

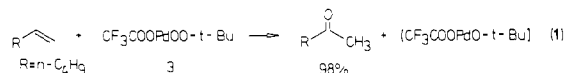
Table IV. Correlation between Force Constants, Orbital Energies, and CASSCF Occupation Numbers for [L-Pd-L] Complexes

ligand	force constant ^a (eV/Å ²)	orbital energy ^a (eV)	CASSCF occ. no.
CH ₃ ⁻	27.6	-7.97	1.925
F ⁻	58.4	-14.97	1.965
OH ⁻	63.4	-16.12	1.981

^aFrom SCF calculations (cf. Table II).

the other hand, there are no reported examples of either cis migration to olefins²⁵ or reductive eliminations for coordinated methoxide, β -diketonate, hydroxide, or fluoride.

The complexes in entries 3-7 (Table I) have a Pd-Nu bond orbital energy ranging from -10.1 to -12.7 eV. The reactivity of these coordinated nucleophiles in migration reactions is more difficult to predict. It is interesting to note that the calculated force constant parallels the energy of the Pd-Nu bond orbital. Thus, for the complexes predicted to undergo migration the force constant is 27-31 eV/Å², and for those predicted not to react in migration reactions the force constant is 57-63 eV/Å². The values of the force constants suggest that the complexes in entries 1-7 would be able to undergo migration reactions, whereas complexes in entries 8-11 would not. Interestingly, peroxide complex 3 oxidizes olefins to ketones (eq 1),²⁶ and it was suggested that the reaction takes place via a cis migration of the peroxide from palladium to coordinated olefin, followed by decomposition to ketone. No stereochemical evidence was provided, but in view



of the fact that peracids cleave alkyl-platinum^{27a} and allyl-pal-

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(25) (a) Methoxypalladation of the conjugated diene 2-methylene-6,6-dimethylbicyclo[3.1.1]hept-3-ene has recently been reported to occur cis.^{15b} This is a special strained diene and methoxypalladation of 1,3-cyclohexadiene, which is less strained, occurs trans.^{15c} (b) Hosokawa, T.; Imada, Y.; Murahashi, S. I. *Tetrahedron Lett.* **1982**, *23*, 3373. (c) Bäckvall, J. E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1980**, 943.

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ladium^{27b} bonds with retention of configuration at carbon, such a mechanism is quite likely. Also, reductive elimination of alkylpalladium cyanides to alkylcyanides with retention of configuration at carbon has been reported.²⁸

The calculations suggest that migration of monodentate carbon coordinated β -diketonates is possible, whereas migration of bidentate O,O-coordinated β -diketonates is unlikely. The reason why only trans attack and no cis migration by these stabilized carbon nucleophiles has been observed in the addition of olefins²⁹ could be that the bidentate O,O-coordinated form is favored when they coordinate.³⁰

In this and our earlier studies the ability of a coordinated nucleophile to undergo a migration reaction has been correlated with the bond strength between the nucleophile and the metal. The simplest way to get a measure of the bond strength has been to use the corresponding orbital energy and the harmonic force constant. A third measure of the bond strength is obtained from CASSCF⁵ calculations. If the bonds are included in the active space it is expected that the bonding orbital of a strong bond will have a high occupation number. For this reason CASSCF calculations were performed with CH₃⁻, F⁻, and OH⁻ as ligands and the resulting occupation numbers are shown in Table IV together with the corresponding SCF force constants and orbital energies. As can be seen from Table IV there is a nearly perfect linear correlation between all these measures of the bond strengths for these three ligands, which gives some confidence to the use of any one of them in the present context.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council for financial support.

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(30) Rearrangement of bidentate O,O-coordinated β -dicarbonyl palladium complexes to the corresponding monodentate C-coordinated form requires the addition of strongly coordinating ligands such as pyridine, triphenylphosphine, or dimethylamine: see ref 14 and 20 and references cited therein.

