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AMIDINES—XVIII[1]

TAUTOMERIC EQUILIBRIA AND pK_a VALUES OF N,N′-DISUBSTITUTED AMIDINES. SUBSTITUENT EFFECTS

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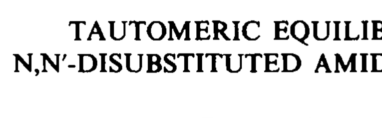
Abstract—The influence of substitution of amidine group on tautomeric equilibria constants and basicities is discussed. Equations based on correlation analysis methods are derived enabling predictions of both, microscopic pK_a values of individual tautomers, measured macroscopic pK_a values of the tautomeric mixture, as well as the tautomeric equilibrium constant (as pK_T). It is shown that pK_{a_m} values of unsymmetrically N,N′-disubstituted amidines should obey a non-linear relation with σ° constants, and only for symmetrically N,N′-disubstituted amidines obey the linear Hammett equation. Tautomeric equilibrium constants of N,N′-disubstituted amidines correlate with σ° substituent constants. The methods of prediction of pK_a value of both tautomers and pK_T value are proposed.

Derived relations are applied to the series of N,N′-diphenylacetamidines and benzamidines.

N,N′-Disubstituted amidines display prototropic tautomerism:



$$\underset{B_1}{R_x{-}N{=}\overset{R'}{C}{-}NH{-}R_y} \underset{K_T}{\rightleftharpoons} \underset{B_2}{R_x{-}NH{-}\overset{R'}{C}{=}N{-}R_y}$$

If the substituents R_x and R_y at nitrogen atoms are not identical the two tautomeric forms are different. Tautomeric equilibrium depends on the effects of both substituents, and is displaced in favour of the tautomer containing the stronger electron-withdrawing group at the imino N atom.

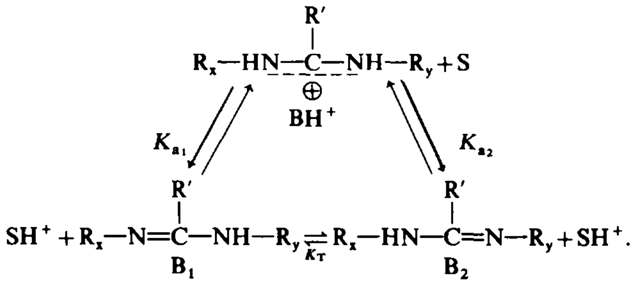
Although prototropic tautomerism of amidines has been known for a long time, and has been reviewed,[2–4] in the literature there are no reported attempts to find quantitative relations between structural parameters and tautomeric equilibria, however, the question which of the tautomers prevails in the mixture and even tautomeric equilibrium constants for some compounds containing the amidine group has been discussed. Prevoršek[5,6] investigating the IR spectra of N-monosubstituted and N,N′-disubstituted amidines has shown that "alkyl groups tend to prefer attachment to the amino nitrogen atom of the amidine group but the reverse is true for aryl groups". His conclusions were in agreement with earlier work on N-arylamidines by Pyman,[7,8] and was supported later by Moritz[9] who criticized the work of Grivas and Taurins.[10,11] Gautier[12] and Reynaud[13] have determined the structure of the predominant tautomer by acylation or alkylation of the mixture of tautomers and further studied the obtained products. Tautomerism of other compounds containing the amidine group such as sulfonylamidines[14–16] and some cyclic amidines[17] was also studied using IR or NMR spectroscopy. However, no quantitative information on the position of tautomeric equilibrium was obtained in the above mentioned papers. Only in recent years Katritzky for some N-monosubstituted acetamidines[18,19] has applied the method of determination of tautomeric equilibrium constant based on measurements of pK_a values of the two corresponding methyl derivatives.

We have found that the constants of tautomeric equilibria of amidines, as well as pK_a values of individual tautomers, can be predicted with good accuracy using the methods of correlation analysis.

