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# First-Principles Molecular Dynamics Study of a Photochromic Molecular Crystal

**Irmgard Frank,* Dominik Marx, and Michele Parrinello**

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany*

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We present first-principles calculations for the thermal reaction in the photochromic molecular crystals of 2-(2′,4′-dinitrobenzyl)-pyridine (DNBP). Under irradiation this dye molecule undergoes a characteristic change of color as a result of an intramolecular proton-transfer reaction. By simulating the thermal reaction with first-principles molecular dynamics, we show that during the thermal proton transfer a hydrogen bond from the *o*-nitro group to the migrating proton is formed intermediately, which serves as a "bridge" between the educt and product forms. Furthermore, we present the experimentally not accessible structures of the crystalline photoisomers. On the basis of our results we conclude that photoisomerization is possible in the crystalline phase. This property is of elementary interest for technical applications of this system.

## Introduction

When irradiated with ultraviolet light, the crystals of 2-(2′,4′-dinitrobenzyl)-pyridine (DNBP) undergo a characteristic change of color from pale yellow to blue−violet. This change is due to a photoinduced proton-transfer reaction that was first described as early as 1925.[1] It has attracted renewed attention in recent years in the context of the development of optical switches and has been investigated thoroughly in the framework of the EU Esprit project PROTIOS.[2−5]

Optical switches are of great interest for optical data processing and optical data storage.[6−10] In order to form the basis for the preparation of optical switches, a system should exhibit bistability, i.e., it should exist in two thermally sufficiently stable states that can be selectively and reversibly converted into each other by irradiation. In the case of DNBP the thermal back reaction occurs within 5 days, which is too fast for most applications. But, by modification of the pyridine ring, it has been possible to obtain derivatives with lifetimes several orders of magnitude longer.[2] Thus, DNBP is a promising system for this kind of application and it is of great interest to understand the interconversion of different isomers in more detail.

It is known from experiment[1,11−18] that the photoreaction of DNBP consists of an intramolecular proton transfer of one of the hydrogen atoms of the methylene group bridging the dinitrobenzene ring and the pyridine ring. Three isomers are involved (Figure 1): first, the stable pale yellow form with both hydrogen atoms located at the methylene group; this form is usually called the "$CH_2$ form". Second, there is the metastable form that is responsible for the blue color of the photoproduct; in this form one of the methylene hydrogen atoms is transferred to the nitrogen atom of the pyridine ring ("NH form"). Third, there exists a short-lived so-called "OH form" in which the hydrogen atom is bound to the *o*-nitro group, forming an NOOH group. The crystal structure of the $CH_2$ form has been determined experimentally by X-ray diffraction,[19] while both the NH and OH forms are too short-lived for a determination of their structures. The possible interconversions between the isomers as postulated by Sixl and Warta[18] are depicted in Figure 1. The mechanisms of the photoreactions and the thermal back reactions are not known in detail. It is found that the presence of the *o*-nitro group is essential for the photoreaction $CH_2 \rightarrow NH$, since only compounds with an *o*-nitro group show such a photoreaction.[14,20]

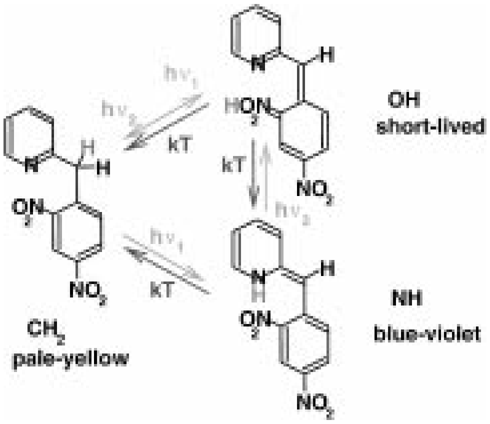

**Figure 1.** Figure 1. Schematic diagram showing the three isomers of DNBP (i.e., the $CH_2$, OH, and NH forms) and their possible interconversions,[18] where $kT$ marks thermal reactions and $h\nu_i$ denotes photoinduced reactions with different excitation energies.

From experiment it could not be decided if the photoreaction was possible in the perfect crystal or only at surfaces and dislocations. Since the reaction $CH_2 \rightarrow NH$ involves a change of hybridization at the methylene bridge, one might doubt that this rearrangement is possible in a rigid crystalline environment. Yet the high conversion rates ($>$ 16%) found for crystalline DNBP layers[4] can hardly be explained without assuming a reaction within the bulk.

