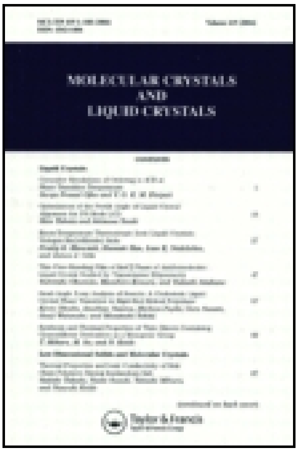

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Controlling of Intermolecular Proton Transfer in the Crystals of Potentially Tautomeric Organic Compounds via Molecular Packing and Structure of Hydrogen Bonds

Sergei Aldoshin [a]
[a] Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka, 142432, Moscow Region, Russia

Version of record first published: 24 Sep 2006

To cite this article: Sergei Aldoshin (1997): Controlling of Intermolecular Proton Transfer in the Crystals of Potentially Tautomeric Organic Compounds via Molecular Packing and Structure of Hydrogen Bonds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 105-114

To link to this article: http://dx.doi.org/10.1080/10587259708036149

Mol. Cryst. Liq. Cryst., 1997, Vol. 298, pp. 105–114
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CONTROLLING OF INTERMOLECULAR PROTON TRANSFER IN THE CRYSTALS OF POTENTIALLY TAUTOMERIC ORGANIC COMPOUNDS VIA MOLECULAR PACKING AND STRUCTURE OF HYDROGEN BONDS

SERGEI ALDOSHIN
Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, Chernogolovka 142432, Moscow Region, Russia

Abstract A possibility to obtain photochromic crystals with photoinitiated intermolecular proton transfer basing on the potentially tautomeric prototropic organic crystals has been shown. The structurre of these compounds, ways of structural modification and syntheis of crystals with such structure of a hydrogen bond which is favorable for intermolecular proton transfer have been studied.

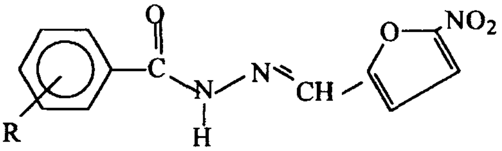
Compounds exhibiting photochromic properties in crystals have some advantages compared to photochromic materials working in other media:

- special working medium is not necessary for photochromic crystals because they work in their own medium;
- due to a high molecular arrangement of photochromic crystals, photochromic transformations can be controlled via the molecules structure and their packing;
- photochromic transformations can be studied carefully by different physical-chemical methods, including X-ray analysis, spectroscopy, tunnel microscopy, etc.

However, high density of molecules packing in crystals can prevent photochromic transformations, result in destruction of crystals and a decrease of a number of inter-exchange cycles. We suppose that these problems can be solved for photochromic crystals with photoinitiated proton transfer. For this purpose, such photochromic prototropic crystals are necessary in which position of heavy atoms is not influenced by the proton transfer. Crystals with intramolecular proton phototransfer (intra-MPT) seem to be promising from this standpoint. Interesting results have been obtained for photochromic crystals of salicylalarylimines (SAI). SAI crystals are characterized by numerous phototransformation cycles. High rate of the dark bleaching and short life time of the photoform are drawbacks of these crystals.

In this connection, we began to study the structure and properties of potentially prototropic crystals with intermolecular hydrogen bonds (inter-MHB) between proton donating and proton acceptor centers, rather than with intra-MHB. In prototropic crystals with inter-MHB a distance between the reactive centers depends on the molecules packing. It means that we can change a distance between the reactive centers and to affect a barrier of the proton transfer and a stability of the photoform by changing the molecules packing. We suppose that intermolecular proton transfer is feasible in the crystals of potentially prototropic molecules containing the amide O-C-N-H group. This group has a trans structure in crystals. Such structure is necessary for the inter-MHB formation. In addition, this group can be of both ketoamine (O=C-N-H) and oxyimine (HO-C=N) structure, thus being potentially tautomeric.

We have found that crystals of benzhydrazide (BH) derivatives are photosensitive.



BH

Fig. 1 shows the structure of BH photosensitive crystals. BHs form crystal hydrates of the 1:1 composition. The BH molecules form stacks packed in the "head to tail" mode. The water molecules are located in the channels between the BH molecules stacks.

The crystal is characterized by polar chains of intermolecular hydrogen bonds with the built-in water molecules.[1]

UV-irradiation of crystals near the long-wave absorption band of BH results in an absorption band of 400-500 nm. The crystals change in color. Spectral changes are irreversible.

