FEATURE ARTICLE

Theoretical Studies of Excited State Proton Transfer in Small Model Systems

Steve Scheiner[†,‡]

Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62901-4409

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Ab initio calculations that address the problem of excited-state proton transfer across an intramolecular hydrogen bond are reviewed. Small molecules, such as malonaldehyde, containing such a H-bond are first examined. This work reveals that in comparison to the ground state, the H-bond is strengthened and the transfer barrier reduced in the $^1\pi\pi^*$ state; opposite trends are noted in the triplet $\pi\pi^*$ as well as $n\pi^*$ states. Replacement of the H-bonding O atoms of malonaldehyde by N has only a small effect upon these results, as does enlargement or reduction of the malonaldehyde ring, coupled with anionic charge. The transfer barrier is linearly related to the equilibrium length of the H-bond in the various states of each system. Attachment of a phenyl ring to malonaldehyde introduces a fundamental asymmetry into the proton transfer potential, as the enol and keto tautomers are inequivalent. Whereas the enol is more stable in the ground and $n\pi^*$ states, a reversal occurs in the $\pi\pi^*$ states, which may be understood on the basis of the level of aromaticity within the phenyl ring. Nonetheless, when this asymmetry is accounted for, the phenyl ring affects the intrinsic barrier to proton transfer in the smaller malonaldehyde by a surprisingly small amount. Because of the high transfer barriers in the $n\pi^*$ states, coupled with low barriers to bond rotation, rotamerization is likely to dominate over proton transfer in these states. This behavior contrasts sharply with the $\pi\pi^*$ states, where proton transfer is far more likely than bond rotations. While it is clear that inclusion of electron correlation is essential to a quantitative reproduction of the proton-transfer process in excited states, the most accurate yet affordable method by which to include correlation remains an open question.

I. Introduction

The transfer of a proton from one species to another is one of the most thoroughly studied phenomena in all of chemistry. Whereas the great majority of the literature has dealt with the ground electronic state, more recent work has begun to reveal a rich panoply of fascinating results in excited states, only some of which are understood. Excited-state proton transfer (ESPT) was first observed in methyl salicylate in the 1950s[1]. Some years later, Taylor et al.[2] found that the first excited singlet of 7-azaindole dimer preferred a different tautomer than does the ground state, the first documented example of concerted biprotonic transfer. In 1979, evidence was provided of proton transfer in an excited state to explain dual fluorescence in 3-hydroxyflavone.[3] Five years later, Chou et al.[4] described a functioning photoinduced proton-transfer laser based on this molecule; the transfer in the excited state occurs in less than 8 ps.[5]

In addition to its relevance to lasers, ESPT has a wide range of other applications under development including energy/data storage devices and optical switching.[4,6−14] Raman filters and hard-scintillation counters,[15] polymer photostabilizers,[16−18] and triplet quenchers.[19,20] Other applications center about electroluminescent materials with photochemical stability, resistance to thermal degradation, and low self-absorption and LED materials.[20] It has been suggested that ESPT has potential for understanding the binding properties of protein,[21,22] as well as optical probes for biomolecules.[23−25] For example, the similarity of 7-azatryptophan to tryptophan makes the former an ideal noninvasive in situ probe.[26,27] The activity of certain naturally occurring fluorescent proteins may well be due to ESPT,[28,29] a process that also shows promise as a monitor of hydrophobic microenvironment, as in a micelle interior,[30] as a molecular probe for certain functional groups,[31] and even has antiviral potential.[32]

One of the prime features common to most excited-state proton transfers is their rapidity, on the femto to nanosecond time scale.[33−41] These rapid transfers are commonly attributed to a barrierless process, or at least one with a very low barrier.[42−48] Also intriguing is the observation that the preferred site of the proton in the ground state of the H-bond commonly loses the proton to its partner upon electronic excitation. That is, if $AH^+\cdots B$ represents the ground-state configuration of the hydrogen bond, $(A\cdots{}^+HB)^*$ is frequently preferred in the excited state, commonly attributed to a large photoinduced change in p*K*.[35,49−52]

A number of systems containing more than one H-bond exhibit multiple proton transfers,[53] and the question as to whether these transfers take place in a stepwise or concerted fashion has generated a great deal of recent interest. The 7-azaindole dimer is illustrative. Whereas Coulomb explosion[54] and femtosecond transient absorption and fluorescence upconversion spectroscopy[55] support a stepwise model, a conclusion supported by dynamics simulations,[56] other workers argue that a reinterpretation of the data leads toward a concerted mecha-

† E-mail: scheiner@chem.siu.edu.
‡ New address effective 15 July 2000: Department of Chemistry & Biochemistry, Utah State University, Logan UT 84322.

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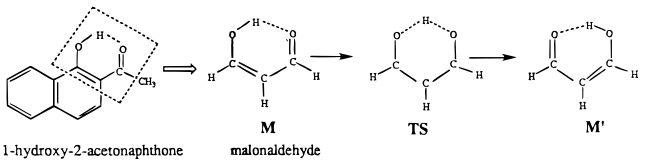

Figure 1. Molecular diagram of a typical ESPT molecule studied by experimental means, and a small model which embodies the intramolecular H-bond. **M** and **M′** refer to the two equivalent tautomers of malonaldehyde, before and after the proton transfer, **TS** to the transition state for this transfer process.

nism.[57] Despite these many measurements over the years, a number of questions remain unanswered about the ESPT process.

Ab initio calculations have several virtues for studying ESPT. It is first possible to study small model systems so as to gain a fundamental understanding of the essence of the process. These systems can be examined in vacuo, free of the many complications arising from surrounding solvent, and then slowly built up, step by step, to approximate the experimental situation. One can freeze the action, so to speak, at any stage of the proton transfer, even at geometries that are not true minima on the surface, e.g. transition states. Although showing signs of blossoming of late, calculations that pertain to excited state proton transfer remain relatively rare. There has been a scattering of semiempirical calculations[58−74] addressing some interesting questions, but semiempirical methods are suspect even for ground states of H-bonded systems; they are likely to be even less reliable when considering excited states.[75−78]

Many of the molecular systems that exhibit the most interesting photochemical behavior are fairly large, containing a number of aromatic rings, as exemplified by 1-hydroxy-2-acetonaphthone,[79] pictured in Figure 1. We are interested in first establishing the fundamental properties of the chemical groups engaged in the intramolecular H-bond, free of the complicating effects of these rings. For this reason, it is convenient to first "detach" the rings and study the smaller and simpler system outlined by the box in the figure. These rings can later be introduced one at a time, as the model is made more reflective of the true systems of interest. A second attractive feature of removal of these rings in Stage 1 is that much more accurate quantum chemical methods, involving larger basis sets and more extensive inclusion of electron correlation, can be brought to bear on a smaller molecule like malonaldehyde, **M**, in Figure 1. Indeed, the sort of intramolecular H-bond contained in malonaldehyde is representative not only of 1-hydroxy-2-acetonaphthone, but also of a wide array of other, related, systems that are of experimental interest.[32,79−83]

II. Malonaldehyde-Like Molecules

Figure 1 illustrates also the transition state (**TS**) for proton transfer, and the tautomer, **M′**, that results from the full transfer. It is important to note at the outset that **M** and **M′** are chemically equivalent so that the proton-transfer potential will of necessity be symmetric. A preliminary set of calculations in this laboratory[84] compared the proton transfer in the S_0 ground state of malonaldehyde and one excited state, the first $\pi\rightarrow\pi^*$ triplet, T_1, using UHF theory. Two different basis sets were examined in order to consider the sensitivity of the results to the presence of certain types of orbitals, in particular polarization and diffuse functions. The 6-31G(d,p) and 6-31+G(d,p) basis sets were found to be sufficient to reproduce the ground-state proton transfer barriers previously computed for this system. Earlier calculations over the years had provided evidence of the importance of including dynamic electron correlation in evaluating barriers to proton transfer in the ground state;[85,86] the same was found to be true in excited states. Consistent with many processes in addition to proton transfer, second-order Møller−Plesset (MP2) appears to reproduce the barriers about as well as the more costly MP4 level. In agreement with other calculations described below, the UHF results suggested that the H-bond is weakened by the $\pi\rightarrow\pi^*$ excitation, resulting in a higher barrier to proton transfer in this excited state. This bond weakening was in turn traced to the lower acidity of the pertinent OH group upon electronic excitation. The nature of this triplet, as well as the ground state, was later pursued in greater detail, comparing a wider range of theoretical approaches.[87] CIS treatment of the triplet led to results in good agreement with UHF and UMP2 in certain respects, as did complete active space (CAS)SCF. All these methods agreed that the barrier is higher in the $^3\pi\pi^*$ than the ground state, although the degree of barrier increase was found to be surprisingly variable from one method to the next.

