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Proton Transfers in Hydrogen-Bonded Systems. 2. Electron Correlation Effects in $(N_2H_7)^+$

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Abstract: Potentials for transfer of the central proton between the NH_3 units of $(H_3NHNH_3)^+$ are calculated via ab initio methods at several levels of sophistication. Double-well potentials are obtained for all internitrogen distances studied which vary between 2.73 and 3.15 Å. All methods indicate that the energy barrier to proton transfer increases as the two NH_3 molecules are further removed from one another. Treatment of electron correlation via the polarization configuration interaction (POL-CI) method leads to barriers substantially smaller than those obtained by restricted Hartree–Fock calculations with use of a basis set of double ζ plus polarization function (RHF/DZP) quality. Inclusion of only intrapair correlations involving the two nitrogen lone pairs with use of the generalized valence bond (GVB) method leads to no decreases in the barriers relative to the DZP Hartree–Fock estimates. Use of the smaller split valence 4-31G basis produces barriers intermediate between the RHF/DZP and POL-CI results. Proton transfers in $(N_2H_7)^+$ in the gas phase are studied using both a rigid model and one which includes relaxation of the R(NN) distance during proton motion. The latter relaxation results in a lowering of the POL-CI barrier from 3.5 to 1.5 kcal/mol.

Transfers of protons from one molecular species to another are known to play a major role in a large number of diverse chemical processes.[1,2] The importance of proton transfers to a wide range of biological phenomena such as membrane transport,[3,4] enzymatic catalysis,[5–9] photosynthesis,[10–12] ATP formation,[13,14] and vision[15,16] is becoming increasingly more apparent. In light of this fact, it would be quite useful to determine the energetics of the proton-transfer processes between various molecules. Molecular orbital methods furnish a valuable means of obtaining the required information as the properties of suitably chosen small model systems may be calculated quite accurately.[17] Internal geometries and relative orientations of reactants and products may be treated with a precision which is difficult to match with experimental techniques. This fact facilitates the calculation of potentials for proton transfers at various different intermolecular distances and relative orientations.[1] In addition, other useful information such as electronic distributions at each stage of transfer may be extracted from the calculated wave functions.

As an example, accurate potentials for proton transfer in the cationic water dimer $(H_5O_2)^+$ have been calculated previously[18–21] at the Hartree–Fock level. Basis sets used have ranged in size from double ζ to larger bases containing polarization functions. However, it is well-known that single-determinant wave functions of the Hartree–Fock type cannot adequately treat processes involving bond dissociation. One might therefore expect that neglect of electron correlation will lead to errors in proton-transfer processes where bonds are being partially broken and formed. Indeed, Meyer et al.[21] have found a substantial lowering of the energy barrier to proton transfer between the two water molecules of $(H_5O_2)^+$ when electron correlation is included. Similar decreases in proton-transfer barriers have been noted also in the anionic dimers[22,23] $(H_3O_2)^-$ and $(HF_2)^-$. Proton transfers of intramolecular type also seem to be affected in the same way as evidenced by a decrease in the calculated barrier in malondialdehyde when correlation effects are included.[24]

Analogous investigations of proton transfers between the biologically important nitrogen-containing molecules are much less complete. Hartree–Fock calculations with a minimal basis set of Gaussian lobe functions[25] yielded a potential wherein the equilibrium position of the hydrogen-bonding proton in $(H_3NHNH_3)^+$ is midway between the two nitrogens. Increasing the basis set size by splitting the valence shells, on the other hand, resulted in a double-well potential with a barrier to the transfer of the proton between the two NH_3 units.[25] Delpuech et al.[26] found double-well potentials also for R(NN) distances between 2.59 and 2.84 Å in $(N_2H_7)^+$ when a double ζ plus polarization function basis

Table I. Basis Sets

atom	primitives	contraction
	4-31G	
N	(8s4p)	[3s2p]
H	(4s)	[2s]
	DZP	
N	(9s5p1d)	[3s2p1d]
H (central)	(5s1p)	[3s1p]
H	(4s)	[2s]

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(1) See Paper 1 in this series: S. Scheiner, *J. Am. Chem. Soc.*, **103**, 315–320 (1981).

(2) "Proton-Transfer Reactions", E. Caldin, V. Gold, Eds., Wiley, New York, 1975; R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, NY, 1973.

(3) (a) W. Stoeckenius, *Sci. Am.*, **234**, **No. 6**, 38–46 (1976); (b) R. Henderson, *Ann. Rev. Biophys. Bioeng.*, **6**, 87–109 (1977); (c) J. F. Nagle and H. J. Morowitz, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 298–302 (1978).

