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Proton and Heavy Atom Motions during the Stepwise Proton Tautomerism of Various Oxalamidines. A Semiempirical PM3–MNDO Study*

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The tautomerism of oxalamidine (OA) and the substituted analogs tetraphenyloxalamidine (TPOA), 2,2'–bis–(4,5–dihydro–1,3–diazole) (OA5), 2,2'–bis–(3,4,5,6–tetrahydro–1,3–diazixine) (OA6) and 2,2'–bis–(4,5,6,7–tetrahydro–1,3–diazepine) (OA7) has been studied theoretically using the semiempirical PM3–MNDO method. According to a previous experimental study, this process consists of an intramolecular degenerate double proton transfer in weak intramolecular N–H···N hydrogen bonds, where the two protons are transferred stepwise involving a zwitterionic intermediate. In addition, evidence was obtained for a substantial heavy atom reorganisation which is strongly dependent on the chemical structure. In the present study, this interpretation is confirmed theoretically by calculation of the energies and geometries of the initial states, transition states and intermediate states of the tautomerism. For AO6 and AO7, *sin*- and *anti*-forms are obtained which differ in the confirmation of methylene bridges. The geometry of *anti*-OA7 agrees remarkably well with the crystal geometry of OA7. Therefore, although the calculated barrier heights of the tautomerism highly exceed the experimental values, the calculated molecular geometries seem to be reliable. Especially interesting is the nature of reorganisation of the molecular skeleton during proton transfer in various oxalamidines. This reorganisation mainly involves a decrease of the nitrogen-nitrogen distances of the hydrogen bond in which the proton transfer takes place, thus lowering the barrier for the tautomerism. The reorganisation energy strongly depends on the chemical structure. In the case of OA and TPOA, compression of the proton transferring hydrogen bond is possible without major changes in the geometry of the other hydrogen bond. By contrast in bicyclic oxalamidines, compression of one hydrogen bond involves elongation of the other bond or a ring deformation, requiring additional energy. Ring deformation requires less energy in OA7 as compared to OA5 and OA6, in accordance with experimental findings.

* Dedicated to the memory of Professor Tibor Škerlak

INTRODUCTION

The mechanisms of degenerate intra- and intermolecular double proton transfer reactions have been studied experimentally in the past mainly by dynamic liquid and solid state NMR techniques.[1–10] However, although it has not yet been possible to calculate reliable rate constants of these processes using *ab initio* methods combined with dynamic reaction theories, theoretical calculations have become a useful source of information concerning the reaction pathway.[11–16] Thus, it has been proposed that the two protons in porphyrins[11–14] and azophenine[15] are transferred stepwise involving a metastable intermediate. These results were confirmed experimentally only recently by analysis of the kinetic HH/HD/DD isotope effects[4–10] and in the case of oxalamidine (Figure 1) by observation of kinetic solvent effects. The latter are not in agreement with an unpolar transition state of a hypothetical concerted reaction pathway as shown in Figure 1 but support the formation of a zwitterionic intermediate during the stepwise reaction.[6,7] Actual experiments were performed on the bicyclic derivate OA7, and also on TPOA[5] and OA6[6,7] whose structure is shown in Figure 2. However, the following problems remained. The observed kinetic HH/HD/DD isotope effects on the OA7 tautomerism were found to be much smaller than in the porphyrin case[2] which was explained in terms of smaller tunneling contributions arising either from a higher energy of the intermediate or from a substantial heavy atom reorganisation during the transfer. It was assumed that this reorganization mainly consists of a compression of the proton transferring hydrogen bond. In addition, an extreme dependence of the barriers of the oxalamidine tautomerism on the chemical structure was observed.[7] *E.g.*, the tautomerism of TPOA is the fastest process observed in the oxalamidine series; in contrast, the tautomerism of OA6 is so slow that it can no longer be detected by NMR;[7] OA7 represents an intermediate case. The question arose whether this structural dependence is associated to the hydrogen bond compression during the reaction.