DISCUSSION

pK_a *Values of* N,N′-*disubstituted amidines*

Protonation of tautomerizing amidine yields only one amidinium cation. It is a conjugate acid (BH^+) of both tautomeric bases (B_1 and B_2), and in the solvent S undergoes dissociation as shown by Eq. (1)



(1)

Microscopic constants[20] are defined as follows

$$K_{a_1} = (B_1)(SH^+)/(BH^+) \tag{2a}$$

$$K_{a_2} = (B_2)(SH^+)/(BH^+). \tag{2b}$$

By any of the direct empirical methods only macroscopic dissociation constant K_{a_m} is measured. Accordingly to Brönsted theory it is defined[20] as $K_{a_m} = \{(B_1)+(B_2)\}(SH^+)/(BH^+)$. Thus the measured dissociation constant is the sum of microscopic constants

$$K_{a_m} = K_{a_1} + K_{a_2}. \qquad (3)$$

In the case when both substituents R_x and R_y are identical both microscopic constants are also identical, i.e. $K_{a_1} = K_{a_2} = K_{a_s}$, and measured p$K_a$ value can be expressed as

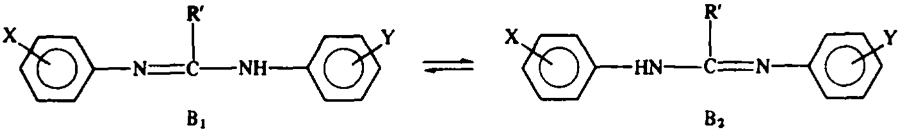
$$\mathrm{p}K_{a_m} = \mathrm{p}K_{a_s} - \log 2. \qquad (4)$$

In the former papers [21–24] we have found that N^1-methyl-N^1,N^2-diphenylamidines containing variable substituents at both phenyl rings obey the disubstituent Hammett equation

$$\mathrm{p}K_a = \mathrm{p}K_a^\circ - \rho_{\mathrm{Im}}\sigma^\circ_{\mathrm{Im}} - \rho_{\mathrm{Am}}\sigma^\circ_{\mathrm{Am}} \qquad (5)$$

where $\sigma^\circ_{\mathrm{Im}}$ and $\sigma^\circ_{\mathrm{Am}}$ are the σ° values of substituents at phenyl rings at imino and amino nitrogen atoms, respectively. It was also shown that for substituents at nitrogen atoms in amidines σ° values should be used.[25]

The values ρ_{Im} and ρ_{Am} depend to a considerable degree on substitution at amidine carbon atom[22,25] but seem to be entirely independent on substitution at the second nitrogen atom.[23,24] Thus it can be assumed that in the case of unsymmetrically disubstituted N,N′-diphenylamidines ($R_x = C_6H_4X$; $R_y = C_6H_4Y$)



(6)

the pK_a values of both tautomers B_1 and B_2 should obey Eqs (7) and (8), respectively

$$\mathrm{p}K_{a_1} = \mathrm{p}K_a^\circ - \rho_{\mathrm{Im}}\sigma^\circ_{\mathrm{X}} - \rho_{\mathrm{Am}}\sigma^\circ_{\mathrm{Y}} \qquad (7)$$

$$\mathrm{p}K_{a_2} = \mathrm{p}K_a^\circ - \rho_{\mathrm{Am}}\sigma^\circ_{\mathrm{X}} - \rho_{\mathrm{Im}}\sigma^\circ_{\mathrm{Y}} \qquad (8)$$

where pK_a° is the microscopic pK_a value of amidine containing at both nitrogen atoms unsubstituted phenyl rings. It can be calculated from measured pK_{a_m} value of such amidine (Eq. 4).

Replacing K_{a_1} and K_{a_2} in Eq. (3) by these terms obtained from Eqs (7) and (8), respectively, after rearrangements is obtained the relation between pK_{a_m} value and substituent constants (Eq. 9)

$$\mathrm{p}K_{a_m} = \mathrm{p}K_a^\circ - \log\left[10^{(\rho_{\mathrm{Im}}\sigma^\circ_{\mathrm{X}} + \rho_{\mathrm{Am}}\sigma^\circ_{\mathrm{Y}})} + 10^{(\rho_{\mathrm{Am}}\sigma^\circ_{\mathrm{X}} + \rho_{\mathrm{Im}}\sigma^\circ_{\mathrm{Y}})}\right]. \qquad (9)$$

