Stepwise Two-proton Transfer within the Formamidine Dimer. A Theoretical Study using *Ab initio* Calculations

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Ab initio calculations at the VDZ and VDZ + P levels of theory of the two-proton transfer reaction within an isolated formamidine dimer give transition states with low symmetry, and with 6-31G* basis sets indicate stepwise two-proton transfers even in the absence of solvent.

Two-proton transfer reactions play an important role in many kinds of catalysis. Previous studies of the potential energy surfaces for such reactions within dimers have shown a concerted transfer with a highly symmetrical transition state in which the protons are located midway between the monomeric subunits.[1,2] In another theoretical investigation at the Hartree–Fock (HF) level of theory (using 3-21G basis set) the formamidine dimer and its two-proton transfer reaction have been studied using the assumption that the reaction path has C_{2h} symmetry.[3] The optimized structure of the highest energy within this restriction (a D_{2h} structure) was assigned as the transition state for the transfer reaction.[3]

As a part of our reaction mechanism studies of bifunctional catalysis[4] we have investigated the potential energy surface for the two-proton transfer reaction between two formamidine molecules at the Hartree–Fock level of theory using GTO basis sets of increasing size and precision, namely STO-3G, 3-21G, 6-31G, 6-31+G, and 6-31G*.[5] Symmetry restricted geometry optimization was performed using various optimization techniques.[6,7] Four stationary points have been located: monomer (M), dimer (D), transition state (TS) (identified as a first order saddle point), and at the 6-31G* level an intermediate, I. All stationary points were characterized by their force-constant matrices, calculated using analytical differentiation methods. The calculations were performed on a Cray 1 computer using the program package COLOGNE88[8] or on a digital Vax 8700 using the program package Gaussian 86.[9] The two packages include routines for all the above mentioned methods.

Using various split-valence basis sets, with and without diffuse functions, gave planar monomer and dimer structures having C_s and C_{2h} symmetries respectively. Analysis of the results suggests that the planarity of M and D found at VDZ level is due to an overestimation of bond polarities,[10] introducing a repulsive force between the nitrogen ligands leading to sp^2 hybridized nitrogens in the amino groups and shorter bonds to the ligands. The STO-3G and 6-31G* basis

Table 1. Energies, relative to the dimer, and the imaginary frequencies for the transition states.

Basis set	$E_{2M} - E_D$ /kcal mol^{-1}	$E_T - E_D$ /kcal mol^{-1}	Imag. freq. /cm^{-1}
STO-3G	11.7	9.0	1311i
3-21G	19.9	16.0	1494i
6-31G	14.3	19.4	432i
6-31+G	12.8	19.4	146i
6-31G*	11.2	25.4[a]	

[a] At this level of theory, the structure with C_{2v} symmetry is a local minimum, not a transition state.

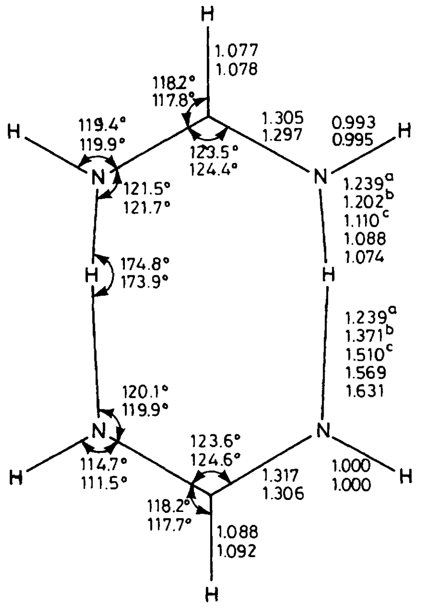

Figure 1. Calculated equilibrium geometries. Bond lengths are given in Å. The values with superscript correspond to (a) STO-3G, (b) 3-21G, and (c) 6-31G. Of the values without reference the upper one corresponds to the 6-31+G and the lower one to the 6-31G* level of theory.

sets gave structures with pyramidal amino groups in both the monomer (C_1 symmetry) and the dimer (C_i symmetry). The dihedral angel τ_{H_tNCN} (H_t is the proton to be transferred) obtained in the 6-31G* calculation was 14.1° for the monomer and 12.0° for the dimer.

The heavy atom distance r_{NN} for the two identical hydrogen bonds in the dimer increased when going to larger basis sets (r_{NN} ranging from 2.826 Å with the STO-3G basis set to 3.103 Å at the 6-31G* level). The bond length r_{H_tN} was slightly longer in the hydrogen bonded complex compared to the monomer structure (6-31G*: 1.006 and 0.998 Å, respectively).

At the STO-3G level we found a highly symmetrical transition state with D_{2h} symmetry (Figure 1), consistent with the general conception of transition states of such reactions.[1,11] In contrast, at the split valence level of theory we found a less symmetrical transition state showing C_{2v} symmetry where the two hydrogens were closer to one of the two amidine subunits than to the other (Figure 1). No transition state structure of D_{2h} symmetry (the two hydrogens exactly midway between the two amidine subunits) could be found. At the 3-21G level, the structure with D_{2h} symmetry (earlier reported as a transition state[3]) was shown to have two imaginary frequencies, as was also the case for the D_{2h} structure at the 6-31G* level. As for the dimer the heavy atom distances for the transition state tend to increase with larger basis sets and the hydrogen bridges become more asymmetric. The potential barrier becomes less curved as the heavy atom distance increases as indicated by a decrease in the imaginary frequency of the transition state (Table 1). When introducing polarization functions the computed C_{2v} structure turned out to be a local minimum instead of a transition state. A ten-point interpolation of all geometry parameters between the C_{2v} and C_i minima, carried out in order to get an approximate description of the activation barrier, led to a maximum 5.6 kcal mol^{-1} higher in energy than the C_{2v} structure (1 cal = 4.184 J). This indicates that there is an ion-pair like intermediate of C_{2v} symmetry on the reaction path of the two-proton transfer reaction. Thus there must be two transition states, both of C_1 or C_s symmetry, one before and the other after the intermediate. These transition states have not yet been localized.

The relative energies related to the lowest lying stationary point (the dimer) at each level of theory are given in Table 1. The true saddlepoint found at 3-21G level lies just 0.04 kcal mol^{-1} lower in energy (a small but significant energy difference) than the D_{2h} structure reported previously as a transition state.[3] The corresponding energy difference at the 6-31G* level is much greater (4.2 kcal mol^{-1}). As we see it, the high energy of the ion-pair like intermediate (compared to D) calculated with the 6-31G* basis set must to a large extent be due to separation of charges. Thus the intermediate, I, may be stabilized in polar solvents. It is interesting to note that systems which were assumed previously to use concerted two-proton transfer pathways make use of stepwise mechanisms involving intermediates even in the absence of solvent.

The reason for asymmetric potentials for the formamidine case and highly symmetrical ones for the formic acid case[1] may be that nitrogen forms weaker hydrogen bonds than oxygen. This results in longer heavy atom distances both in the dimer and the transition state. A more ion-pair like structure will therefore be favoured.

We have performed MP2/6-31G* calculations on D, I, and the maximum on the interpolation path. The relative energy $E_I - E_D$ decreases from 25.4 to 18.8 kcal mol^{-1} and the energy difference between the interpolation maximum and I decreases from 5.6 to 2.7 kcal mol^{-1}. Thus these results suggest that the inclusion of electron correlation effects will not change the symmetry of the potential energy surface.

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