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HEATS OF SOLUTION OF SOME PYRIMIDINES, PURINES AND RELATED COMPOUNDS IN DIMETHYLSULFOXIDE

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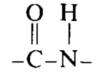
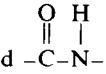
ABSTRACT

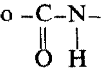
The heats of solution of some pyrimidines, purines and related compounds are combined with their heats of vaporization or sublimation to yield the enthalpies of transfer from the gas phase to dimethylsulfoxide and to water. The isolation of H-bonding terms from these enthalpies by various methods is difficult and the preferred method based on Taft-Kamlet correlations suffers from the lack of independent values for the solute solvatochromic parameters. Nevertheless, our data show strong interactions of the $-NH_2$ and  $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$ groups with Me_2SO. The calculated group enthalpies of transfer from water to Me_2SO indicate a marked stabilization of the $>N-H$, $-NH_2$, $-OH$, and  $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$ groups in Me_2SO so that H-bonding interactions between these groups and the H-bond donor water are less important.

INTRODUCTION

We are currently studying the protonation of nucleic acid bases in various media [1]. Within the framework of this research, we have supplemented data in the literature by determining the heats of solution of some biologically important pyrimidines, purines and related compounds in dimethyl sulfoxide (Me_2SO). For the purpose of comparison, additional determinations in water were called for. We present here the results of our calorimetric study. We have used Me_2SO as solvent because it is widely used in research on nucleic acids on account of its good solubilizing properties. Furthermore, a step in understanding solvation in Me_2SO, a dipolar solvent with no H-bond donor (HBD) properties but good H-bond acceptor (HBA) properties, might be a starting point in unravelling the complex H-bonding interactions in water, which has both HBD and HBA properties.

Base	Abbreviation	R_2	R_6	R_9
Purine	Pur	H	H	H
Adenine	Ade	H	NH_2	H
Adenosine	Ado	H	NH_2	Ribose
9-Methyladenine	MeAde	H	NH_2	CH_3
N^6,N^6-Diethyladenine	Et_2Ade	H	Et_2N	H
Hypoxanthine	Hyp	H	OH [a]	H
Guanine	Gua	NH_2	OH [a]	H

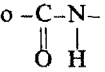
[a] Tautomerization to



$-\underset{\substack{\| \\ O}}{C}-\underset{\substack{| \\ H}}{N}-$

Base	Abbreviation	R_2	R_4	R_5	R_6
Pyrimidine	Pym	H	H	H	H
Cytosine	Cyt	OH [a]	NH_2	H	H
Uracil	Ura	OH [a]	OH [a]	H	H
Thymine	Thy	OH [a]	OH [a]	CH_3	H
4-Amino-2,6-dimethylpyrimidine	Dap	CH_3	NH_2	H	CH_3

[a] Tautomerization to



$-\underset{\substack{\| \\ O}}{C}-\underset{\substack{| \\ H}}{N}-$

EXPERIMENTAL

Materials

Sources of most of the compounds used have been previously reported [1]. 4-Aminopyridine (Ampy) (Aldrich) and naphthalene (Naph) were used as received. N^6,N^6-Diethyladenine was prepared as follows [2]: 5 g 6-chloropurine (Aldrich), 8.6 ml Et_2NH and 30 ml n-butanol were heated under reflux for 90 min. After cooling, the precipitate was filtered, washed with 25 ml water, and recrystallized from absolute ethanol. All samples were checked for purity by acid–base titrations or UV measurements. Me_2SO (BDH, analytical grade) was used without further purification.

Calorimetry

The heats of solution were measured at $25.00 \pm 0.01°C$ with an L.K.B. model 8725-2 isoperibol calorimeter as previously described [1]. The amount of base dissolved (1×10^{-4} to 3×10^{-3} mol) in 100 ml of Me_2SO or water was deduced from the masses of the glass ampoules.

The heats of solution of Et_2Ade and Hyp in water could not be determined directly because the bases were either too insoluble or dissolved too slowly. These values were obtained indirectly by measuring first the heat of solution, ΔH_{nw}, of solid Et_2Ade and Hyp respectively in aqueous 0.12 M and 0.58 M $HClO_4$. Then, the heat of reaction of aqueous Et_2Ade with an excess of 5.8 M $HClO_4$ was measured to yield the heat of protonation, ΔH_{pw}, after a correction for the dilution of $HClO_4$. Our ΔH_{pw} values were combined with ΔH_{nw} to give $\Delta H_w(Et_2Ade)$ according to $\Delta H_w = \Delta H_{nw} - \Delta H_{pw}$. For Hyp, ΔH_{pw} was taken from the literature [3] and then combined with our ΔH_{nw} to give ΔH_w(Hyp).