To broaden the scope to excited states other than the first triplet, the next step was a test of the CIS procedure[88] as a tool to examine higher triplets and singlets above the ground state, viz. the singlet $\pi\pi^*$ and $n\pi^*$ states, and $^3n\pi^*$.[89] The CIS results first confirmed the earlier UHF finding that the transfer barrier is higher in $^3\pi\pi^*$ than in S_0. With regard to the ordering of the various states, the two triplets were found lower in energy than the singlets:

$$\text{energy} \qquad S_0 < {}^3\pi\pi^* < {}^3n\pi^* < {}^1n\pi^* < {}^1\pi\pi^* \qquad (1)$$

This pattern conforms to ideas generally applicable to aromatic systems,[90,91] suggesting a generality to them. The barriers to proton transfer $E^\dagger$ were computed in each of these states, and it was found that most of the excited states had a higher barrier than did the ground state with one notable exception, $^1\pi\pi^*$.

$$E^\dagger \qquad {}^1\pi\pi^* < S_0 < {}^3\pi\pi^* < {}^1n\pi^* < {}^3n\pi^* \qquad (2)$$

Examination of the optimized structures revealed a strong correlation between the barriers in eq 2 and the strength of the intramolecular H-bond in each of the excited states. The topologies of the π HOMO and the MO just below it, of $\sigma(n)$ symmetry, permitted a simple explanation of the different geometries of the $\pi\pi^*$ and $n\pi^*$ states, particularly the CC and CO bond stretches and contractions that occur within the ring upon electronic excitation. As a specific example, the excitation from an orbital containing a bonding interaction within a given CC bond, to one where the interaction is antibonding, yields a lengthening of this bond.

In an effort to examine the effects of dynamic electron correlation, MP2 calculations were applied to the geometries optimized at the CIS level of each state, yielding substantial reductions in some of the barriers to proton transfer. In fact, after inclusion of correlation, the barriers in the excited states vanish for the most part. This barrier reduction is consistent with the ground-state trend, where the barrier is also reduced, but is even more dramatic in the case of the excited states. Many of the above conclusions were later confirmed by a series of CASSCF and CASPT2 calculations of the ground and excited singlets of malonaldehyde.[92] Similar correlation-induced excited-state barrier lowerings were observed in later calculations of various systems in which the correlation is computed by an entirely different procedure,[93−95] and another study went so far as to suggest there is no barrier at all in the $^1\pi\pi^*$ state.[96] A

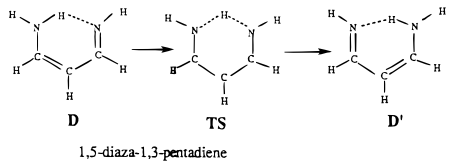

Figure 2. Molecular diagram of 1,5-diaza-1,3-pentadiene, **D**, its equivalent tautomer **D′**, and the proton-transfer transition state, **TS**.

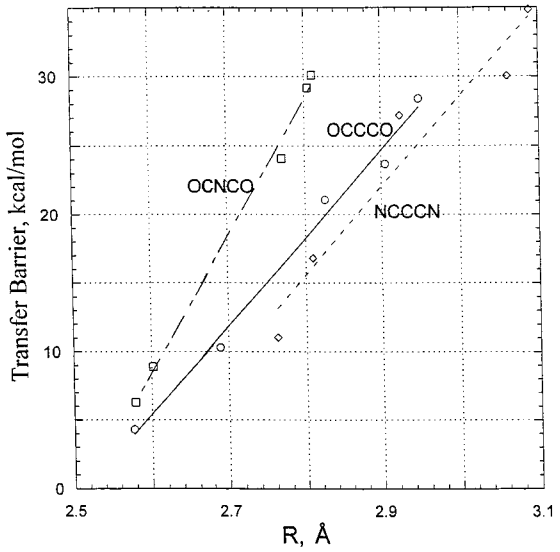

Figure 3. Comparison of the ground and excited-state proton-transfer barriers in a number of systems. Malonaldehyde, labeled by its OCCCO skeleton, is represented by circle data points and solid line, the NCCCN skeleton of 1,5-diaza-1,3-pentadiene by the diamonds, and formimidol OCNCO by square data points. All barriers computed at the CIS/6-31+G** level. R refers to the distance between heavy atoms in the intramolecular H-bond, either O···O or N···N.

later experiment, making use of nonlinear degenerate four-wave mixing spectroscopy of malonaldehyde,[97] suggested that the prediction of a low barrier in the nπ* state might not be far off the mark. However, on the basis of later benchmark calculations, described below in section IV, it is likely that the MP2 lowering of the barriers is exaggerated.

A. Nitrogen Substitution. Replacement of the two O atoms of malonaldehyde that are involved in the intramolecular H-bond by NH leads to 1,5-diaza-1,3-pentadiene (**D**), illustrated in Figure 2 along with its tautomer **D′** and intervening transition state. **D** is isoelectronic with malonaldehyde and maintains the symmetry of the proton transfer potential, so one can focus purely on the effect of changing the character of the H-bonding atoms from O to N. Calculations[98] revealed that the pertinent MOs of **D** are quite similar to those of malonaldehyde, further facilitating the comparison. The highest occupied MO is of π type, and the second highest of σ symmetry, resembling in many respects a lone pair on the proton-accepting atom.

As in the case of malonaldehyde, the $^3\pi\pi^*$ state of **D** is the lowest-lying of the excited states. Again, at the CIS level, all of the excited states have a higher proton-transfer barrier and longer H-bond than the ground state, with the same notable exception of $^1\pi\pi^*$ where the barrier is lower and the H-bond shorter. Indeed, the CIS barriers of **D** follow precisely the same trend as in Eq (2). Perhaps the most informative comparisons between **M** and **D** can be visualized by Figure 3 which correlates the proton-transfer barrier and the length of the H-bond in each of the various states, including S_0. Just as was found in numerous studies of proton transfers in the ground state, longer H-bonds are typically associated with a higher transfer barrier, given similar systems. Indeed, such sensitivity is also noted in excited states.[95,99−101]

The line labeled NCCCN in Figure 3 refers to the internitrogen transfer in the **D** molecule, and OCCCO to the OH···O interaction in malonaldehyde. There is a horizontal displacement of some 0.05 Å, which indicates that the NH···N bond can be longer by this amount and still have the same transfer barrier as the interoxygen H-bond. In alternate language, the internitrogen H-bond has a lower proton-transfer barrier than does OH···O by 2 to 3 kcal/mol, given the same bond length. It was encouraging to note a very similar result had been found earlier for the ground states,[85] suggesting that the rules governing excited state proton transfer are not entirely changed upon electronic excitation.

Another point of similarity with the ground state is the lowering effect of electron correlation upon the proton-transfer barrier. MP2 treatment of correlation reduces the barriers in the excited states to the point that it is questionable whether any of these states contain a double well potential. Intriguingly, a CASSCF treatment leads to the opposite result of excited-state proton-transfer barriers that are higher than ground-state data. This curious methodological dependence of these results is addressed in some detail below.

One might expect a smaller perturbation to the malonaldehyde system if the N atom replaces not one of the H-bonding O atoms, but rather one of the C atoms. When the central CH group of malonaldehyde is replaced by N, the resulting OCNCO skeleton retains the OH···O character of the intramolecular H-bond, as well as the symmetry of the proton transfer potential. Not only does this substitution avoid the H-bonding atoms, but the N atom is separated from the site of the H-bond by one C atom, providing additional insulation of a sort. Calculations of this altered system, formimidol, were carried out,[102] and the perturbations were generally small. The ordering of excited states was preserved, as was the H-bond weakening caused by n$\rightarrow\pi^*$ excitation.

