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Quantum Chemical Studies on the Double Proton Transfer in Benzoic and o-Chlorobenzoic Acid Dimers*

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The double proton transfer process has been studied for the benzoic (BAC) and o-chlorobenzoic acid (o-Cl-BAC) dimers in the gaseous state and for crystalline form at the non-empirical level. The correlation energy corrections have been taken into account at the MP2 level and zero-point energy as well as crystal field effects were considered. The results of calculations enable a reasonable interpretation of low potential barriers observed by NMR for some molecular crystals involving carboxylic dimers. The role of substituents and a possible mechanism of the double proton transfer are considered.

Key words: double proton transfer, benzoic acid, o-chlorobenzoic acid

Proton transfer reactions are the simplest and important in many chemical problems as well as in some biological processes. It appears that the low-barrier hydrogen bond (LBHB) may play a fundamental role in stabilizing intermediates in enzymatic reactions and in energy lowering of transition states [1]. On the other hand, the multiple proton transfer seems to play an important role in quantum chemical interpretation at molecular level of some biological processes like mutations, aging and cancerogenic action [2].

The possible role of hydrogen bonding and the proton transfer processes were also considered in relation to the electrical conductivity and its anisotropy [3–5]. As an alternative mechanism for the proton transport, the soliton-like cooperative excitation of proton within the chain of the hydrogen bonds was considered as well [6].

As the evaluation of the potential energy surface with a good accuracy is of great importance for the dynamics and the interpretation of the proton transfer mechanism, the proton transfer in hydrogen bonded systems has been studied in many groups by both semiempirical and non-empirical quantum chemical methods [7–13], including density functional theory (DFT) with different functionals [14,15].

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*Dedicated to the memory of Professor Krzysztof Pigoń.

Dimers of benzoic and o-chlorobenzoic acid

In some crystalline dicarboxylic acids the NMR measurements demonstrated the coexistence of two interconverting molecular conformations due to the double proton transfer process. Solid state NMR investigations showed that the activation energies of this reactions for some crystalline carboxylic acids are of the order of 1.2 kcal/mole [16–19]. Thus, the experimental barrier heights for carboxylic acids are much lower than those evaluated even by sophisticated quantum chemical calculations. It is assumed that in the gaseous state the hydrogen bond protons displace between the two symmetrical potential minima of equivalent tautomers (Fig. 1). In condensed phases, however, because of interactions with environment, the initial and final states may be trapped in some configurations [20]. Thus, the role of the crystal field in the proton transfer reactions may be important, but still not clearly understood. In this situation a comparison of the potential energy hypersurfaces for isolated gaseous dimers and those for the crystal lattice enables a deeper understanding of the proton transfer mechanism.

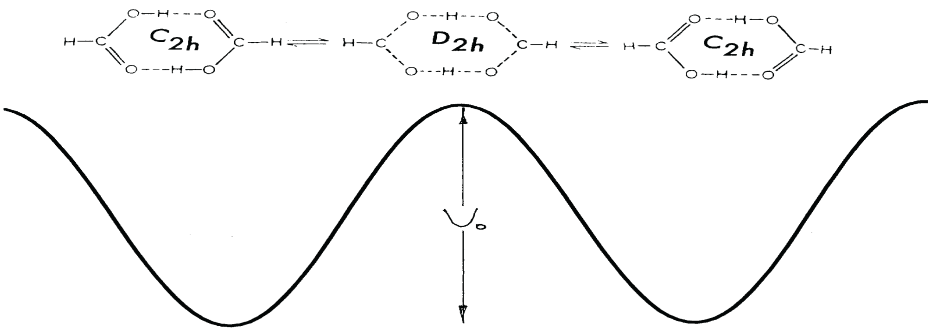

Figure 1. Stationary points: C_{2V} (equilibrium geometry), and D_{2h} (transition state) on the potential energy hypersurface for synchronous double proton transfer in the formic acid dimer. The potential barrier height is denoted by V_o.

The crystal structures of benzoic and o-chlorobenzoic dimers (Fig. 2) are similar. Benzoic acid (BAC) crystallizes in monoclinic system of the $P2_1/c$ space group with dimensions $a = 5.52$, $b = 5.14$, $c = 21.90$ Å and $\beta = 97°$ [21]. The closest approach distance occurs between the oxygen atoms of the carboxyl groups, which are related by a centre of symmetry. The O–H···O distance is 2.64 Å and all other intermolecular approach distances are over 3 Å (Fig. 3). On the other hand, o-chlorobenzoic acid (o-Cl-BAC) crystallizes in the monoclinic system of the $C2/c$ space group in a unit cell of dimensions $a = 14.73$, $b = 3.90$, $c = 25.50$ Å and $\beta = 112° 40'$ [22]. Similarly to the benzoic acid, the closest approach distance occurs between the oxygen atoms of the carboxyl groups, which are related by a centre of symmetry. The O–H···O distance is 2.63 Å and all other intermolecular approach distances are over 3 Å, and correspond to normal van der Waals interactions.