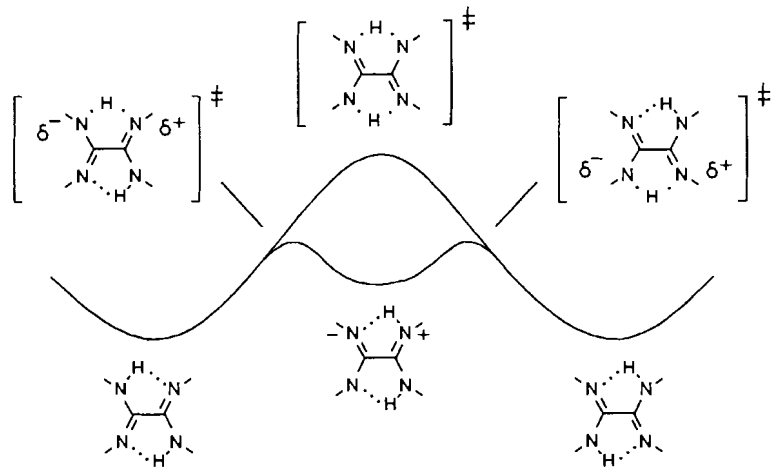

Figure 1. Reaction profiles for the stepwise and the concerted intramolecular tautomerism of bicyclic oxalamidines.

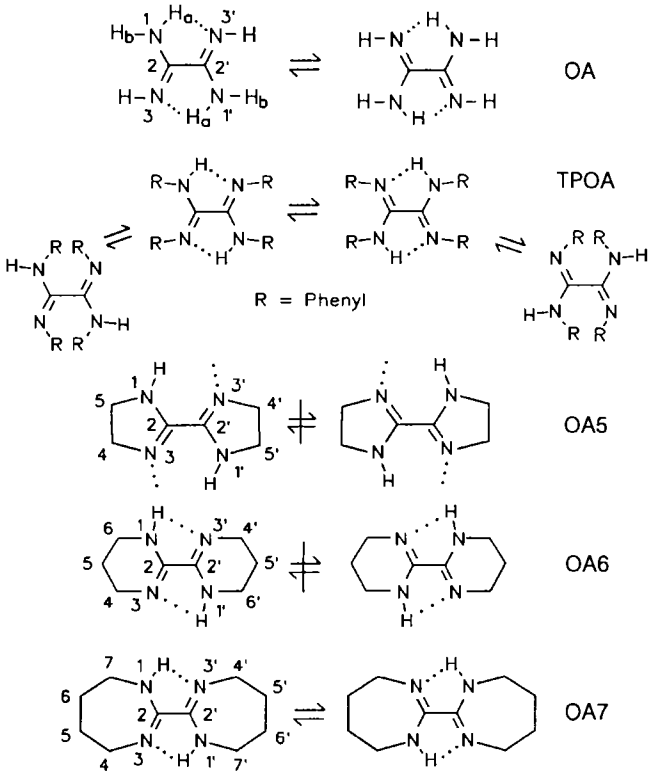

Figure 2. Structures of bicyclic oxalamidines calculated in this study using the semiempirical PM3–MNDO method, as implemented in MOPAC.[18] OA: parent compound; TPOA: tetraphenyloxalamidine[5]; OA5: 2,2'-bis-(4,5-dihydro-1,3-diazole);[7] OA6: 2,2'-bis-(3,4,5,6,-tetrahydro--1,3-diazixine);[7] OA7: 2,2'-bis-(4,5,6,7-tetrahydro-1,3-diazepine).[7]

In order to study these questions further, we have undertaken the present theoretical study of the tautomerism of oxalamidines. Up to date, no theoretical studies of this reaction have been reported. We would have liked to perform *ab initio* calculations for this purpose; however, in view of the decisive role of large substituents and the hugeness of this task, we confined ourselves to semiempirical calculations based on the MNDO method.[17,18] We are aware that only qualitative and quantitative comparisons with experimental data are possible in view of the many approximations made. In order to get a better feeling for the role of the substituents, we performed calculations not only on the analogs TPOA, OA6 and OA7, which were studied experimentally, but also on the parent compound OA and the five-membered bicyclic compound OA5 (Figure 2). In the following, the results are reported and discussed.

