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Solid-State Photochromism of 5-*tert*-Butyl-2-hydroxyisophthalaldehyde

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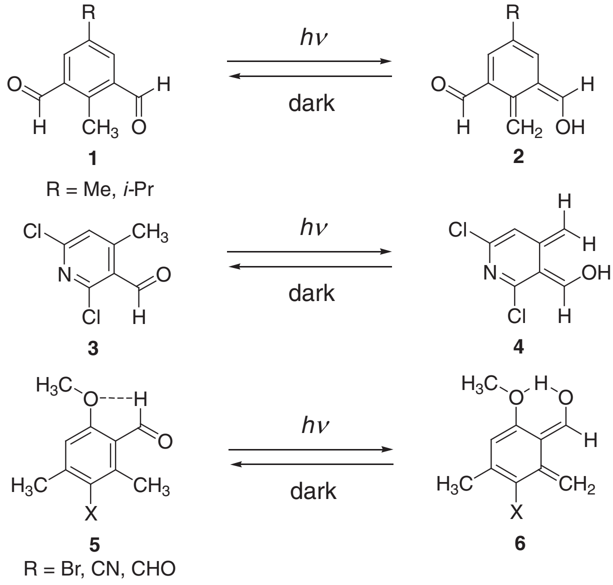
Colorless crystals of 5-*tert*-butyl-2-hydroxyisophthalaldehyde change to an orange-red color upon brief exposure to UV–vis radiation ($\lambda > 300$ nm). The colored crystals revert to colorless in the dark. X-ray diffraction revealed different packing patterns for the crystals of nonphotochromic and photochromic compounds.

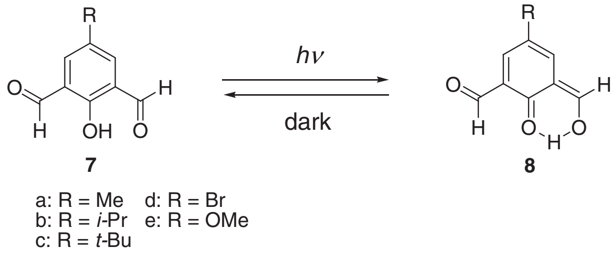
Photochromic compounds have received considerable attention in recent years owing to their potential applications, such as information storage, electronic display systems, optical switching devices, ophthalmic glasses, and macroscale mechanical motion of materials.[1] Several types of organic photochromic compounds, such as azobenzenes, diarylethenes, naphthopyrans, spiropyrans, fulgides, chromenes, and *N*-salicylideneanilines, have been discovered, and their photochromic properties have been studied.[2]

However, there are few reports on the solid-state photochromism involved in the photoenolization of carbonyl compounds (Scheme 1). Kumar and Venkatesan reported that some isophthalaldehydes **1**[3] exhibit photocoloration from colorless to red upon exposure to sunlight. The red color fades within approximately 5 min after storage in the dark. Sarkar et al. first reported the solid-state photochromism of 2,6-dichloro-4-methyl-3-pyridinecarbaldehyde (**3**),[4] colorless crystals of which turn deep orange-red on exposure to sunlight. The colored crystals revert to colorless within approximately 40 min in the dark. Moorthy reported that some anisaldehydes **5**[2j] change to brick-red color upon brief exposure to UV–vis radiation. The red color, attributed to (*E*)-xylylenol **6**, persists for approximately 10 h.

During the course of our study on the photochromism of chiral Schiff-base macrocycles,[5] we had the experience of studying the photochemistry of 2-hydroxyisophthalaldehyde derivatives **7**. Herein, we report on the solid-state photochromism of 5-*tert*-butyl-2-hydroxyisophthalaldehyde (**7c**), which can potentially be a family of photochromic compounds (Scheme 2).



Scheme 1.



Scheme 2.

