

## Menschutkin Reactions of *N*-Methylimidazole and of *N*-Methylbenzimidazole with Methyl Iodide in Acetonitrile–Methanol. Family-dependent and Family-independent Properties

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Rate constants and activation parameters have been determined for the reactions of the aromatic amines *N*-methylimidazole and *N*-methylbenzimidazole with methyl iodide in acetonitrile–methanol. The enthalpies of solution have also been determined for the relevant species in the same solvent mixtures. Activation enthalpies in acetonitrile and the specific interaction enthalpies between the amine and methanol show a linear correlation with  $pK_a$  values determined in water only over a narrowly defined type of structure. However, transition-state indices for the two reactions defined in terms of physical interaction energy,  $\alpha_{\text{phys}}$  and  $\beta_{\text{phys}}$ , show the behaviour anticipated by analogy with reactions of pyridine derivatives (*i.e.*, family-independent character).

Acidity or basicity as represented by  $pK_a$  values determined in water has often been used as reactivity index in various forms of correlation analysis,<sup>1,2</sup> selected more on the basis of experimental conditions rather than of theoretical rigour; direct thermodynamic measurements on the relevant system are often limited by various experimental difficulties but  $pK_a$  values in water are conveniently available. However, application to mechanistic problems has not been straightforward, as revealed by contrasting phrases such as dipolar aprotic *versus* protic solvent effects,<sup>3–5</sup> proton *versus* methyl cation affinity,<sup>6</sup> internal electronic energy and molecular motion *versus* external solvation,<sup>7,8</sup> and kinetic *versus* equilibrium reactivity.<sup>9–11</sup>

In previous work on the Menschutkin reactions, comparative discussion has been directed to the various aspects of the transition-state characteristics, in relation to the aliphatic *versus* aromatic amine reaction series.<sup>12–14</sup>

Imidazole and pyridine have a structural analogy; both are characterized as aromatic amines with an imino nitrogen as a reaction site. Studies of the reaction of imidazole with methyl iodide, combined with previous results on aliphatic and aromatic amine reactions, would be desirable for deducing the scope and limitations of the use of  $pK_a$  values determined in water as a reactivity index for mechanistic criteria.

In this work, kinetic and thermodynamic measurements on the reactions of *N*-methylimidazole and *N*-methylbenzimidazole with methyl iodide reactions have been carried out in acetonitrile–methanol.

### Experimental

**Materials.**—*N*-Methylimidazole, a commercial product, was dried over calcium hydride and distilled twice under reduced pressure. *N*-Methylbenzimidazole was prepared from benzimidazole and methyl iodide as described elsewhere,<sup>15</sup> and the crude product, dissolved in tetrahydrofuran, was dried over calcium hydride and distilled under reduced pressure. The distilled product, after solidification by chilling with ice, was recrystallized twice from hexane–ether (Found: C, 72.5; H, 6.0; N, 21.25. Calc. for  $C_8H_8N_2$ : C, 72.7; H, 6.1; N, 21.2%). *N,N'*-Dimethylimidazolium iodide was prepared from *N*-methylimidazole and methyl iodide in acetonitrile and recrystallized three times from butan-2-one–propan-2-ol mixtures (Found: C, 26.5; H, 4.0; N, 12.3; I, 56.6. Calc. for  $C_5H_9IN_2$ : C, 26.8; H, 4.05; N, 12.5; I, 56.6%). *N,N'*-Dimethylbenzimidazolium

iodide was prepared from *N*-methylbenzimidazole and methyl iodide in acetonitrile and recrystallized three times from ethanol–propan-2-ol (Found: C, 39.2; H, 4.0; N, 10.2; I, 45.85. Calc. for  $C_9H_{11}IN_2$ : C, 39.4; H, 4.05; N, 10.2; I, 46.3%). Other materials were treated as described elsewhere.<sup>12–14</sup>

**Kinetic Measurements.**—Kinetic measurements were carried out as described elsewhere.<sup>12–14</sup> Rate constants were determined at four of the following temperatures, 20.0, 30.0, 40.0, 50.0, and 60.0 °C. Experimental errors were estimated to be 2% from duplicate or triplicate runs.