Cation Binding Effect on Hydrogen Bonding

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Contribution from the Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899. Received January 22, 1985

Abstract: Cation binding effects on nearby H bonds are studied for the imidazole dimer. The binding of the cations, H⁺, Na⁺, Zn(OH)⁺, and Zn²⁺, is found to have a significant effect on both the H bond energy and the equilibrium internuclear separation of the H bond. The net stabilization energy ranges from 8.0 kcal for Na⁺ to 28.0 kcal for Zn²⁺. The polarization of the dimer is also appropriate to increase the binding of another imidazole. Proton transfer is also studied for the dimer itself and the cation perturbed dimer. Double wells are found in all cases in the energy curve for proton transfer with a fixed N-N' distance between the imidazole monomers. With the exception of Zn²⁺ a substantial barrier is calculated for the proton transfer reaction. Compact effective potentials (CEP) were used in the calculations. Comparisons of the orbital energies and gradient optimized geometry of the CEP calculation for imidazole with a GTO 4-31G all-electron calculation are quite satisfactory.

I. Introduction

Metal cation binding to biomolecules is often an essential element in their function. In addition to the ion-multipole contribution to the intermolecule binding one of the consequences of the cation binding is the polarization of the attached ligands

which strengthens the H bond. Rode has already noted that these polarization effects can alter the donor-acceptor interaction in hydrogen-bonded systems, influence the binding energies, and substantially alter the equilibrium geometry of the H bond.¹⁻⁴

[†]Bar Ilan University, Israel and National Foundation for Cancer Research Associate at NBS.

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Table I. Comparison of Imidazole Geometries

	CEP	4-31G	3G ^a	exptl ^b
N1-C2	1.380	1.362	1.38	1.364
C2-N3	1.322	1.299	1.32	1.314
N3-C4	1.399	1.386	1.40	1.382
C4-C5	1.391	1.350	1.35	1.364
C5-N1	1.396	1.377	1.39	1.377
N1-H1	0.997	0.989	1.02	0.998
C2-H2	1.074	1.062	1.08	1.078
C4-H4	1.071	1.062	1.08	
C5-H5	1.071	1.062	1.08	
C5-N1-C2	107.2		107	106.9
N1-C2-N3	111.7		111	112.0
C2-N3-C4	105.9		104	104.9
N3-C4-C5	109.8		111	110.7
C4-C5-N1	105.3		106	105.5
C2-N1-H1	126.5		127	
N3-C2-H2	125.3		126	
C5-C4-H4	128.2		128	
N1-C5-H5	123.0		122	

^aReference 17. ^bReference 15.

Rode focussed his attention on the net stabilization energy (NSE) of the hydrogen bonds due to cation binding and optimization of the H bond geometry. Although some test calculations with extended bases were performed, the majority of calculations were done with minimal bases. The restricted bases will not represent the polarizability adequately. For example, the polarization effect can contribute over 40% to the binding of pyrimidine to Pt-(NH₃)₃²⁺.⁵ By implication any error in the polarizability will lead to errors in the cation effect on hydrogen bonding.

The effect of cation binding then can even be greater than Rode has already indicated for the DNA bases. In this paper we will explore an H-bonded system of two aromatic molecules, imidazole (ImH) hydrogen bonded to imidazole. The H-binding energy will be optimized for both the N-H and N-N distances. The N-N distance for the maximum NSE is then frozen while the proton is transferred between the two imidazoles. This procedure is intended to model one mode of proton transfer in a biochemical system where the constituents or residues are fixed geometrically by other covalent interactions like the hydrogen-bonded bases in a duplex nucleic acid strand. In this mode the proton is not transferred to the solvent at "infinity" but is retained on the nearest neighbor. The metal cation stabilizes the zwitterion that results. Proton transfer in hydrogen-bonded imidazole dimers has been studied theoretically by Chojnacki and Lipinsky⁶ and Bredas et al.⁷

Study of the proton transfer bears on the question first raised by Löwdin⁸ whether a double well is generated as the proton transfers along its hydrogen bond. In studies of the motion of a single hydrogen atom in the guanine-cytosine (GC) pair and the dimeric form of formic acid^{9,10} Clementi et al. have not found such a double well. In the case of the imidazole dimer, we do calculate a double well. This ion-pair well is calculated to be substantially stabilized by cation interactions.

