solute–solvent interactions.

In the case of the 3-substituted 5-nitro-2-pyrrolidin-1-ylthiophenes (**2C**) acidity measurements for **2Cg** and **2Cd** did not give direct evidence (see above) for protonation of the carbonyl group, but indirect pieces of evidence for this are the fact that the measured pK_{BH^+} values seem to be, in absolute terms, too low and the fact that on exclusion of these two points from the correlation with the thiophenic σ_p^- values [1f] a significant improvement of statistical parameters is observed [compare eqns. (2) and (3), see also below].

$$(-pK_{BH^+})_{2C} = (5.09 \pm 0.96)\sigma_p^- + (1.06 \pm 0.70) \quad (2)$$

$$(r = 0.894, n = 9, \text{C.L.} > 99\%)$$

$$(-pK_{BH^+})_{2C} = (5.43 \pm 0.45)\sigma_p^- + (1.39 \pm 0.33) \quad (3)$$

$$(r = 0.983, n = 7, \text{C.L.} > 99.9\%)$$

It must be remarked that for **2Ab**,[3] **2Bb**[3] and **2Cb**, *i.e.*, for 2-amino-5-nitrothiophenes (no substituent at C-3) similar pK_{BH^+} values (−1.64, −1.92 and −1.74) have been measured and similar values of λ_{max} (444, 448 and 448 nm) and log ε (4.49, 4.50 and 4.55) have been observed, and this indicates a similar conjugative ability of the three amino groups, when their electronic interactions with the nitro group are free from steric interactions.

In contrast, for **1Ab**,[2] **1Bb**[3] and **1Cb**, *i.e.*, for 2-amino-3-nitrothiophenes (amino moiety and nitro group *ortho* to each other) significant differences in log ε values (3.81, 3.75 and 3.97, at λ_{max} 400, 398 and 408 nm, respectively) and large differences in pK_{BH^+} values (1.69, 1.07 and 2.28) have been observed. The occurrence of significant differences in pK_{BH^+} values and in the UV–VIS spectroscopic behaviour for **1Ab**, **1Bb** and **1Cb** appears dependent on the different steric interactions between nitro and amino groups which affect the protonation of the amino nitrogen atom.

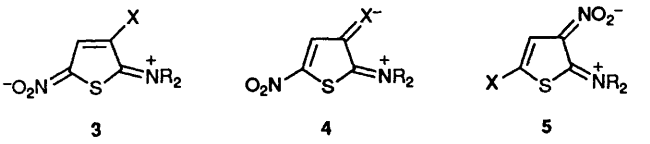
Furthermore, the results of the cross-correlations [eqns. (4) and (5)] show that the transmission of the substituent effects

$$(-pK_{BH^+})_{1C} = (1.16 \pm 0.09)(-pK_{BH^+})_{1A} + (0.07 \pm 0.45) \quad (4)$$
$$(r = 0.987, n = 6, \text{C.L.} > 99.9\%)$$

$$(-pK_{BH^+})_{1C} = (1.09 \pm 0.07)(-pK_{BH^+})_{1B} + (1.23 \pm 0.27) \quad (5)$$
$$(r = 0.990, n = 7, \text{C.L.} > 99.9\%)$$

is similar in the three series. This indicates that the effect responsible for the different basicity observed for **1Ab**, **1Bb** and **1Cb** remains the same within each series irrespective of the 5-substituent. This seems to confirm the above interpretation of our results and to exclude the possibility that the differences in basicity are a consequence of a different extent of conjugation.

From an examination of pK_{BH^+} values in Tables 1 and 2 one can observe that on going from **1Cj** = **2Cj** (X = NO_2), which contains a strong electron-withdrawing substituent, to other **1C** and **2C** compounds there is a larger and larger spread in pK_{BH^+} values [$(\Delta pK_{BH^+})_{X=Me}$ *ca.* 1], **2C** compounds being more basic than the corresponding **1C** ones. This fact points out once again the relevance of the hyper-*ortho* relationship in thiophene derivatives and the different weight of formulae **3** and **4** in **2C** as



3 **4** **5**

a function of the present substituent. As a matter of fact for X = Me, H, Br, **2C** is more basic than **1C**: in this case the difference in basicity between the compounds compared depends on the electronic interactions between nitro and pyrrolidinyl groups and these interactions are more efficient in an *ortho*-like **5** than in a *para*-like **3** relationship. The stronger the electron-withdrawing substituent present at C-3 in **2C**, the more relevant are the electronic interactions between this substituent and the pyrrolidinyl group at C-2 (see structure **4**); as a consequence pK_{BH^+} values measured for **2C** and **1C** are similar.

The relevance of electronic effects (practically unaffected by proximity effects) in determining pK_{BH^+} values of **1C** and **2C** accounts for the excellent cross-correlation between $(-pK_{BH^+})_{2C}$ and $(-pK_{BH^+})_{1C}$ ($s = 1.19 \pm 0.06$, $i = 1.35 \pm 0.29$, $r = 0.992$, $n = 9$, C.L. > 99.9%). Proximity effects or variable solute–solvent interactions, which would be affected by the *ortho*-substituent (variable in **2C**, constant in **1C**), do not influence the measured pK_{BH^+} values. It is interesting to observe that acetyl and amido substituted derivatives (**1Cg, d** and **2Cg, d**) do not have to be excluded from the cross-correlation, so confirming that also in the series **2C** in these compounds the protonation occurs at the carbonyl group (see above).