(4) S. Scheiner, *Ann. N.Y. Acad. Sci.*, in press.

(5) D. M. Blow, J. J. Birktoft, and B. S. Hartley, *Nature (London)*, **221**, 337–340 (1969).

(6) S. Scheiner and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 432–436 (1976).

(7) W. P. Jencks in "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969, Chapter 3.

(8) G. M. Maggiora and R. L. Schowen in "Bioorganic Chemistry", Vol. 1, Academic Press, New York, 1977, pp 173–229.

(9) W. N. Lipscomb, *Chem. Soc. Rev.* **1**, 319–336 (1972).

(10) K. Sauer, *Acc. Chem. Res.*, **11**, 257–264 (1978).

(11) K. R. Miller, *Sci. Am.*, **241**, 102–113 (1979).

(12) P. Mitchell, *Science (Washington, DC)*, **206**, 1148–1159 (1979).

(13) T. Pozzan, F. DiVirgilio, M. Bragadin, V. Miconi, and G. F. Azzone, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 2123–2127 (1979).

(14) S. M. Cohen, S. Ogawa, H. Rottenberg, P. Glynn, T. Yamane, T. R. Brown, R. G. Shulman, and J. R. Williamson, *Nature (London)*, **273**, 554–556 (1978).

(15) K. Peters, M. L. Applebury, and P. M. Rentzepis, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3119–3123 (1977).

(16) B. Honig, T. Ebrey, R. H. Callender, U. Dinur, and M. Ottolenghi, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 2503–2507 (1979).

(17) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, MA, 1972.

(18) P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **92**, 6101–6107 (1970).

(19) R. Janoschek, E. G. Weidemann, H. Pfeiffer, and G. Zundel, *J. Am. Chem. Soc.*, **94**, 2387–2396 (1972).

(20) W. P. Kraemer and G. H. F. Diercksen, *Chem. Phys. Lett.*, **5**, 463–465 (1970).

0002-7863/81/1503-2169$01.25/0

set was used. There has, however, been no previous attempt to determine the effects of electron correlation upon the proton-transfer potentials in the latter system. One might expect significant changes in these potentials as were found[21-24] for the isoelectronic $(H_5O_2)^+$ system and others mentioned above. The present paper reports calculations of correlation-induced changes in proton-transfer potentials in $(N_2H_7)^+$. Potentials are calculated at various levels of sophistication for R(NN) distances between 2.73 and 3.15 Å.

Methods

A. Basis Sets. Calculations were carried out with the use of two basis sets, both of which were contractions of groups of Gaussian-type functions. The 4-31G basis set[27] consists of a single-orbital representation of the nitrogen inner shell and a twofold splitting of the valence shells of N and H. The second basis set is essentially of double ζ plus polarization function (DZP) quality. For N centers, Huzinaga's 9s5p set of primitive Gaussian functions[28] was contracted to a valence double ζ set.[29] To this was added a single set of d functions with orbital exponent 0.80.[29] (The $x^2 + y^2 + z^2$ combination of d functions having s symmetry was not included in the calculations.) The basis set of the central hydrogen being transferred consisted of a [3s][30] contraction of (5s) primitive Gaussians[28] augmented by a single set of three p orbitals with exponent 1.00.[29] All the above orbitals were left unscaled. The remaining six hydrogen atoms were each represented by a double ζ [2s] contraction of four primitive Gaussians[29] with scale factor 1.2. The basis sets described above are summarized in Table I.

B. Hartree–Fock Level. The GAUSSIAN-70 package of programs[31] was used to carry out all calculations with the 4-31G basis set. Integrals involving the DZP basis set were evaluated by using the BIGGMOLI program of R. C. Raffenetti.[30] The GVBTWO program written by F. Bobrowicz and W. Wadt was used to perform the molecular orbital calculations.

C. Electron Correlation. The process being considered here consists of the motion of the central proton in $[H_3N\text{-}H\cdots NH_3]^+$ along the already existing hydrogen bond to form $[H_3N\cdots H\text{-}NH_3]^+$. The partial breaking and concurrent strengthening of the respective bonds to the central hydrogen may alternatively be described as the transfer of the proton from the lone pair of one nitrogen to that of the second. The orbitals expected to undergo the largest change as a result of the transfer are therefore the "lone pairs" of the two nitrogens. The remaining occupied orbitals which include the nitrogen inner shells and the other NH bonding orbitals are expected to be much less affected by the motion of the central proton.