RESULTS

Solution enthalpies

The heats of solution Q of solid Naph, 2-hydroxypyridine (Hypy), Ampy and Cyt in Me_2SO (Q_s) and that of Hypy in water (Q_w) were plotted against the quantities of base dissolved. The slopes of the corresponding least-squares lines gave the molar enthalpy of a solution of B, $\Delta H_{s\text{ or }w}(B)$, which refers to eqn. (1)

$$B(c) = B(s \text{ or } w) \tag{1}$$

For Et_2Ade, Hyp, and caffeine (1,3,7-trimethylxanthine, Caf), because of the low rate of dissolution of the base in Me_2SO, the quantity of base dissolved could not be varied significantly so that the solution enthalpies reported are an average of two to four separate determinations.

The $\Delta H_{s\text{ or }w}(B)$ values are taken to be equal to $\Delta H^{\ominus}_{s\text{ or }w}(B)$ because no concentration dependence was observed in the concentration range used (10^{-3}–10^{-2} M). The $\Delta H^{\ominus}_{s\text{ or }w}(B)$ values are given in Table 1 together with literature data [1,4–16].

Enthalpies of vaporization and sublimation

In order to calculate and discuss the enthalpy changes corresponding to the transfer of the bases from the gas phase to Me_2SO or water, we needed the enthalpies of vaporization or of sublimation of the bases.

The vaporization enthalpies, $\Delta H^{\ominus}_{vap}$, for benzene (ϕH) [4,5], methylbenzene (ϕCH_3) [5], aniline (ϕNH_2) [14], *N*,*N*-dimethylaniline (ϕNMe_2) [17], pyridine (Py) [4,14], and pyrimidine (Pym) [4] given in Table 2, are literature values. For *N*-methylimidazole (MeImid), $\Delta H^{\ominus}_{vap}$ was estimated from the extrapolated linear relation between $\Delta H^{\ominus}_{vap}$ and the normal boiling points given by Wadsö [18] for tertiary amines, since we also found this relation to hold for the cyclic compounds Bz, Py, pyrrole, and 1,2-diazine.

TABLE 1

Solution enthalpies (kJ mol^{-1}) of bases and related compounds in Me_2SO, $\Delta H_s^{\ominus}$, and water, $\Delta H_w^{\ominus}$, at 25 °C

Base	$\Delta H_s^{\ominus}$	$\Delta H_w^{\ominus}$	Base	$\Delta H_s^{\ominus}$	$\Delta H_w^{\ominus}$
Cyt	+8.3±0.2	+27.2 [a]	Pur	+13.7 [e]	+18.3 [e]
Ura	+10.2 [b]	+29.4 [c]	Ade	+10.0 [e]	+33.5 [e]
Thy	+7.9 [b]	+24.3 [d]	Ado	+1.3 [e]	+32.3 [e]
Dap	+14.6 [e]	+9.7 [e]	MeAde	+6.5 [e]	+26.1 [e]
Pym	+0.22 [e]	−9.8 [e]	Et_2Ade	+21.2±0.3	+16.1±0.8
Ampy	+8.86±0.08	+16.7 [f]	Hyp	+10.1±0.6	+26.7±0.1
Hypy	+13.3±0.2	+9.6±0.2	Gua		+49.2 [l]
Py	+1.2 [g]	−9.7 [g]	Caf	+19 ±1	+14.2 to +15.1 [m]
ϕNMe_2	+3.51 [g]		BzImid	+11.3 [e]	+19.0 [e]
ϕNH_2	−9.36 [g]	+1.84 [g]	MeImid	−0.1 [e]	−9.6 [e]
ϕOH	+13.3 [h]	+9.6 [i]	Imid	+11.0 [e]	+12.8 [e]
ϕCH_3	+3.8 [j]	+3.2 [j]	Naph	+18.99±0.02	+29.8 [n]
ϕH	+2.7 [j,k]	+3.0 [j]			

[a] Ref. 8. [b] Ref. 9. [c] Ref. 10. [d] Ref. 11. [e] Ref. 1. [f] Ref. 7. [g] Ref. 14. [h] Ref. 16. [i] Ref. 15. [j] Ref. 5. [k] Ref. 4. [l] Ref. 12. [m] Ref. 13. [n] Ref. 6.