II. Details of the Calculation

Compact effective potentials (CEP) were used to eliminate core electrons for all the atoms.¹¹ The d electrons in Zn were retained

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Table II. Orbital Energies for Imidazole (eV)

	CEP	4-31G	exptl ^a
σ orbitals			
10	37.57	36.99	
9	32.45	31.94	
8	28.27	27.80	
7	22.92	22.60	
6	22.10	21.84	
5	21.11	20.91	
4	16.66	16.67	15.3
3	16.66	16.53	14.0
2	15.80	15.68	13.7
1	11.47	11.39	10.3
3	16.59	16.38	14.7
2	10.93	10.74	10.3
1	9.12	8.96	8.78

^aReference 16.**Table III.** Proton Transfer Energetics

	ΔH^a (kcal/mol)
1. ImH + ImH \rightarrow Im ⁻ + ImH ₂ ⁺	121.1
2. Zn ImH ²⁺ + ImH \rightarrow ZnIm ⁺ + ImH ₂ ⁺	-77.9
3. NaImH ⁺ + ImH \rightarrow NaIm + ImH ₂ ⁺	40.0
4. ImH ₂ ⁺ + ImH \rightarrow ImH + ImH ₂ ⁺	0
5. (OH)ZnImH ⁺ + ImH \rightarrow (OH)ZnIm + ImH ₂ ⁺	5.9
6. ImH + H ⁺ \rightarrow ImH ₂ ⁺	-244 (248) ^b
7. ImH \rightarrow Im ⁻ + H ⁺	364
8. NaImH ⁺ \rightarrow NaIm + H ⁺	283
9. ZnImH ²⁺ \rightarrow ZnIm ⁺ + H ⁺	165 (166.7) ^c
10. (OH)ZnImH ⁺ \rightarrow (OH)ZnIm + H ⁺	249

^aNo zero-point energy correction. ^bReference 12; an experimental proton affinity of 219.8 kcal/mol has been reported for M. Mautner in a review: S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, **13**, 695 (1984). ^cD. Demoulin and A. Pullman, *Theor. Chim. Acta*, **49**, 161 (1978); for binding of Zn to the N3 site.

in the core. The basis sets are double- ζ (DZ) quality for the valence electrons, and the calculated properties of test systems such as CH₄, C₂H₂, and C₂H₄ have been shown to accurately reproduce all-electron calculations. The SCF calculations were performed with the HONDO¹² code which was modified for the effective potentials. Energy gradient optimized geometries were obtained for all fragments whose geometries are given in Figure 1. A bridged binding site for Zn²⁺ to the imidazole anion was found to have the lowest energy and is reported in detail elsewhere.¹³ The comparison of the CEP solutions to DZ quality all-electron results is favorable for the case of the imidazole and protonated imidazole monomers. The energetics are not sensitive to small changes in the optimized geometries for the different basis sets. The geometries reported by Kollman and Hayes¹⁴ were obtained by gradient optimization with use of a minimal STO-3G basis. However, their proton affinity, which was calculated with the 4-31G basis at the STO-3G geometries, agrees with the results reported here to within 4 kcal. The 4-31G gradient optimized geometry is in better agreement with the microwave structure¹⁵ than either the CEP or STO-3G structures as seen from Table I, but gradient calculations¹³ with more accurate 10s/5p all-electron bases find that the structure using the more accurate basis is intermediate between the CEP and 4-31G structure.

The orbital energies for the CEP and 4-31G calculations are compared to experimental values¹⁶ in Table II. Although the