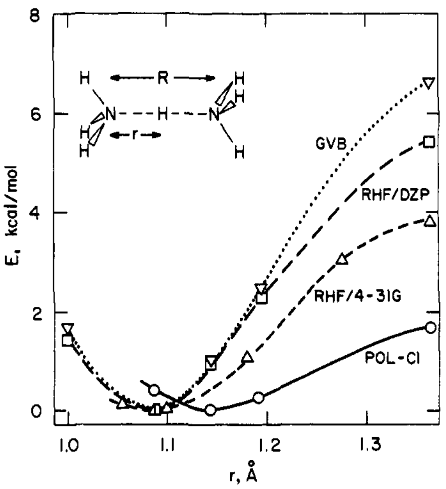

Figure 1. Energetics of proton transfer in $(N_2H_7)^+$. R is equal to 2.731 Å.

In order to take full advantage of the above fact, a generalized valence bond (GVB) wave function[32] of the form

$$\mathcal{A}[1a_1{}^2 2a_1{}^2 3a_1{}^2 4a_1{}^2 1e_x{}^2 1e_y{}^2 2e_x{}^2 2e_y{}^2 \phi_{1a}{}^1 \phi_{1b}{}^1 \phi_{2a}{}^1 \phi_{2b}{}^1 \chi_s] \quad (1)$$

where $\mathcal{A}$ is an n-electron antisymmetrizer was constructed from the DZP basis set for the $(N_2H_7)^+$ system of C_{3v} symmetry. $1a_1$ and $2a_1$ represent the nitrogen inner-shell orbitals and $3a_1$, $4a_1$, $1e_x$, $1e_y$, $2e_x$, $2e_y$ the NH bond pairs. The remaining ϕ_i are obtained by correlating the nitrogen lone pairs into two pairs of singly occupied orbitals. All spatial orbitals are evaluated to self-consistency.[32] The spin function χ_s has the form

$$\chi_s = \chi(8)\chi_{4eS} \quad (2)$$

where $\chi(8)$ is the spin eigenfunction of the eight doubly occupied orbitals.

$$\chi(8) = \alpha\beta\alpha\beta\alpha\beta\alpha\beta\alpha\beta\alpha\beta\alpha\beta\alpha\beta \quad (3)$$

Two restrictions imposed on our GVB wave function are designated strong orthogonality and perfect pairing.[32] The former restriction requires each orbital be orthogonal to all orbitals except for its mate in the same pair. The perfect pairing approximation requires in addition the spin function χ_{4eS} to consist of two singlet coupled pairs.

$$\chi_{4eS} = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \quad (4)$$

The overlapping GVB orbitals ϕ_i may alternatively be replaced by orthogonal natural orbitals $5a_1$, $6a_1$, $7a_1$, $8a_1$ defined as

$$\begin{aligned}
\phi_{1a} &= (1 + \lambda_1{}^2)^{-1/2}(5a_1 + \lambda_1 7a_1) \\
\phi_{1b} &= (1 + \lambda_1{}^2)^{-1/2}(5a_1 - \lambda_1 7a_1) \\
\phi_{2a} &= (1 + \lambda_2{}^2)^{-1/2}(6a_1 + \lambda_2 8a_1) \\
\phi_{2b} &= (1 + \lambda_2{}^2)^{-1/2}(6a_1 - \lambda_2 8a_1)
\end{aligned} \quad (5)$$

where

$$\lambda_i{}^2 = \frac{1 - S_{i\,a/b}}{1 + S_{i\,a/b}} \qquad S_{i\,a/b} = \langle\phi_{ia}|\phi_{ib}\rangle \quad (6)$$

This leads to a multiconfiguration self-consistent field (MCSCF) wave function which is completely equivalent to the perfect pairing GVB wave function (eq 7).

$$\mathcal{A}\left\{1a_1{}^2 2a_1{}^2 3a_1{}^2 4a_1{}^2 1e_x{}^2 1e_y{}^2 2e_x{}^2 2e_y{}^2 \chi(8) \left\{\begin{matrix} 5a_1{}^2 6a_1{}^2 \\ 5a_1{}^2 8a_1{}^2 \\ \\ 6a_1{}^2 7a_1{}^2 \\ 7a_1{}^2 8a_1{}^2 \end{matrix}\right\} \chi_{4eS}\right\} \quad (7)$$

The GVB wave function is expected to contain a significant amount of the correlation energy of the system. In particular, the intrapair "left–right" correlation in each of the nitrogen lone pairs should be largely accounted for.