The sublimation enthalpies for the solid bases, $\Delta H_{subl}^{\ominus}$, are given in Table 2. Values for Naph [19], imidazole (Imid) [20], phenol (ϕOH) [21], Hypy [22], and Ampy [23] were taken from the literature. For the nucleic acid bases and some of their derivatives (Cyt, Ura, Thy, Ade, MeAde, Hyp, Gua, and Caf), $\Delta H_{subl}^{\ominus}$ values were deduced from literature values corresponding to higher temperature [24–29] and corrected to 25 °C according to

TABLE 2

Enthalpies of transfer from the gas phase to Me_2SO, $\Delta H_{gs}^{\ominus}$, and from water to Me_2SO, $\Delta H_{ws}^{\ominus}$, at 25 °C (kJ mol^{-1})

Base	$\Delta H_{vap,subl}^{\ominus}$ [a]	$\Delta H_{gs}^{\ominus}$	$\Delta H_{ws}^{\ominus}$	Base	$\Delta H_{vap,subl}^{\ominus}$ [a]	$\Delta H_{gs}^{\ominus}$	$\Delta H_{ws}^{\ominus}$
Cyt	+157	−149	−18.8	Pur	+104	−90	−4.6
Ura	+127	−117	−19.2	Ade	+134	−124	−23.5
Thy	+130	−122	−15.4	Ado			−31.0
Dap	+104	−89	+4.9	MeAde	+126	−119	−19.6
Pym	+50.0	−49.8	+10.0	Et_2Ade	+123	−102	+5.1
Ampy	+88.1	−79.2	−7.8	Hyp	+166	−156	−16.5
Hypy	+86.6	−73.3	+3.7	Gua	+199		
Py	+40.2	−39.0	+10.9	Caf	+107	−88	+4
ϕNMe_2	+52.8	−49.3		BzImid	+106	−95	−7.7
ϕNH_2	+55.6	−65.0	−11.2	MeImid	+54	−54	−9.5
ϕOH	+67.8	−71.0	−15.9	Imid	+74.5	−63.5	−1.8
ϕCH_3	+38.0	−34	+0.6	Naph	+72	−53	−10.8
ϕH	+33.8	−31	0				

[a] See text.

Burkinshaw and Mortimer's equation [24]. The sublimation enthalpies for the other bases were not available and had to be estimated from data for related compounds by using suitable group contributions. $\Delta H^{\ominus}_{\mathrm{subl}}(\mathrm{Pur})$ was obtained by subtracting from $\Delta H^{\ominus}_{\mathrm{subl}}(\mathrm{Ade})$, 30 kJ mol^{-1} for the loss of the amino group. This correction is an average of the enthalpy changes for the loss of the amino group when passing from Gua to Hyp (-33 kJ mol^{-1}) and from 5-aminouracil to uracil (-27 kJ mol^{-1}) [27]. $\Delta H^{\ominus}_{\mathrm{subl}}(\mathrm{Et_2Ade})$ was obtained by adding 3 kJ mol^{-1} to the value for N^6,N^6-dimethyladenine (120 kJ mol^{-1}) [29]. $\Delta H^{\ominus}_{\mathrm{subl}}$ of benzimidazole (BzImid), 106 kJ mol^{-1}, was calculated from $\Delta H^{\ominus}_{\mathrm{subl}}(\mathrm{Imid}) = 74$ kJ mol^{-1} to which we added 32 kJ mol^{-1} for the attachment of the α,ω-butadienyl group to the imidazol moiety. This latter contribution ($+32$ kJ mol^{-1}) was calculated according to a method developed to estimate the enthalpies of planar aromatic hydrocarbons [30]. $\Delta H^{\ominus}_{\mathrm{subl}}$ of Dap was taken as 104 kJ mol^{-1} from $\Delta H^{\ominus}_{\mathrm{subl}}(\mathrm{Ampy}) = 88$ kJ mol^{-1} to which we added first 10 kJ mol^{-1} to pass from pyridine to pyrimidine, then an additional 6 kJ mol^{-1} to account for the two methyl groups. This 104 kJ mol^{-1} value is in good agreement with 106 kJ mol^{-1} deduced from a correlation line we obtained between $\Delta H^{\ominus}_{\mathrm{subl}}$ and molecular weights for the related bases Imid, Ampy, Hypy, Pur, BzImid and MeAde. $\Delta H^{\ominus}_{\mathrm{subl}}(\mathrm{Ado})$ could not be estimated.

