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Solid-State Photochromism and Photoreactivity of *o*- and *p*-Anisaldehydes. Remarkable Stabilization of *o*-Xylylenols

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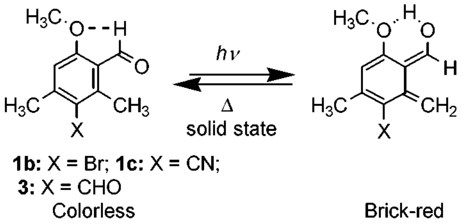
ABSTRACT

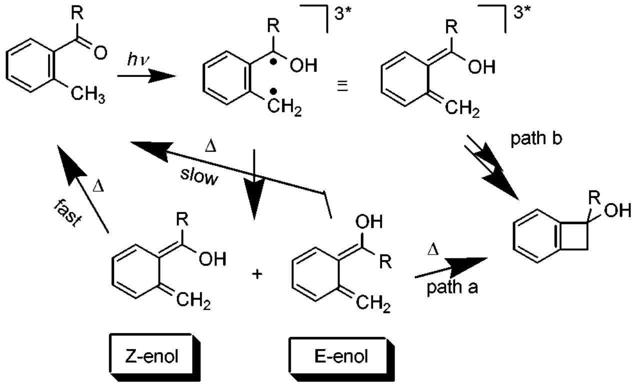


1b: X = Br; **1c:** X = CN;
3: X = CHO

All of the crystalline *o*-anisaldehyde derivatives 1 and 3 change to brick-red color upon brief exposure to UV–vis radiation. The red color, attributed to (*E*)-xylylenol, is remarkably persistent for hours (ca. 10 h) in the case of 1c; such a long lifetime for the reactive *o*-xylylenols is unprecedented. In contrast, the *p*-anisaldehydes 2 undergo cyclization. Solid-state photolysis of 2b affords the benzocyclobutenol 7b regioselectively, which is not accessible from solution-phase photolysis.

Photoenolization of *o*-alkyl aromatic carbonyl compounds is a very useful transformation to access an important class of reactive intermediates, namely, α-hydroxy *o*-quinodimethanes or photoenols.[1,2] The reaction involves abstraction of a γ-hydrogen by the triplet-excited carbonyl to yield a triplet biradical (= triplet enol),[3] which decays to (*Z*)- and (*E*)-enols/xylylenols (Scheme 1).[3−5] Available evidence suggests that (*Z*)-enols are very short-lived (ca. 100 ns) and undergo rapid 1,5-sigmatropic shift to regenerate the precursor carbonyl compound. On the other hand, (*E*)-enols are remarkably longer-lived (seconds), and the chemical trapping chemistry known so far is in aggrement with its stereochemistry.[1] Wagner and co-workers have convincingly shown that the dienols, in the absence of added dienophiles, undergo

Scheme 1



[†] Indian Institute of Technology.
[‡] Panjab University.
(1) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.
(2) Segura, J. L.; Martin, N. *Chem. Rev.* **1999**, *99*, 3199.
(3) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.
(4) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.
(5) For usage of the term “*o*-xylylenol”, see: Wagner, P. J.; Sobczak, M.; Park, B.-S. *J. Am. Chem. Soc.* **1998**, *120*, 2488.
(6) Wagner, P. J.; Subrahmanyam, D.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 709.

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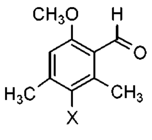
thermal conrotatory ring closure to synthetically important intermediates, viz., benzocyclobutenols (path a, Scheme 1).[6]

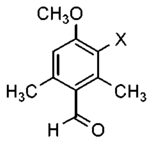
That the photoenols are colored has been known for a while.[7,8] With an ultimate objective of developing efficient photochromic systems based on photoenolization, Ullmann and co-workers carried out a systematic investigation on carbonyl compounds.[9] Employing an approach that involved stabilization of the photoenols through intramolecular hydrogen bonding, they successfully demonstrated photochromism of certain chromone derivatives in benzene solutions at 25 °C. Subsequently, virtually no attention has been paid toward exploring carbonyl compounds as photochromic materials. To the best of our knowledge, only three reports of fortuitous observation of solid-state photochromism in carbonyl compounds have appeared.[10−12]