**Heat of Solution Measurements.**—Heats of solution were measured with a Tokyo Riko twin isoperibol calorimeter (TIC-2D) at  $25.0 \pm 0.05$  °C as described elsewhere.<sup>12–14</sup> Final concentration ranges of solutes were  $0.67\text{--}1.73 \times 10^{-1}$  mol dm<sup>-3</sup> for *N*-methylimidazole,  $0.98\text{--}1.51 \times 10^{-2}$  mol dm<sup>-3</sup> for *N*-methylbenzimidazole, and  $0.54\text{--}1.32 \times 10^{-2}$  mol dm<sup>-3</sup> for salts. Experimental errors were estimated to be 2% from duplicate or triplicate runs.

### Results

Rate constants (at 30.0 °C) and activation parameters are summarized in Table 1. Enthalpies of solution for neutral bases and for salts are summarized in Table 2.

Transfer enthalpies for neutral bases are reproduced by equations (1) and (2),<sup>12–14</sup> with a maximum deviation of  $\pm 0.2$  kJ mol<sup>-1</sup> and the parameters derived are summarized in Table 3.

$$\Delta H_t^{\text{AN} \rightarrow \text{MeOH}} = \Delta H_{t,\text{phys}}^{\text{AN} \rightarrow \text{MeOH}} + \Delta H_{t,\text{SI}}^{\text{AN} \rightarrow \text{MeOH}} \quad (1)$$

$$\Delta H_t^{\text{AN} \rightarrow \text{mix}} = \Delta H_{t,\text{phys}}^{\text{AN} \rightarrow \text{MeOH}} x_{\text{MeOH}} + \frac{\Delta H_{t,\text{SI}}^{\text{AN} \rightarrow \text{MeOH}} K_{\text{se}} x_{\text{MeOH}}}{(x_{\text{AN}} + K_{\text{se}} x_{\text{MeOH}})} \quad (2)$$

The relative values of transfer enthalpy for the salt as defined by the middle part of equation (3) were reproduced by the right-hand side of equation (3),<sup>16</sup> with a maximum deviation of 0.4 kJ mol<sup>-1</sup>. The parameters determined are summarized in Table 3.

**Table 1.** Rate constants (at 30.0 °C) and activation parameters in acetonitrile-methanol

$x_{\text{MeOH}}$	<i>N</i> -Methylimidazole + MeI			<i>N</i> -Methylbenzimidazole + MeI		
	$10^5 k$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$10^6 k$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\text{kJ mol}^{-1}$	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\text{kJ mol}^{-1}$	$\text{J K}^{-1} \text{mol}^{-1}$
0	91.7	54.6	-123.1	199.1	57.4	-126.6
0.10	38.2	64.4	-98.1	108.6	63.5	-111.5
0.25	17.9	68.1	-92.2	62.3	67.7	-102.3
0.50	8.15	71.1	-88.9	28.8	72.9	-91.5
0.75	4.07	73.6	-86.3	14.9	75.3	-89.0
1.0	1.55	76.9	-83.5	6.07	79.8	-81.7

$x_{\text{MeOH}}$  = Mole fraction of methanol.

**Table 2.** Enthalpies of solution in acetonitrile-methanol at 25 °C (kJ mol<sup>-1</sup>)

$x_{\text{MeOH}}$	<i>N,N'</i> -Dimethylimidazolium		<i>N,N'</i> -Dimethylbenzimidazolium	
	<i>N</i> -Methylimidazole	iodide	<i>N</i> -Methylbenzimidazole	iodide
0	0.895	4.73	15.9	12.5
0.10	-6.95	1.34	10.1	9.04
0.25	-9.31	2.55	7.64	9.93
0.50	-9.35	7.05	7.10	14.7
0.75	-8.55	12.35	7.74	19.5
0.90		17.1		24.65
1.0	-7.07	21.7	9.20	29.1

**Table 3.** Constituent terms and parameters for transfer enthalpy<sup>a</sup>

	<i>N</i> -Methylimidazole	<i>N</i> -Methylbenzimidazole	<i>N,N'</i> -Dimethylimidazolium cation	<i>N,N'</i> -Dimethylbenzimidazolium cation
$\Delta H_t^{\text{AN} \rightarrow \text{MeOH}}$	7.03	7.3	8.30	7.90
$\Delta H_t^{\text{PHYS} \rightarrow \text{MeOH}}$	-15.0	-14.0	-4.50	-5.10
$\Delta H_t^{\text{SI} \rightarrow \text{MeOH}}$	12.0	8.0		
$K_{\text{sc}}$	1	1		
$Z$	1	1		