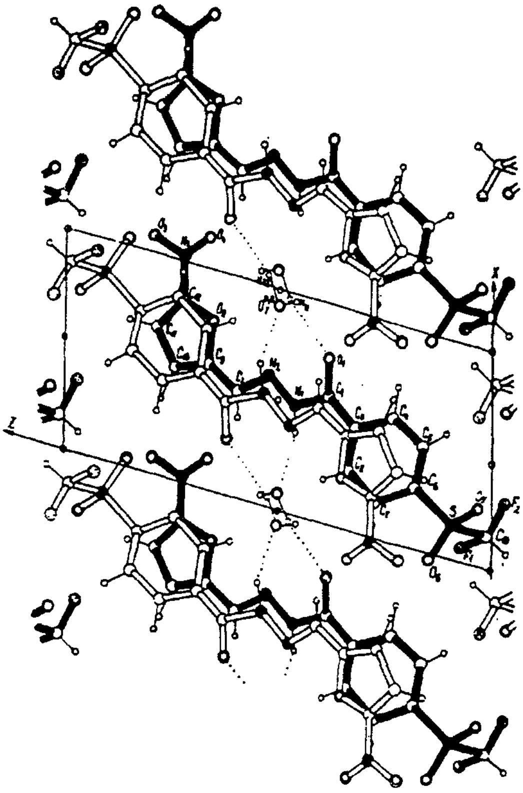


FIGURE 1 Structure of photosensitive BH crystals

Non-photosensitive BH crystals have different crystal structure.

- BH molecules form crystal hydrates and polar chains of inter-MHB, similar to photosensitive crystals. But molecules do not form stacks, so channels are not available in the crystal;

- molecules form crystal hydrates and form stacks. But channels are absent in crystals, and molecules are not linked by polar inter-MHB chains;

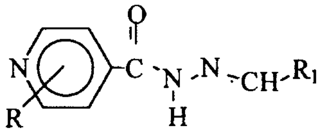
- molecules do not form crystal hydrates, polar inter-MHB chains, and stacks, so there are no channels in crystals.

Based on the structural data obtained, we suppose that photochemical transformations in photosensitive BH crystals are due to the intermolecular transfer of the amide proton from the BH molecule to the water one. A channel structure of the BH crystal hydrates with the polar inter-MHB chains and the built-in water photoinitiated intermolecular proton transfer and the photoproduct stabilization.

We tried to introduce structural modifications in this photochromic system taking into account suggested structural scheme of phototransformation., i.e., to obtain crystal hydrates of 1:2 rather than of 1:1 composition. We believed that a dimeric associate would possess higher proton donating properties, and hence, higher photosensitivity. To obtain a crystal hydrate of the 1:2 composition, a channel size should be increased. For this purpose, we have synthesized BH with different substituents in o- and m-positions of the benzene moieties. We managed to obtain crystals of the necessary structure using BH with nitro-substituents in meta-positions. Molecules form crystal hydrates of the 1:2 composition, they are linked by the polar inter-MHB chains, arranged in stacks. There are channels in the crystals in which dimeric water associates are built. These crystals are characterized by the highest photosensitivity.

The results obtained suggest that photochromic crystals with intermolecular proton transfer can be formed. Properties of such crystals depend on the inter-MHB structure. So, our objective is to find a possibility to control the hydrogen bonds structure and to create crystals with a desired structure and inter-MHB.

In this connection, we have studied conditions of formation and inter-MHB structure of isonicotinhydrazide derivatives (INH), compounds that are similar to BH. The INH molecules have a proton donating amide center, and two proton acceptor centers, the carbonyl group (similar to BH), and the nitrogen atom of the pyridine moiety. The INH molecule is potentially tautomeric. It can exist in either keto-amino form (O=C-NH-), or oxy-imino (HO-C=N-) and zwitterionic (HN(Py)...-N-) forms.



INH

Different crystal structures with different inter-MHB nature were shown to be obtained depending on the synthesis and/or crystallization conditions.[2] So, potentially tautomeric crystals with different channels of intermolecular proton transfer can be obtained. The channel is determined by the inter-MHB type. When crystallization occurs from alcohol (methanol), crystals with N-H...N(Py) inter-MHB between the amide NH-group and the nitrogen atom of the pyridine cycle are formed. This is a rare case when the C=O carbonyl group does not participate in inter-MHB. We have found that in such crystals the C=O group can participate in specific intermolecular interactions with the energy close to that of inter-MHB.