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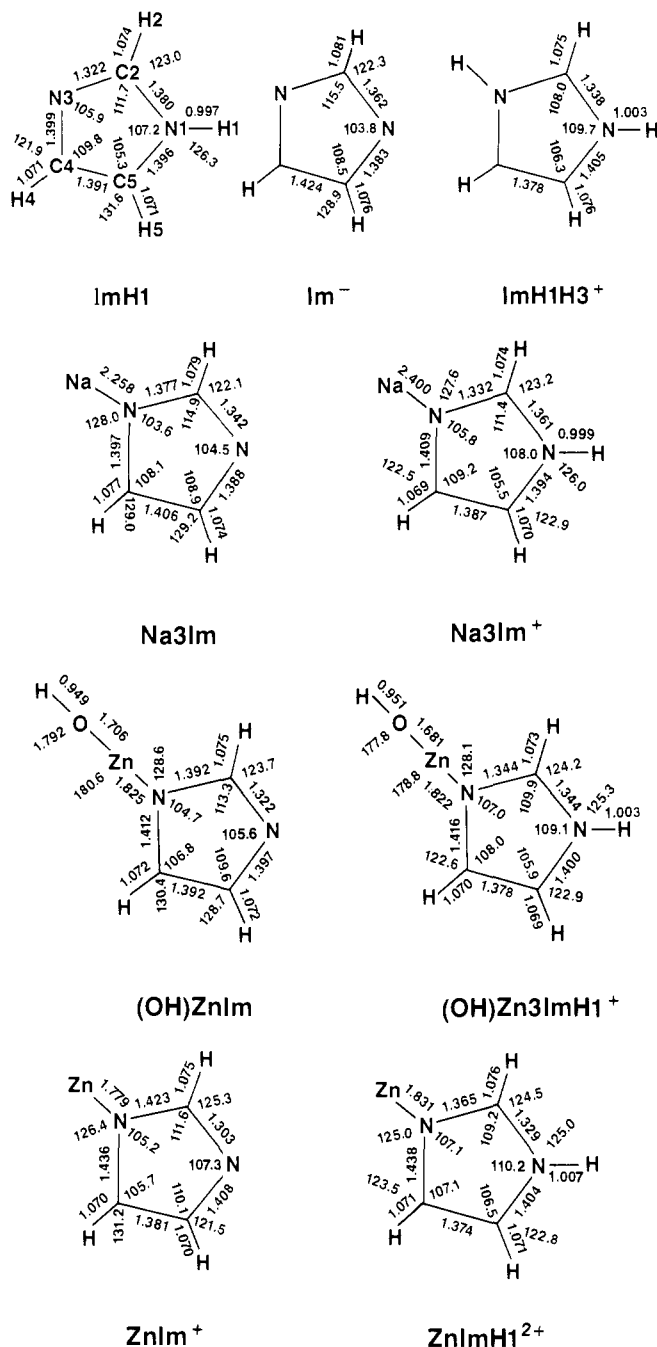


Figure 1. Gradient optimized geometries are presented for all the species considered in the proton transfer reactions: ImH , Im^- , ImH_3^+ , NaIm , NaImH^+ , $(\text{OH})\text{ZnIm}$, $(\text{OH})\text{ZnImH}^+$, ZnIm^+ , and ZnImH_2^{2+} .

calculated values are in reasonable agreement, the experimental values bear little resemblance to the calculated ones except for the lowest π ionization potential. Without the considerable effort of calculating the relaxed excited ion electronic states and calculating or estimating the correlation energy, it is not possible to assign the spectra from these calculations.

The proton transfer energies and proton affinities of the species considered are shown in Table III. To determine the potential energy curves for proton transfer, the fragment geometries are frozen and then allowed to interact through linear N1-H-NC hydrogen bonds connecting coplanar monomers in the conformation shown in Figure 2. Since the fragments relax substantially when the proton is transferred, calculations were performed relative to both the neutral and zwitterion asymptotes with the appropriate

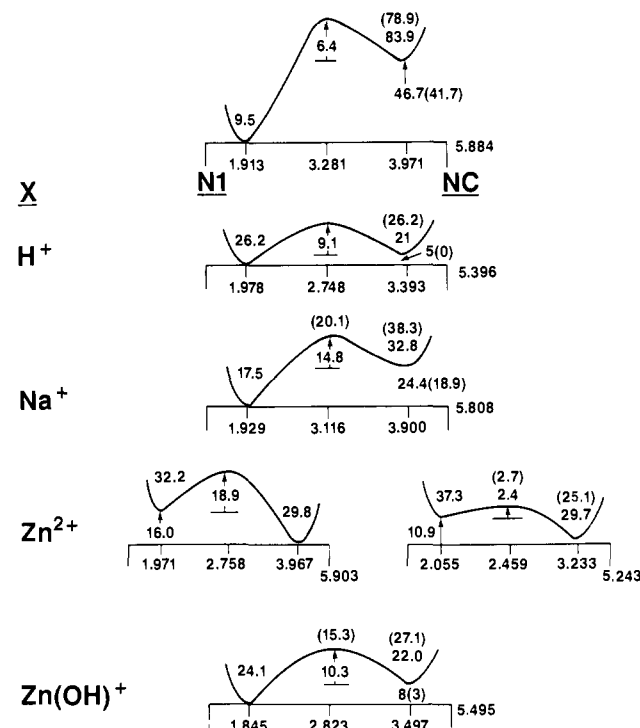
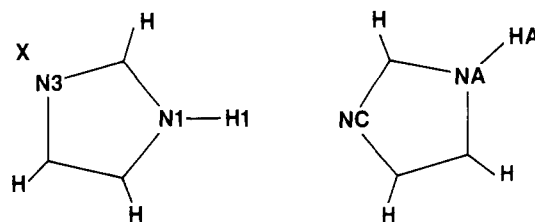