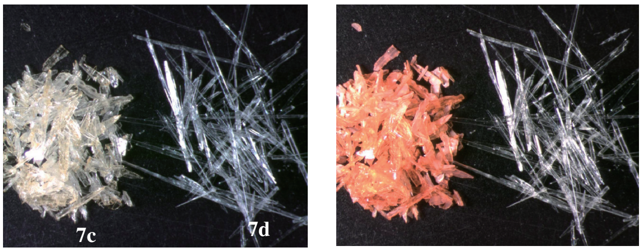


Figure 1. Photographs of **7c** and **7d** before (left) and after irradiation (right).

All 2-hydroxyisophthalaldehyde derivatives, **7**, were synthesized from readily available 4-substituted phenols by the Duff reaction.[6] Upon brief exposure to UV–vis radiation ($\lambda >$ 300 nm), colorless crystals of 5-*tert*-butyl-2-hydroxyisophthalaldehyde (**7c**) changed to an orange-red color (Figure 1). The crystals reverted to the colorless form on standing at room temperature in the dark for approximately 12 h. Figure 2 shows that the UV–vis absorption changes in the region 400–600 nm before and after irradiation may be due to the formation of the (*E*)-enol **8c**. In contrast, the crystals of other 2-hydroxyisophthalaldehyde derivatives **7a**, **7b**, **7d**, and **7e** did not exhibit any photocoloration and no UV–vis spectral changes occurred after photoirradiation (Figure 2).

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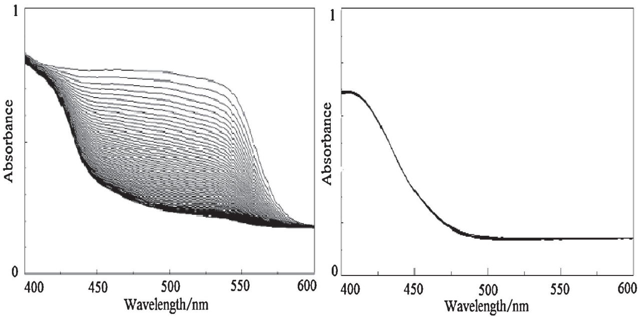

Figure 2. UV–vis spectral changes of **7c** (left) and **7d** (right) in the solid state. Successive measurements were recorded every 10 min from the top (after irradiation of the light for 10 min) to the bottom (after keeping 12 h in the dark).

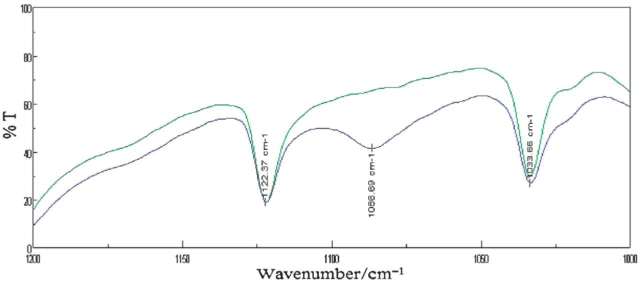

Figure 3. IR spectral changes of **7c** before (green) and after (blue) photoirradiation in KBr pellet.

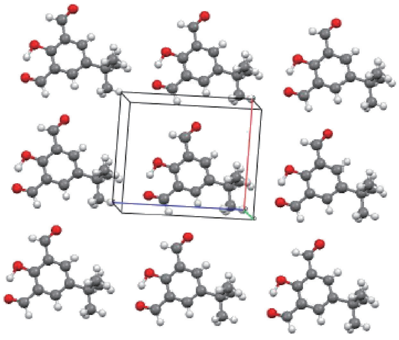

Figure 4. View down the *b* axis showing the planar arrangement of **7c** molecules.

With the aim of understanding the mechanism of the photochromism of **7c**, we investigated the IR spectra of **7c** before and after photoirradiation (Figure 3). After irradiation, a new sharp band attiributable to the νC–O band for an enol form appeared at $1086\,\mathrm{cm}^{-1}$. However, there are no significant changes in another region of the spectra.

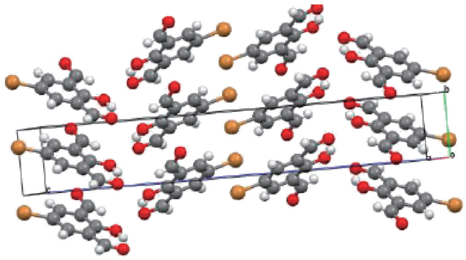

Figure 5. Herringbone structure observed in the crystal of **7d**.