More importantly, however, the GVB wave function provides a space of 12 occupied (valence) and 34 virtual orbitals which

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[21] W. Meyer, W. Jakubetz, and P. Schuster, *Chem. Phys. Lett.*, **21**, 97–102 (1973).

[22] B. O. Roos, W. P. Kraemer, and G. H. F. Diercksen, *Theor. Chim. Acta*, **42**, 77–82 (1976).

[23] A. Stogard, A. Strich, J. Almlof, and B. Roos, *Chem. Phys.*, **8**, 405–411 (1975).

[24] G. Karlstrom, B. Jonsson, B. Roos, and H. Wennerstrom, *J. Am. Chem. Soc.*, **98**, 6851–6855 (1976).

[25] P. Merlet, S. D. Peyerimhoff, and R. J. Buenker, *J. Am. Chem. Soc.*, **94**, 8301–8308 (1972).

[26] J.-J. Delpuech, G. Serratrice, A. Strich, and A. Veillard, *Mol. Phys.*, **29**, 849–871 (1971).

[27] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724–728 (1971).

[28] S. Huzinaga, *J. Chem. Phys.*, **42**, 1293–1302 (1965).

[29] T. H. Dunning, Jr., and P. J. Hay in "Methods of Electronic Structure Theory", H. F. Schaefer, Ed., Plenum Press, New York, 1977, pp 1–27.

[30] R. C. Raffenetti, *J. Chem. Phys.*, **58**, 4452–4458 (1973).

[31] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *QCPE*, GAUSSIAN-70, Program No. 236, (1974).

[32] (a) W. A. Goddard and L. B. Harding, *Annu. Rev. Phys. Chem.*, **29**, 363–396 (1978); (b) W. A. Goddard, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368–376 (1973); (c) B. J. Moss, F. W. Bobrowicz, and W. A. Goddard, *J. Chem. Phys.*, **63**, 4632–4639 (1975).

Table II. Optimized Bond Lengths (Å) and Total Energies (au) for $(N_2H_7)^+$

	method			
R, Å	RHF/4-31G	RHF/DZP	GVB	POL-CI
		Bond Lengths (r_0)		
2.73	1.087	1.077	1.079	1.144
2.95	1.062	1.053	1.063	1.102
3.15	1.048	1.040	1.056	1.085
30.0	1.011	1.005	1.029	1.041
		Total Energies (E_0)		
2.73	−112.61322	−112.78188	−112.80650	−112.87099
2.95	−112.61079	−112.78187	−112.80854	−112.87043
3.15	−112.60634	−112.77909	−112.80705	−112.86752
30.0	−112.56388	−112.74408	−112.77310	−112.82826

serves as a convenient and efficient starting point from which large-scale configuration interaction calculations may be performed. All single and double excitations from the four configurations in (7) were allowed with the restrictions that only a single electron was permitted into the virtual space and no excitations were allowed out of the nitrogen inner shell orbitals $1a_1$ and $2a_1$. This POL-CI[33] treatment leads to 8972 space/spin configurations arising from 5475 spatial configurations.

Integral transformations were executed with the use of R. C. Raffenetti's TRAOMO program. CIGEN, written by R. C. Ladner and B. D. Olafson, and modified by T. H. Dunning, Jr., and S. P. Walch, was used to generate the configuration lists. CI calculations were carried out with the CITWO program, written by F. W. Bobrowicz and modified by S. P. Walch.

D. Molecular Geometries. The $(N_2H_7)^+$ system studied here is depicted in Figure 1. The structure, obtained from a full-geometry optimization with use of the valence double ζ 4-31G method,[27] is of C_{3v} symmetry. All HNH bond angles are tetrahedral, and the two NH_3 units are staggered with respect to one another. The optimized R(NN) distance is 2.731 Å. At this intermolecular separation, the optimum distances between the central hydrogen and each of the two nitrogens are 1.087 Å and 1.644 Å. The optimized structure may thus be described by the formula $(NH_4)^+NH_3$ as the central proton is more closely associated with one of the NH_3 groups. The remaining NH bond distances are 1.009 Å in the $(NH_4)^+$ moiety and 1.004 Å in NH_3.