Figure 2. Schematic of the double well potentials for proton transfer. The potential at the top is for the neutral dimer. The well at the left represents the optimized hydrogen bond, $\text{N1-H}\cdots\text{NC}$, energy and internuclear distance. The N1-NC distance is calculated to optimize the hydrogen bond energy and then fixed. The barrier to the transfer of the H1 proton and the binding energy and distance for binding H1 to NC are also given. The energies in parentheses were obtained by using the monomer geometries at the zwitterion asymptote. All the energies are in kcal/mol and the distance is given in atomic units (1 au = 0.52917 Å). The binding energy for the minimum on the left is determined relative to $\text{XImH} + \text{ImH}$ where X is nothing, H^+ , Na^+ , Zn^{2+} , or $\text{Zn}(\text{OH})^+$ while the value on the right is relative to $\text{XIm}^- + \text{ImH}_2^+$.

fragment geometries for the two types of calculations. Complete geometry optimization along the reaction path is expensive and the curve shapes, including the barrier height for the transfer reaction, can be adequately estimated by this approximation. For example, the transfer of a proton from protonated imidazole to imidazole yields an error of about 5 kcal in the asymptotic energy if the ion-pair geometry is not relaxed. Gradient optimization for the entire energy curve would necessarily yield a symmetric curve with a reduction of the barrier for proton transfer of at most 2 kcal.

The stationary points in the energy curve for proton transfer varying both the distance between N1-H and the distance between NC-H are shown schematically in Figure 2 as a function of various cation perturbations. In the case of Zn^{2+} interacting with the dimer, the proton transfer is exothermic and the two curves in Figure 2 illustrate the behavior of the energy surface for reaction as a function of the N1-NC distance. Except for the Zn^{2+} case with $R(\text{N1-NC}) = 5.903$ au, the schematic curves are given for the N1-NC distance for which the maximum N1-H1 bond energy is obtained. The net stabilization energies for the neutral hydrogen bond interactions are 8.0, 16.7, 14.6, and 28.0 kcal for Na^+ , H^+ , ZnOH^+ , and Zn^{2+} bonding.

The effect on the charge distribution of both the hydrogen bonding and the subsequent perturbation of the dimer by metal

(16) S. Cardock, R. H. Findlay, and M. H. Palmer, *Tetrahedron*, **29**, 2173 (1973).

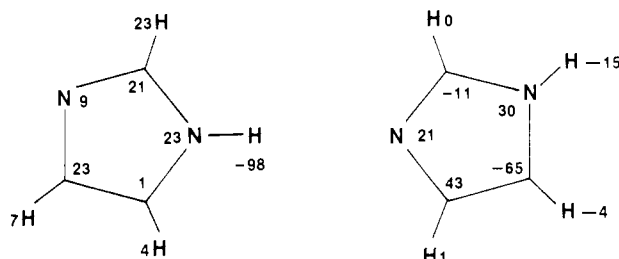


Figure 3. The Mulliken population differences ($10^{-3} e$) in the $(\text{ImH})_2$ dimer illustrate the electronic basis for positive cooperativity in the H bond energy in a chain of imidazoles.

cation binding was examined with a Mulliken population analysis. The results of such an examination are very qualitative since the atomic populations are basis set dependent. The shifts in population do mirror the polarization and charge transfer effects and are useful when the basis set dependence is recognized and absolute populations are not emphasized.

