Although a similar two-dimensonal mechanism involving only one chain is feasible for S_3N_3, we would prefer a three-dimensional approach. This is best envisaged for the vaporization step where two possibilities appear feasible. One would involve an SNS unit in the chain along the $\bar{1}02$ plane coupling to an NSN unit in the plane behind, i.e., coupling occurs approximately along the 100 plane. This produces the required six-membered ring with the central atom of the three from each chain flipped up. Such a process can continue down each pair of chains taking three atoms at a time from each. This process is facilitated by the close interaction between such units; S···N distances are 3.39 Å, close to the van der Waals radii (3.35 Å). The alternative mechanism is to take an NS fragment from one chain and insert it into a planar SNSN unit in the plane behind. This process would be considerably enhanced if one $(SN)_x$ chain were to rotate relative to the other. Such interchain coupling has already been shown to exist,[50-52] and from band structure calculations it is evident that this is a requirement for large π band splittings and the subsequent electrical properties of $(SN)_x$. Thus, although the individual chains can exhibit a one-dimensional Peierls instability (hence semiconducting) the three-dimensional solid exhibits metallic character. In both cases a distorted S_3N_3 ring will be produced initially, and it is therefore of some interest to determine the potential barrier for rearrangement to a planar structure. Such studies are at present underway; we have shown above that the chair/boat C_s symmetry $S_3N_3{}^\circ$ readily converts to the planar C_{2v} form. The reverse of either of the above mechanisms is a preferred topochemical polymerization, i.e., condensation of S_3N_3 units to $(SN)_x$ would require stacks of S_3N_3 ring units, not unlike those proposed for the S_2N_2 crystal structure.[6] Such cofacial π systems are currently the subject of some interest.[53] The "red monomer" can be obtained as an unstable crystalline solid;[7] the crystal structure would be of considerable interest in the context of the above discussion.

In closing, we reiterate that our ab initio CI calculations for the radical and cationic states support a planar ring geometry for the $S_3N_3{}^\circ$ species: essentially D_{3h} with a possible distortion to C_{2v}, and a shortening of the N–S–N bonds about the C_2 axis. The radical is ${}^2A_2$; the ground-state cation is ${}^3A_2{}'$, preferred over ${}^1A_1{}'$. This is analogous to the situation in the first-row NH_2 radical,[54] although this cation ordering is reversed in the second-row PH_2 species.[55] The agreement with the PES is remarkably good considering the complexity of ionic states.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. We thank Drs. McDowell and Frost (UBC) for their interest and Dr. M. F. Guest (Daresbury) for assistance with the MRDCI program.

Registry No. S_3N_3, 64885-69-4; $(SN)_x$, 56422-03-8; S_4N_4, 28950-34-7; NS_2, 12033-57-7; S_2N_2, 25474-92-4.

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Electrostatic Proximity Effects in the Relative Basicities and Acidities of Pyrazole, Imidazole, Pyridazine, and Pyrimidine[1]

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Contribution from the Department of Chemistry, University of California at Irvine, Irvine, California 92717, the Departamento de Quimica Fisica y Quimica Cuantica, Universidad Autonoma de Madrid, Cantoblanco 28049, Madrid, Spain, and the Instituto de Quimica Medica, CSIC, Juan de la Cierva 3, 28006, Madrid, Spain. *Received August 30, 1985*

Abstract: The relative gas-phase and solution basicities of pyridazine and pyrimidine and of pyrazole and imidazole, as well as the relative gas-phase and solution acidities of the latter diazoles, have been accounted for approximately by considering important NH^+ and lone pair electrostatic interactions that act from the 2-position.

The acid/base behavior of above titled compounds is widely recognized for its importance to the life sciences.[2] The gas- and aqueous-phase basicities of pyrimidine (1,3-diazine, I) are known to be distinctly *smaller* by 3.4[3] and 1.1[4] pK_b units, respectively, than that of pyridazine (1,2-diazine, II). We have found that *in contrast* the gas-phase basicity of imidazole (1,3-diazole, III) is *larger* (as is also the aqueous basicity[5]) by significantly greater amounts (8.0 and 4.6 pK_b units, respectively) than that of pyrazole (1,2-diazole, IV). This very large basicity difference (in either phase) has not previously been satisfactorily explained.