<sup>a</sup> Enthalpies and the coefficient,  $A(\text{RR}'_3\text{N}^+)$ , are all given in kJ mol<sup>-1</sup>.

$$\begin{aligned} & \delta_{\text{R}} \Delta H_t^{\text{AN} \rightarrow \text{mix}} (\text{RR}'_3\text{N}^+) \\ &= \Delta H_t^{\text{AN} \rightarrow \text{mix}} (\text{RR}'_3\text{N}^+\text{I}^-) - \Delta H_t^{\text{AN} \rightarrow \text{mix}} [\text{Bu}_4\text{N}^+\text{I}^-] \\ &= \delta_{\text{R}} \Delta H_t^{\text{AN} \rightarrow \text{MeOH}} (\text{RR}'_3\text{N}^+) x_{\text{MeOH}} + A(\text{RR}'_3\text{N}^+) x_{\text{AN}} x_{\text{MeOH}} \end{aligned} \quad (3)$$

## Discussion

In empirical energy correlations, a logarithmic rate constant has been one of the most frequently selected parameters of interest, since it is more tractable than other functions because of rather mild as well as regular responses to the perturbations introduced; rather drastic as well as unique responses have effectively been compensated between activation enthalpy and activation entropy. For further critical analysis activation enthalpy and/or activation entropy would be a suitable parameter. In Figure 1 the activation enthalpies for the Menshutkin reactions measured in acetonitrile, *i.e.*, for the reactions of methyl iodide with various amines indicated in the Figure, are plotted against  $\text{p}K_{\text{a}}$  values for the relevant amines determined in water, where the term  $\log(q/p)$  stands for the statistical correction on the protonation-deprotonation equilibria.<sup>1</sup> Some of the features, which are clearly revealed in the correlation, have been blurred in other forms of empirical energy correlations.

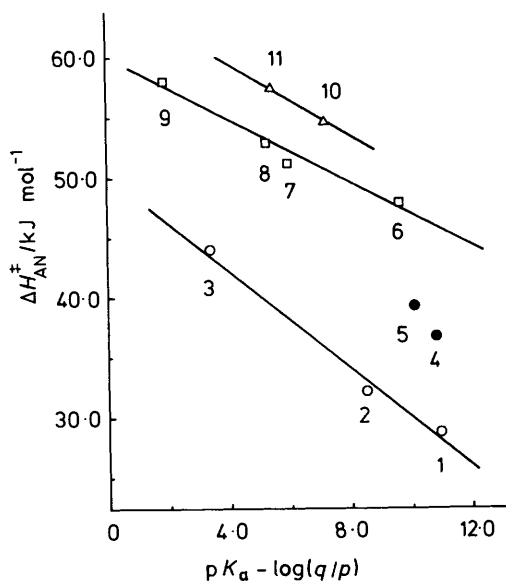
It is interesting to note that aliphatic amine reactions are separated into two families according to the steric requirement of amines, *i.e.*, open chain or bicyclic, and pyridine and imidazole reactions are classified into different families in spite of the seemingly analogous structural requirements, *i.e.*, aromatic amine with a imino nitrogen as a reaction site.

Structural variation in a nucleophile is likely to introduce

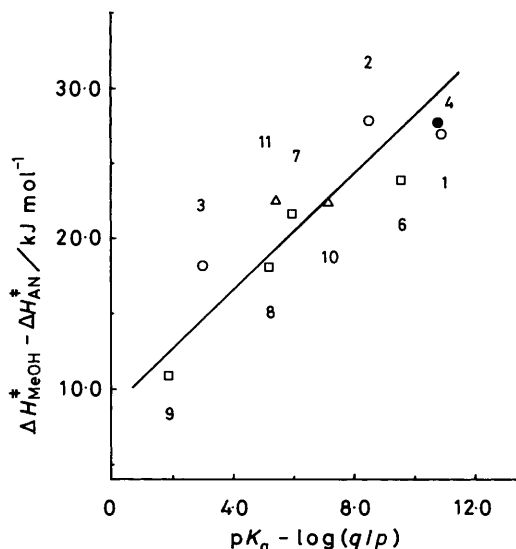
dual effects into the activation enthalpy; a particular intercept is assigned to a narrowly defined type of structure, a family, and, within a family, activation enthalpy gives a linear correlation with  $\text{p}K_{\text{a}}$ . Slope values are -2.0 and -1.3 kJ mol<sup>-1</sup> per unit  $\text{p}K_{\text{a}}$  increment for the bicyclic amine and for the pyridine families, respectively.