This N replacement slightly weakens the intramolecular H-bond in the ground state and in the singlet and triplet $\pi\pi^*$ states, while apparently strengthening the interaction in the two nπ^* states. Although the proton-transfer barrier in the ground state of formimidol (**F**) is lower than in **M**, the barriers in all four excited states are higher in the N-analogue. In other words, the N-substitution enhances the effect of electronic excitation upon the transfer barriers. This substitution also dampens the effect of the n$\rightarrow\pi^*$ excitation upon the H-bond. This effect was connected with the ability of N to partially insulate the proton-acceptor O atom from electron density loss which accompanies n$\rightarrow\pi^*$ excitation.

Examination of Figure 3 reveals the clear linear correlation between proton-transfer barriers and the length of the H-bond in this **F** system, as was noted above for **M** and **D**. The curve fit to the OCNCO barriers is slightly steeper than the curve fits for the OCCCO and NCCCN systems, but retains its near linearity. The vertical displacement of the OCNCO line above OCCCO indicates that the N substitution, even separated from the H-bond as it is, endows the molecule with a higher proton-transfer barrier, given a particular H-bond length. Indeed, the OCNCO line is further separated from OCCCO than is NCCCN, leading to the conclusion that in some sense, N-substitution at a non-H-bonding location affects the proton-transfer barrier by a greater amount than does substitution of the H-bonding atoms themselves.

B. Ring Size and Charge. All of the systems considered thus far are five-membered rings (not including the bridging

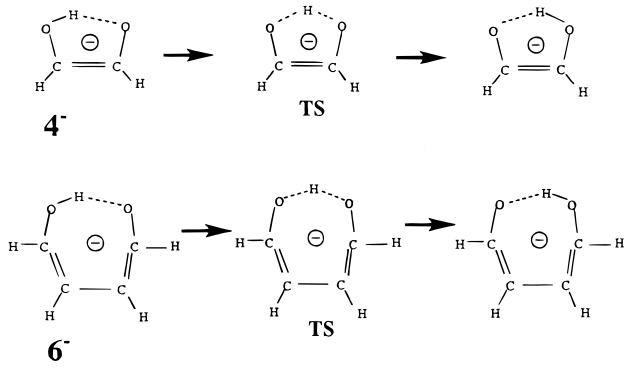

Figure 4. Diagrams of anionic four and six-membered ring systems $\mathbf{4}^-$ and $\mathbf{6}^-$, respectively.

H). It is logical to be curious as to how the patterns might be altered if the rings were of a different size. Another point of similarity of the rings above is that all are electrically neutral. A number of additional systems were devised so as to examine the effect of both ring size and electrical charge upon the proton-transfer properties. Moieties $\mathbf{4}^-$ and $\mathbf{6}^-$, illustrated in Figure 4, contain four and six heavy atoms, respectively. Like malonaldehyde, they include an intramolecular OH···O bond, but differ in that they each bear a negative charge.

These anions were compared to neutral malonaldehyde in a series of ab initio calculations,[103] which showed the ground state H-bond to be progressively strengthened as the ring is enlarged from three to four to five atoms, as measured by both a shorter R(O···O) separation and a greater stretch of the covalent r(OH) bond, coupled with a reduction in the angular strain of the θ-(OH···O) angle. All systems exhibit strong evidence of H-bond weakening upon n→π^* excitation, whether singlet or triplet. As an interesting point of distinction, on the other hand, the $\pi\rightarrow\pi^*$ triplet excitation strengthens the H-bond in the two anions, which contrasts with the neutral wherein the H-bond is weakened in the $^3\pi\pi^*$ state. Another difference engendered by the overall charge is a shift in the energy ordering of the excited states. In comparison to the ordering of the neutrals in eq 1 above, the order in the two anions is as follows:

$$\text{energy} \qquad S_0 < {}^3\pi\pi^* < {}^1\pi\pi^* < {}^3\mathrm{n}\pi^* < {}^1\mathrm{n}\pi^* \qquad (3)$$

i.e., the $^1\pi\pi^*$ state is lowered relative to the others. A more minor discrepancy is associated with the skeletal bond lengths. Whereas the CC and CO bonds of the neutral vary a good deal as the proton moves along its transfer coordinate, there is much less alteration in the two anions. This distinction can be rationalized on the basis of the simple Lewis bonding diagrams of Figures 1 and 4 where the transfer changes double bonds to single and vice versa in malonaldehyde, but there are no such changes required in the two anions.

The close correspondence between the strength of the H-bond, as measured by energetics as well as geometric markers, and the barrier to proton transfer remains largely intact as the ring is enlarged or as charge is added to the system. The persistence of this relationship, with a certain degree of experimental support,[40,104,105] hence strongly suggests a causal relationship that is fairly universal. The relationship is expressed more quantitatively by Figure 5 which further indicates that the enlargement of malonaldehyde **M** by one C atom, and the addition of a negative charge, to produce the $\mathbf{6}^-$ anion, has a very small effect indeed upon the parameters of the linear relationship. The situation is somewhat different in the smaller anion: the higher barriers here can be simply attributed to the much greater degree of ring strain for a given R(O···O) separation. For example, the values of θ(OH···O) for $\mathbf{4}^-$ are in the range of 35−51°, as compared to only 6−15° for $\mathbf{6}^-$. This large increase of barrier associated with angular strain of the H-bond is characteristic of other systems as well.[106]

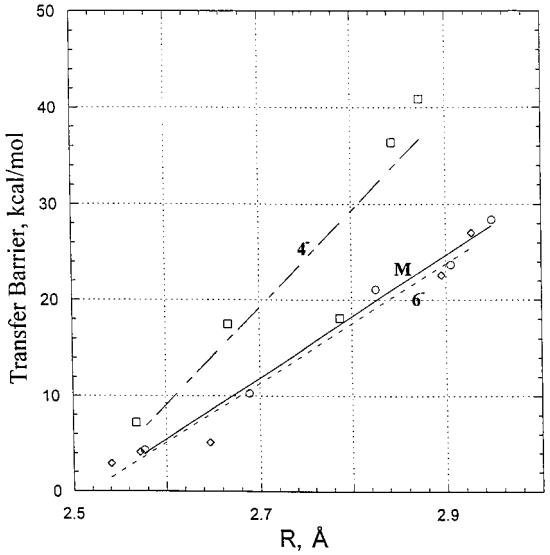

Figure 5. Comparison of the proton-transfer barriers in neutral malonaldehyde (**M**), represented by circle data points and solid line, and two anionic systems. $\mathbf{4}^-$ and $\mathbf{6}^-$ refer to systems illustrated in Figure 4, indicated by square and diamond data points, respectively. All barriers computed at the CIS/6-31+G** level. R refers to the O···O H-bond distance.

One can exploit the connection between barrier height and H-bond strength by probing more deeply into the factors that affect the latter property. Since the H-bond is dependent upon electron density in the lone pair of the acceptor atom, and the n orbital consists largely of this lone pair, it is easy to understand the weakening of the H-bond caused by n→π^* excitation. This density loss is confirmed by monitoring the Mulliken charge of the proton-acceptor atom. Indeed, the changes in this atom's charge are consistent with the curious observation that the H-bonds are weakened in the $^1\pi\pi^*$ states of the anions, whereas a strengthening occurs in the same state of the neutral malonaldehyde.

This comparison of ring sizes also pursued the matter of how the results are affected by the choice of basis set. Both the H-bond energy and the proton transfer barrier are quite insensitive to basis set, once a "threshold" is surpassed. For these molecules in their ground states, the smallest basis that can be recommended is 6-31G*; addition of diffuse or more polarization functions affects the results to only a small extent. The bar is raised a bit upon consideration of the excited states, where diffuse functions, e.g., 6-31+G*, appear to be required for good accuracy. While electron correlation perturbs the H-bond energies to only a small degree, there is a dramatic effect upon the transfer barriers. MP2 barriers are much smaller than CIS values, whereas coupled cluster barriers[95] suggest values intermediate between those two extremes (see below).