We have also found that the gas-phase basicity of the conjugate base of imidazole (III′) is significantly *smaller* (by 2.6 pK_b units) than that of the conjugate base of pyrazole (IV′). That is, III is a stronger acid than IV. The same order of relative acidities applies in dimethyl sulfoxide solution (III is stronger than IV by

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(1) This work was supported in part by a grant from the U.S.-Spain Joint Committee for Scientific and Technological Cooperation.

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(3) Houriet, R.; Schwarz, H.; Zummack, W.; Androde, J. G.; Schleyer, P. v. R. *Nouv. J. Chim.* **1981**, *5*, 505. The value given is from our determinations, which are in reasonable accord with this reference. We find the gas-phase basicity of II to be equal (±0.1 kcal/mol) to that of ethylamine and to be 1.1 kcal/mol (±0.1) greater than that of 3-chloropyridine. Compound I was found to be 1.4 ± 0.2 kcal/mol more basic than 4-CNC_5H_4N, all using the methods described in ref 14. Gas-phase $\Delta pK_b = \Delta G^\circ(g)/2.303RT$, where ΔG° is for the indicated proton-transfer equilibrium.

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0002-7863/86/1508-3237$01.50/0

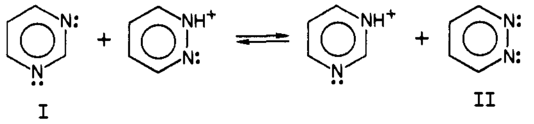
Table I. Comparison of Observed and Calculated Values (kcal/mol) of $\Delta G°(g)$ and $\Delta G°(aq)$ for Reactions 1–7[a]

	gas phase		aqueous phase	
reactn	$\Delta G°(g)$	$\Delta G°(g)_{calcd}$	$\Delta G°(aq)$	$\Delta G°(aq)_{calcd}$
1	4.6	4.5 = 6.5 + 2.0 − 12.5 + 8.5	1.5	1.0 = 2.5 + 1.0 − 7.8 + 5.3
2	−10.9	−11.5 = −6.5 − 1.0 − 12.5 + 8.5	−6.1	−5.5 = −2.5 − 0.5 − 7.8 + 5.3
3	3.6	3.5 = 6.5 + 1.0 − 12.5 + 8.5	−0.3	0.5 = 2.5 + 0.5 − 7.8 + 5.3
4	9.6	8.5 = 8.5	5.4	5.3 = 8.5/1.6
5	8.4	8.5 = 8.5	4.6	5.3 = 8.5/1.6
6	5.0	4.0 = −6.5 − 2.0 + 12.5	4.0	4.3 = −2.5 − 1.0 + 7.8
7	4.8	5.0 = −6.5 − 1.0 + 12.5	4.9	4.8 = −2.5 − 0.5 + 7.8

[a] See text for descriptions of structural parameters used for calculated values.

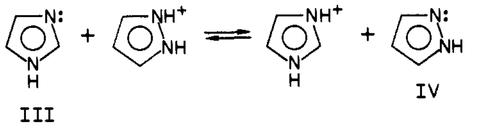
1.3 pK_a units)[6] but in aqueous solution IV is stronger than III by 0.2 pK_a units.[5a] The apparent enigma of the above basicities is interpreted herein, as are also the solvent effects on each comparison.