RESULTS

For the semiempirical calculations, we employed the PM3–MNDO method using the MOPAC package version 6.0.[18] In each proton transfer step the geometry of all other atoms was optimized. In all the cases studied, the reaction was found to be

stepwise, *i.e.* to involve a saddle point with only one proton in flight, and a metastable intermediate, in agreement with experimental findings.[6,7] The concerted pathways were, therefore, not studied in detail. The calculated energies of the ground state, transition state and the intermediate state are assembled in Table I together with calculated nitrogen-nitrogen distances. Surprisingly, the energy of the intermediate is almost independent of the molecular structure, *i.e.* always between 100 and 120 kJ mol^{-1} larger than the ground state. In contrast, the energies of the transition states vary strongly with the chemical structure. Geometries of the stationary states are visualized in Figures 3 to 7. To facilitate discussion, the various compounds are discussed separately in the following.

Parent Compound Oxalamidine (OA)

The parent compound OA comes out as essentially planar, as illustrated in Figure 3. Both hydrogen bonds are equivalent. The hydrogen bonded protons are located in the molecular plane; only the non-hydrogen bonded protons of the NH_2-groups are located outside the plane, allowing some pyramidalization at the neighboring nitrogen atom. In the transition state, the proton in flight is located approx. midway between the proton donating nitrogen atom 1N and the proton accepting nitrogen atom 3' N in comparison with the initial state, the distance between the latter is decreased from 2.8 Å to 2.4 Å. This decrease considerably reduces the barrier of proton transfer. On the other hand, there is only a slight increase of the distance between the other two nitrogen atoms, 3N and 1' N. Position of the other atoms of the skeleton do not change substantially. The intermediate state is remarkably lower in energy than the transition state and it has essentially the same geometry as the initial state, with the exception of the transferred proton.

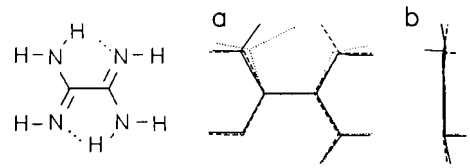

Figure 3. Calculated geometries of the ground state (solid line), transition state (broken lines) and the intermediate state (dashed line) of the tautomerism of the parent compound oxalamidine (OA).

Tetraphenyloxalamidine (TPOA)

A very similar result is obtained for TPOA (Figure 4) where motion of the phenyl groups is associated with the motion of the nitrogen atoms. In the transition state, the displacement of the proton donating nitrogen atom is more pronounced relative to the other nitrogen atoms. The energies of both the transition state and the intermediate state are decreased as compared to OA, an effect that can be interpreted in terms of energy gain by delocalization of the charges created. In the intermediate state, the nitrogen distances within the two proton transfer units are remarkably different, *i.e.* there seems to be energy gain if one hydrogen bond is stronger than the other.

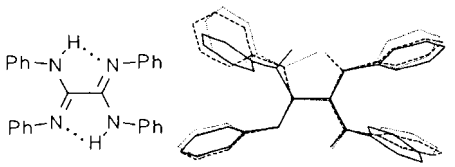

Figure 4. Calculated geometries of the ground state (solid line), transition state (broken lines) and the intermediate state (dashed line) of the tautomerism of the tetraphenyloxalamidine TPOA.

2,2'-Bis-(4,5-dihydro-1,3-diazole) (OA5)

According to Figure 5, OA5 is essentially planar, with the exeption of the mobile protons which are now located outside the molecular plane so as to allow for a certain degree of pyramidalization at the attached nitrogen atoms. We note a large increase of nitrogen distances in the proton transfer units as a result of the reduced 1N–2C–3N angles. Thus, there is almost no intramolecular hydrogen bond formation, and intermolecular hydrogen bond formation will be facilitated, which could explain why OA5 is not soluble in organic solvents. As compared to OA, we note a large increase of the transition state energy, although the energy of the intermediate state is comparable. This increase arises essentially from the following circumstance. The topologies of the five-membered rings remain remarkably constant during the reaction because the ring deformation energy is very large. Therefore, the 1N–3'N distance reduction from 3.0 Å to 2.6 Å, necessary for proton transfer, is only possible by in-plane bending of the two rings. This process is associated with a considerable increase in the nitrogen distances of the non-proton transferring unit 3.0 Å to 2.6 Å, as illustrated in Figure 5. It is clear that these processes require much more energy as compared to OA and TPOA, where the motion of the two nitrogen atoms involved in the transfer is essentially decoupled from the motion of the other atoms. In the intermediate state of OA5, the transition state strain is released, resulting in an energy comparable with those of OA and TPOA.