C. Asymmetric Systems. The next step in the investigation of malonaldehyde-related systems was to remove the symmetry while retaining the basic electronic structure. This was accomplished by changing the CH═O group on one side of the malonaldehyde molecule to N═NH.[107] The resulting glyoxal-monohydrazine (**G**) pictured in Figure 6, is isoelectronic with malonaldehyde. Unlike the latter, the two tautomers of **G** are inequivalent to one another, lending an asymmetry to the proton-

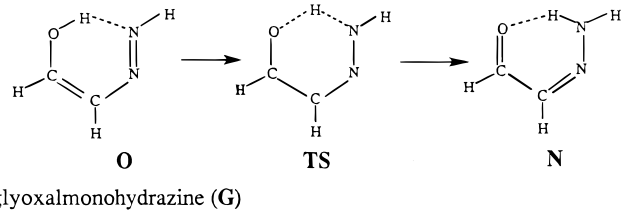

Figure 6. Molecular diagram of glyoxalmonohydrazine (**G**), containing an asymmetric proton-transfer potential. The **O** tautomer is commonly referred to as keto and **N** as enol.

transfer potential of each state. The **N** tautomer (also known as the keto) was computed to be more stable than **O** (the enol) by about 10 kcal/mol in the ground state, not surprising in view of the greater basicity of nitrogen. Correlation has only a minor effect upon this energy difference. The barrier to proton transfer from O to N is 11 kcal/mol at the SCF level, but is reduced to less than 2 kcal/mol when MP2 correlation is included. Despite the asymmetry of the **G** molecule, the frontier MOs of the **O** and **N** tautomers are surprisingly similar. A number of similarities were found also between the manifolds of excited states in **G** and malonaldehyde, notwithstanding the asymmetry of the former. In the first place, the energy ordering of both the **O** and **N** tautomers corresponds to eq 1 above, although there are some minor modifications. Second, CIS calculations of both molecules suggest that the proton-transfer barrier is higher in the excited states than in S_0, with the usual exception of $^1\pi\pi^*$.

What makes **G** most interesting is the asymmetry of its proton-transfer potential, and how this asymmetry is affected by electronic excitation. At all levels of theory considered, with and without correlation, the **N** tautomer is more stable in the two $\pi\pi^*$ states, but the situation reverses and **O** is favored in the singlet and triplet nπ^* states. Reversals in stability of this type are well-known in ESPT reactions, and are commonly attributed to changes in pK caused by excitation.[91,108] At the correlated MP2 level, it appeared that the transfer potentials for the ground and singlet and triplet $\pi\pi^*$ states are rather similar to one another, containing a single **N** minimum, with only the hint of a second well corresponding to **O**. The ^{1}nπ^* and ^{3}nπ^* states, on the other hand, are each associated with a double-well potential, with an energetic bias toward **O**.

The work on asymmetric glyoxalmonohydrazine was compared to a very similar system, **G′**, in which the nonbridging H atom bound to the nitrogen is replaced by a methylene, and a hydrogen is added to the other nitrogen. The **O** tautomer is preferred in the ground state,[109] unlike **G** where **N** is more stable. In fact, for **G′**, there is no minimum in the ground-state potential corresponding to **N**. However, the two molecules behave more similarly in their $\pi\pi^*$ states: Excitation of an electron from the π to the π^* MO, in either the singlet or triplet configuration, changes the character of the potential such that **N** is more stable than **O**, as it is in **G**. Later DFT computations [110] found that attachment of aromatic systems of various sizes to the basic **G′** unit causes only a minor perturbation in the transfer energetics; all exhibit the characteristic transition from one tautomer to the other upon excitation. Moreover, the characters of the relevant MOs in the neighborhood of the H-bond are essentially unchanged by the presence of the aromatic rings.

Other calculations have also addressed analogous asymmetric systems. 1-amino-3-propenal, for example, is very much like **G** except that its skeleton is of the NCCCO type rather than NNCCO. The ^{1}nπ^* state is computed to have a higher proton-transfer barrier than either S_0 or $^1\pi\pi^*$, the latter of which probably has no barrier at all.[93] Later computations using CIS and MP2 [111] confirmed that the energy barrier to proton transfer is quite small in the $^1\pi\pi^*$ state, and the transfer potential is of perhaps single-well character.

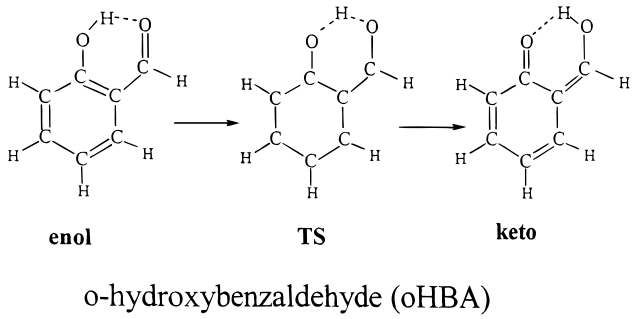

Figure 7. Molecular diagram of o-hydroxybenzaldehyde (oHBA), illustrating the enol and keto tautomers, and the transition state separating them.

III. Aromatic Systems

As stated earlier, most of the ESPT molecules that have been studied experimentally, and which show the most interesting behavior, contain an aromatic system of some sort connected directly to the intramolecular H-bond. It thus becomes important to investigate how the behavior of the various smaller moieties discussed above is perturbed when connected to an appropriate aromatic system. When attached to a simple phenyl ring, the malonaldehyde molecule resembles *o*-hydroxybenzaldehyde (oHBA), as illustrated in Figure 7. The so-called enol form contains an intramolecular H-bond linking the phenol OH with the aldehydic O acceptor. After the transfer has occurred, the resulting system, commonly referred to as the keto form, contains a H-bond to an O acceptor atom, double-bonded directly to the phenyl ring. Unlike the smaller malonaldehyde where the system is symmetrically equivalent before and after the transfer, the enol and keto forms of the larger oHBA are chemically distinct, with different energies. In fact, a simple Lewis diagram of the two forms suggests that there is a loss of aromaticity in the keto form, with important implications discussed below.

Despite the differences in size between malonaldehyde and oHBA, and the aromaticity of the latter, ab initio computations revealed a surprisingly small difference between the two with respect to the frontier molecular orbitals involved in the first few electronic excitations.[112] While there is of course a good deal of density connected with the π and π^* MOs that appears within the confines of the aromatic ring of oHBA, the topologies of these orbitals, including their nodal structures, in the vicinity of the H-bonded ring are essentially unchanged from malonaldehyde. Another point of strong similarity concerns the geometrical properties of the intramolecular H-bond in each tautomer, as well as the computed energy of this interaction. Just as for malonaldehyde, the H-bond in oHBA is greatly weakened in the two nπ^* states, less so in $^3\pi\pi^*$, but significantly strengthened in $^1\pi\pi^*$.

The difference in energy between the keto and enol tautomers of oHBA goes to the heart of one of the central issues of ESPT chemistry, reflecting as it does the reversal in pK_a that is associated with certain electronic excitations.[13,44,45,82,113] The enol is clearly favored over the keto in the ground state, while the reverse is true in the singlet and triplet $\pi\pi^*$ states, regardless of whether correlation is included. The magnitude of this change is dramatic; the 16 kcal/mol preference for the enol in S_0 is reversed to a favoring of the keto in the $^3\pi\pi^*$ state by as much

as 20 kcal/mol. The situation is slightly less clear in the nπ* states. The ^{3}nπ* enol is more stable than the keto by 20 kcal/mol at the CIS level, but this margin slims down to only 2 kcal/mol with MP2 correlation. In the case of the singlet nπ*, the 17 kcal/mol CIS preference for the enol is reversed by correlation, leaving the nπ* states an unresolved question.