Equations 1–3 give the proton-transfer equilibria of the above basicity comparisons:[8,10]



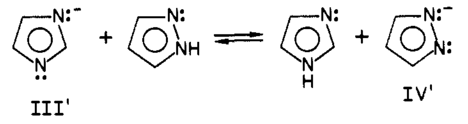
(1)

$\Delta G°(g) = +4.6 \pm 0.2$ kcal/mol
$\Delta G°(aq) = +1.46 \pm 0.2$ kcal/mol



(2)

$\Delta G°(g) = -10.9 \pm 0.2$ kcal/mol
$\Delta G°(aq) = -6.34 \pm 0.2$ kcal/mol



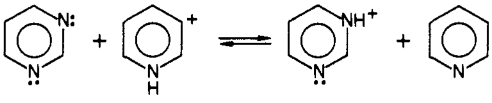
(3)

$\Delta G°(g) = +3.6 \pm 0.2$ kcal/mol
$\Delta G°(Me_2SO) = +1.8 \pm 0.2$ kcal/mol
$\Delta G°(aq) = -0.3 \pm 0.2$ kcal/mol

It will be observed that in the gas phase the positions of equilibrium for all three reactions 1–3 are in the direction expected for the dominant effect to be the relief of the destabilization imparted to either neutral base or ion by electrostatic repulsion between either adjacent lone pair electrons[7] or adjacent NH^{+}[8] pair centers, i.e., left for reactions 1 and 3 and right for reaction 2. Another significant contribution to the $\Delta G°$ values for reactions 1–3 is the field/inductive effect of the electronegative aza substituent, which is less at the 3- than the 2-position.[9a] This aza substituent effect destabilizes cations but stabilizes anions. Second-order attractive interactions are probably also involved in all three reactions between the lone pair electrons and the adjacent NH^{+}[9b] or NH in the conjugate acid of II or of IV, respectively.

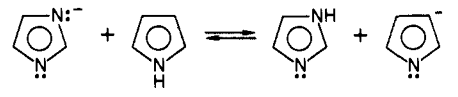
In reaction 2, all three of the above effects act to shift the equilibrium to the right giving a negative $\Delta G°$ value that is in magnitude the largest of those for reactions 1–3. The attractive electrostatic interaction in the conjugate acid of II and the predominant lone pair repulsion in II are opposed by a favorable aza substituent effect in reaction 1. This accounts for the positive $\Delta G°(g)$ value observed for reaction 1 and its intermediate magnitude compared to those of reactions 2 and 3. In reaction 3, the predominant lone pair repulsion in IV′ is supported by the weak lone pair/NH attraction in pyrazole, but these are opposed by the favorable aza substituent effect with the consequence that $\Delta G°(g)$ is only a relatively small positive value.

In order to account more quantitatively for the contributing effects to $\Delta G°(g)$ values for reactions 1–7, the following simplified assumptions have been made: (a) the intrinsic adjacent NH$^+$/NH$^+$ pair and adjacent lone pair electronic repulsions are taken to be equal and of approximately 6.5 kcal/mol in magnitude; (b) the corresponding electrostatic interactions from the 3- (rather than the 2-) position are taken to be negligible; (c) the electronegative 2-aza substituent effect is taken to be approximately 12.5 kcal/mol (favorable in anions, unfavorable in cations), and the 3-aza substituent is taken to be approximately 8.5 kcal/mol; (d) the adjacent NH$^+$/lone pair attraction is taken equal to approximately 2.0 kcal/mol, whereas that for the adjacent NH/lone pair attraction is taken to be approximately 1.0 kcal/mol. These assumpions reproduce within 1 kcal/mol the $\Delta G°(g)$ values for reactions 1–7 as shown in Table I. Reactions 4–7 are as follows:



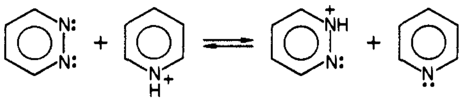
(4)

$\Delta G°(g) = +9.6$ kcal/mol[8]
$\Delta G°(aq) = +5.4$ kcal/mol[4]



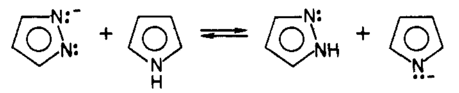
(5)

$\Delta G°(g) = +8.4$ kcal/mol[11]
$\Delta G°(Me_2SO) = +6.1$ kcal/mol[6]
$\Delta G°(aq) = +4.6$ kcal/mol[5]



(6)

$\Delta G°(g) = +5.0$ kcal/mol[12]
$\Delta G°(aq) = +4.0$ kcal/mol[2]



(7)

$\Delta G°(g) = +4.8$ kcal/mol[11]
$\Delta G°(Me_2SO) = +4.4$ kcal/mol[6]
$\Delta G°(aq) = +4.9$ kcal/mol

Solvation by water in reactions 1–3 (and to a lesser extent by $(CH_3)_2SO$ in reaction 3) is expected to preferentially stabilize that

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[5] (a) Catalán, J.; Claramunt, R. M.; Elguero, J.; Laynez, J.; Menéndex, M., unpublished results; (b) Yagil, G. *Tetrahedron* **1967**, *23*, 2855.