III. Analysis of Metal Binding

(a) Imidazole Dimer. The imidazole dimer features ImH as both a proton donor and acceptor. For ImH-OH_2 dimers, Del Bene and Cohen¹⁷ have calculated a 9.6 kcal hydrogen bond for ImH as donor and 5.6 kcal for ImH as acceptor using a minimal STO-3G basis. The 9.5 kcal bond energy calculated here agrees well with the value reported by Bredas et al.⁷ The $\text{N1-H1}\cdots\text{NC}$ bond length is found to be 3.11 Å which is considerably larger than the experimental value of 2.86 Å found in the imidazole crystal.¹⁸ Bredas et al.⁷ obtained a bond energy of 9.9 kcal/mol using a 4-31G basis but for a geometry constrained to correspond to that found in the crystal. The minimum energy structure, obtained for a dihedral angle of 90° , is calculated to be 0.8 kcal/mol below that at 0° . Optimization of the $\text{N1}\cdots\text{H1}\cdots\text{NC}$ distance reduces the value by 0.01 Å in going from 0° to 90° . Since the energy difference between the 0° and 90° structure is small and there is no qualitative difference in the bonding behavior, the planar structures only were considered to simplify the calculation.

The appreciable difference between the bond lengths for the calculated dimer and the crystal hydrogen bonds suggests a cooperative effect in the bonding as a function of the number of hydrogen bonds. An error of 0.25 Å is larger than expected for basis set or correlation errors in the equilibrium geometry of an electrostatically bound system. The atomic population of ImH-ImH indicates substantial polarization of both the donor and acceptor molecules. The H1 atom on the proton donor becomes more positive and the NC acceptor more negative which contributes to the strong hydrogen bond. In addition, the N3 atom on the donor molecule becomes slightly more negative while the HA atom on the acceptor is slightly more positive. The N3 and HA atoms are polarized in the right direction to enhance any subsequent hydrogen bonds as shown in Figure 3.

In the case of the ImH-OH_2 dimer, the calculated populations were interpreted as representing substantial charge transfer to the proton donor molecule.¹⁷ However, this may be an artifact of the small basis. In the case of the ImH dimer, the calculated populations do not indicate any charge transfer as seen in Figure 3. A transfer of 0.06 e is reported by Bredas et al.⁷ for the 4-31G basis. The present results suggest essentially no charge transfer, but the calculated $R(\text{N-N})$ distance between monomers is 3.11 Å as opposed to the shorter crystal distance of 2.86 Å. In addition, the more accurate orbital tails of the CEP basis⁵ compared to the 4-31G basis would reduce the probability of superposition effects that are interpreted as charge transfer.

Proton transfer in the absence of a stabilizing field is unlikely. Transferring the proton with the N1-NC distance fixed at the

dimer equilibrium value finds a local energy minimum 46.7 kcal/mol above the neutral energy minimum with a barrier of 6.4 kcal/mol. The zwitterion is stable by 84 kcal relative to the ion-pair asymptote. If the calculation is done with the ionic geometries, then the local minimum is found at 41.7 kcal but the barrier is increased to 10.2 kcal. Full gradient optimization of the reaction curve is too expensive, but these results indicate that no qualitative changes should be expected.

(b) $\text{Na}^+(\text{ImH})_2$. Attaching cationic species to the nonbonded nitrogen of the proton-donor imidazole polarizes the system and stabilizes both the neutral hydrogen-bonded dimer and the zwitterionic species. We have studied the effect of several cationic perturbers and find that, of those studied, the sodium cation perturbs the dimer the least. Gradient optimization was used to determine the structures of NaImH^+ and NaIm that are shown in Figure 1. These structures were then used in a study of the hydrogen bonding and proton transfer as shown in Figure 2. The net stabilization energy (NSE) of the hydrogen bond between the imidazoles due to the presence of the Na^+ is 8.0 kcal/mol. The equilibrium hydrogen bond distance decreases by less than 0.1 Å. However, the ion-pair minimum is now only about 19 kcal above the minimum of the neutral dimer. The presence of Na^+ stabilizes the ion-pair conformer by nearly 22 kcal. The barrier between the two minima is substantially increased, though. Since the N1-H1 bond is weakened by the presence of Na^+ , the barrier reflects the increased binding of the ion pair. Since the N1-NC distance was not varied to optimize the zwitterion binding, the barrier location and height are only approximate but suggest that proton transfer may be inhibited by large barriers in cases where the base-base distances are relatively fixed.