It is possible to draw connections between the relative stabilities of the two tautomers and the degree of aromaticity in the phenyl ring. The latter was quantified using the idea that a fully aromatic benzene ring would have all of its C−C bonds of equal length.[112] Hence, one can define a nonaromaticity index η as the difference in length between the longest and shortest of the C−C bonds within the phenyl ring. This parameter is of course equal to zero in benzene, our prototype aromatic system. It is equal to 0.028 Å in the enol oHBA geometry of S_0, but rises to 0.124 Å in the keto, confirming the notion that aromaticity is lost in the keto. η exhibits a similar increase from enol to keto in the two nπ* states, consistent with the observation that enol is favored over keto in these two excited states. The situation is quite different for the $\pi\pi$* states, which show an energetic preference for the keto over the enol. As an electron has been excited from a π bonding to a π* antibonding orbital, it is not surprising that some aromaticity is lost in these states of the enol. Indeed, the nonaromaticity index is three or four times higher in the $\pi\pi$* enol states, as compared to S_0. Having already lost much aromaticity in the enol, there is little left to lose by tautomerization to keto, and in fact η is little changed by this proton transfer.

A comparison of the transfer barriers in malonaldehyde and oHBA is complicated by the differing energies of the two tautomers of the latter. That is, if one starts with any symmetric proton-transfer potential, as in malonaldehyde, and then skews the potential by raising the energy of one side, say the right, the barrier for transfer from left to right will of course rise while the transfer barrier in the reverse direction will diminish. This dual barrier obscures the fundamental question as to what effect the addition of the ring has upon the *intrinsic* barrier. One means of estimating the intrinsic barrier in this asymmetric potential is to adopt a philosophy akin to Marcus theory, and "wash out" the asymmetry by taking an arithmetical average of the forward and reverse barriers.

The outcome of this procedure is outlined in Figure 8 which plots proton-transfer barriers against the equilibrium R(O···O) distance. The solid line labeled **M** represents the best straight-line fit of the barriers in the malonaldehyde system (square data points) as our point of reference. The "x" and "+" data points refer to the same data for the transfers from enol to keto, and vice versa respectively, of oHBA. There is clearly a great deal of scatter in these values. On the other hand, when the aforementioned averaging is concluded, one obtains the points represented by the circles in Figure 8. These averages obey a nearly linear relationship, visualized by the broken line labeled oHBA. The latter line is nearly parallel to the analogous curve of **M**, and only a little higher.

In summary, it appears that addition of the aromatic ring to the basic malonaldehyde unit perturbs its hydrogen bonding and proton transfer properties by surprisingly little. The largest change arises from the introduction of a high degree of asymmetry into the proton transfer potential. The ring preferentially stabilizes the enol tautomer in the ground and nπ* states, but the keto in the $\pi\pi$* states. These opposing trends can be understood largely on the basis of the degree of aromaticity in the ring, and how this property is affected by each electronic excitation. The asymmetry introduced into each proton transfer

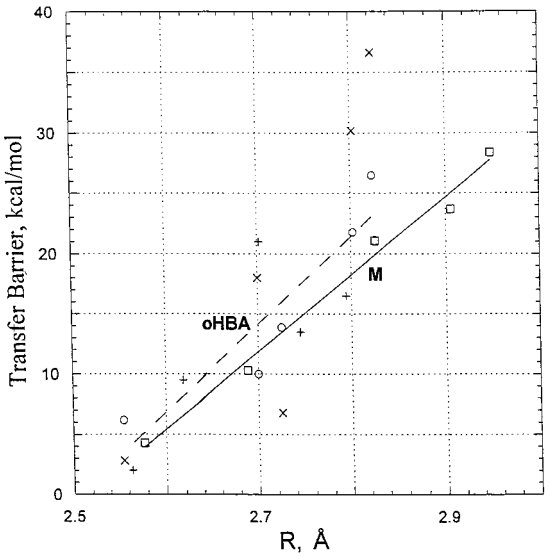

Figure 8. Comparison of the proton-transfer barriers in malonaldehyde (**M**), represented by square data points and solid line, and oHBA, as a function of equilibrium R(O···O) for a number of states. The broken line indicates the average barriers in oHBA, represented by circle data points; "x" and "+" signs refer respectively to the enol → keto and reverse barriers in oHBA. All barriers computed at the CIS/6-31+G** level.

potential by the aromatic ring skews the barriers for transfer in the two directions, one rising and the other falling. But when this skewing effect is averaged out, the aromatic ring is found to affect the transfer barrier of malonaldehyde by only a small amount. Indeed, later work confirmed the similarity of the behavior of the singlet and triplet $\pi\pi$* states, and suggested that addition of even more phenyl rings would perturb the transfer energetics by smaller and smaller amounts.[77]

Other computations of aromatic systems are consistent with our conclusions above. Early calculations of oHBA with a minimal basis set had suggested an enol → keto tautomerization induced by excitation to the $^1\pi\pi$* state,[114] and the authors made some attempt to rationalize the behavior of certain of the excited states based on nodal patterns.[115−119] CASSCF and CASPT2 calculations of oHBA confirm the much higher transfer barrier for the ^{1}nπ* state as compared to $^1\pi\pi$*,[94] as well as the reversal in stability between the two tautomers that occurs in the latter state. The similar salicylic acid also undergoes a preferential stabilization of the keto upon excitation to the $\pi\pi$* states,[73] as does 3-hydroxychromone and a number of its derivatives.[77] In all fairness, however, it should be mentioned that other calculations of oHBA, and closely related congeners, have raised the question as to whether excitation to the $^1\pi\pi$* state results in a full tautomerization or merely in a small shift of the bridging proton.[120,121] Another word of caution derives from other calculations that suggest the addition of an aromatic ring to a small system can produce stronger perturbations in different situations.[122]

CIS and MP2 computations [111] of the asymmetric H-bond in the ground state of 1-amino-3-propenal, indicate a preference for the O···HN keto to the OH···N enol, understandable from the standpoint of the greater basicity of N. Adding an aromatic ring, thereby forming salicylaldimine, reverses this preference, entirely consistent with the aromaticity arguments described above for oHBA. Importantly, the addition of the aromatic ring does not alter the conclusion that the keto tautomer is preferred in the excited $^1\pi\pi$* state, although it does appear to lower transfer barriers in the various states. The same reversal within

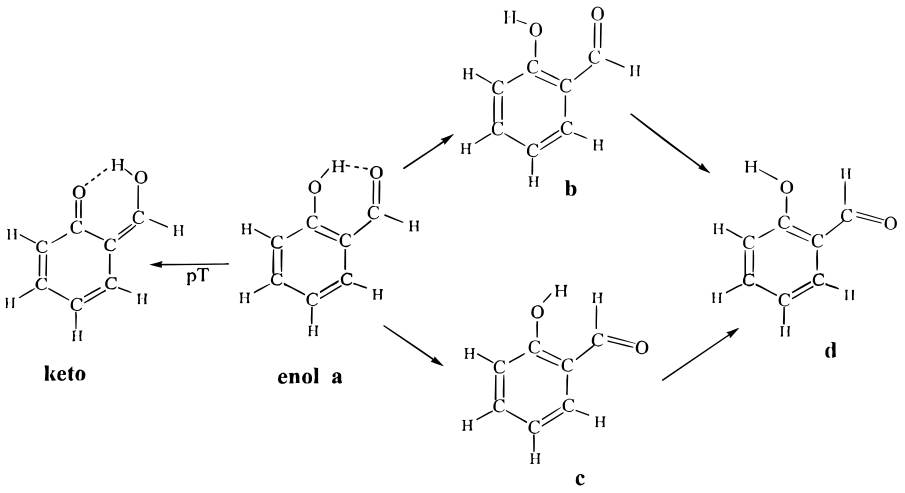

Figure 9. Structures of the keto and enol tautomers of oHBA, as well as various rotamers of the latter.