Since **2Ab**,[3] **2Bb**[3] and **2Cb** show similar pK_{BH^+} values, the introduction of the variable 3-X substituent causes the occurrence of different trends in the series **2A–C** for the protonation at the amino nitrogen atom. This can be accounted for by considering the role played by the proximity effects in the three series, which decreases on going from **2B** to **2A** and **2C**.

Accordingly, the goodness of the fits for **2A**, **2B** and **2C** improves as the steric interactions between variable *ortho*-substituent and amino group become smaller [$(r)_{2B} = 0.902$, $(r)_{2A} = 0.953$ and $(r)_{2C} = 0.983$]. The corresponding susceptibility constants also seem to change in the same order [$(\rho)_{2B} = 3.87 \pm 0.76$, $(\rho)_{2A} = 4.32 \pm 0.56$ and $(\rho)_{2C} = 5.43 \pm 0.45$] and this behaviour can depend on the same factors, even though differences in solute–solvent interactions (also depending on the previous effects) seem able to affect the electronic interactions.

Table 3 Physical data[a] for 5-substituted 3-nitro-2-pyrrolidin-1-ylthiophenes (**1C**) and 3-substituted 5-nitro-2-pyrrolidin-1-ylthiophenes (**2C**)

Compound	X	Crystallization solvent	Colour	M.p./°C
1Ca	Me	ligroin–benzene	yellow-orange	80–1
1Cb	H[b]	ligroin–benzene	yellow-orange	86–7
1Cc	Br	methanol	yellow	112–13
1Cd	$CONH_2$	methanol–dioxane	orange-red	243
1Ce	$CONMe_2$	methanol	orange	152–3
1Cf	CO_2Me	methanol	orange	141–2
1Cg	Ac	methanol	orange-red	157–8
1Ch	SO_2Me	methanol–dioxane	orange	162–3
1Ci	CN	methanol	yellow	145–6
1Cj = **2Cj**	NO_2	methanol–dioxane	orange	124–5
2Ca	Me	methanol–dioxane	orange	197–8
2Cb	H	methanol–dioxane	orange	169–70
2Cc	Br	methanol–dioxane	red	157–8
2Cd	$CONH_2$	dioxane–methanol	yellow-orange	248–9
2Cf	CO_2Me	methanol	yellow	118–19
2Cg	Ac	methanol	orange	119–20
2Ch	SO_2Me	methanol–dioxane	orange	195–6
2Ci	CN	methanol–dioxane	orange	180–1

[a] All the compounds gave correct analyses. [b] Data from G. Consiglio, C. Arnone, D. Spinelli and R. Noto, *J. Chem. Soc., Perkin Trans. 2*, 1982, 721.

Moreover a DSP analysis[13] of pK_{BH^+} data can be carried out according to eqn. (6).

$$-pK_{BH^+} = \rho_I\sigma_I + \rho_R\sigma_R + i \quad (6)$$

The results are not statistically more significant than those obtained by the single-parameter treatment but interesting results can come from some comparisons. The parameters calculated for **1C** ($\rho_I = 3.39 \pm 0.74$, $\rho_R = 5.55 \pm 0.79$, $i = 2.50 \pm 0.25$, $n = 7$, $R = 0.9914$, $F = 114$, C.L. > 99.9%) show susceptibility constants higher than those calculated for **1A** and **1B**, but with a similar blending coefficient ($\lambda = \rho_R/\rho_I = 1.4$; compare with 1.4 and 1.2 for **1A** and **1B**). The results obtained for **2C** appear very interesting ($\rho_I = 5.00 \pm 0.91$, $\rho_R = 6.11 \pm 0.97$, $i = 1.65 \pm 0.30$, $n = 7$, $R = 0.9906$, $F = 105$, C.L. > 99.95%), because the blending coefficient calculated [$(\lambda)_{1C}$ 1.2] is very large compared with those for **1A** and **1B** [$(\lambda)_{1B} = 0.34$ and $(\lambda)_{1A} = 0.52$], clearly showing that because the steric interactions between 2-amino group and 3-X (variable *ortho*-substituent) on going from **2B** to **2A** and **2C** are reduced, the relevance of resonance interactions strongly increases and becomes similar for *ortho*-substituted **2C** and *para*-substituted **1C** compounds.

Experimental

Materials.—Compounds **1Ca–j** and **2Ca–d, f–j** were prepared according to the general methods previously reported.[14] The relevant physical data are reported in Table 3.

pK_{BH^+} *Measurements.*—Acid dissociation constants K_{BH^+} were determined as previously reported.[2,3] The cautions previously described to prevent decomposition of substrates in highly concentrated acid solutions were adopted.[3] Data treatments (according to HAFM, BOM and EAM methods) and corrections were made as previously described.[2,3]

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