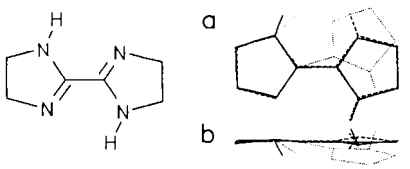

Figure 5. Calculated geometries of the ground state (solid line), transition state (broken lines) and the intermediate state (dashed line) of the tautomerism of OA5.

2,2'-Bis-(3,4,5,6-tetrahydro-1,3-diazixine) (OA6)

The case of OA6 is similar, but a complication arises because the methylene bridges are no more planar. This leads to the formation of a *syn*- and an *anti*-conformer of OA6, as illustrated in Figure 6. Each conformer forms two interconverting degenerate *syn*- and *anti*-conformers. In the more stable *syn*-conformer, the two rings

are not in the same plane, the torsion angle φ around the central bond being 56°. The energy gain associated with this torsion is only 8 kJ mol^{-1} and corresponds almost entirely to energy difference between the two conformers. The potential wells of the two conformers seem to be very shallow, implying a small barrier of interconversion. The NMR experiments performed show an equivalence of the protons within each CH_2-group, which either implies a fast interconversion between different conformers or the existence of a single symmetric conformer. In view of the lack of experimental data, the pathways of interconversion between the different conformers were not further studied in detail.

The proton transfer pathway in the *anti*-conformer of OA6 resembles the pathway of OA5, although the energy necessary to reach the transition state has decreased. But, still a substantial inplane bending of the two rings with respect to each other is needed in order to reduce the nitrogen distance in the proton transferring unit. The corresponding increase in the nitrogen distance of the non-proton transferring unit is less pronounced. Proton transfer starting from the more stable *syn*-conformer requires first a reduction of the torsional angle around the central bond, *i.e.* planarization of the oxalamidine unit. Thus, the differences between the *syn*- and *anti*-conformers have disappeared in the transition and the intermediate states, as illustrated in Figure 6.

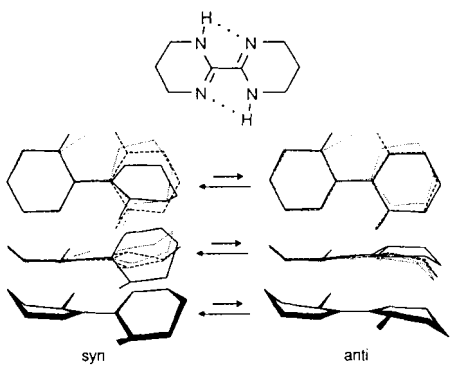

Figure 6. Calculated geometries of the ground state (solid line), transition state (broken lines) and the intermediate state (dashed line) of the tautomerism of OA6.

2,2'-Bis-(4,5,6,7-tetrahydro-1,3-diazepine) (OA7)

In the case of OA7, depicted in Figure 7, the seven-membered rings have a large influence on the molecular structure and dynamics. Firstly, we also find *syn*- and *anti*-conformers, where the former are slightly more stable than the latter, like in the case of OA6. Again, the potential wells are shallow and the interconversion was not studied in detail. In the more stable *syn*-conformer, the four nitrogen atoms are again no more located in the same plane because of a torsion between the two seven-membered rings. The torsion angle φ between the two rings is 53°. In the *anti*-conformer φ is close to zero; the geometry of the rings in all conformers is very similar.