In this situation, there is hope that theory can complement experiment and thus help us to understand this process in greater depth. This was our motivation for investigating various isomers of DNBP both in the gas phase and in the crystalline phase. To this end we employ Hohenberg−Kohn−Sham density functional theory[21,22] and Car−Parrinello molecular dynamics.[23]

## II. Methodology

The method of choice for investigating periodic systems of organic molecules is density functional theory in the Hohen-

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* Present address: Institut für Physikalische Chemie, LMU München, Butenandtstrasse 5-13, Haus E, 81377 München.

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berg−Kohn−Sham formalism;[21,22] see refs 24 and 25 for reviews. On one hand this method is, in contrast to quantum-chemical multideterminant methods, fast enough for calculations on systems consisting of about one hundred atoms. On the other hand, it is superior to semiempirical methods that are parameterized on the basis of data for small molecules when dealing with unconventional geometries and/or periodic systems. The investigation of the reaction dynamics is done with Car−Parrinello molecular dynamics,[23] which represents a very efficient way of simulating the dynamics of complex molecular systems on the basis of Kohn−Sham theory, see refs 26−28 for reviews. With this method, first-principles simulations are possible on a time scale of several picoseconds. Hence, it is not feasible to simulate straightforwardly the full thermal back reaction that takes many hours in real life. There are several ways to handle the problem of simulating reactions that involve high barriers. The one that we use here consists of locating the transition state structure beforehand and initializing the MD propagation at this point in configuration space. We run two independent trajectories, one that finds the educt state and one that ends up in the product state, which are both lower in potential energy than the initial transition state. Since the MD method has no preferred direction of time, we obtain in this manner a full trajectory from the educt state to the product state. Of course, the generated time evolution has no physical meaning in the sense that it could be used to determine rate constants for this reaction. Rather, we investigate in this way the central part of a reaction such as, in our case, the primary proton-transfer event.

The calculations were performed using the CPMD code developed in our group.[29] This code uses plane waves for the expansion of the wave function. To reduce the number of plane waves necessary, the inner electrons are described by supersoft pseudopotentials of the Vanderbilt type.[30] This allows to use plane waves only up to an energy cutoff of 35 Rydberg. For the calculation of the isolated molecules, a large orthorhombic, periodically repeated unit cell was employed with the cell dimensions 20 × 30 × 20 au. For the crystal calculations we used the experimental dimensions of the monoclinic cell (19.0865 × 28.6827 × 14.5227 au, $\beta = 101.4°$).[19] We employed the Becke−Lee−Yang−Parr (BLYP) density functional[31,32] since this functional is known to be very well suited for the description of organic molecules. Also, hydrogen bonds are well described. The wave functions were optimized with the method of direct inversion in the iterative subspace (DIIS).[33,34] The geometry optimizations were performed using DIIS combined with a quasi-Newton method that employs the BFGS update for the Hessian matrix.[33,35,36] For the location of the transition states, a rational functional optimization (RFO) algorithm[37] was used in combination with the Powell update[38] for the Hessian matrix. For the Car−Parrinello molecular dynamics runs, a time step of 0.12 fs (5 au) was employed.

## III. Results and Discussion

We have performed full geometry optimizations for the ground-state structures of the three isomers in the gas phase. In addition, the two transition states between the NH and $CH_2$ forms and the OH and $CH_2$ forms have been determined. The results are depicted in Figure 2 and are compared to results obtained earlier[39] with the semiempirical method PM3.[40] It must be emphasized that we did not intend to locate the absolute minima for each structure, but geometries that are comparable to the ones in the crystalline environment. In organic molecules with several single bonds, many structures of similar energy exist. We checked this by optimizing the structures of some other conformers and found energies in a range of roughly ± 1 kcal/mol with respect to the energies of the presented structures. Hence, rotation around these single bonds is of minor importance when discussing the relative energies of the three isomers relevant in the crystalline phase. Of course, the same is true for the transition states. Because of the difficulty of locating transition states in systems with many degrees of freedom, it is certainly not possible to determine all of them. Yet, from the calculations we have performed starting from different initial geometries, we are positive that there are no transition states that are significantly lower in energy.

