

Proton transfer in some periodic molecular systems

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Abstract The electronic structure of representative hydrogen bonded systems: hydrogen cyanide, imidazole and malonic acid have been studied at the non-empirical level. The role of the dimensionality on the potential barrier for the proton transfer has been examined. It was shown that it depends on the crystal structure and only in some cases like hydrogen cyanide or imidazole the relevant crystals may be considered as one-dimensional. However, for more complicated crystallographic structures, e.g. malonic acid, the evaluated barrier is strongly dependent on the dimensionality taken into account in our calculations.

Keywords Density of states · Hydrogen bonding · Periodic systems · Proton transfer

Introduction

The proton transfer reactions are the simplest but very important in many chemical problems as well as in some biological processes. It appears that the low-barrier hydrogen bond (LBHB) for this displacement may play a fundamental role in stabilizing intermediates in enzymatic reactions and in energy lowering of transition states [1]. There is considerable evidence that a LBHB may be important in the reaction catalyzed by Δ^5 -3-ketosteroid isomerase [2]. Recent computational and gas phase experimental studies [3] have also shown that LBHB can exist in the gas phase systems. 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 [4].

The possible role of hydrogen bonding and the proton transfer processes were also considered in relation to the electrical conductivity and its anisotropy [5–7]. 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 [8].

It is preferably assumed that in the gaseous state the hydrogen bond protons displace between the two symmetrical potential minima of equivalent tautomers. In a condensed phases, however, because of interactions with environment, the initial and final states may be trapped in some configurations [9]. 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 deeper understanding of the proton transfer mechanism.

Model systems

As a model one-dimensional (1D) hydrogen bonded systems tetragonal hydrogen cyanide (space group C_{4v}^9 , two molecules in the unit cell and strictly linear chains) and imidazole have been chosen. Imidazole crystal belongs to the monoclinic system (space group $P2_1/c$, with four molecules per cell and chains extending along crystallographic *c* axis) [11] (Fig. 1). Furthermore, triclinic malonic acid (*Pi* space group with two molecules in the unit cell) [12] have been chosen (Fig. 2) which represents three-dimensional hydrogen bonded structures. Because of highly anisotropic structures in these first two systems, the relevant properties may be discussed

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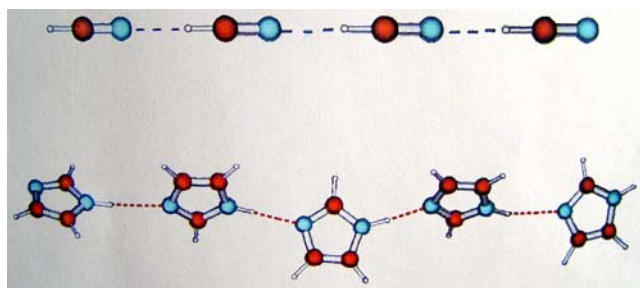


Fig. 1 Hydrogen cyanide [10] (upper) and imidazole [11] (lower) chains in their crystalline phases

assuming their structures as the one-dimensional chains. In the case of the triclinic form of the malonic acid at room temperature the centro-symmetric dimers are staggered along the crystal *c* axis and bound to each other by hydrogen bonds formed by the carboxylic groups [12]. On the other hand, the malonic acid is the simplest dimeric system for which the experimental barrier for the double proton transfer has been determined by the NMR spin-lattice relaxation time T_1 method [13].

Computational

Calculations of electronic structures have been performed at the non-empirical *ab initio* model taking into account the interelectronic correlation. In the case of periodic systems three different bases have been used, i.e. Huzinaga including polarization functions [14], 4-31G* [15] and correlation consistent cc-pVTZ [16]. In the computation with B3LYP density functional the GAUSSIAN-03 [17] computer program was used.

Results and discussion

Recently, growing interest in experimental and theoretical, mainly quantum chemical studies on the proton transfer in crystal systems may be observed [18]. The density functional theory has also been applied for investigations of structure and stability of ionic liquid of hydrogen fluoride and imidazole chains [19]. The cooperative hydrogen bonding and the proton transfer effects have been adapted for interpretation of the water structure [20] or mutations processes [21].

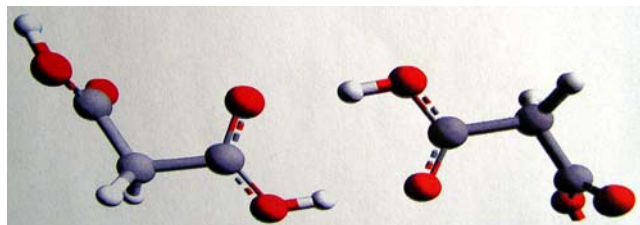


Fig. 2 Malonic acid dimers aligned along the *c* axis in the crystal [12]

Table 1 Potential barriers [kcal mol⁻¹] for the proton transfer in hydrogen cyanide and imidazole hydrogen bonds calculated at DFT level within the cc-pVTZ basis set (two or four protons within the unit cell)

SYSTEM	2-PROTONS	4-PROTONS
HCN		
ISOLATED UNIT CELL	73.96	77.67
1D	65.74	66.29
2D	66.19	68.05
3D	66.23	68.08
IMIDAZOLE		
ISOLATED UNIT CELL	51.60	137.82
1D	33.33	56.82
2D	34.31	57.25
3D ^a	31.77	51.96

^a Results for cc-pVDZ basis set

Our results for the potential barrier height [kcal mol⁻¹] for hydrogen cyanide and imidazole are listed in Table 1, whereas those for malonic acid are given in Table 2. The relevant values were evaluated for one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) crystals, respectively. Both in the case of hydrogen cyanide and imidazole the influence of dimensionality on the barrier height seems to be rather small. This is true for the considered two protons and four protons of the hydrogen bonds in the unit cell transferring within these chains. However, for malonic acid the above-mentioned role of dimensionality seems to be very important. This effect may be ascribed to different crystal structure which cannot be approximated by the one-dimensional chain.