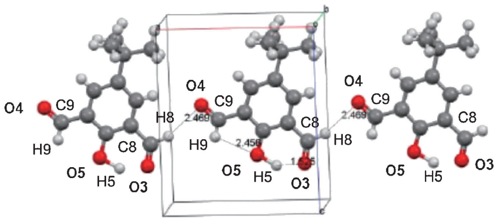

Figure 6. Infinite hydrogen-bonded chains in crystals of **7c**; intramolecular H-bond geometry: O5–H5···O3: O5···O3 2.610(5) Å, H5···O3 1.53(6) Å, angle 147(5)°; C9–H9···O5: C9···O5 2.811(6) Å, H9···O5 2.46(6) Å, angle 102(4)°; intermolecular: C8–H8···O4 [$x + 1$, $+y$, $+z$], C8···O4 3.478(6), H8···O4 2.47(6) Å, angle 161(5)°.

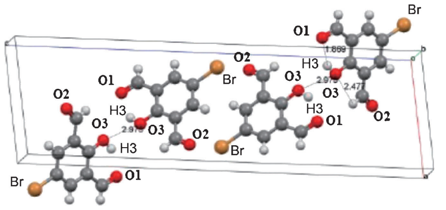

Figure 7. Hydrogen-bonding pattern in crystals of **7d**: intramolecular O3–H3···O1: O3···O1 2.623(2) Å, H3···O1 1.87(4) Å, angle 146(4)°; C5–H5···O3: C5···O3 2.791(3) Å, H5···O3 2.48 Å, angle 100°; intermolecular dimers: O3–H3···O3 [$-x + 1/2, y + 1/2, -z + 1/2$], O3···O3 2.974(3) Å, H3···O3 2.48(4) Å, angle 117(4)°; Br···Br distance 3.877(2) Å.

Crystals of **7c** and **7d** suitable for X-ray analysis were obtained by recrystallization from cyclohexane, and were investigated by X-ray crystallography to elucidate the structural factors that explain the presence of photochromic properties only in the crystals of **7d**. The crystal lattice of both compounds is modulated by the presence of only one formal hydrogen-bond donor (phenolic H-atom) and three hydrogen-bond acceptors. This favors the presence of two intramolecular hydrogen bonds: one between the hydroxy H-atom and one of the aldehyde oxygen atoms, and the other between the phenol oxygen and the H-atom of the second aldehyde group. Crystals of compounds **7c** and **7d** revealed planar (Figure 4) and herringbone (Figure 5) arrangements of the molecules, respectively. The geometry of intra- and intermolecular hydrogen bonds is shown in Figure 6 (**7c**) and Figure 7 (**7d**). The intermolecular hydrogen bonds and intermolecular nonbonding contacts in both compounds are within the upper limits. The Br···Br distance is slightly above the higher limit than that reported by Navon et al. (3.7 Å max).[7] One can assume that the electronic structure of the phenol ring differs because of presence of the electron-donating group in **7c** (*t*-Bu) and/or weakly electron-withdrawing group (Br, **7d**). Indeed, the phenol proton in **7d** is located closer to the phenol-oxygen atom O3, whereas in **7c**, it is localized between the hydroxy and aldehyde oxygen atoms.

In addition, molecules in **7d** form dimeric structures, in which geometric measures for the intermolecular hydrogen bond is ideal (O3–H3···O3 angle is only 117°, Figure 7); however, the O3···O3 distance is sufficiently short to facilitate proton exchange.

The presented data show that in the case of photochromic compound **7c**, infinite linear hydrogen bonding is observed, whereas in case of photoinert derivative **7d** hydrogen bonds are localized to the dimeric system. It is possible that although crystal irradiation excites molecules of both compounds, excited state in the case of compound **7c** is somehow better stabilized and can be experimentally detected. The unusually stable photo-enol of **8c** compared to Kumar and Venkatesans' compounds may be due to the intra- and intermolecular hydrogen bonding.