an asymmetric OH···N bond occurs in a larger system like 2-(2′-hydroxyphenyl)oxazole and some of its derivatives,[123−126] or in [2,2′-bipyridine]-3,3′-diol where a double proton transfer takes the system from a pair of intramolecular OH···N bonds in the di-enol to two O···HN (di-keto).[127,128] It might be added parenthetically that there is evidence that calculations of this type can accurately reproduce experimental quantities, such as the excitation-induced change in dipole moment and polarizability of a molecule like *o*-hydroxyacetophenone.[129]

Experimental work on oHBA is not entirely conclusive. Early emission spectroscopy indicated little proton transfer takes place in the $^1\pi\pi^*$ state[82,113] but transfer through a low barrier has been observed in a series of closely related derivatives[104] by spectroscopic methods such as time-resolved thermal lensing,[118] fluorescence excitation and dispersed emission,[79] and femtosecond time-resolved multiphoton ionization.[130] It may turn out that the photophysical properties are rather sensitive to substituents on the ring, as suggested by fluorescence experiments.[83,131,132]

A. Competitive Bond Rotations. The proton transfer in molecules like malonaldehyde and oHBA takes place within the preexisting intramolecular H-bond. If this bond were broken prior to transfer, such a transfer could not occur. Since the H-bond is typically not very strong, on the order of several kcal/mol, it is not difficult to imagine that this bond might be broken fairly easily.[133−135] Figure 9 illustrates how the enol configuration of oHBA might have its H-bond broken by rotation around one of two bonds. Rotation around the indicated C−O bond moves the hydroxyl H atom away from the H-bond axis, yielding configuration **b**. Alternately, a rotation around the neighboring C−C bond breaks the H-bond by moving the carbonyl O away from the H, leading to configuration **c**. The H-bond is also broken if rotation occurs around both bonds as in **d**.

Calculations were conducted to evaluate the energetics of each of these energetic pathways so as to compare with the proton-transfer process.[136] It was found in the ground state that configurations **b**−**d** are higher in energy than the enol by some 8−10 kcal/mol. The energy barriers computed for these bond rotations are rather high, varying between 13 and 16 kcal/mol. Since the transfer of a proton to yield the keto is also energetically uphill, by about 16 kcal/mol, neither bond rotation nor proton transfer to form the keto is likely to take place in the enol ground state.

We turn our attention now to the excited states. Like S_0, the keto is higher in energy than the enol for the singlet and triplet $n\pi^*$ states by some 16−20 kcal/mol. When this observation is coupled with the high barrier separating the two tautomers, a proton transfer to form the keto is unlikely. On the other hand, the geometries resulting from bond rotations are comparable in energy to the enol in the two $n\pi^*$ states; in fact, **d** is predicted to be somewhat more stable than the enol for these two excited states. Moreover, the energy barriers computed for these bond rotations are fairly low, less than 5 kcal/mol. Consequently, bond rotations are far more likely to occur in the $n\pi^*$ states than is tautomerization to the keto.

The situation is quite different in the singlet and triplet $\pi\pi^*$ states, where the proton transfer to form the keto is exoergic by 7−14 kcal/mol. The barriers impeding this transfer are rather low, 3 and 7 kcal/mol for the singlet and triplet, respectively, facilitating a rapid proton transfer. Bond rotations cannot compete with the proton-transfer process in the $\pi\pi^*$ states. In the first place, the **b** and **c** configurations are higher in energy than the enol by 12−17 kcal/mol for the singlet and 6−8 for the triplet. Second, the barriers obstructing these bond rotations are computed to be rather high, particularly for the singlet, a result that is consistent with prior experimental measurements of oHBA in rare gas matrix.[80]

Summarizing the total picture for oHBA, excitation to either of the $\pi\pi^*$ states would be conducive to proton transfer as the enol → keto tautomerization would be favored over any rotamerization that might preclude the transfer in these excited states. If excited to a $n\pi^*$ state, on the other hand, oHBA would likely rapidly rotamerize to a configuration like **d** which cannot undergo an intramolecular proton transfer.

B. Effects of Chemical Substitution. Many of the systems investigated experimentally contain not only aromatic systems, but one or more non-hydrogen substituents occur in various positions. Indeed, it has been suggested that the proton transfer properties may be heavily influenced by substituents on the aromatic ring.[83,101,131,132,137] It is therefore important to examine in a systematic way how such chemical substitution might alter the proton-transfer properties of the various excited states. Salicylaldimine, a cousin of oHBA in which the C═O of the aldehyde is replaced by the imine C═NH functionality, was taken as a model for this study. As illustrated in Figure 10, the enol tautomer contains a OH···N intramolecular H-bond, which transitions to O···HN in the keto. Two positions were considered for replacement of H by the F atom. X_1 is located on the aromatic ring, on the C atom adjacent to the carbon bearing the O atom. Closer to the H-bond is site X_2 bonded to the same carbon as is the N.

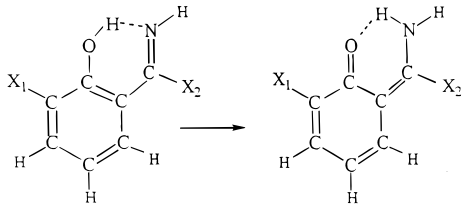

Figure 10. Structures of the keto and enol tautomers of salicylaldimine and its fluoroderivatives, with X_1 and X_2 = H or F.

As in the similar case of oHBA, the enol is more stable than the keto in the ground state of salicylaldimine, which can again be understood on the basis of a loss of aromaticity in the keto.[138] The energy difference is smaller in salicylaldimine, 7−9 kcal/mol as compared to 16−17 kcal/mol in oHBA, even though the replacement of the C═O of oHBA by the C═NH of salicylaldimine appears to strengthen the H-bond in the enol by several kcal/mol. More importantly, replacement of the H at X_1 by a F atom lessens the energetic preference of the enol by 1 kcal/mol while the opposite effect of an increase in ΔE occurs when the substitution takes place at X_2. These changes can be understood on the basis of inductive effects of F. When placed at X_1, F is close to O, so it can enhance the acidity of this atom by stabilizing the partial negative charge that accumulates on the unprotonated O in the keto tautomer; atomic charges verified this presumption. Precisely analogous arguments explain the tendency of the X_2 substitution to increase the relative stability of the enol, by enhancing the acidity of the proximate N atom.

Also as in the case of oHBA, and many of the smaller molecules discussed above, the H-bond is weakened by the various excitations of salicylaldimine, with the singular exception of the $^1\pi\pi^*$ state which undergoes a H-bond strengthening. The tautomer preference switches from the enol in the ground state to the keto in the singlet and triplet $\pi\pi^*$ states.[138] This energy reversal is equally dramatic in salicylaldimine, amounting to a total of as much as 30 kcal/mol, and is again consistent with the degree of aromaticity in the phenyl ring. More to the point, the effects of fluorosubstitution in these excited states can be rationalized on the basis of electronegativity. Just as in the ground state, placement of an F atom at site X_1 adds to the preference for the keto, whereas the opposite effect is observed for substitution at X_2. It is worth stressing that these inductive effects are observed even in the absence of explicit inclusion of electron correlation. Effects of fluorosubstitution at both X_1 and X_2 upon the proton transfer barrier are generally small but tend to obey the rules noted above, in that the barriers follow the patterns dictated by the changes in ΔE. For example, just as a F atom at X_1 "pushes" a proton across from O to N, stabilizing the keto, so too is the barrier for this direction of transfer reduced. It should be noted finally that some of the trends computed for the $n\pi^*$ state are not simply explained by these principles, and may warrant additional work.

In conclusion, it appears that with few exceptions, many of the effects of chemical substitution, including perturbations of H-bond strength and the proton-transfer potential, can be understood in terms of the same inductive arguments that have been so useful in characterizing the ground electronic state over the years.