In the Edward equation and its sophisticated version,<sup>1,2</sup> two types of variables are required for quantitative assessments of a nucleophilic reactivity; basicity as represented by  $\text{p}K_{\text{a}}$  values in water and polarizability (or logarithmic molar refraction). Furthermore, the more polarizable reagent has implicitly been assumed to introduce a more stabilizing effect at the bond-elongated transition state. In fact, the increasing trend in activation enthalpy along the sequence triethylamine < pyridine < *N*-methylimidazole reaction, 36.6,<sup>12</sup> 52.9,<sup>12</sup> and 54.6 kJ mol<sup>-1</sup>, respectively, although partly fortuitous, coincides with the decreasing trend in reactivity as expected from the molar refraction for the respective amines, 33.8, 24.1, and 23.3 cm<sup>3</sup> mol<sup>-1</sup> (these were evaluated from  $n_{\text{D}}$  values, molecular weight, and density at 20 °C<sup>22</sup>).

Quinuclidine (1-azabicyclo[2.2.2]octane), triethylamine, and 4-dimethylaminopyridine have comparable  $\text{p}K_{\text{a}}$  values, *i.e.*, 10.95,<sup>17</sup> 10.8,<sup>17</sup> and 9.58,<sup>17</sup> respectively, and the activation enthalpy for the respective reaction could be taken as an analogous quantity to the intercept for the relevant family. Decreasing reactivity along the sequence quinuclidine > triethylamine > 4-dimethylaminopyridine, as judged from the activation enthalpy, is associated with the increasing trend in the degree of charge development as judged from  $\alpha_{\text{phys}}$  values, 0.22, 0.35, and 0.64, for the quinuclidine,<sup>14</sup> triethylamine,<sup>12</sup> and



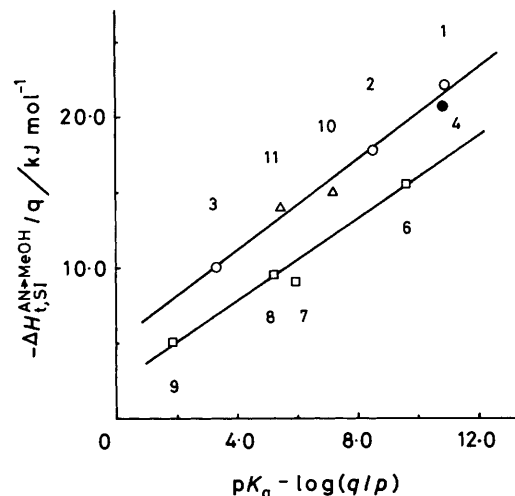
**Figure 1.** Activation enthalpies for reactions of the following amines with methyl iodide in acetonitrile *versus* statistically corrected  $pK_a$  values for the relevant amine in water. The marking is ○ for bicyclic aliphatic amines, ● for aliphatic amines, □ for pyridines, and △ for imidazoles. The numbering of the amines is as follows: 1, Quinuclidine; 2, 1,4-diazabicyclo[2.2.2]octane; 3, *N*-methyldiazabicyclo-octanium ion; 4, triethylamine; 5, *N*-methylpiperidine; 6, 4-dimethylaminopyridine; 7, 4-*t*-butylpyridine; 8, pyridine; 9, 4-cyanopyridine; 10, *N*-methylimidazole; 11, *N*-methylbenzimidazole. Activation enthalpies other than those given in Table 1 were taken from refs. 12–14.  $pK_a$  Values were taken from refs. 17–21



**Figure 2.** Differential activation enthalpy,  $\Delta H_{\text{MeOH}}^{\ddagger} - \Delta H_{\text{AN}}^{\ddagger}$ , *versus* statistically corrected  $pK_a$  values in water. The marking and numbering of the amines are given in Figure 1. Activation enthalpies other than those given in Table 1 were taken from refs. 12–14

4-dimethylaminopyridine reaction,<sup>14</sup> respectively. Seemingly sequential variation in the index,  $\alpha_{\text{phys}}$ , along with the variation in reactivity would be beyond the scope of the Edward-type treatments.