Enthalpies of transfer

The enthalpies of transfer of the bases from the gas phase to solvents, $\Delta H^{\ominus}_{\mathrm{gs}}(\mathrm{B})$ and $\Delta H^{\ominus}_{\mathrm{gw}}(\mathrm{B})$, respectively for $\mathrm{Me_2SO}$ and water, are given in Table 2. These values which refer to the process

$$\mathrm{B(g)} = \mathrm{B(s\ or\ w)} \tag{2}$$

are calculated from data in Tables 1 and 2 according to

$$\Delta H^{\ominus}_{\mathrm{gs\ or\ gw}}(\mathrm{B}) = \Delta H^{\ominus}_{\mathrm{s\ or\ w}}(\mathrm{B}) - \Delta H^{\ominus}_{\mathrm{subl\ or\ vap}}(\mathrm{B}) \tag{3}$$

The enthalpies of transfer of B from water to $\mathrm{Me_2SO}$, $\Delta H^{\ominus}_{\mathrm{ws}}(\mathrm{B})$, calculated from

$$\Delta H^{\ominus}_{\mathrm{ws}}(\mathrm{B}) = \Delta H^{\ominus}_{\mathrm{s}}(\mathrm{B}) - \Delta H^{\ominus}_{\mathrm{w}}(\mathrm{B}) \tag{4}$$

and data in Table 1 are also given in Table 2.

DISCUSSION

H-Bonding contribution to enthalpy of solvation

H-Bonding interactions between solutes and solvents play a major role in the interpretation of biophysical processes and attempts have been made to isolate from solution enthalpy data of nucleic acid bases, the enthalpy term which characterizes their H-bonding interactions with the solvent. We will assume with Krishnan and Friedman [5,31], the following additive contributions to the enthalpy of solvation of B, i.e. the transfer of B from the gas phase to the solvent

$$\Delta H^{\ominus}_{\mathrm{gs}} = \Delta H_{\mathrm{cav}} + \Delta H_{\mathrm{vdw}} + \Delta H_{\mathrm{str}} + \Delta H_{\mathrm{HB}} \tag{5}$$

where ΔH_{cav} is due to the creation in the solvent of a cavity, ΔH_{vdw} includes the van der Waals interactions of B with the solvent and polarization–dipole and dipole–dipole interactions, ΔH_{str} corresponds to structural changes produced in the solvent and is particularly relevant for water, and ΔH_{HB} refers to H-bonding interactions between B and the solvent.

Clearly isolating ΔH_{HB} is difficult and various approaches have been used. First, some authors have calculated ΔH_{cav} as a first step, but the values of ΔH_{cav} are relatively high and they vary according to the method of calculation used. This is shown in the results of a group of workers who first obtained values of 31 and 36 kJ mol^{-1} for the bases uracil and thymine respectively [25], then values of 89 and 101 kJ mol^{-1} [32] for the same compounds. Abraham and Nasehzadeh [33] have tested cavity and interaction theories of solution against experimental values for the simple non-polar solute Me_4Sn. These authors concluded that "the methods tested were as yet not refined enough to lead to generally quantitative data on cavity effects".

The solvation enthalpy (SE) method uses a second approach to reach ΔH_{HB}, or more generally specific interactions: a model compound M is chosen to cancel ΔH_{cav} and ΔH_{vdw}, and presumably ΔH_{str}, so that $\Delta H^{\ominus}_{\mathrm{gs}}(\mathrm{B}) - \Delta H^{\ominus}_{\mathrm{gs}}(\mathrm{M}) = \Delta H_{\mathrm{HB}}$. Then, in a third related approach, the pure base (PB) method [34], ΔH_{HB} is taken as the difference between the enthalpies of solution of B and of M in the solvent minus the difference of the enthalpies of solution of B and M in an inert solvent such as cyclohexane or CCl_4. The choice of the model compound to compensate for ΔH_{vdw} in both SE and PB methods is obviously crucial, as shown by Stephenson and Fuchs [35] who have compared enthalpy data for the solution of 1-octanol and five model compounds in thirteen non-polar or dipolar aprotic solvents. These authors recommend the use of another method, the non-hydrogen-bonding baseline (NHBB) method which takes advantage of correlations with the Taft–Kamlet dipolarity–polarizability solvent parameters $\Pi^{\star}$ [36] to obtain a meaningful compensation for ΔH_{vdw}.