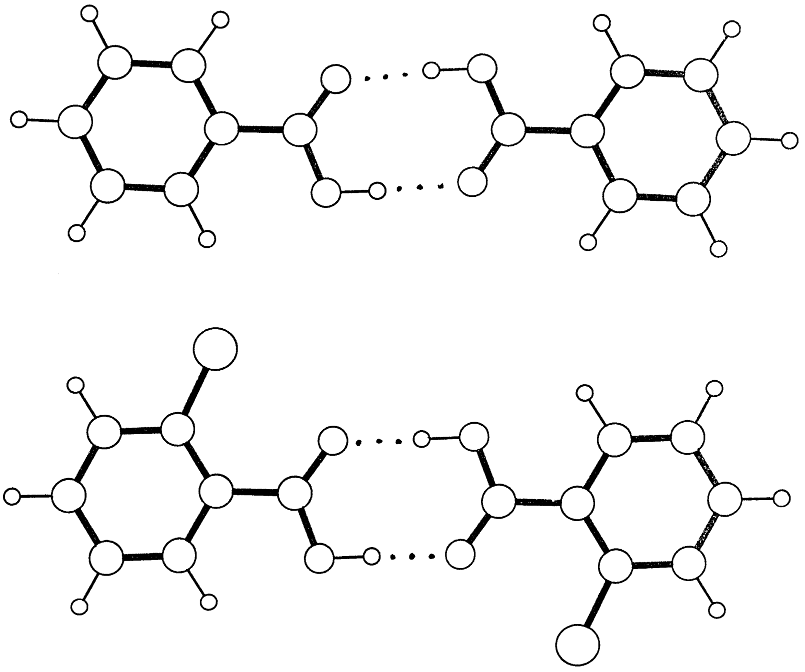

Figure 2. Molecular structures of the benzoic acid (at the top) and o-chlorobenzoic acid (at down) dimers. The dotted lines denote the respective hydrogen bonds between the dimers.

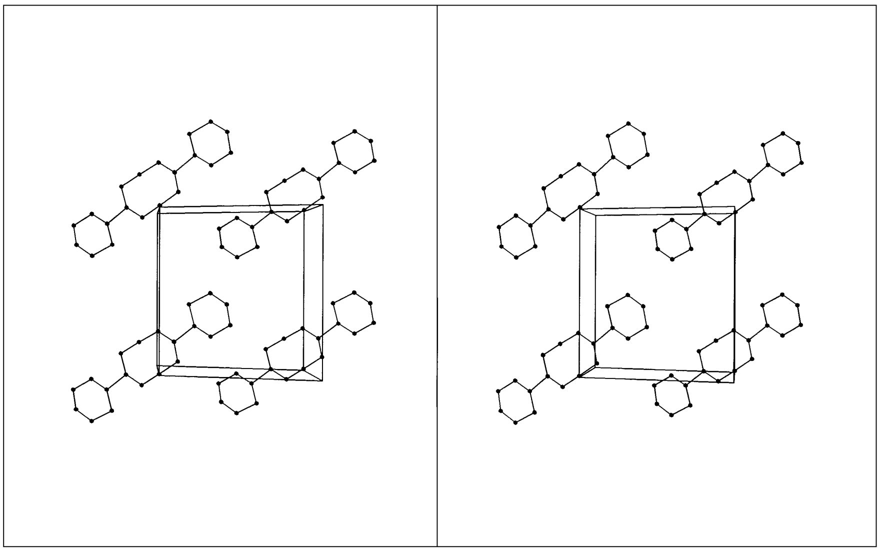

Figure 3. The unit cell of the benzoic acid crystal: left – standard proton position; right – proton located in the middle of the hydrogen O–H···O bonds [21].