While crystallizing INH from the aqueous acetic acid, we managed to lock the proton acceptor center N(Py) by solvating this center with the acetic acid molecule. The structure of the crystals obtained is similar to that of photosensitive BH crystals: stack packing, channels, filled with the water molecules, polar inter-MHB chains. A channel C=O...H_2O...HN is formed in the crystals.

We have found the conditions which provide elimination of the acetic acid molecules from the crystals with keeping the water ones. A loss of acetic acid molecules is accompanied by a two-step structural rearrangement. Three types of hydrogen bonds are formed in crystals of the resulting form: N--H...H_2O, C=O...H_2O and H_2O...N(Py), and two channels for the proton transfer: C=O...H_2O...H-N and N-H...H_2O...N(Py). We have studied formation conditions for crystals with different inter-MHB types for the INH derivatives class, as well as these crystals mutual transitions. This allows us to obtain photosensitive crystals with a desired channel of intermolecular proton transfer. These channels have different barriers of the proton transfer, thus providing the formation of photoproducts of various chemical origin, structure and spectral properties.

By modifying structure and spectral properties of compounds with the amide group, we have obtained derivatives of ortho-amidoanilines. [3] As distinct from BH, they have a benzene ring between the nitrogen atoms, which expands the π-system. X-ray analysis showed that the stack packing in a "head to tail" mode is the most favorable for these compounds both from the standpoint of van der vaals and dipole-dipole interactions (Fig. 2). With such arrangement, the amide groups have opposite orientation., and inter-MHB fail to be formed in crystals. The crystals are non-photosensitive.

By analyzing the packing features, we see that ortho-substituents in the benzene moiety should prevent the formation of such stacks. So, we have synthesized a compound with the ortho-nitro-substituent in the benzylidene fragment.

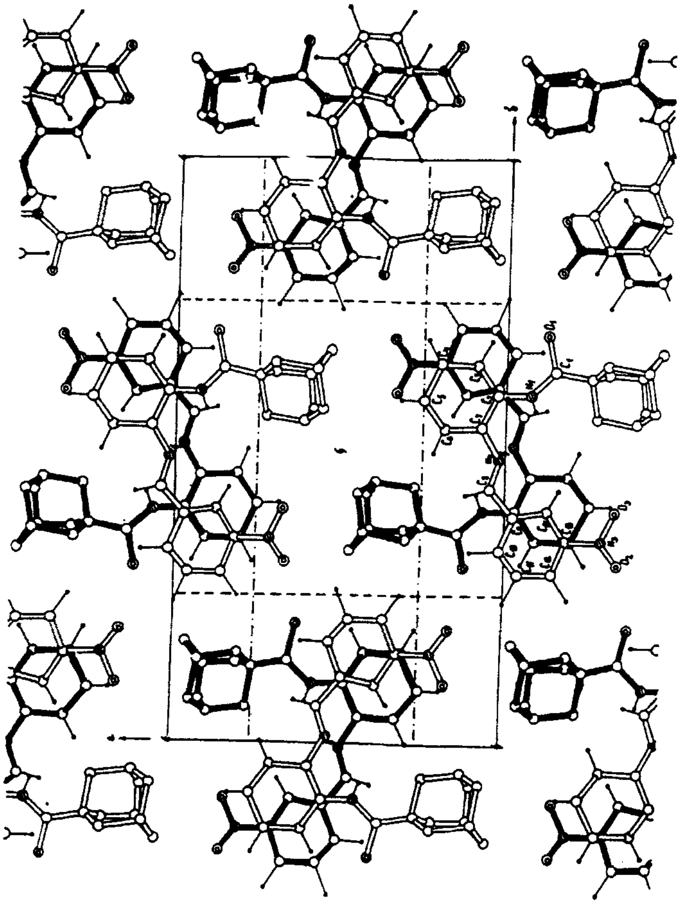
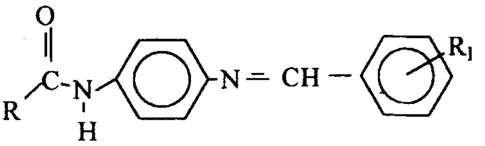


FIGURE 2 A typical stack structure of ortho-amidoaniline crystals



We have succeeded to obtain the C=O...H-N inter-MHB in this crystal, which connects the translation molecules in chains (Fig.3). The chains direction almost coincides with the direction of the dipole moment vector of the molecules. As it has been mentioned such structure is favorable for the proton transfer in the BH crystal. The crystals actually appeared to be photosensitive.