In view of the recent surge of interest in photochromic materials due to their application in photonic devices,[13] we were motivated to explore photochromism in carbonyl compounds based on photoenolization in the solid state, in particular. Incidentally, among a vast number of photochromic compounds known so far, only a few have been found that are photochromic in the solid state.[14] Herein, we have designed the anisaldehydes **1**−**3** and examined the influence of intramolecular stabilization of the (*E*)-enol and lack thereof on the photochemical pathways exemplified in Scheme 1. While the (*E*)-enols **4** of *o*-anisaldehydes **1** and **3** derive stabilization through intramolecular O−H···O hydrogen bonding, the enols **5** and **6** of *p*-anisaldehydes **2** lack such stabilization. Our preference for crystalline aldehydes to ketones was based on the following considerations:

- The formyl hydrogen can be exploited for C−H···O hydrogen bonding to orient the carbonyl group toward that of methyl for γ-hydrogen abstraction.
- Bond rotations associated with the formation of (*E*)-enol in the crystal lattice would be difficult with any group larger in size than hydrogen.
- Substitution of aromatic ring does not appear to cause state-switching of excited states.[15]



1



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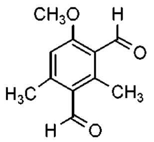
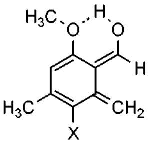


3

a: X = H; **b:** X = Br; **c:** X = CN



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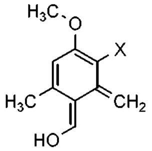

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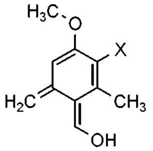

6

All of the aldehydes **1**−**3** were synthesized starting from readily available 3,5-dimethylphenol and fully characterized (IR, ^{1}H and ^{13}C NMR, and MS). The aldehydes **1a** and **2a** were found to be liquids, and their photochemistry is not considered here. Upon brief exposure to UV−vis radiation ($\lambda > 300$ nm, high-pressure Hg lamp), colorless crystals of anisaldehydes **1b,c**, **2c**, and **3**, with the exception of **2b**, change to a brick-red color. Reversion to the colorless form occurs on standing the crystals at room temperature. While it takes ca. 5 min for complete reversion in the case of **2c** and **3**, the red color in the case of **1b** and **1c** is persistent for several hours (ca. 10 h). Figure 1 shows the UV−vis absorption and IR spectra (inset) typically recorded for **1c** before and after irradiation. The absorption in the region between 400 and 600 nm and the appearance of a broad O−H stretching band with concomitant disappearance of the carbonyl stretching band (1687 cm^{-1}) clearly establish the formation of (*E*)-enol. Indeed, the (*E*)-enol of *o*-methylbenzaldehyde has been matrix-isolated (N_2 and Xe) and characterized through UV−vis and IR spectroscopy at 12 K.[16] In this case, the stretching due to O−H has been shown to appear as a sharp band at ca. 3600 cm^{-1}, suggesting the absence of hydrogen bonding. In contrast, a broad band at 3454 cm^{-1} in Figure 1 clearly attests to the fact that the (*E*)-enol is intramolecularly hydrogen-bonded (**4c**, X = CN). The order of lifetimes of the enols is typically found to be **1c** > **1b** > **3** ≈ **2c**.

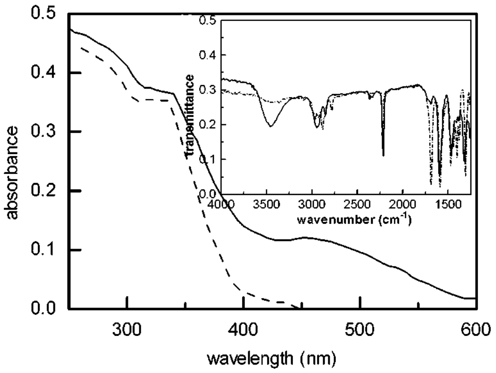

Figure 1. The UV−vis absorption and IR spectra (inset) of **1c** before (dotted line) and after (solid line) exposure to UV−vis radiation.

As mentioned earlier, photolysis of the crystals of aldehyde **2b** did not lead to photochromism. In contrast, extended irradiation in a Rayonet reactor ($\lambda_{max} = 350$ nm) for 24 h led to loss of crystallinity and formation of a single

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[7] Yang, N. C.; Rivas, C. *J. Am. Chem. Soc.* **1961**, *83*, 2213.

[8] Zwicker, E. F.; Grossweiner, L. I.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2213.