[6] Bordwell, F. G., private communication.

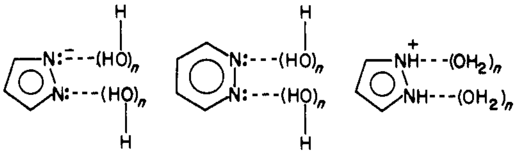
[7] Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

[8] Del Bene, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3617 has reported (nonoptimized) calculations at the 4-31G level which give for reaction 1 $\Delta E°_{calcd}$ = 2.5 kcal/mol and for reaction 4 $\Delta G°_{calcd} = +9.6$ kcal/mol.

[9] (a) As an indication, the gas-phase basicity of 2-CN pyridine is 1.3 kcal/mol less than that of 3-CN pyridine. (b) We are indebted to a referee for pointing this out.

[10] (a) Catalán, J.; Elguero, J. *J. Chem. Soc., Perkins Trans. 2*, **1983**, 1869 have obtained structure-optimized calculations for reaction 2 of $\Delta E° = -12.8$ kcal/mol (Indo). In work to be published, $\Delta E°_{calcd} = -18.3$ (STO-3G) and −14.3 kcal/mol (4-31G with 3G optimized geometries) have also been obtained. (b) Jen, J.; Hehre, W. J.; Taft, R. W. (unpublished results) have obtained structure-optimized 3-21G and 3-21+G calculations for reaction 3 of $\Delta E° = +3.5$ and +4.0 kcal/mol, respectively, and for reaction 5 $\Delta E° = +10.4$ kcal/mol (3-21G).

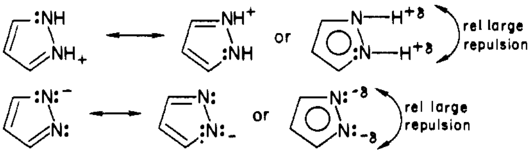
neutral or ion which is internally destablized.[12,13] The result is smaller or reversed equilibrium shifts in solution compared to the gas phase.[12,13] It will be noted for all three reactions (1-3) that $\Delta G°(aq)$ values are shifted from the corresponding $\Delta G°(g)$ values by ca. 4.0 kcal/mol in the direction that relieves by H-bonding solvation the NH^+ or lone pair repulsion in the 1,2-diazine or diazole system, as represented by the following structures:



In accounting for values of $\Delta G°(aq)$ for reactions 1-7, we estimate that (a) 6.5 - 4.0 = 2.5 kcal/mol is the magnitude for the reduced electrostatic repulsion between adjacent lone pair electrons or adjacent HN^+ pairs which applies in water; (b) a reduction factor of 1.6 for the 2- and 3-aza substituent effects applies in water (giving magnitudes of 7.8 and 5.3 kcal/mol, respectively); (c) a reduction factor of 2.0 applies for the attractive lone pair/NH^+ or NH interactions (giving 1.0 and 0.5 kcal/mol, respectively, for the magnitudes of these). These structural parameters give satisfactory agreement between calculated and observed values of $\Delta G°(aq)$ for reactions 1-7 as shown in Table I.

The generally good agreement btween observed and calculated values of $\Delta G°(aq)$ in Table I appears to indicate that other hydration effects not considered above tend to approximately cancel between opposite sides of these equilibria.