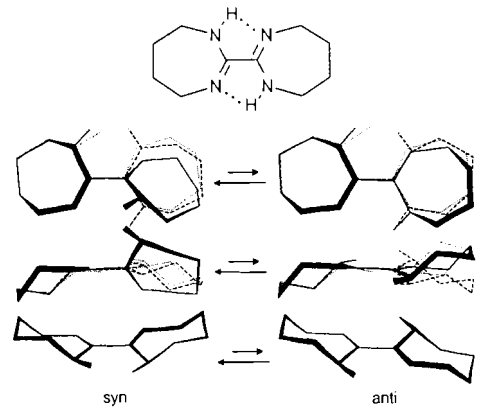

Figure 7. Calculated geometries of the ground state (solid line), transition state (broken lines) and the intermediate state (dashed line) of the tautomerism of OA7.

We note that the geometry of the *syn*-conformer resembles closely the geometry of OA7 in the crystal,[7,19] besides the φ-value which is close to zero in the crystal. Favoring of an angle $\varphi = 0$ in the crystal could be intrinsic or arise from intermolecular interactions. In this context, it is interesting to note that also biphenyl seems to be more or less planar in the solid state,[20] whereas in the gas phase there is an angle of 42° between the phenyl groups,[21] a result which has been well reproduced by the AM1 method.[22] Therefore, we are convinced that the occurrence of the two conformers of OA7 (and of OA6) might be real, although difficult to verify by NMR because of the fast ring dynamics. In the anti-conformer, the nitrogen distances within the proton transfer units are similar to those calculated for the parent compound OA and for TPOA; in the *syn*-conformer, these distances are slightly increased because of the ring torsion. As compared to OA6, the rings are much more flexible, reducing the strain on the oxalamidine unit. Thus, hydrogen bonding and at the same time pyramidalization at the protonated nitrogen atoms is more pronounced in OA7, which well reproduces the trend observed by NMR, as disscussed in the proceeding section. Ring flexibility also allows for a decrease of the nitrogen distances within the proton transferring unit in the transition state without any increase of the distance in the other unit. The calculated energy necessary to reach the transition states is, therefore, substantially reduced as compared to OA6, in agreement with the experiment. The mechanism of proton transfer in the two conformers of OA7 is not very different; in both molecules there are ring conformational changes related to the proton transfer. In the *anti*-conformer, the torsional angle is essentially reduced both in the transition and intermediate states, like in the case of OA6. Besides the solvent motion, the ring motion could be responsible for the quite small kinetic HH/HD/DD isotope effects of tautomerism.

DISCUSSION AND CONCLUSIONS

We have explored the tautomerism of various oxalamidines using semiempirical MNDO calculations. We are aware that the calculated barrier energies are much larger than the experimental ones because of the known inherent approximations

of the method used. Nevertheless, it is interesting to discuss the processes studied in the light of this method.

First of all, the method reproduces well the experimental geometry of OA7, for which a crystal structure is available. In addition, the calculated nitrogen-nitrogen distances of 3.0/2.8 Å for OA6 and OA7 and 2.8 for TPOA correlate well with the increasing strength of the intramolecular hydrogen bond found experimentally[7] in the series OA6, OA7, TPOA. As far as the mechanism of the proton transfer is concerned, a stepwise proton transfer involving a zwitterionic intermediate is predicted, like previously for porphyrins[11–14] and for azophenine,[15] in agreement with experimental findings.[6,7] Furthermore, we find here a substantial decrease of the nitrogen-nitrogen distances of the proton transferring hydrogen bond in the transition state.

Whereas energy differences between the intermediate and initial state are relatively insensitive to the chemical structure (see Table I), large substituent effects on the barriers of tautomerism are observed, which correlate well with the experimental trend, although the absolute barrier energies are much too large due to the known limitations of the method. We note that the introduction of flexible phenyl or methylene groups into OA reduces the barrier energy substantially, though the transition state geometry of the molecular skeleton is very much the same. We relate this effect to a stabilization of the charges created by the polarizable phenyl or methylene groups. Very interesting is the influence of bicyclic methylene bridges. The hydrogen bonds in OA5 and OA6 are much weaker than in OA7 and TPOA; consequently, much more energy is necessary for hydrogen bond compression during the proton transfer. Moreover, whereas hydrogen compression in OA and TPOA takes place without any major distortion of the other parts of the molecule, it involves, especially in the bicyclic compounds OA5 and OA6, a major elongation of the other hydrogen bond containing the bound mobile proton (Figure 5) requiring additional energy. The alternative, the distorsion of the methylene rings, would require even