With the replacement of the aldehyde H of oHBA by a methyl group, viz. o-hydroxyacetophenone (oHAP), rotation of the aldehyde group around the C−C bond in the enol is largely ruled out due to steric crowding between this methyl and the hydroxyl H. Other than this particular restriction, this methyl substitution perturbs the oHBA molecule very little. Calculations[139] verify that the preferred tautomer in the S_0 state of oHAP corresponds to the enol, but that this situation is reversed and keto is more stable in the $^1\pi\pi^*$ state. This energy difference is 17.7 kcal/mol, quite similar to the value computed for oHBA. Also, like oHBA, $\pi\rightarrow\pi^*$ excitation reverses the stabilities of the two oHAP tautomers, favoring the keto. These computed results were consistent with the observed fluorescence spectra of the molecule,[6,104] as well as later calculations.[129]

IV. Methodological Investigations

The computational study of hydrogen bonds and proton transfers in their ground states has been sufficiently extensive that there exists a general understanding of the errors incurred by the use of any particular method. For example, it is widely recognized that enlargements of basis set lead to higher transfer barriers, while electron correlation reduces the barrier.[140−145] Moreover, there is every indication that most of the popular means of including correlation, i.e., MP2, MP4, QCISD, coupled cluster, etc., are in fair agreement concerning transfer barriers.[146−153] Transfers in excited states, on the other hand, have been studied far less extensively, so that there is no consensus yet as to which methods are most appropriate and accurate. Indeed, this issue is not limited to the proton transfer problem; computational methodology for excited states of molecular systems is generally much less mature than for closed-shell ground electronic states. For this reason, a comprehensive understanding of the ESPT process would be incomplete without some testing and comparison of a range of different theoretical approaches on prototype systems.

One sort of approach that has been tested in our laboratory is the multiconfiguration SCF (MCSCF) method.[147,154] MCSCF takes as its starting point a definition of "active space", a subset of occupied and virtual molecular orbitals that are allowed to participate in formal electronic excitations which in turn define the various electronic configurations. Because this choice is somewhat arbitrary, it thus becomes necessary to examine the sensitivity of the results to the particular set of orbitals which are included in the active space. Calculations[154] highlighted the dangers of an unbalanced choice of active orbitals, identified those orbitals whose inclusion is largely unnecessary, and pointed toward a set of guidelines to be used in selecting a balanced set. It was learned that a localization of the MOs prior to the MCSCF procedure can greatly simplify the choice of active MOs, and lead to a less arbitrary selection, and to a more reproducible, consistent set of data, with the added benefit of a smaller, i.e., cheaper, collection of active MOs. This work was followed up by a parallel study[147] that emphasized means of including dynamic correlation following a MCSCF calculation via configuration interaction approaches. It was found first of all that standard CI calculations using a single reference configuration conform nicely to results obtained for the proton-transfer barriers using Møller−Plesset treatment of correlation, even if only a small number of occupied MOs are included in the excitation list, provided these MOs are chosen judiciously. It is not necessary to go beyond double excitations for reliable results. Following MCSCF by CI removes much of the sensitivity to the particular choice of correlated space. When the CI expansion is based on a MCSCF wave function, there is reduced danger of skewed results with an unbalanced choice of occupied and virtual MOs. With this caveat in mind, the MCSCF + CI approach can be quite successful, particularly if both singles and doubles are included. The need for undue

concern about MO imbalance is lessened when the MOs are localized prior to the MCSCF treatment.

Tangential to an understanding of the ESPT process is elucidation of the factors that contribute to proton affinities of relevant species in their excited states. To this end, we considered how analysis of wave functions based on natural bond orbitals may be of use in monitoring the precise nature of various electronic excited states. One study[155] focused on small molecules containing the sorts of functional groups likely to participate in proton transfers in systems of interest. In particular, the double-bonded carbonyl group was investigated, along with its isoelectronic congeners wherein the O is replaced by C or N. It was demonstrated how one might identify the various localized orbitals that are populated or depopulated in any given excitation. In ethylene, for example, the first excited singlet ($^1B_{3u}$) can be identified as an excitation from the CC π bond to a 3s type of Rydberg on C; the next singlet ($^1B_{1u}$) is predominantly of $\pi \rightarrow \pi^*$ type, but also contains a significant amount of excitation into a carbon Rydberg orbital. It was found that the deprotonation energy of the various molecules tends to be reduced following electronic excitation. This trend appears to be rooted in a charge shift away from the more electronegative atom upon excitation.

A more recent work[156] consisted of a detailed comparison of a number of different theoretical methods applied to a set of well-defined prototype systems. The molecules investigated were the five-membered rings described above: malonaldehyde (**M**) and formimidol (**F**) both contain a symmetric OH···O intramolecular H-bond, an analogous NH···N bond exists within diazapentadiene (**D**), and glyoxalmonohydrazine (**G**) contains the asymmetric OH···N. For each of these systems, preliminary calculations examined how the total energy is affected by choice of active space within the complete active space SCF formalism (CASSCF), a more complete version of MCSCF.[156] The optimum choice, in either the 4-31G or 6-31+G** frameworks, appeared to include one σ and two π MOs from the occupied space, coupled with one σ^* and three π^* virtual MOs; this set is designated (12/13). Results obtained with (12/13) were compared with data from a slightly altered set (13/13) to which a third occupied π MO was added. In addition to CASSCF, CASPT2 calculations were carried out that add second-order perturbation treatment of correlation directly to the CASSCF formalism. Other theoretical methods compared were CIS, and its MP2 derivative which includes dynamic correlation, CCSD and CCSD(T) variants of coupled cluster, and finally density functional theory (DFT), using B3LYP functionals to include both exchange and correlation.

All methods considered were unanimous in the ordering of the four excited states of **M**, reproducing the CIS order of eq 1 above, although there were substantial variations in the quantitative aspects of the energy spacings. Similar levels of agreement were observed in the other molecules as well. It is worth mentioning that this ordering obtained with 6-31+G** is largely reproduced by the much smaller 4-31G basis set. The agreement is poorer when comparing the barriers to proton transfer. In the case of the ground state of malonaldehyde, for example, the various correlated methods are in fair agreement, providing barriers of several kcal/mol. Not unexpectedly, the SCF barrier is too high, as compared to the correlated methods, by several kcal/mol. The CASSCF barrier, on the other hand, is a drastic overestimate, by as much as 20 kcal/mol. Indeed, the CASSCF barriers are much too high for all of the excited states as well. As illustrated in Figure 11, it also appears that the small variance in active space, between (12/13) and (13/13), yields a disturbingly large change in the barrier of a number of the excited states. Examination of Figure 11 also reveals that while the CIS barriers are larger than the correlated values, the CIS overestimates are not as extreme. CIS, like CASSCF(12/13), predicts that the transfer barrier for the triplet nπ^* state is substantially higher than for the singlet, a pattern which is not reproduced by most of the correlated methods below.

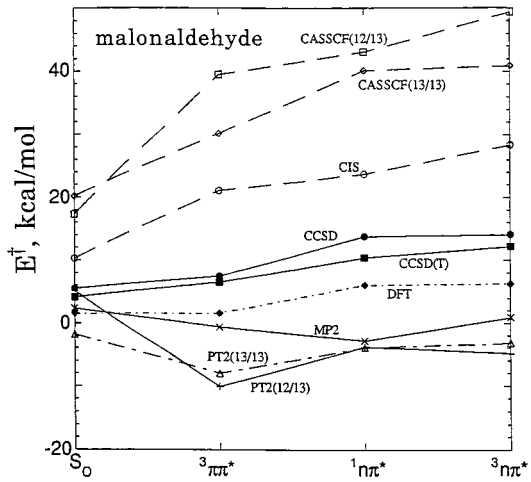

Figure 11. Barriers to proton transfer, $E^\dagger$, computed for the ground and several excited states of malonaldehyde by various methods.

With regard to the methods that include dynamic correlation, there is no overall agreement for the excited states. The CCSD and CCSD(T) barriers are all positive and of magnitude 10 kcal/mol or less. These results also suggest that the singlet and triplet nπ^* barriers are similar in magnitude to one another, and both larger than the ground state and $^3\pi\pi^*$ barriers. Although of smaller magnitude, the DFT barriers mimic this pattern. The MP2 barriers are underestimates compared to CCSD, indeed falling below zero in a number of cases. (A negative barrier indicates that the energy of the midpoint of the transfer is of lower energy than the transfer starting point configuration OH···O.) Whereas both CCSD and DFT yield the highest barriers for the two nπ^* states, the reverse is predicted by MP2. Lowest of all are the barriers computed by CASPT2. Indeed, all of the CASPT2 barriers are negative with the sole exception of the ground state when the (13/13) active space is employed. One point that is unanimous among the various methods is that the transfer barrier for the $^1\pi\pi^*$ state (not shown in figure) is the smallest of all, lower even than the S_0 barrier.