The polarization of the imidazoles that was identified in the previous section as leading to cooperative hydrogen bonding stabilization is enhanced by the presence of Na^+ . The unshielding of HA on the acceptor imidazole shown in Figure 2 is 80% larger when Na^+ is attached to N3 of the donor molecules.

(c) $\text{H}^+(\text{ImH})_2$. When a proton is attached to imidazole at N3, there is considerable delocalization of the positive charge among the imidazole hydrogens. Hence, the H1 atom is more unshielded than for the case of the Na^+ perturber and a stronger effect on the hydrogen bond is expected. The NSE of the hydrogen bond due to the proton perturber is 16.7 kcal/mol. Also, the N1-NC distance and hydrogen bond length are reduced by nearly 0.5 au relative to the unperturbed system. A comparably strong hydrogen bond is found experimentally for the protonated pyridine dimer.¹⁹

Transfer of the proton in this case should be perfectly symmetrical. However, using the optimized neutral geometry for the acceptor molecule leads to an error of about 5 kcal/mol and a slightly unsymmetrical barrier. The calculated barrier height is 9.1 kcal/mol.

The polarization of the imidazoles is very strong for the proton perturber. The unshielding of HA on the acceptor molecule is 2.5 times that calculated for the unperturbed dimer. Adding a proton to the N3 of the terminal molecule would considerably enhance the hydrogen bonding of a chain of imidazoles.

(d) $\text{Zn}^{2+}(\text{ImH})_2$. Direct binding of a divalent metal cation to a base is not realistic, but the results for the Zn^{2+} interaction illustrate the magnitude of the perturbation due to a multiply charged cation. Without the stabilizing binding of other ligands, the complex will dissociate into two singly charged species, $\text{Zn}^{2+}(\text{ImH})_2 \rightarrow \text{ZnIm}^+ + \text{ImH}_2^+$. Two points on the reaction surface are described in Figure 2. The Zn^{2+} is bound, in the curve on the left, to a dimer constrained approximately to the N1-NC distance of the unperturbed dimer. At the initial N1-NC distance of 5.9 bohr, the NSE is 22.7 kcal and there is an 18.9-kcal barrier to proton transfer. In the curve to the right, the N1-NC distance in the dimer is 5.24 bohr to maximize the hydrogen bond energy in the field of the Zn^{2+} . At this distance the NSE is 27.8 kcal/mol and the barrier to proton transfer is greatly reduced to only 2.4 kcal/mol. The barrier is now sufficiently low that motion of the complex toward a smaller N1-NC distance may provide an ul-

(17) J. E. Del Bene and I. Cohen, *J. Am. Chem. Soc.*, **100**, 5285 (1978).

(18) B. M. Craven, R. K. McMullan, J. D. Bell, and H. C. Freeman, *Acta Crystallogr.*, **33B**, 2585 (1977).

(19) M. Meot-Ner (Mautner), *J. Am. Chem. Soc.*, **101**, 2396 (1979).

timate pathway for proton transfer.

The binding of Zn^{2+} distorts both the geometry and electronic structure of the directly ligated ImH very substantially. The energy of this polarized ImH is 4.9 eV higher than the optimized asymptotic ImH molecule. The NSE of the H bond is the resultant of large ionic and polarization effects, but it is difficult to assign weights to them because the direct ligation and polarization energy is much larger than the NSE and the calculations required to isolate the effects are not possible with present codes.

(e) $(ZnOH)^+(ImH)_2$. The perturbing effect of multiply charged cations will be ameliorated by other ligands attached to the cation. The $(ZnOH)^+$ molecule is intended to model such a case. As in the case of the Zn^{2+} perturbation, the maximum NSE for this perturber (14.6 kcal/mol) occurs for a reduced N1-NC distance of 5.495 bohr. Binding of the cation strengthens the H bond and tends to reduce the distance between the monomer fragments. In this case the ion-pair species is almost as bound as the neutral species. Using the ion-pair geometries, the excitation energy for proton transfer is only 3 kcal. Again, a substantial barrier, between 10-15 kcal, is obtained.