In a later paper we will give further comparisons with theoretical calculations, ionic solvation energies obtained from a thermodynamic cycle, and further considerations of the rough quantitative assessments made in this paper. We note in closing that while the intrinsic basicity effects in reactions 1-3 may be viewed as originating largely from the effects of simple electrostatic repulsions and attractions, the observed effects undoubltedly also include similar considerations as they effect the relative π electron delocalization energies. That is, for example, stabilization by π-electron delocalization in the conjugate acid of IV and in the conjugate base IV′ are very likely reduced compared to that for the corresponding 1,3-diazole systems as represented in the valence bond forms:



Experimental Section

Gas-phase basicities[14] and acidities[11,15] have been obtained as previously described. IV was found to be 0.5 kcal/mol more basic than $(CH_3CO)_2CH_2$ but 0.2, 0.6, and 1.0 kcal/mol less basic than 4-$CF_3C_5H_4N$, $(CH_3O)_3PO$, and $(tert\text{-}C_4H_9)_2S$, respectively. III was found to be 0.6 kcal/mol less basic than 3-$CH_3C_5H_4N$ but 0.9. and 1.8 kcal/mol more basic than *tert*-amylamine and 2-$CH_3OC_5H_4N$, respectively. IV was found to be 0.5 kcal/mol more acidic than *i*-PrSH, but less acidic by 0.6 and 1.1 kcal/mol than *m*-$CNC_6H_4NH_2$ and *m*-$NO_2C_6H_4NH_2$, respectively. III was found to be 0.2, 0.9 and 1.5 kcal/mol less acidic than *m*-$CH_3C_6H_4OH$, C_6H_5OH, and *p*-$CNC_6H_4NH_2$, respectively.

Acknowledgment. We are pleased to acknowledge helpful discussions with Professor W. J. Hehre and the unpublished data provided by Professor F. G. Bordwell.

Registry No. I, 289-95-2; II, 289-80-5; III, 288-32-4; III′, 36954-03-7; IV, 288-13-1; IV′, 23303-11-9; pyridine conjugate acid, 17009-97-1; pyrazole conjugate acid, 17009-91-5; imidazole conjugate acid, 17009-90-4; pyrimidine conjugate acid, 17009-95-9; pyridine conjugate acid, 16969-45-2; pyrrole, 109-97-7; pyridine, 110-86-1; pyrrole conjugate base, 23303-09-5.

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[11] Obtained in this work on the gas-phase acidity scale of: Bartmess, J. W.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

[12] Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247.

[13] Mishima, M.; McIver, R. T., Jr.; Taft, R. W; Bordwell, F. G.; Olmstead, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 2717.

[14] Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. t.; Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417. A temperature correction has been applied as given in: Bromilow, J.; Abbound, J. L. M.; Lebrilla, C. B.; Taft, R. W.; Scorrano, G.; Lucchini, V. *J. Am. Chem. Soc.* **1981**, *103*, 5448.

[15] Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

On the Surface Tension of Organic Liquids

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Abstract: An earlier correlation between surface tension and dielectric constant has been modified, leading to a choice of a "best" function of dielectric constant for the correlation. This has been accomplished by a correlation between surface tension and compressibility. The relationship permits calculation of the temperature coefficient of surface tension. A rationale has been given for the relationship between surface tension and compressibility.

Some years ago the surface tension of liquids was correlated with their dielectric constants.[1] Subsequently, Holmes showed that it was difficult to choose mathematically a "best" function of dielectric constant for the correlation since the various functions he studied behaved very much like the constant itself.[2] The purpose of the present paper is to show that a best function may be chosen through the correlation of surface tension with compressibility.

The correlation of surface tension, in the normal range, with $(\text{density}/\text{compressibility})^{1/2}$ and the correlation with compressibility of surface tension at the triple point has been shown (ref 3 and references therein). In the present paper, surface tension (γ), in the normal range, is shown to be simply related to the

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[1] Papazian, H. A. *J. Am. Chem. Soc.* **1971**, *93*, 5634.

[2] Holmes, C. F. *J. Am. Chem. Soc.* **1973**, *95*, 1014.

[3] Sanchez, I. C. *J. Chem. Phys.*, **1983**, *79*, 405.

0002-7863/86/1508-3239$01.50/0