In summary, we have observed the solid-state photochromism of 5-*tert*-butyl-2-hydroxyisophthalaldehyde (**7c**), a new family of photochromic compounds. On the basis of available crystallographic data and inspection of reflectance FT-IR spectra for monocrystals before and after irradiation, it is difficult to predict whether the solid-state photochromism of **7c** is derived from inter- or intramolecular proton hopping. Further studies on the mechanism of this type of photochromic compound are currently underway.

Experimental

Preparation of 2-Hydroxyisophthalaldehyde Derivatives. 2-Hydroxyisophthalaldehyde derivatives **7a**–**7e** were prepared according to a previously reported method, as follows.[6] For example, a mixture of 4-*tert*-butylphenol (8.29 g, 55.2 mmol) and hexamethylenetetramine (15.5 g, 110 mmol) in trifluoroacetic acid (100 mL) was heated under reflux for 24 h. After addition of 4 M HCl (200 mL), the reaction mixture was extracted with dichloromethane. The organic layer was evaporated to give a yellow solid. The product was purified by column chromatography on silica gel using dichloromethane as the eluent to yield 5-*tert*-butyl-2-hydroxyisophthalaldehyde (**7c**) as a colorless solid (3.8 g, 33% yield). Mp 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.49 (s, OH, 1H), 10.25 (s, CHO, 2H), 7.99 (s, Ar, 2H), 1.36 (s, *t*-Bu, 9H). IR: 3352 (νOH), 1686 cm^{-1} (νC=O).

X-ray Structural Determinations. X-ray data for **7c** and **7d** were collected on a Bruker APEX-II CCD diffractometer using Cu Kα radiation ($\lambda = 1.54178$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares using SHELXS97 and SHELXL97[8] programs. All non H-atoms were refined anisotropically; all H-atoms bonded to carbon atoms were placed on geometrically calculated positions and refined using a riding model. The hydroxy H-atoms in the two structures were located from $\Delta\rho$ maps and refined isotropically. Compound **7c**: $C_{12}H_{14}O_3$, MW: 206.23, $a = 8.5087(3)$, $b = 6.6259(2)$, $c = 10.0713(3)$ Å, $\beta = 90.482(3)°$, $V = 567.78(3)$ Å^3, $F(000) = 220$, $D_{calcd} = 1.206$ Mg m^{-3}, μ(Cu Kα) $= 0.704$ mm^{-1}; monoclinic, space group $P2_1/m$, $Z = 2$. A total of 5162 reflections were collected, 1083 of which were unique, with $R(\text{int}) = 0.0320$. Multiscan absorption correction was applied with $T_{\min} = 0.6640$ and $T_{\max} = 0.9570$. Final $R1 = 0.0902$ and $wR2 = 0.2317$ for 2476 reflections with F. The phenol hydrogen atom was found from difference Fourier maps and refined. Compound **7d**: $C_8H_5BrO_3$, MW: 229.03, $a = 7.5479(2)$, $b = 3.9898(1)$, $c = 26.0154(6)$ Å, $\beta = 96.979(1)°$; $V = 777.64(3)$ Å^3, $F(000) = 448$, $D_{calcd} = 1.956$ Mg m^{-3}, μ(Cu Kα) $= 6.910$ mm^{-1}; monoclinic space group $P2_1/n$, $Z = 4$. A total of 6727 reflections were collected, 1357 of which were unique with $R(\text{int}) = 0.0319$. Multiscan absorption correction was applied with $T_{\min} = 0.1667$ and $T_{\max} = 0.8628$. Final $R1 = 0.0827$ and $wR2 = 0.227$ for 1233 reflections with $I > 2\sigma(I)$. CCDC-856311 and CCDC-856310 contain the supplementary crystallographic data for **7c** and **7d**, respectively. These data can be obtained free of charge at "http://www.ccdc.cam.ac.uk/conts/retrieving.html" (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; E-mail: deposit@ccdc.cam.ac.uk).

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