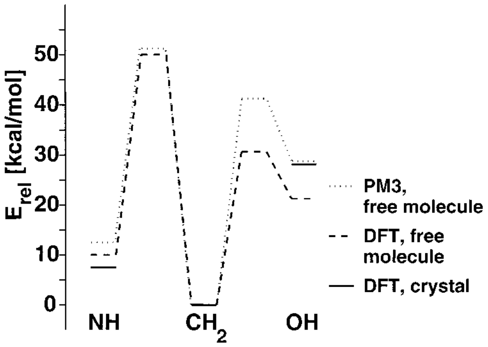

**Figure 2.** The relative energies of the DNBP isomers for the free molecules and for the crystalline forms. For comparison semiempirical PM3 results for the isolated molecules[39] are also included.

From comparison with the semiempirical results, it is evident that both methods perform equally well for the $CH_2$ and NH forms and for the transition state between these two forms. In contrast, for the OH form, and also for the transition state between the OH and $CH_2$ forms, a characteristic shift is observed: the semiempirical result is too high by ≈ 10 kcal/mol. This deviation can be explained by the unusual arrangement in these systems, with the migrating hydrogen atom bound to or close to the nitro group. Obviously the NOOH functionality is not well parameterized in the semiempirical scheme. In contrast, DFT yields results of comparable quality for any geometry.

As a second step we performed similar geometry optimizations for the molecular crystals that contain four molecules in the monoclinic unit cell. We did not try to optimize the cell constants but used the experimental ones, since the corresponding gradients were initially very small. Hence, trying to optimize the cell constants for the soft lattice of this molecular crystal would probably yield meaningless results. For the crystals, we located the minima only, since the determination of the transition states would have been too expensive.

From the results (Figure 2) it is evident that the crystalline environment does not greatly affect the relative energies. A look at the crystalline arrangement of the $CH_2$ form (Figure 3) reveals that the packing of the molecules in the crystal is indeed quite loose, so a major effect of the molecules on each other is not to be expected. Comparison with the experimental structure shows that the calculated geometry is very similar to the X-ray structure.[19] In fact, the largest deviations are found for the hydrogen atoms that were not well located by the experiment. Apart from the crystal structure of the $CH_2$ form, we can also present the geometry of the NH and OH photoproducts in the molecular crystal.[41] For a clearer comparison we show only one of the molecules, cut out from the optimized crystal structure, together with the corresponding gas-phase structures (Figure 4). It is evident that the three isomers in the crystal differ almost only in the position of the proton, while the relative position of the two rings is hardly affected. In contrast, in the free molecules

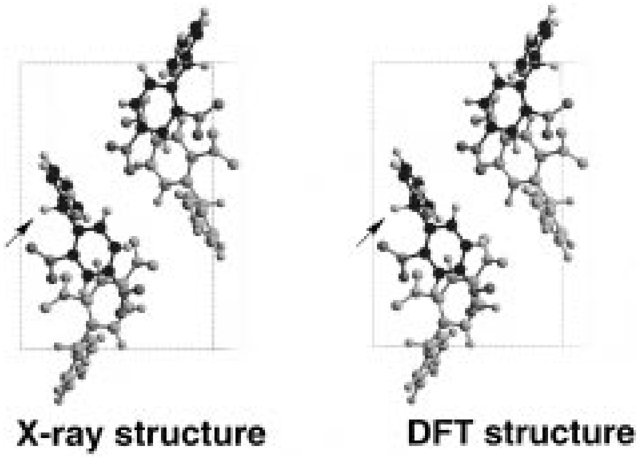

**Figure 3.** The calculated structure of the DNBP crystal with four molecules in the unit cell in comparison to the X-ray structure.[19] The arrows mark the relevant proton.

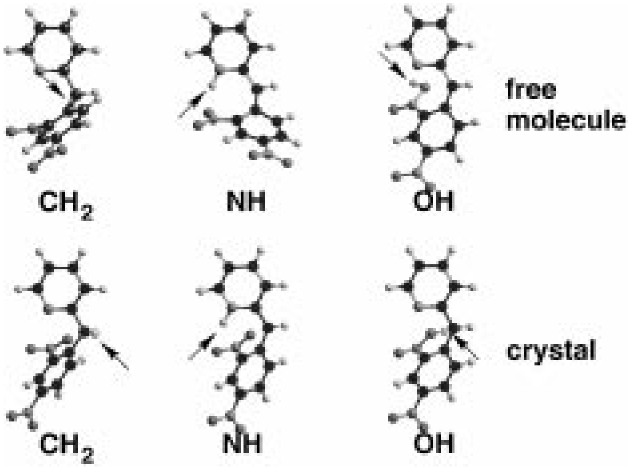

**Figure 4.** The optimized structures of the three isomers (i.e., the $CH_2$, OH, and NH forms) for the free molecules and for the molecules in the crystal. The arrows mark the relevant proton.