In the case of the N,N′-diphenylamidine series with only one variable substituent X relation (10) is obtained

$$\mathrm{p}K_{a_m} = \mathrm{p}K_{a_s} - \log\left[10^{\rho_{\mathrm{Im}}(\sigma^\circ_{\mathrm{X}} - \sigma^\circ_{\mathrm{Y}})} + 10^{\rho_{\mathrm{Am}}(\sigma^\circ_{\mathrm{X}} - \sigma^\circ_{\mathrm{Y}})}\right] \qquad (10)$$

where pK_{a_s} is the pK_a value of the symmetrically disubstituted (X = Y) N,N′-diphenylamidine. The plot of this relation is presented on Fig. 1.

The pK_a°, or correspondingly pK_{a_s}, value can be calculated from measured pK_{a_m} of the corresponding amidine (Eq. 4), i.e. unsubstituted N,N′-diphenylamidine (pK_a°) or symmetrically disubstituted N,N′-diphenylamidine (pK_{a_s}).

The ρ_{Im} and ρ_{Am} values can be obtained from investigation of the corresponding series of trisubstituted amidines such as N^1-methyl-N^1,N^2-diphenylamidines because, as it was shown[23,24] substitution at the second N atom has no significant influence on these values. But it has to be pointed out that only those trisubstituted amidines can be used which contain the same substituent at amidine C atom as considered tautomerizing ones, because substitution at this site bears considerable influence on both ρ values.[22,25]

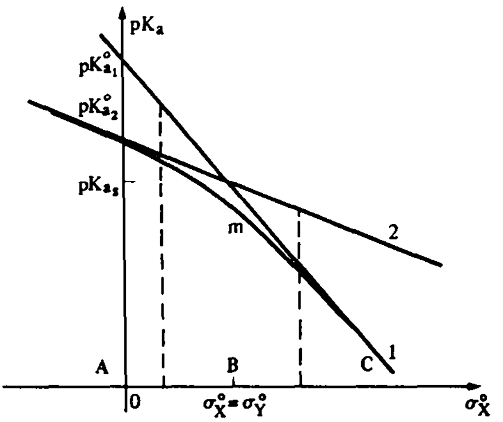


Fig. 1. Plot of pK_a values vs σ° for N,N′-disubstituted amidines containing only one variable substituent: pK_{a_m}, curve m (Eq. 10), pK_a of tautomers: B_1, line 1 (Eq. 7); and B_2, line 2 (Eq. 8).

As the ρ_{Im} and ρ_{Am} values are not identical[21–24] the relation between pK_{a_m} values and substituent constants is by no means a straight line. For this reason any linear regression between pK_a values of tautomerizing amidines encountered in the literature[26–29] is meaningless, as based on erroneous assumption. Reported apparent ρ values obtained by the least squares method depend in such cases mainly on the range (A, B or C on Fig. 1) in which is found the majority of the experimental points. The only exceptions are symmetrically disubstituted N,N′-diphenylamidines (X = Y). Equation (9) or (10) implies that in such a case pK_{a_m} values should obey the linear Hammett Eq. (11) where the observed ρ value is the sum of ρ_{Im} and ρ_{Am}

$$\mathrm{p}K_{a_m} = \mathrm{p}K_a^\circ - \log 2 - (\rho_{\mathrm{Im}} + \rho_{\mathrm{Am}})\sigma^\circ_{\mathrm{X}}. \qquad (11)$$

It seems probable that using some other values representing polar effects of substituents instead of σ constants, it will be possible to derive equations enabling prediction of pK_a values for tautomerizing amidines containing substituents of any kind, as in the case of trisubstituted amidines[25,30,31] and symmetrically N,N′-disubstituted amidines.[32]

Tautomeric equilibria of N,N′*-disubstituted amidines*

In the case of N,N′-disubstituted amidines the equilibrium constant between tautomers B_1 and B_2 (Eq. 1) is defined as

$$K_T = (B_1)/(B_2) = x/1 - x$$

where x is the molar fraction of B_1. The ratio of tautomers concentrations is evidently determined by their basicities. Dividing Eqs (2a) and (2b) and taking the logarithm we obtain

$$\mathrm{p}K_{\mathrm{T}} = \mathrm{p}K_{\mathrm{a}_1} - \mathrm{p}K_{\mathrm{a}_2}. \qquad (12)$$

Relation (12) implies that if the difference between pK_{a} values of individual tautomers is about 1, the tautomeric mixture contains 91% of the less basic tautomer, and if it is about 2, it contains practically one (99%) tautomer.