TABLE I

Experimental and calculated parameters of hydrogen bonding and intramolecular double proton transfer in oxalamidines

	E_a^{HH}	E_0	$E^{+}-E_0$	E_i-E_0	$r^{o}_{1N3'N}$	$r^{o}_{3N1'N}$	$r^{+}_{1N3'N}$	$r^{+}_{3N1'N}$	$r^{i}_{1N3'N}$	$r^{i}_{3N1'N}$
OA	–	0	174	120	2.8	2.8	2.4	2.9	2.75	2.75
TPOA	43.0[b]	0	143	114	2.8	2.8	2.4	2.8	2.5	2.7
OA5	–	0	220	102	3.0	3.0	2.6	3.3	3.0	3.0
$OA6_{syn}$	>90.0	0	172	112	3.0	3.0	2.4	3.0	2.8	2.8
$OA6_{anti}$		8	164	105	2.8	2.8	2.5	2.9	2.8	2.8
$OA7_{syn}$	56.2[a]	0	123	118	3.0	3.0	2.5	2.9	2.8	2.8
$OA7_{anti}$	57.6[b]	6	142c	115	2.8	2.8	2.6[c]	2.9[c]	2.8	2.9

E_a^{HH}:experimental energies of activation of double proton transfer in kJ mol^{-1}; E_0, E°, E_i/kJ mol^{-1}: E_0, E^{+}, E_i/kJ mol^{-1} energies of the initial, transition and intermediate states of the stepwise oxalamidine tautomerism, calculated using the semiempirical PM3–MNDO method implemented in the MOPAC calculation package;[18] r^{o}_{nm}, r^{+}_{nm}, r^{i}_{nm} calculated distances between nitrogen atoms n,m = 1N, 3' N of the proton transferring unit and 3N,1'N of the unit containing the bound mobile proton (for atom numbering see Figure 2) in the ground state (0), transition state ($^{+}$) and the intermediate state (i). a: solvent acetonitrile, b: solvent methylcyclohexane, both values are averages for *syn*- and *anti*-conformer, see Ref. 7. c: not fully optimized transition state.

more energy. OA7 represents an intermediate case. Here compression of proton transfering hydrogen bond is only associated with a very slight elongation of the other bond since the seven-membered rings are so flexible that the energy required for their distortion is relatively small, as compared to the five- and six-membered rings.

In conclusion, the concept of a substantial compression of proton transferring unit, coupled in the five- and six-membered cyclic oxalamidines to an elogation of the other hydrogen bond can explain why the proton tautomerism of OA6 is experimentally not observable, in contrast to OA7 and TPOA. The circumstance that the main part of the barrier energy refers to a heavy atom reorganization and not to proton transfer – in contrast to the case of porphyrin tautomerism – enables proton tunneling only at high energies, slightly below the top of the barrier, which is related to the substantially smaller kinetic hydrogen/deuterium isotope effects, as it has been observed experimentally.[6,7] Thus, the oxalamidine tautomerism is a good model system for the study of heavy atom motions during an intramolecular proton process.

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SAŽETAK

Micanje protona i teških atoma za vrijeme protonske tautomerije korak po korak kod različitih oksalamidina. Semiempirijsko proučavanje metodom PM3–MNDO

Gerd Scherer and Hans-Heinrich Limbach

Tautomerija oxalamidina i substituiranih analoga tetrafeniloksalamidina studirana je s pomoću semiempirijske metode PM3–MNDO. Prema prethodnoj eksperimantalnoj studiji tautomerija oksalamidina se sastoji od intramolekulskoga degeneriranog dvostrukog protonskog prijenosa u slabe intramolekulske vodikove veze N–H···N, kod kojih se dva protona prenose korak po korak, a taj prijenos uključuje zwitterionski međuprodukt. Također je utvrđeno da u tom procesu dolazi do znatne reorganizacije teških atoma. Ta reorganizacija jako ovisi o strukturi molekulskog sustava. U ovom radu ta su eksperimentalna opažanja poduprli teorijski računi, kojima su dobivene vrijednosti za energije i geometrije početnih stanja, prijelaznih stanja i međuprodukata tautomerije.