The $(ZnOH)^+$ fragment tends to withdraw electrons from the HA atom in the dimer comparably to the proton. The Zn^{2+} perturbation is calculated to be the largest as expected, but the loss of electron population at HA for the $ZnOH^+$ perturbation is 80% of the loss due to Zn^{2+} at the same N1-NC distance.

IV. Conclusion

The imidazole dimer H bond is significantly strengthened in all cases by the presence of cationic perturbers. Because of the aromatic character of the imidazole substantial population shifts are observed at atoms on the other side of the ring. The perturbation is even transmitted through the ring in a fashion to promote a positively cooperative effect on H-bonding energies and

distances for a chain of imidazoles. In all the singly charged species there is a substantial barrier to proton transfer and a double well is evident in all cases where the N1-NC distance is frozen at the value for the unperturbed dimer.

The double well has been sought in other hydrogen-bonded systems without success.^{8,9} It is possible that stabilization of the ion-pair conformation results from the polarization of the fragments which is better described by the flexible CEP bases. The data for calculated polarizabilities for the larger aromatic bases are incomplete with regard to basis set dependence, and this will be investigated. The calculations with the Zn^{2+} perturber provide another clue to the origin of the double well. As the N1-NC distance is decreased, the barrier height decreases substantially. Qualitatively, this removal of the barrier can be seen as resulting from the overlap of two energy curves, due to the proton removal in the N1-H1 bond and proton binding in the H1-NC bond, crossing at lower energies as the N1-NC distance is shortened. In polymeric stabilized species the hydrogen bonds are shorter than they are for the dimer and a lower barrier would be expected.

The proton and $ZnOH^+$ perturbers resulted in a substantial reduction in the N1-NC distance. Such cationic perturbations could have significant biochemical consequences if they are not ameliorated by solvent effects. Cations mostly interact with the bases through their H_2O ligands, but there are reports of direct binding of, for example, a $(H_2O)_5 Mg^{2+}$ to a base in an oligomer of DNA.²⁰

Registry No. ImH, 288-32-4; Im^- , 36954-03-7; ImH_2^+ , 17009-90-4; NaIm, 5587-42-8; NaImH⁺, 98900-93-7; (OH)ZnIm, 98900-94-8; (OH)ZnImH⁺, 98900-95-9; ZnIm⁺, 72147-22-9; ZnImH²⁺, 72147-21-8.

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Calculation of Group Electronegativity

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Abstract: A simple relation is presented to calculate orbital electronegativity, viz., $\chi_{A,i} = \chi_{A,i}^0 (1 + 0.5 \sum_{j \neq i} \delta_{A,j} + 1.5 \delta_{A,i})$ (where A is the atom being considered, i is the bonding orbital on A that is being considered, $\chi_{A,i}^0$ is the orbital electronegativity of the neutral A atom, $\delta_{A,i}$ is the charge on A in orbital i , and the summation is over all bonds to A except i). This equation is a simple modification of a relation presented in an earlier paper. The $\delta_{A,i}$ are calculated assuming charge conservation and electronegativity equalization within each bond in the group. If A is the central atom of the group G (e.g., A is C in CH_3) and i is the orbital to be bonded then $\chi_G = \chi_{A,i} (\delta_{A,i} = 0)$. It is shown that this formalism leads to group electronegativity values that reproduce empirical trends more faithfully than methods using total electronegativity equalization and at least as well as other methods developed specifically to treat substituent effects.

Group electronegativity is a concept which has proven quite useful in chemistry and especially in organic chemistry. Lately there has been a significant amount of work done that deals with the evaluation and use of group electronegativity.¹⁻⁶ A method

was introduced in a recent paper¹ (herein called paper 1) that can be used to calculate both atomic and group electronegativity in a simple manner. The method requires only a screened nuclear charge obtained from modified Slater's rules, an effective principal quantum number and a value for fractional p character in the atomic orbital being considered. It was shown to effectively reproduce previous results for the entire periodic table as well as treat charge effects in molecules and groups.

However, it had deficiencies, viz., it could not differentiate between isomeric groups (e.g., CH_2CH_2F and $CHFCH_3$), it could not easily handle multiple bonds, and as will be seen below it tends to overestimate the effect of other atoms or groups attached to the central atom of the group (e.g., the effects of the H atoms on C in CH_3). The present paper describes a simple modification

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