It was found that the lowering of the barrier is dependent on the interelectron correlation taken into account in the calculation [22] and its some limiting value is reached when more than 60% of the correction energy is taken into account. It has been pointed out that the lowering of the barrier for the proton transfer seems to be roughly proportional to the correlation energy taken into account in the calculation [23]. Our calculations indicate that, at least for some density functionals, the correlation energy might be slightly overestimated [24]. Thus, the DFT results seem to underestimate the potential barrier height for this kind of process.

Table 2 Potential barriers [kcal mol⁻¹] for the protons transfer in malonic acid hydrogen bonds calculated at DFT level within the 6-31G** basis set (four protons within the unit cell)

System	Protons
SINGLE UNIT CELL	147.98
1D	93.06
2D	92.16
3D	29.41

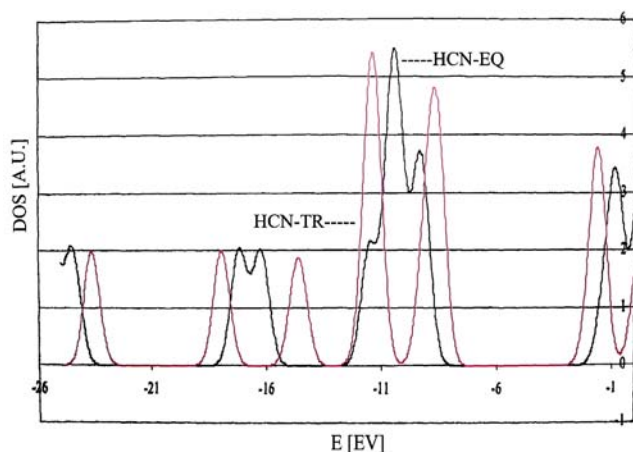


Fig. 3 Density of states for the hydrogen cyanide dimer: HCN-EQ- standard proton position, HCN-TR- proton position in the middle of the hydrogen bond

The possible role of the basis set superposition error (BSSE) in the proton displacement potential has been studied by Latajka, Scheiner and Chałasiński [25]. It was concluded that the BSSE is comparable for the endpoint and midpoint of the proton position and therefore has only a negligible effect upon the barrier to proton movement.

In some crystalline dicarboxylic acids the NMR measurements demonstrated the coexistence of two interconverting molecular conformations taking place by the double proton transfer process. The solid state NMR investigations showed that the activation energies of this reactions for some crystalline carboxylic acids are of the order of $1.2 \text{ kcal mol}^{-1}$ [26–28]. The results demonstrate that experimental barrier heights for carboxylic acids are much lower than those evaluated even by sophisticated quantum chemical calculations.

The role of electrostatic crystal field effects up to now is difficult to understand clearly in the case of molecular crystals. In our case they have been taken into account by using the

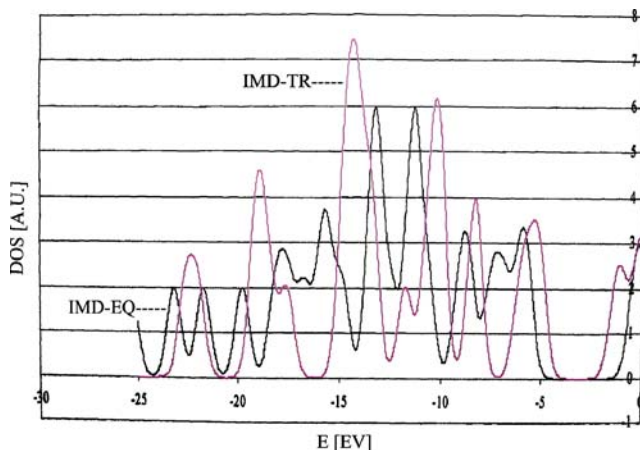


Fig. 4 Density of states for the imidazole dimer: IMD-EQ- standard proton position, IMD-TR- proton position in the middle of the hydrogen bond

monopole charges evaluated within the *ab initio* calculations. The influence of higher multipoles was shown to be not very important or at least unclear, however the crystal field role seems to be obvious [29]. It should be noted that the estimated field effect for crystalline malonic acid is of the order of 0.80 kcal/mole , enhancing the barrier. Thus, the final barrier is $1.49 \text{ kcal mol}^{-1}$. Therefore, taking into account the accuracy of quantum chemical calculations, it seems that the barrier height of malonic acid is quite close to the respective experimental result of $1.33 \text{ kcal mol}^{-1}$ [13].

The difference in the density of states can be seen for the standard proton position and the transition one (Figs. 3 and 4). It is the largest for the highest molecular orbitals and points out on the dependence of the occupation numbers on the proton position within the respective hydrogen bonds.

We assume that in the case of moderate potential barrier height for the proton displacement, both classical and quantum mechanical processes are important [22, 30]. 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, mainly at low temperatures [30].

The results of this calculations may be important for molecular dynamic simulations. In the case of the benzoic acid dimers some discrepancies between theoretical results and the relevant experimental studies [31] were explained by excitation of normal modes coupled to the reaction path [32]. On the other hand, it was pointed out that the dynamical potential barrier seemed to play an important role in the dynamic processes like proton transfer [33].

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