In order to illustrate the wide range of values obtained for ΔH_{HB} by the three methods, we have compared data for ΔH_{HB} of pyridine and pyrimidine in water using benzene as model compound. The SE method gives -19 kJ mol^{-1} for Py and an unexpected -29 kJ mol^{-1} for the less basic Pym, while the PB method leads to a much lower -13 kJ mol^{-1} for Py. Using the NHBB method, since water and Me_2SO have very close $\Pi^{\star}$ values, 1.09 and 1.00 respectively [36], we take our $\Delta H^{\ominus}_{\mathrm{gs}}$ value for Me_2SO as the base line value for water and obtain -11 kJ mol^{-1} (Py) and -10 kJ mol^{-1} (Pym) from data in Table 2. These ΔH_{HB} values are easier to reconcile with the enthalpy of formation of the complexes of Py and Pym with phenol (a stronger acid than water) in CCl_4 [37], -27 kJ mol^{-1} (Py) and -22 kJ mol^{-1} (Pym), than are the values obtained earlier with the SE method, -19 and -29 kJ mol^{-1} respectively. Nevertheless, these latter figures have been used as a starting point to evaluate the enthalpy of interaction of imidazole, purines, and pyrimidines with solvent water [4,38,39].

To conclude, this short discussion has emphasized the problems involved in the estimation of the ΔH_{HB} term in water even for simple non HBD bases such as Py and Pym. Obviously, when we consider substituted pyrimidines and purines with both HBA and HBD properties, the difficulties are compounded. This is apparent when examining the enthalpy data for the solution of *m*-cresol versus toluene in alcohol solvents [40] where both types of H-bonding interactions also operate.

Enthalpies of solvation in Me_2SO

Turning now to the simpler HBA solvent, Me_2SO, we have taken the first step in expressing enthalpy of solvation values $\Delta H_{gs}^{\ominus}$ as a function of the Taft–Kamlet solvatochromic parameters [36]. By using data for the solution of non-polar pentane, hexane, heptane ($\Pi_2^{\star} = -0.08$) and cyclohexane ($\Pi_2^{\star} = 0$) we obtain

$$\Delta H_{gs}^{\ominus} = -19.17(\bar{V}_2/100) - 0.9 \text{ (kJ mol}^{-1}) \tag{6}$$

where $\bar{V}_2$ is the solute molar volume.

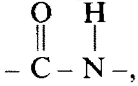
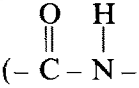
Then adding $\Delta H_{gs}^{\ominus}$ data for the solution of eleven polar non HBD solutes in Me_2SO [31,40–42] we calculate

$$\Delta H_{gs}^{\ominus} - \left(-19.17(\bar{V}_2/100) - 0.9\right) = -33.44\Pi_2^{\star} + 4.3 \text{ (kJ mol}^{-1}) \tag{7}$$

($r = 0.987$), so that the solvatochromic equation becomes

$$\Delta H_{gs}^{\ominus} = -19.17(\bar{V}_2/100) - 33.44\Pi_2^{\star} + 3.4 \text{ (kJ mol}^{-1}) \tag{8}$$

Equation (8) allows us to estimate $\Pi_2^{\star}$ values for a non HBD liquid solute: for example, for Pym we find $\Pi_2^{\star} = 1.14$. However, in order to use eqn. (8) directly to calculate the $\Delta H_{cav} + \Delta H_{vdw}$ terms for our bases, we need their $\bar{V}_2$ and $\Pi_2^{\star}$ values. Then, the difference between the experimental $\Delta H_{gs}^{\ominus}$ (total interaction) and the calculated value (eqn. (8)) would yield ΔH_{HB} which might correlate with the α_2 acidity Taft–Kamlet parameter of the HBD bases. Since as yet we do not have independent values of $\Pi_2^{\star}$ and α_2 for the bases [36], we have fallen back on the SE method to evaluate group contributions to $\Delta H_{gs}^{\ominus}$ of the bases. We take pairs of selected solutes and their $\Delta H_{gs}^{\ominus}$ values from Table 2 to calculate $\Delta\ \Delta H_{gs}^{\ominus}$ which gives the interaction enthalpy of the group with Me_2SO, provided that the $\bar{V}_2$ and $\Pi_2^{\star}$