The pK_{a} values of individual tautomers are not experimentally accessible, because tautomerization of amidines, on account of formation of dimeric associates,[4,33,34] is a very fast reaction. For example in the case of N,N'-dimethylformamidines[33] the lifetime of the tautomer at 25° in $CDCl_3$ solution is about 10^{-4} s, and in the case of N,N'-di-*p*-fluorophenylformamidine[35] is between 10^{-2} and 10^{-3} s, depending on temperature (−70 to 62°). But the pK_{a_1} and pK_{a_2} values can be fairly accurately predicted using the above relations (Eqs 7 and 8).

The pK_{T} values should obey the Hammett equation. If in Eq. (12) the pK_{a_1} and pK_{a_2} are replaced by the expressions from Eqs (7) and (8), respectively after rearrangement Eq. (13) is obtained, where $\rho_{\mathrm{T}} = \rho_{\mathrm{Im}} - \rho_{\mathrm{Am}}$

$$\mathrm{p}K_{\mathrm{T}} = -\rho_{\mathrm{T}}(\sigma^{\circ}_{\mathrm{X}} - \sigma^{\circ}_{\mathrm{Y}}). \qquad (13)$$

This equation can be also used for prediction of tautomeric equilibria on the basis of ρ_{Im} and ρ_{Am} values obtained from trisubstituted amidines.

RESULTS

Derived equations were applied to the two series of tautomerizing amidines: N,N'-diphenylacetamidines (ADPh) and N,N'-diphenylbenzamidines (BDPh). The following compounds were investigated

We have measured pK_{a} values of these amidines in 95.6% ethanol (azeotrope) at standardized conditions ensuring high reproducibility[25,30,31] and comparability with the former results for trisubstituted amidines.[23–25,30,31] Obtained pK_{a} values and calculated confidence intervals at the significance level of 0.05 are summarized in Table 1.

As ρ_{Im} and ρ_{Am} were taken from values obtained previously from investigation of N^1-alkyl-N^1,N^2-diphenylamidines in the same conditions, namely N^1-methyl-N^1,N^2-diphenylacetamidines[23] ($\rho_{\mathrm{Im}} = 2.88 \pm 0.18$; $\rho_{\mathrm{Am}} = 1.42 \pm 0.16$) for calculation of p$K_{\mathrm{a}}$ of ADPh, and N^1-methyl-N^1,N^2-diphenylbenzamidines[24] ($\rho_{\mathrm{Im}} = 2.99 \pm 0.32$; $\rho_{\mathrm{Am}} = 1.66 \pm 0.33$) for calculation of p$K_{\mathrm{a}}$ of BDPh series. The pK°_{a} values were calculated according to Eq. (4) from measured pK_{a_m} values of unsubstituted N,N'-diphenylamidines (compounds 2 and 10, respectively). Thus for prediction of macroscopic pK_{a_m} values the following relations should be applied:

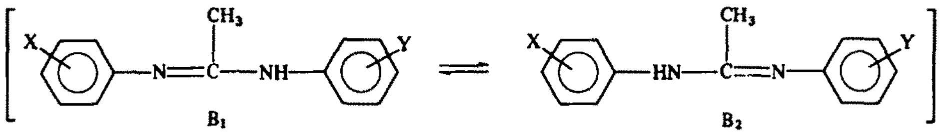
for ADPh according to Eq. (9)

$$\mathrm{p}K_{\mathrm{a}_m} = (7.27 \pm 0.03) - \log\{10^{[(2.88\pm0.18)\sigma^{\circ}_{\mathrm{X}} + (1.42\pm0.16)\sigma^{\circ}_{\mathrm{Y}}]} + 10^{[(1.42\pm0.16)\sigma^{\circ}_{\mathrm{X}} + (2.88\pm0.18)\sigma^{\circ}_{\mathrm{Y}}]}\}$$