Potentials for proton transfer were calculated for three intermolecular separations, R. One of these was the 4-31G optimized value of 2.731 Å, and the others chosen were 2.95 Å and 3.15 Å. In order to determine the hydrogen-bond energy of the $(NH_4)^+NH_3$ system, it was necssary to carry out calculations at the very large intermolecular separation of 30 Å where the interaction between the $(NH_4)^+$ and NH_3 moieties may be expected to be negligible. So that a large number of expensive geometry optimizations could be avoided, the rigid-molecule approximation was used in this study wherein all nuclei are held stationary as the central proton is moved along the internitrogen axis. (Full-geometry optimizations at each stage of the transfer carried out at R = 2.73 Å were found to have a negligible effect on the results.)

Results and Discussion

The energies calculated for various values of the NH internuclear distance, r, are shown in Figure 1 for the fixed intermolecular separation R = 2.731 Å. Calculations at the Hartree–Fock level are represented by the RHF/4-31G and double ζ plus polarization (RHF/DZP) basis set results. GVB energies are obtained using the DZP basis set via the previously described "splitting" of the two nitrogen lone-pair orbitals. Inclusion of extensive configuration interaction yields the curve labeled POL-CI. Each curve depicts energies relative to that found for r_0, the optimum value of r as calculated by the appropriate method.

Table III. Calculated Barriers[a] to Proton Transfer, $E^\dagger$

	method			
R, Å	RHF/ 4-31G	RHF/ DZP	GVB	POL-CI
2.73	3.8	5.4	6.6	1.7
2.95	11.4	14.6	15.4	7.3
3.15	20.6	25.0	25.0	14.7

[a] kcal/mol.

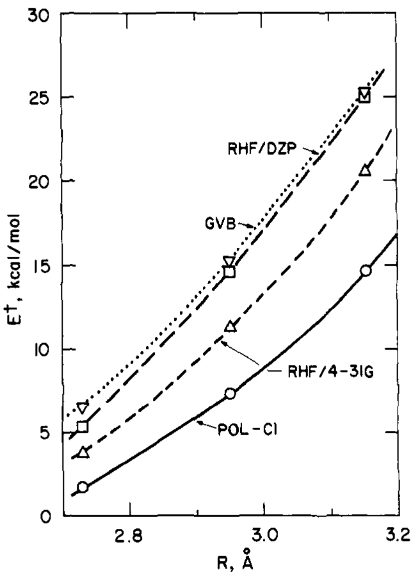

Figure 2. Calculated energy barriers to proton transfer.

These values of r_0 are presented in Table II for each different intermolecular separation. It may first be noted that at all levels of approximation, the optimized value of r is found to increase as the two molecules are allowed to approach one another, i.e., as R decreases. This result is quite reasonable since the lone pair of NH_3 is expected to exert an attractive force upon the hydrogen-bonding proton of $(NH_4)^+$. At the Hartree–Fock level, the DZP values of r_0 may be seen to be roughly 0.01 Å smaller than the corresponding 4-31G distances. Inclusion of polarization functions therefore appears to preferentially strengthen the covalent N–H bond as compared to the hydrogen bonding H···N interaction. Correlation of the lone pairs in the GVB perfect pairing approximation increases the optimized value of r by a variable amount with the difference between r_0^{GVB} and $r_0^{RHF/DZP}$ rising with increasing R. More extensive inclusion of electron correlation effects via the POL-CI method produces a much more substantial lengthening of r_0. It should be noted, however, that the POL-CI treatment typically leads to an overestimate of correlation-induced bond lengthening.[33] The lengthening of the X–H covalent bond in hydrogen bond complexes X–H···Y as a result of inclusion of correlation effects has been noted previously[21-23] for $(H_5O_2)^+$, $(H_3O_2)^-$, and $(HF_2)^-$.

Total energies, E_0, calculated for each optimized structure described above are also presented in Table II. Enlargement of the basis set from 4-31G to DZP results in a lowering in the total RHF energies of approximately 0.17 au. Inclusion of extensive CI further lowers the energies by ca. 0.09 au. The GVB wave functions in which the motions of the electrons in each nitrogen lone pair are partially correlated account for about 30% of the total energy lowering of the POL-CI technique.