In Figure 2, the differential activation enthalpies,  $\Delta H_{\text{MeOH}}^{\ddagger} - \Delta H_{\text{AN}}^{\ddagger}$ , are plotted against the same set of  $pK_a$  values as used in Figure 1. The line shown is arbitrarily drawn parallel to the two lines, *i.e.*, one line drawn through the points for 2, 11, and 3, and another line linking the two extreme values for 4 and 9. Slope



**Figure 3.** Negative values of the specific interaction enthalpy per unit basis site,  $-\Delta H_{t,\text{SI}}^{\text{AN} \rightarrow \text{MeOH}}/q$ , *versus* statistically corrected  $pK_a$  values in water. The marking and numbering of the amines are given in Figure 1. The enthalpies other than those given in Table 3 were taken from refs. 12–14

value is 1.9  $\text{kJ mol}^{-1}$  per unit  $pK_a$  increment. Most of the contributions which have brought about the particular intercept to the relevant family in the correlations shown in Figure 1 are effectively compensated between the two solvents and all the values are incorporated into one correlation in Figure 2, although incomplete compensation and subtle difference in reaction characteristics result in some scatter in the correlation.

This is one example which expresses the notion<sup>14</sup> that structural variation introduces multiple effects into transition-state characteristics, while solvent effects provide a probe for detecting a more singular property.

When the activation enthalpy in methanol,  $\Delta H_{\text{MeOH}}^{\ddagger}$ , is plotted against  $pK_a$  values, the slope of the plot is given as a sum of two constituent slopes, *i.e.*, slope of the correlation given in Figure 1 and that given in Figure 2. Respective values amount to  $-0.1$  ( $-2.0 + 1.9$ ) for the bicyclic amine reaction family and  $0.6$  ( $-1.3 + 1.9$ ) for the pyridine reaction family. Constituent analysis of the activation enthalpy,  $\Delta H_{\text{MeOH}}^{\ddagger} - \Delta H_{\text{AN}}^{\ddagger}$ , in terms of physical and specific interaction enthalpy as described elsewhere,<sup>12,14</sup> combined with the specific interaction enthalpy *versus*  $pK_a$  correlation shown in Figure 3, leads to the conclusion that the most significant component for a nucleophile which brings about variations in the term is the specific interaction enthalpy,  $\Delta H_{t,\text{SI}}^{\text{AN} \rightarrow \text{MeOH}}$ . Alternatively, the relative contribution of the specific interaction enthalpy in the observed slope value, 1.9  $\text{kJ}$  per unit  $pK_a$  increment, could be evaluated through the division of the slope for the correlation given in Figure 3 by that in Figure 2, as *ca.* 79 and 71% for the bicyclic amine and for the pyridine families, respectively. In other words, the slope value of the empirical energy correlation for the system which includes a protic solvent–base or protic solvent–nucleophile combination is significantly affected by the specific interaction between base (or nucleophile) and protic solvent, *i.e.*, the quantity which does not reflect the characteristics of an activated complex, and can hardly be taken as a transition-state index.

In Figure 3, specific interaction enthalpies per unit basis site, which have been determined so far by the authors,<sup>12,14</sup> are plotted against  $pK_a$  values in water. Here, the two features which remind us of the pattern of behaviour described for the activation enthalpy *versus*  $pK_a$  correlations (Figure 1) are also noted; dispersion of bicyclic amine reactions and of pyridine

**Table 4.** Brønsted coefficients,  $\alpha_{\text{phys}}$ , and isokinetic temperatures,  $\beta_{\text{phys}}$ <sup>a</sup>

	<i>N</i> -Methylimidazole + MeI	<i>N</i> -Methylbenzimidazole + MeI
$\alpha_{\text{phys}}$	0.48 (0.50)	0.44 (0.39)
$\beta_{\text{phys}}/\text{K}$	700 (653)	530 (423)

<sup>a</sup> Numbers in parentheses are estimated values (see text).