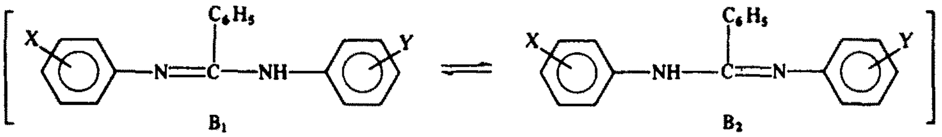
for BDPh according to Eq. (10)

$$\mathrm{p}K_{\mathrm{a}_m} = (6.45 \pm 0.04) - \log[10^{(2.99\pm0.32)\sigma^{\circ}_{\mathrm{X}}} + 10^{(1.66\pm0.33)\sigma^{\circ}_{\mathrm{X}}}].$$

As it is seen (Table 1) calculated pK_{a_m} values are within accuracy limits nearly identical with experimental ones. This provides strong support for the above assumption that for tautomerizing amidines the ρ_{Im} and ρ_{Am} values of amidines containing the same substituent at functional carbon atom can be applied. Therefore pK_{a_1}, pK_{a_2} and pK_{T} values can be calculated



ADPh



BDPh

Compound No.	ADPH X	ADPH Y	Compound No.	BDPh X	Compound No.	BDPh X
1	*p*-Me	*p*-Me	7	*p*-OMe	13	*p*-Cl
2	H	H	8	*p*-Me	14	*p*-Br
3	*p*-Br	*p*-Me	9	*m*-Me	15	*p*-I
4	*p*-Br	H	10	H	16	*m*-Cl
5	*p*-Br	*p*-Br	11	*m*-OMe	17	*m*-Br
6	*p*-Cl	*p*-Cl	12	*p*-F	18	*m*-NO_2

Table 1. pK_a and pK_T values for N,N′-diphenyl-acetamidines and benzamidines in 95.6% ethanol at 25±0.1°

Compound No.	Formula	R′	X	Y	pK_{a_m}		pK_{a_1}	pK_{a_2}	pK_T	% B_1 (mol)
					Exp	Calc				
1	$C_{16}H_{18}N_2$	Me	p-Me	p-Me	7.66±0.03	7.55±0.07	7.96±0.03		0	50
2	$C_{14}H_{14}N_2$	Me	H	H	6.97±0.03		7.27±0.03		0	50
3	$C_{15}H_{15}N_2Br$	Me	p-Br	p-Me	6.51±0.03	6.60±0.05	6.70±0.07	7.28±0.07	−0.58±0.14	79±6
4	$C_{14}H_{13}N_2Br$	Me	p-Br	H	6.19±0.05	6.36±0.08	6.51±0.05	6.89±0.05	−0.39±0.09	71±4
5	$C_{14}H_{12}N_2Br_2$	Me	p-Br	p-Br	5.52±0.10	5.52±0.11	5.82±0.10		0	50
6	$C_{14}H_{12}N_2Cl_2$	Me	p-Cl	p-Cl	5.63±0.12	5.63±0.11	5.93±0.11		0	50
7	$C_{20}H_{18}N_2O$	Ph	p-OMe	H	6.78±0.04	6.64±0.10	7.12±0.11	6.89±0.11	0.23±0.14	37±7
8	$C_{20}H_{18}N_2$	Ph	p-Me	H	6.52±0.04	6.45±0.08	6.84±0.08	6.67±0.08	0.18±0.09	40±5
9	$C_{20}H_{18}N_2$	Ph	m-Me	H	6.36±0.03	6.29±0.06	6.64±0.06	6.55±0.06	0.09±0.04	45±2
10	$C_{19}H_{16}N_2$	Ph	H	H	6.15±0.04		6.45±0.04		0	50
11	$C_{20}H_{18}N_2O$	Ph	m-OMe	H	6.04±0.02	5.91±0.07	6.15±0.07	6.28±0.07	−0.13±0.07	57±4
12	$C_{19}H_{15}N_2F$	Ph	p-F	H	5.90±0.03	5.76±0.10	6.00±0.09	6.20±0.09	−0.20±0.10	61±5
13	$C_{19}H_{15}N_2Cl$	Ph	p-Cl	H	5.46±0.03	5.56±0.12	5.73±0.12	6.05±0.12	−0.32±0.16	68±8
14	$C_{19}H_{15}N_2Br$	Ph	p-Br	H	5.42±0.03	5.50±0.12	5.66±0.12	6.01±0.13	−0.35±0.17	69±9
15	$C_{19}H_{15}N_2I$	Ph	p-I	H	5.43±0.08	5.47±0.13	5.62±0.13	5.99±0.13	−0.37±0.18	70±9
16	$C_{19}H_{15}N_2Cl$	Ph	m-Cl	H	5.23±0.05	5.24±0.16	5.36±0.16	5.84±0.16	−0.48±0.24	75±11
17	$C_{19}H_{15}N_2Br$	Ph	m-Br	H	5.25±0.03	5.23±0.16	5.35±0.16	5.84±0.16	−0.49±0.24	76±12
18	$C_{19}H_{15}N_3O_2$	Ph	m-NO$_2$	H	4.24±0.04	4.27±0.27	4.32±0.27	5.27±0.28	−0.84±0.46	87±16