values for both compounds are close. First, comparing the thymine–uracil and toluene–benzene pairs, we find that the addition of a $-CH_3$ gives a contribution of -5 and -3 kJ mol^{-1} respectively, which compares favourably with -3 kJ mol^{-1} for aliphatic solutes [31]. Then, looking at the $-NH_2$ group with both pairs Et_2Ade–Ade and ϕNMe_2–ϕNH_2, we obtain -16 kJ mol^{-1} (after subtracting -6 kJ mol^{-1} for the extra $-CH_2-$ of Et_2Ade) in good agreement with Stephenson and Fuchs' values [42] of -16 kJ mol^{-1} calculated for the H-bonding interactions using the NHBB method (ϕNH_2 vs. ϕH). Taking the pairs Ade–Pur and ϕNH_2–ϕH would have given -34 kJ mol^{-1} which emphasizes the importance of proper correction for the dipolar–polarizability contribution. If we now consider the $-OH$ group, the pair ϕOH–ϕH gives -40 kJ mol^{-1} in agreement with Friedman's value [31] of -35 kJ mol^{-1} for aliphatic alcohols. However, these high values must include a non H-bonding term since from Stephenson and Fuchs' data [40] we calculate -25 kJ mol^{-1} (*m*-cresol vs. toluene) for an aromatic $-OH$ and -16 kJ mol^{-1} (pentanol vs. BuOMe) for the less acidic aliphatic $-OH$. At any rate, for an $-OH$ group which tautomerizes to  $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$, we obtain much higher values: for Hyp–Pur and Dap–Cyt, -66 and -68 kJ mol^{-1} (after correction for $-CH_3$), although these values are likely to include some dipolar–polarizability contributions. Finally, comparing the pairs MeAde–Ade and MeImid–Imid gives -5 kJ mol^{-1} and -9 kJ mol^{-1} respectively, i.e. a relatively small contribution for $>$N–H interactions. There are two noteworthy features which emerge from these comparisons. First, the H-bonding interaction due to an $-NH_2$ group is large and near that of an aliphatic $-OH$. Second, the tautomerized $-OH$ group ( $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-$) whether on pyrimidines or purines gives rise to strong interactions with Me_2SO.

Enthalpies of transfer from water to Me_2SO

We have also considered the enthalpies of transfer of the bases from water to Me_2SO, $\Delta H^{\ominus}_{ws}$, given in Table 2. We have compared the $\Delta H^{\ominus}_{ws}$ of pairs of bases to isolate the transfer contributions of selected groups. Since water and Me_2SO have similar $\Pi^{\star}$ values, the ΔH_{vdw} contribution to solvation should nearly cancel in $\Delta H^{\ominus}_{ws}$. Furthermore by comparing $\Delta H^{\ominus}_{ws}$ for pairs of selected bases, we also eliminate the ΔH_{cav} term so that we should be left with $\Delta\ \Delta H^{\ominus}_{ws}$ representing mostly changes in H-bonding contributions when passing from water to Me_2SO, with possibly some residual ΔH_{str} contribution. The $\Delta\ \Delta H^{\ominus}_{ws}$ values calculated for the $>$N–H, $-NH_2$, $-OH$ groups all indicate stabilization in Me_2SO, suggesting that the dominant H-bonding interactions are between the above groups acting as

HBD and both solvents, Me_2SO being the stronger HBA solvent [43]. Apparently, the H-bonding interactions between the previous groups and water, acting as HBD, play a minor part. Nevertheless, we could not find a correlation between the $\Delta\ \Delta H^{\ominus}_{ws}$ values and H-bond strength parameters. For example, in the series ϕNH_2, 4-Ampy, 4-Ampym, 9-MeAde, $\Delta\ \Delta H^{\ominus}_{ws}$ does not correlate with pK values for the deprotonation of the $-NH_2$ groups, which might reflect the HBD strength.

In conclusion, it would seem as if the unravelling of the complex interactions between the nucleic acid bases and the solvents in terms of enthalpy contributions to their heats of solvation will have to pass through an independent evaluation of their $\Pi^{\star}_2$, α_2, and β_2 Taft–Kamlet solvatochromic parameters.

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