reactions into different families, and within a family, linear correlation with  $\text{p}K_{\text{a}}$  values. Slope values amount to 1.35 and 1.5  $\text{kJ mol}^{-1}$  per unit  $\text{p}K_{\text{a}}$  increment for the pyridine and for bicyclic amine families. In addition, higher basicity for a bicyclic amine family as represented by vertical displacement upwards of the  $-\Delta H_{\text{t,SI}}^{\text{AN} \rightarrow \text{MeOH}}/q$  line is reflected in a higher nucleophilic reactivity, *i.e.*, vertical displacement downwards of the  $\Delta H_{\text{AN}}^{\ddagger}$  line (see Figures 1 and 3). Either in the activated complex of the reaction or in a hydrogen-bonded complex, partial bond-making and -breaking proceed simultaneously along the bond linking three atoms. The analogies observed in the two types of enthalpy would be a natural consequence.

Brønsted coefficients,  $\alpha_{\text{phys}}$ , and isokinetic temperatures,  $\beta_{\text{phys}}$ , both due to physical interaction have been determined according to the procedures described elsewhere,<sup>12,14</sup> and summarized in Table 4. *N*-Methylimidazole is characterized by the larger dipole moment and  $\text{p}K_{\text{a}}$  values than those for pyridine, *i.e.*, 3.71 D and  $\text{p}K_{\text{a}}$  7.20 for *N*-methylimidazole, and 2.2 D and  $\text{p}K_{\text{a}}$  5.40 for pyridine,<sup>23</sup> even though both share a common structural feature, *i.e.*, heterocyclic aromatic amine. Substituent effects on protonation energies are generally found to be attenuated on going from gas phase to aqueous solution, and the attenuation factor for *N*-methylimidazoles is almost twice as great as that for pyridines.<sup>24</sup> As the cationic charge is more delocalized over the ring, a larger number of solvent molecules can participate in solute-solvent interactions, leading to a more stabilized cation. The less endothermic enthalpy of transfer for *N,N'*-dimethylimidazolium ion,  $\delta_{\text{R}}\Delta H_{\text{t}}^{\text{AN} \rightarrow \text{MeOH}} = 8.3 \text{ kJ mol}^{-1}$ , than that for *N*-methylpyridinium ion,  $\delta_{\text{R}}\Delta H_{\text{t}}^{\text{AN} \rightarrow \text{MeOH}} = 9.4 \text{ kJ mol}^{-1}$ ,<sup>16</sup> supports this view.

The larger extent of charge development at the transition state, as evaluated from  $\alpha_{\text{phys}}$ , and the higher isokinetic temperature,  $\beta_{\text{phys}}$ , for the *N*-methylimidazole reaction than those for the pyridine reaction (0.48 and 700 K for *N*-methylimidazole reaction and 0.38 and 393 K for pyridine reaction<sup>12</sup>) would be a reflection of delocalization of incipient cationic charge over the ring accompanied by more favourable solute-solvent interactions.

Within an aromatic amine family, various transition-state indices are expected to indicate concordant variations with  $\text{p}K_{\text{a}}$  values (see Figure 1 of this paper and discussion section in ref. 14). The two types of coefficients,  $\alpha_{\text{phys}}$  and  $\beta_{\text{phys}}$ , have been interpolated from the corresponding values for pyridine and for 4-dimethylaminopyridine reactions,<sup>14</sup> under the assumption of linear dependence on  $\text{p}K_{\text{a}}$  values, and indicated in parentheses in Table 4. The agreement between the observed and the estimated values is fair for the *N*-methylimidazole reaction. The

decrease in these coefficients on going from the *N*-methylimidazole to the *N*-methylbenzimidazole reaction is also predicted by the procedures.

Through these analyses, it is concluded that the *N*-methylimidazole and *N*-methylbenzimidazole reactions exhibit dual character; on the thermodynamic quantity for which the contribution from the intrinsic electronic and steric properties of the nucleophile is significant, *i.e.*,  $\Delta H_{\text{AN}}^{\ddagger}$  and  $\Delta H_{\text{t,SI}}^{\text{AN} \rightarrow \text{MeOH}}$ , they show family dependent character, whereas for the quantity for which the contribution from the intermolecular solvation plays a major role, *i.e.*,  $\alpha_{\text{phys}}$  and  $\beta_{\text{phys}}$ , they follow the trend as anticipated from those for the reactions of pyridine derivatives (family-independent property).

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