using Eqs (7), (8) and (13), respectively. The following relations are applied:

for ADPh

$$pK_{a_1} = (7.27\pm0.03)-(2.88\pm0.18)\sigma^\circ_X-(1.42\pm0.16)\sigma^\circ_Y$$

$$pK_{a_2} = (7.27\pm0.03)-(1.42\pm0.16)\sigma^\circ_X-(2.88\pm0.18)\sigma^\circ_Y$$

$$pK_T = -(1.46\pm0.34)(\sigma^\circ_X-\sigma^\circ_Y)$$

for BDPh

$$pK_{a_1} = (6.45\pm0.04)-(2.99\pm0.32)\sigma^\circ_X$$

$$pK_{a_2} = (6.45\pm0.04)-(1.66\pm0.33)\sigma^\circ_X$$

$$pK_T = -(1.33\pm0.65)\sigma^\circ_X.$$

Calculated pK_a values of individual tautomers, tautomeric equilibrium constants (as pK_T values) and amount of the tautomer containing substituent X at phenyl ring at imino nitrogen atom are summarized in Table 1. Our results provide confirmation for literature qualitative conclusions[5–9,12,13,18,19] that in tautomeric equilibrium the tautomer containing the stronger electron-withdrawing substituent at imino N atom predominates (i.e. tautomer B_1 for compounds 3, 4 and 11–18, and tautomer B_2 for compounds 7–9). They also provide explanation for some criticized conclusions that certain amidines exist only in one of the two tautomeric forms.[4] If the difference between pK_{a_1} and pK_{a_2} values is over 2 pK_a units (this may be the case for N-alkyl-N′-aryl-amidines), concentration of one of the two tautomers (more basic one) can be just undetectable.

EXPERIMENTAL

N,N′-*Diphenylamidines*

N,N′-Diphenylacetamidines and N,N′-diphenylbenzamidines were obtained in our laboratory by procedures used for corresponding trisubstituted acetamidines[23] and benzamidines.[22] Most of them were already known (compounds: 1,[36,37] 2,[38,39] 5,[40] 6,[39] 7,[41] 8,[40,42] 10,[40,43] 13,[44] 14,[44] and 18[45]), their physical constants were consistent with those reported in the literature. All of them were of purity above 95% as adjudged by the titration volumes, and free of unreacted amines, as it was confirmed by the TLC or respectively GLC method. Their structures were confirmed by ^{1}H- and ^{13}C-NMR spectra recorded for CDCl$_3$ solns. The numbers of corresponding atoms in each group are consistent with the structures assigned. Chemical shifts of carbon atoms are in good agreement with additivity parameters (SCS) derived for amidines.[1]

pK_a *Measurements*

pK_a values of investigated amidines were determined by potentiometric titration in 95.6% EtOH (azeotrope) at 25 ±0.1°. Discussion of details ensuring reproducibility of results was given in previous papers.[25,30,31] Obtained pK_a values and calculated confidence intervals at the significance level of 0.05 are given as pK_{a_m} values in Table 1.

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