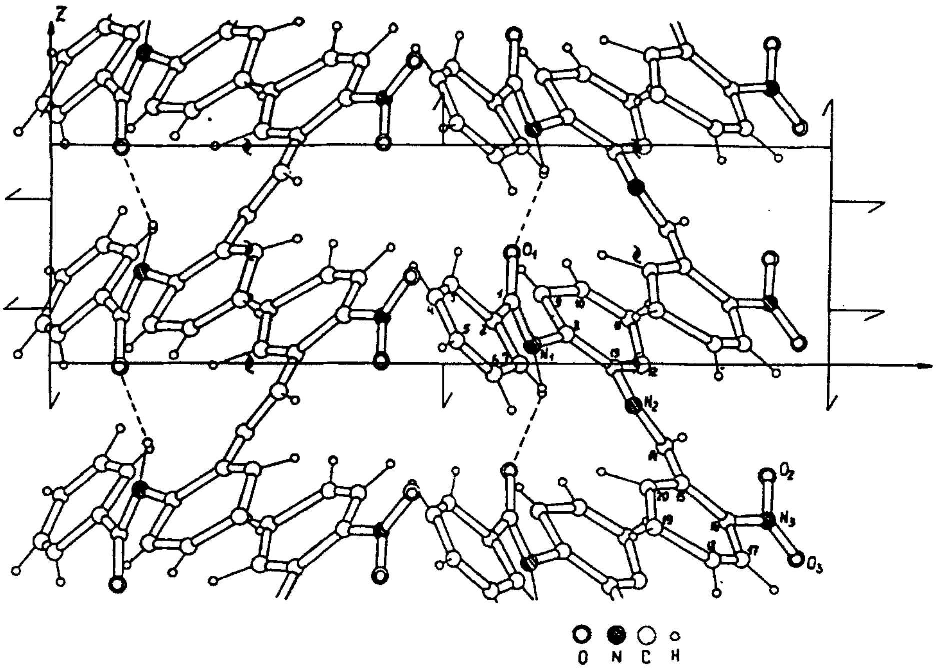
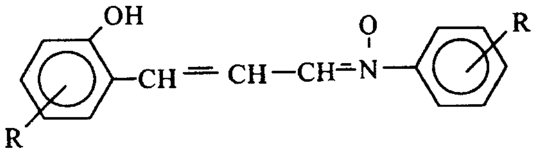


FIGURE 3 Formation of inter-MHB in crystals of ortho-amidoanilines

The data obtained show that a potentially tautomeric amide group provides a possibility to create photosensitive crystals with the N-H...O and N-H...N inter-MHB. We supposed it to be interesting to study a possibility of synthesis of photosensitive compounds with the O-H...O inter-MHB type. We believed that such inter-MHB could occur in OH-derivatives of aldonitrons vinilogs (OH-nitrons). M.I.Knyazhanskii with co-workers showed that introduction of the OH-group in the molecule resulted in the formation of short-lived quinoid photoform in solutions. This fact can be an evidence of the photoinitiated proton transfer from the OH-group.[4]

We have synthesized and studied the crystals of various derivatives of these compounds.



OH-nitrons

The reflection spectrum shows that a quinoid structure is formed in solid state, similar to solutions.

From X-ray study we have determined that there are two different types of OH-nitrons molecules packing in crystals. In the crystal molecules of OH-nitrons are connected either in dimeric associates (Fig.4) or chains by inter-MHB (Fig.5).