the relative position of the rings is controlled by the hybridization at the methylene bridge that connected the two rings. We conclude that the methylene bridge is floppy enough to allow an adjustment of the molecular geometry to the crystalline environment. Thus, our calculations show that the intramolecular proton-transfer reaction can indeed take place in the crystalline phase.

Finally, we performed an MD run for the thermal reaction NH → $CH_2$ in the gas phase starting from the point of highest energy along the reaction pathway, see section II for details of this procedure. Single snapshots of the MD run are presented in Figure 5. It can be seen that the transfer of the proton itself occurs on a time scale of roughly 100 fs (snapshots 2 to 4). On this time scale the rest of the molecule hardly moves. The relaxation of the two rings takes more than 1 ps, and it is not completed at the end of the MD simulation.

What insights can be gained from this unconstrained dynamical simulation? During its transfer, the proton approaches the *o*-nitro group up to hydrogen bond distance, see the fourth snapshot in Figure 5. Thus, the hydrogen-bonded OH intermediate serves as a bridge for the proton during its migration from the NH form to the $CH_2$ form. This has already been concluded from semiempirical calculations.[39] Obviously the interaction of the proton with the *o*-nitro group is characteristic for this type of reaction. When comparing to the previous semiempirical study, it is very likely that the interaction with the OH form is even more important in the excited state. Of course, the experimental observation that the presence of the *o*-nitro group is essential for the reaction[14,20] could also be explained by the acidification of the methylene bridge by nitro groups in the benzene ring, yet a direct interaction would correlate with the extraordinary role of nitro groups in *o*-position. Furthermore, it has been found that some of the DNBP derivatives formed crystals that were not photochromic.[42] By analyzing the X-ray structures of these crystals, it is found that in the nonphotochromic crystals the two rings have a relative position that differs from that in the DNBP crystal. Because of this different intramolecular arrangement a direct interaction of the *o*-nitro group with the migrating proton is not possible. Hence, the assumption that the direct interaction with the *o*-nitro group is essential for these reactions could explain the fact that some of the DNBP derivatives are nonphotochromic.

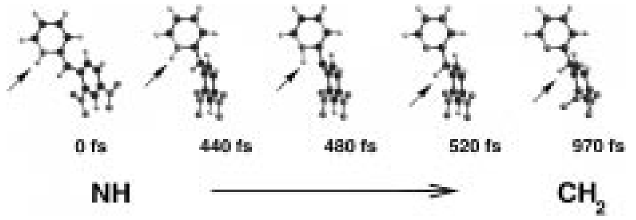

**Figure 5.** Snapshots from the first-principles simulation of the thermal reaction NH → $CH_2$ according to the procedure outlined in section II. The arrows mark the relevant proton.

In this study we have investigated the ground-state reaction only. To obtain a complete picture of the photoinduced processes in this complex system, ab initio molecular dynamics had to be performed in the excited state of the molecular crystal. A methodology that might allow such calculations was developed by us only recently.[43]

## IV. Conclusions

Using electronic structure methods based on first principles, we have investigated intramolecular proton transfer in the photochromic system 2-(2′,4′-dinitrobenzyl)-pyridine both in the gas phase and in the molecular crystal. The calculations show that density functional theory yields essentially the same results for the isolated system as do semiempirical methods, except when unusual functional groups are involved, where density functional theory (here BLYP) is more reliable. We present for the first time the crystal structures of the photoproducts. These structures show that the molecules are very flexible and that structural changes connected to proton transfer concern almost only the migrating hydrogen atom. The results indicate that the reaction is indeed possible in the molecular crystal itself, which implies broader possibilities of technical application of this photochromic system. Our molecular dynamics simulation of the reaction shows, in agreement with previous semiempirical calculations, that the thermal back reaction involves the formation of a short-lived hydrogen bridge of the migrating proton to the *o*-nitro group, which corroborates the experimental finding that this group is essential for the reaction.

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