Most of the trends enunciated above for malonaldehyde persist for the other symmetric H-bonds in **D** and **F**. All methods agree that the barrier is smallest for $^1\pi\pi^*$, followed by the ground state. There is some ambiguity concerning the other excited states. The uncorrelated CIS and CASSCF methods predict the barriers in these states to be quite a bit higher than in S_0, while this question remains open for the correlated methods.

In terms of recommendations for level of calculation, the CASSCF method ought to be avoided due to its large overestimate of transfer barrier, and its apparently high sensitivity to choice of active space. CASPT2 overcompensates for these errors, yielding strong underestimates of the barriers, retaining some of the undesirable sensitivity to choice of space. Like CASSCF, CIS barriers are also overestimates but less drastic ones; moreover, CIS appears to correctly reproduce the trends from one state to the next, i.e., a nearly uniform error. MP2 barriers are also underestimated, but not by very much. The DFT approach offers surprisingly good reproduction of the

CCSD results, producing uniform underestimates of the barriers by roughly 5 kcal/mol.

In an asymmetric system like **G**, one must also be concerned with ΔE, the difference in energy between the OH···N and O···HN tautomers. All methods concur that the latter is the more stable of the two in the ground state, with remarkably small variance in the estimated energy difference of 9−12 kcal/mol. As in the symmetric systems, some of this uniformity is lost when attention is focused upon the excited states. While all of the methods agree that O···HN is more stable than OH···N in the two $\pi\pi^*$ states, there is quite a discrepancy in the amount of this energy difference, varying from 1 to 13 kcal/mol. Analogously for the $^3n\pi^*$ state, all methods predict that the order reverses and that OH···N is more stable, but the amount of this preference varies between 9 and 35 kcal/mol. The CASPT2 values of ΔE are quite high, probably unrealistically so. The same is true for the $^1n\pi^*$ state where the CASPT2 energy differences are much higher than those predicted by the other methods. In summary, the CASSCF and CASPT2 yield several values of ΔE that conflict with each other and with the other methods as well, so cannot be recommended for computations of this energy difference in the excited states, particularly for $n\pi^*$. CIS, too, overestimates the preference for the OH···N configuration in the $n\pi^*$ states, but is otherwise satisfactory. MP2 and DFT seem to offer the most reasonable estimates of ΔE in the ground and excited states.

These calculations struck a number of familiar chords from prior work which had shown that the DFT and MP2 barriers of the $^3\pi\pi^*$ state of malonaldehyde are lower than coupled cluster, while CIS values are much higher.[95] Indeed, CIS and the CIS/MP2 approach to include dynamic correlation, have had mixed success for excited states of related systems.[157−162] The dramatic reduction in CASSCF barriers noted when PT2 correlation is added was noted in these and larger molecules.[94,96,128,159] Other work confirmed the general similarity of CIS and CASSCF proton-transfer potentials, and the much lower barriers computed with CASPT2.[120,121] A recent paper[163] has carried out a thorough and systematic evaluation of the ability of CASSCF and CASPT2 in regard to the proton-transfer potentials of 1-amino-3-propenal. Consistent with our own results described above, a good deal of sensitivity to choice of active space was encountered with the CASSCF barriers. Taking the $^1n\pi^*$ state as an example, barriers varied between 14 and 31 kcal/mol. However, improved uniformity was noted at the CASPT2 level where barriers remained within the narrow range of 3−6 kcal/mol.

V. Summary and Perspectives

Ab initio calculations have brought to light a number of fundamental principles of the excited state proton transfer, but a number of important issues remain incompletely resolved. It appears that small molecules of the malonaldehyde type are capable of reproducing many of the essential features of larger systems containing an extended aromatic system. The topologies of the relevant frontier MOs, which control the excitation-induced geometry changes, are affected to only a minor degree by the presence of aromatic rings. Excitation to the $^1\pi\pi^*$ state brings about a strengthening and contraction of the intramolecular H-bond and a concomitant lowering of the barrier to proton transfer. The triplet $\pi\pi^*$ behaves in a contrasting fashion, with a weakened H-bond and higher transfer barrier; the singlet and triplet $n\pi^*$ states even more so. This very different behavior between the singlet and triplet $\pi\pi^*$ states is intriguing and further analysis is clearly desirable.

Replacement of the two H-bonding O atoms by N has a fairly small effect upon the proton-transfer properties, lowering the barrier uniformly by several kcal/mol. Substitution of one of the peripheral CH groups by a nitrogen atom also produces only a small perturbation, raising the barrier by a small amount. Enlargement or reduction of the malonaldehyde ring size, coupled with introduction of a negative electrical charge, also leads to minor changes, but with one or two exceptions: the H-bond in the $^3\pi\pi^*$ state is strengthened in the four and six-membered anions, opposite to the weakening observed in the neutral. Perhaps most notably, a nearly linear correlation is apparent between the height of the proton transfer barrier, and the equilibrium length of the H-bond in which it occurs, in each system examined. This relationship is surprisingly constant, whether the system is charged or uncharged, contains H-bonding O or N atoms, and is little affected by ring size.

The proton-transfer potential of an asymmetric NH···O H-bond is of course itself asymmetric, and the NH···O and N···HO tautomers are of unequal stability. The former is typically more stable in the ground state, a pattern which remains correct for the singlet and triplet $\pi\pi^*$ states as well. $n\rightarrow\pi^*$ excitation, on the other hand, reverses this ordering, making N···HO more favorable. Future work would be helpful in understanding more completely the reason the latter excitation favors the normally less stable N···HO tautomer.

Attachment of an aromatic phenyl ring to malonaldehyde introduces a different sort or asymmetry into the proton-transfer potential of the OH···O H-bond of *o*-hydroxybenzaldehyde (oHBA). The enol tautomer is favored over the keto in the ground state, easily understood on the basis of a loss of aromaticity in the latter. Indeed, this same principle can be used to understand the reversal in stability between the enol and keto that occurs upon $\pi\rightarrow\pi$ excitation, a reversal which does not occur in the $n\pi^*$ states. This behavior is characteristic not only of oHBA but of a wealth of different but related molecules. For that reason, a more detailed analysis that might permit a quantitative prediction of the aromaticity of a given state would be immensely useful. While the addition of the aromatic ring and the asymmetry it introduces into the proton-transfer potential of course affects the barriers to proton transfer, these modifications have little effect upon the *intrinsic* barrier, of the smaller, fully symmetric, malonaldehyde-like system.

The barriers to proton transfer are quite high in the $n\pi^*$ states of oHBA, whereas the H-bond that obstructs rotation around given bonds is quite weak. Consequently, rotamerization is expected to dominate over ESPT in the corresponding excited states of oHBA and related systems. Opposite trends in the $\pi\pi^*$ states lead to the supposition that ESPT will occur prior to rotamerization. Experimental testing of these predictions would be most welcome. It appears that the effects of chemical substitution upon proton-transfer energetics in excited states can be understood by the same inductive arguments that have been so useful over the years for the ground state.

In comparison to the ground state, computational methodology for study of excited electronic states is relatively immature. There are real questions concerning which particular methods are most appropriate to each of these states, while also being affordable, particularly for larger molecules containing aromatic systems. There are a number of points on which most of the methods tested agree, such as the reduced proton-transfer barrier in the $^1\pi\pi^*$ state, reversal of stability between the two tautomers of oHBA upon certain excitations, and so on. It also appears quite evident that electron correlation is absolutely essential for any sort of quantitative assessment of transfer barriers, and for comparison of tautomer energies. Despite some sanguine results of late, there remains a certain amount of uncertainty concerning

which method of electron correlation ought to be used, including particular details of each. Future studies which might provide definitive guidance concerning method selection would be an extremely constructive step toward further progress in this field.

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