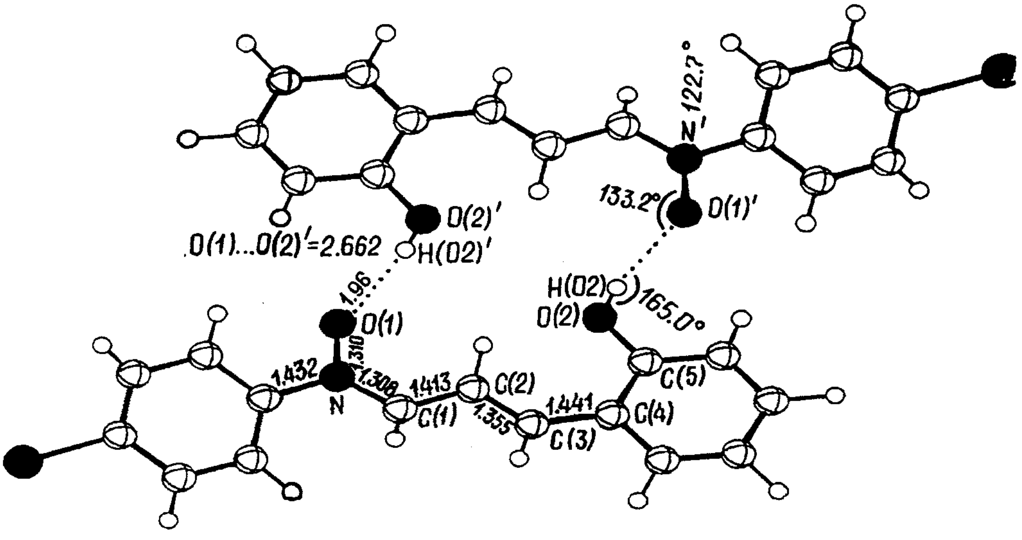


FIGURE 4 Structure of dimeric associates in crystals of OH-nitrons

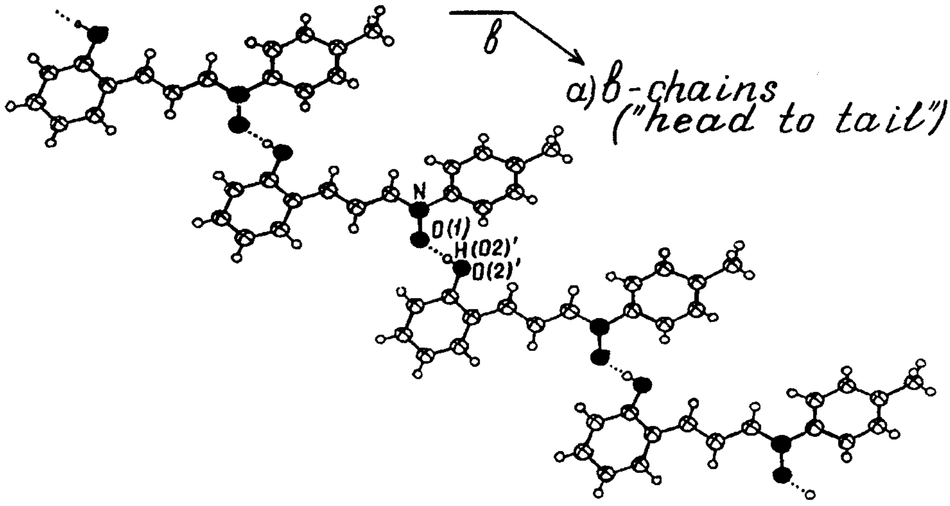


FIGURE 5 Structure of molecular chains in crystals of OH-nitrons

The nitron N→O group forms a hydrogen bond with the hydrogen atom of the OH-group. Dimeric associates are formed by anti-cis-isomers, while different types of chains are formed by syn- and anti-trans-isomers.

Quantum-chemical calculations showed that energies of these conformers differ insignificantly.

We have studied a coordinate of the reaction of the proton transfer along the hydrogen bond in the centrosymmetrical dimeric associate in the ground electron state. A movement of two protons appeared to begin asynchronously, however, the transition state is centrosymmetrical. The data obtained indicate that dimeric associates of OH-nitrons are typical tautomeric systems.

Geometrical modeling points out that after the proton has been transferred, inter-MHB in the quinoid structure weakens. This is due to the increase of intermolecular distance =O...O-H and strong distortion of the OHO angle. Such changes are due to rehybridization of the oxygen atoms of OH- and N→O groups after the proton transfer. Weakening of inter-MHB will increase a barrier of the reverse proton transfer and stabilize the resulting quinoid photoform.

Dipole-dipole intermolecular interactions provide another possibility of the quinoid form stabilization in crystals. Efficiency of these interactions depends on mutual molecules arrangement in the crystal structure, i.e., on the location of molecules in dimeric associates and chains. So, crystals of OH-nitrons of the desired structure and, hence, photosensitivity can be obtained by varying the conditions of synthesis and crystallization.[5]

In conclusion, the performed study suggests an optimistic outlook for the formation of photochromic crystal systems with different types of prototropic re-arrangements (N→O, N.→ N, O→O). There are practicable ways of the inter-MHB structure management in such crystals, and hence, of photosensitivity of crystals.

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