The right terminus of each curve in Figure 1 corresponds to the halfway point for proton transfer, i.e., $r = R/2$. Further motion of the proton beyond this point would result in a potential curve for full proton transfer in which the right half is the mirror image of the left half shown in Figure 1. The full potential for proton transfer thus contains two minima, each of which corresponds to a structure in which the central proton is more closely associated with one NH_3 unit or the other. The energy barrier $E^\dagger$ separating

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[33] (a) P. J. Hay and T. H. Dunning, Jr., *J. Chem. Phys.*, **64**, 5077–5087 (1976); (b) S. P. Walch and T. H. Dunning, Jr., *ibid.*, **72**, 3221–3227 (1980); (c) T. H. Dunning, Jr., *ibid.*, **65**, 3854–3862 (1976).

the two minima is equal to the difference in energy between the midpoint and the bottom of either well.

$$E^\dagger = E(R/2) - E(r_0)$$

Barriers calculated by each method are presented in Table III for several values of R. All methods predict that greater intermolecular separations result in increasingly larger barriers as may be seen in Figure 2 where the barriers are shown as functions of R. Calculations at the Hartree–Fock level show that a decrease in basis set size from DZP to 4-31G results in smaller barriers for all values of R. Inclusion of extensive configuration interaction with the DZP basis set leads to a more drastic decrease in the barrier heights. For example, the POL-CI value of $E^\dagger$ for R = 2.95 Å is less than the RHF/DZP result by a factor of 2. The lowering influence of electron correlation upon the barriers to proton transfer between nitrogens observed here appears to be a manifestation of a more general effect as it has been observed also for proton transfers between oxygen atoms in cationic and anionic dimers of water[21-23] and in malondialdehyde[24] as well as between fluorine atoms[23] in $(FHF)^-$.

It is interesting that the GVB procedure does not result in a decrease of the calculated barrier height as does the POL-CI treatment. In fact, the GVB barriers are slightly higher than the RHF/DZP values for which no electron correlation effects at all are included. The barrier increase obtained with GVB is greater for small values of R and in fact vanishes at R = 3.15 Å.

In order to explain this result, it is first necessary to point out that the only electron correlation treated by our GVB wave function is the *intra*pair correlation between electrons in each of the nitrogen lone pairs. A large number of *inter*pair correlations such as that between a lone-pair electron and an NH bonding electron are ignored. The POL-CI calculations indicate that the total of the latter correlations, neglected by GVB, are of more than twice the magnitude of the former.

A second important point is that the energy barrier represents a *difference* in energy between two different geometries. Any correlation, even one of large magnitude, which produces similar energy lowerings in the two geometries will have a negligible effect on the calculated energy barrier. Thus, the totals of the intrapair correlations treated by GVB, even though of approximate magnitude 17 kcal/mol, are nearly the same in the initial and midpoint stages of the proton transfer, resulting in little difference between the GVB and DZP barriers. The interpair correlations, on the other hand, are significantly different in the two geometries and hence substantially alter the barrier.

Meyer et al.[21] noted similar effects in their study of proton transfer in the isoelectronic $(H_5O_2)^+$ system. The intrapair correlations involving the analogous lone pairs of the oxygens, although of large magnitude, were found to only slightly alter the barrier while interpair correlations, involving only one electron from a given lone pair, played the dominant role. Another similarity between the $(H_5O_2)^+$ calculations of Meyer et al.[21] and those reported here for $(N_2H_7)^+$ may be noted in that the total energy lowering produced by the latter interpair correlations is of slightly greater than twice the magnitude of the former intrapair correlations in either case.

Some of the correlations not included in our POL-CI treatment are those double excitations not involving either nitrogen lone pair. Although there are a very large number of such excitations possible, one would not expect the resulting total energy lowering to be substantially different in the end point and midpoint structures. This supposition is indeed supported by the study[21] of $(H_5O_2)^+$ in which the latter excitations were found to have a very small effect on the proton-transfer barrier.

The results presented in this report have been calculated for fixed values of the intermolecular separation R. Some interesting and useful additional information may be extracted from optimization of the latter distance. Such information is expected to be directly relevant to the $(N_2H_7)^+$ system in the gas phase and to have some applicability to the cation in solution as well. The equilibrium values of R, designated R_0, and the corresponding total energies were determined by fitting the values of R and E_0 of each column in Table II (not including R = 30 Å) to a parabola. The hydrogen-bond energy, E_{HB}, of the $(NH_4)^+NH_3$ system is defined here as the difference between the latter energy, $E(R_0)$, and that of the structure in which R = 30 Å.