The results of high-resolution solid state ^{13}C NMR and the proton spin-lattice relaxation time T_1 measurements, as well as shift tensors of the carboxyl carbon, confirmed the existence of an energy difference between the two configurations [17]. On this basis the rate and the activation energy for the proton transfer have been estimated, basing on the proton T_1 results. Meier, Graf and Ernst reported related studies on the proton transfer in p-toluic acid (p-CH_3-BAC) [16] leading to similar conclusions. It was found that in the low temperature region the plot $\ln T_1$ *vs* 1/T markedly deviates from what the relaxation theory for classical jumps predicts [23]. This deviation has been ascribed to arise from the quantum mechanical tunneling effect. On the other hand, for the proton transfer in the crystalline forms of BAC [16,17] as well as in p-CH_3-BAC [16] these deviations were found to be much lower than those resulting from microvawe [24] and IR [25] studies, as well as from quantum chemical calculations for the carboxylic acid dimers [7–14]. It seems, therefore, desirable to examine whether or not such low activation energies may be generally found in the systems considered. It is also worthwhile to recognize the role of substituents [25].

RESULTS AND DISCUSSION

The lowering of the barrier is dependent on the interelectron correlation taken into account [26] and some limiting value is reached when more than 60% of the correction energy is taken into account. On the other hand, we have found that experimental geometry of the formic acid dimer and a number of other carboxylic acids dimers may be well reproduced within the 6-31G** basis and the second order Møller-Plesset perturbation (Table 1), whereas the results δ tresemble those of the complete basis set of Petersson *et al*. [27]. Therefore, we decided to study the proton transfer for the benzoic and o-chlorobenzoic acid dimers within the 6-31G** basis set at the correlation MP2 level. The full geometry optimization, which essentially influences the final results, has been carried out for the equilibrium and transition states.

Table 1. O···O hydrogen bond lengths [Å] and potential barriers [kcal/mole] for the double proton transfer in carboxylic acid dimers evaluated within the 6-31G** basis set without (V_o) and with (V_o-ZPE) zero-point energy corrections with full geometry optimization at the MP2 level.

Dimer	O···O HB length	V_o	V_o-ZPE
Formic acid	2.704	8.08	4.62
Acetic acid	2.694	9.43	2.76
Oxalic acid	2.674	8.98	2.51
Malonic acid	2.700	9.85	1.41
Benzoic acid	2.675	7.07	1.10
o-Cl-Benzoic acid	2.682	14.98	8.56

The hydrogen bond length for BAC was found to be 2.675 Å and for o-Cl-BAC dimer 2.682 Å in a good agreement with experimental data (Table 1). For simultaneous double proton transfer (Fig. 3), the potential energy barrier for the gaseous dimeric system of the BAC, calculated within the 6-31G** basis set at the MP2 correlation level, equals 14.98 kcal/mole. The difference of zero-point energies calculated is 5.97 kcal/mole, lowering the potential barriers. With this correction the potential barrier for the synchronous double proton transfer in the oxalic acid crystal was found to be 1.10 kcal/mole. For the isolated o-Cl-BAC dimer the relevant values are 14.98, 6.42 and 8.56 kcal/mole. Thus, it seems, that there is a reasonable agreement of the quantum chemical calculations with the experimental results (Table 1).

The possible role of the basis set superposition error (BSSE) in the proton displacement potential has been studied [28]. It was concluded that the BSSE is comparable for the endpoint and midpoint of the proton positions and, therefore, has a negligible effect on the barrier proton movement. It has been pointed out that the lowering of the barrier for the proton transfer seems to be roughly proportional to the correlation energy [26]. Our calculations indicate that, at least for some density functionals, the correlation energy might be slightly overestimated [11]. Thus, the DFT results seem to underestimate the potential barrier height for such processes.

The role of electrostatic crystal lattice effects in molecular lattices, in our case for the surrounding simulation, have been taken into account for three-dimensional crystal lattices by using the monopole atomic charges from *ab initio* calculations. It should be noted that the estimated field effect on the potential barrier, in the case of the simultaneous double proton transfer, is negligible for the benzoic acid dimer, being about 2.66 kcal/mole (enhancing the barrier). Therefore, taking into account the accuracy of our calculations, it seems that in both cases the barrier height is quite close to the experimental value 1.17±0.02 for benzoic acid and 14±2 kcal/mole for o-chlorobenzoic acid dimers [17]. Our results are comparable with Grabowski and Krygowski [29] atom-atom potential calculations for benzoic and α-methyl-*trans*-cinnamic acid, being aware of approximations used. The role of higher multipoles has been shown to be not very important or at least unclear [30], however, the crystal field influence seems to be obvious when comparing the results for benzoic and o-chlorobenzoic acids (Table 1). This means, that the substituents and heavy atoms in particular, essentially modify the hypersurface of the proton transfer processes.

We assume that in the case of moderate potential barrier height for the proton displacement, both classical and quantum mechanical processes are important [31,32]. This assumption may allow, at least for a qualitative interpretation of the experimental NMR results, pointing out that in the crystal the tunneling effect plays an important role in the proton transfer mechanism, especially at low temperatures [17].

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