Table IV. Calculated Energetics for Optimized Intermolecular Distances

	method			
property[a]	RHF/ 4-31G	RHF/ DZP	GVB	POL-CI
R_0, Å	2.73	2.84	2.96	2.80
r_a, Å	1.09	1.06	1.06	1.13
E_{HB}, kcal/mol	31.0	24.0	22.2	26.9
$E_a\dagger$, kcal/mol	3.8	9.6	15.6	3.5
$E_b\dagger$, kcal/mol	2.1	4.2	7.3	1.5
R_b, Å	2.59	2.60	2.65	2.68

[a] R_0 and r_a refer to the equilibrium NN and NH distances, respectively. E_{HB} is the hydrogen-bond energy of the equilibrium structure. $E_a\dagger$ is equal to the difference in energy between the structure with the proton midway between the two nitrogen nuclei ($r = R_0/2$) and the equilibrium geometry ($r = r_a$), both with $R(NN) = R_0$. R_b is the optimized NN distance in the midpoint configuration (transition state). $E_b\dagger$ refers to the difference in energy between the transition state and equilibrium structures.

Examination of the data presented in Table IV reveals that the 4-31G basis set predicts an equilibrium intermolecular separation 0.1 Å smaller than does the larger DZP basis set at the Hartree–Fock level. Inclusion of extensive correlation effects via the POL-CI method results in a similar albeit smaller decrease of R_0. Partial inclusion of correlation via the GVB perfect pairing approximation, however, leads to an opposite effect with R_0^{GVB} being 0.1 Å *longer* than $R_0^{RHF/DZP}$. These trends are consistent with the calculated hydrogen-bond energies in that those methods predicting shorter equilibrium distances also yield stronger interactions between $(NH_4)^+$ and NH_3. The stronger hydrogen bond predicted by the 4-31G method may be explained in part by the superposition effect in which the insufficient basis set of one molecule (e.g., NH_3) is augmented by that of the other and vice versa. The use of small basis sets thus tends to produce spuriously inflated interaction energies when compared to the Hartree–Fock limit. The POL-CI technique leads to a slight increase in the hydrogen-bond energy compared to the RHF/DZP value, consistent with previous observations[22,23,34,35] for $(HO–HOH)^-$, $(H_2O–HOH)$, $(F–HOH)^-$, and $(F–HF)^-$. The GVB method again produces an opposite trend, here a decrease in the interaction energy.

The hydrogen bond energy of 26.9 kcal/mol calculated with the POL/CI method is slightly higher than the experimental value[36] of 24.8 ± 0.4 kcal/mol determined for the gas-phase association of $(NH_4)^+$ and NH_3. However zero-point energies have not been included in the theoretical result. Estimates of corrections for zero-point vibrations in similar hydrogen-bonded systems by Diercksen et al.[34] are decreases in amounts ranging between 1 and 3 kcal/mol. A similar correction of the theoretical value for $(N_2H_7)^+$ will result in extremely good agreement with the experimental hydrogen-bond energy.

It is of some chemical importance to determine the barrier to proton transfer in $(N_2H_7)^+$ with no external restrictions imposed on its geometry. The proton-transfer process may be envisioned as occurring via one of two mechanisms. The first considers the heavy nuclei as unable to adjust their positions during the rapid transfer of the much lighter proton. The transfer process thereby takes place with R(NN) held fixed at its equilibrium value of R_0, already listed in Table IV. (This type of transfer is of relevance

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(34) G. H. F. Diercksen, W. P. Kraemer, and B. O. Roos, *Theor. Chim. Acta*, **36**, 249–274 (1975).

(35) F. Keil and R. Ahlrichs, *J. Am. Chem. Soc.*, **98**, 4787–4793 (1976).

(36) (a) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504–3510 (1973); (b) J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Can. J. Chem.*, **51**, 3242–3249 (1973).

also to any system in which the two nitrogen nuclei are held stationary via some external constraint as might occur if the nitrogens were part of a macromolecular structure.) The barriers obtained by each quantum mechanical technique via the latter mechanism are denoted $E_a^\dagger$ in Table IV. These barriers were obtained by estimating the functional value of each curve in Figure 2 at the corresponding distance R_0 in Table IV. For example, on the basis of the RHF/DZP curve in Figure 2, the barrier expected for $R_0 = 2.84$ Å is 9.6 kcal/mol. The smaller 4-31G basis set predicts a much lower barrier of only 3.8 kcal/mol. The large difference between DZP and 4-31G RHF barriers arises from two factors. The 4-31G basis set yields smaller barriers than does DZP at any given value of R and, in addition, predicts a smaller value of R_0. A similar combination of effects also results in a POL-CI barrier much smaller than the RHF/DZP value. Interestingly, the RHF/4-31G barrier is quite similar to the POL-CI/DZP result. This near agreement is a result of the smaller 4-31G value of R_0 coupled with its inherently larger barriers when compared with POL-CI. The GVB barrier is substantially larger than any other, being nearly 5 times greater than the POL-CI barrier.

A second mechanism whereby the proton might be transferred allows relaxation of the R(NN) distance at each stage of transfer. Optimization of R(NN) for the midpoint structure (top of the barrier) yields R_b (see Table IV). The difference in energy between this geometry and the optimized end point structure with $R = R_0$ yields the barrier denoted as $E_b^\dagger$ in Table IV. These barriers are substantially lower than $E_a^\dagger$ obtained by the first mechanism involving fixed values of R(NN). For example, the POL-CI barrier of 3.5 kcal/mol obtained for fixed $R_0 = 2.80$ Å is lowered to 1.5 kcal/mol by allowing the two nitrogens to move closer together by 0.12 Å in the midpoint geometry. As was found for the previous mechanism, the Hartree–Fock procedures overestimate the barrier height with 4-31G predicting a value closer to POL-CI than does the DZP basis set. Previous calculations[25,26] which did not include correlation contributions have also resulted in barriers to proton transfer appreciably higher than the value of 1.5 kcal/mol calculated here with the use of POL-CI. Delpuech et al.[26] obtained a barrier of 2.5 kcal/mol using a basis set of essentially DZP quality whereas a smaller basis excluding polarization functions led to a value of 1.9 kcal/mol.[25] These results fit the general conclusion that at the Hartree–Fock level, increasing the size of the basis set leads to higher barriers whereas inclusion of correlation effects produces a substantial lowering.

There is no currently available experimental information concerning the barrier to proton transfer in $(N_2H_7)^+$ in the gas phase although NMR work[37] indicates the barrier is quite small in aqueous solution. This observation appears to be in good agreement with the theoretical results reported here. The difference between the equilibrium and barrier energies was found by POL-CI to be only 1.5 kcal/mol. Consideration of the ground vibrational energy may be expected to lead to a barrier to proton transfer somewhat less than the latter value.

As a final point it should be noted that although the POL-CI method has not been applied previously to proton-transfer reactions, results achieved for other reactions have been quite good. For example, the activation barrier calculated for the abstraction of an H atom from CH_4 by $O(^3P)$ was within the range of experimental values.[33b]

Conclusions

All the methods investigated, which include different basis set sizes and inclusion of varying amounts of correlation effects, predict the same qualitative increase in barrier height with larger intermolecular separations. The magnitudes of these barriers, however, differ significantly from method to method. At the Hartree–Fock level, the smaller 4-31G basis set yields smaller barriers than does DZP. Inclusion of configuration interaction with POL-CI greatly decreases the barriers while intrapair correlations alone (GVB) produce a slight increase. Extensive configuration interaction would thus appear to be necessary in order to obtain reliable values for the height of the barrier at each distance.

Similar trends were noted also for proton-transfer energetics at the optimized intermolecular distances and for hydrogen-bond energies in that decrease of basis set size at the Hartree–Fock level and inclusion of configuration interaction produce similar effects, opposite to those predicted by GVB. The results indicate that intrapair correlations in the nitrogen lone pairs, although of considerable magnitude, follow opposite trends, as a function of molecular geometry, to more complete treatments of electron correlation which are necessary for accurate calculation of transfer energetics.

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[37] (a) T. M. Connor and A. Loewenstein, *J. Am. Chem. Soc.*, **83**, 560–563 (1961); (b) M. T. Emerson, E. Grunwald, and R. A. Kromhaut, *J. Chem. Phys.*, 33, 547–555 (1960).

Gas-Phase Proton Affinities for H_2O, C_2H_4, and C_2H_6

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Abstract: Rate and equilibrium constant measurements are reported which provide proton affinities for H_2O, C_2H_4, and C_2H_6 and heats of formation for the corresponding protonated species at 298 K, on the basis of the well-established proton affinity of CO. The values recommended for the proton affinities are 165.3 ± 1.8, 163.0 ± 1.7, and 142.1 ± 1.2 kcal mol^{-1} for H_2O, C_2H_4, and C_2H_6, respectively. The proton affinity obtained for H_2O is lower than accepted values. The results obtained for C_2H_4 agree almost exactly with those obtained in a very recent photoionization (PIPECO) study by Baer. The measurements with C_2H_6 provide a new accurate determination of its proton affinity.

Recent photoionization studies of the formation of $C_2H_5^+$ and $C_3H_7^+$ from C_2H_5I and C_3H_7I, respectively, have provided important new heats of formation for these ions.[1] A significant discrepancy with previously accepted values was evident for the

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