[9] Huffman, K. R.; Loy, M.; Ullman, E. F. *J. Am. Chem. Soc.* **1965**, *87*, 5417.

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[11] Kumar, V. A.; Venkatesan, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 829.

[12] Sarkar, T. K.; Ghosh, S. K.; Moorthy, J. N.; Fang, J.-M.; Nandy, S. K.; Sathyamurthy, N.; Chakraborty, D. *Tetrahedron Lett.* **2000**, *41*, 6909.

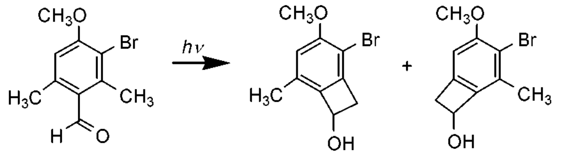
[13] For a recent special issue on "Photochromism: Memories and Switches", see: *Chem. Rev.* **2000**, *100*, issue 5.

[14] Benard, S.; Yo, P. *Chem. Commun.* **2000**, 65 and references therein.

[15] For example, mesitaldehyde is known to afford the 1,4-biradical with a quantum yield of 0.84; see ref 3.

[16] Gelicki, J. Krantz, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1623.

photoproduct at ca. 40% conversion (^{1}H NMR). The photoproduct was isolated and established to be the cyclobutenol **7b** (eq 1).[17,18] As the reactions in solid state are most often topochemically controlled,[19−21] the regiochemistry of the photoproduct must be **7b** as demanded by the molecular structure of its precursor aldehyde **2b** in the solid state (vide infra). Interestingly, photolysis of its benzene solution (0.1 M) for 12 h in a Rayonet reactor (λ_{max} = 350 nm) led to a highly intractable mixture of products; ^{1}H NMR (400 MHz) analysis of the mixture indicated no evidence for the cyclobutenol.[22] Thus, the solid-state photolysis in the present instance leads to a product that is regioselective and also inaccessible from solution-phase photolysis.



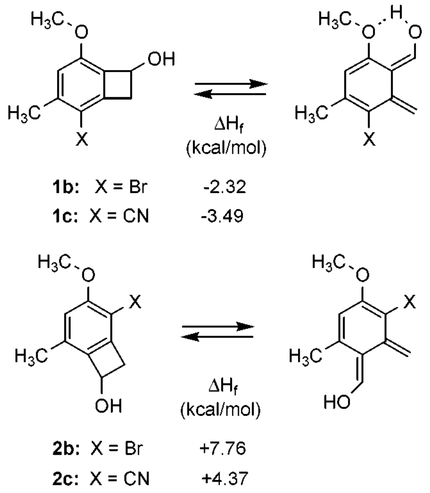
2b **7b** **8b**

(eq 1)

To understand the observed photochromism (*o*-xylylenol) in **1b,c** and **3** and photoreactivity (cyclobutenol) in the case of **2b**, we undertook the X-ray crystal structure analyses of **1b,c** and **2b**.[23] The crystal structures of **1b** and **1c** clearly established that the formyl hydrogens participate in intramolecular hydrogen bonds with the oxygen of the methoxy group, thereby forcing the carbonyl group toward that of methyl for hydrogen atom abstraction. In the case of **2b**, the formyl group is found to be oriented toward the methyl that is *ortho* to the bromo group (cf. Supporting Information). Since the aldehydes **1b** and **2b** differ only in the relative positions of the bromo and formyl groups but display a striking difference in their photobehavior, a comparison of their crystal structures was made to understand the photochromism in one and photoreactivity in the other.[24] The analyses of crystal packing suggest that both **1b** and **2b** are equally close-packed, which is also borne out from similar calculated crystal densities (1.66 g cm^{-3}). Thus, lack of observation of photochromism in **2b** cannot be taken to imply that the crystal lattice in the latter does not permit bond rotations associated with the formation of the long-lived (*E*)-enol. Two explanations may be considered to account for the absence of photochromism in **2b**. First, the (*E*)-enol may indeed be formed but may undergo rapid thermal cyclization as a result of lack of any stabilization (path a, Scheme 1). Second, the triplet-excited biradical presumably collapses to cyclobutenol directly (path b).[25,26] We find it difficult to understand why **2b** should follow the latter, while its cyano-substituted analogue **2c** exhibits photochromism.

The observation of photochromism in **1** and **3** suggests that the stability of the (*E*)-enols in these cases is comparable to or higher than that of their respective cyclobutenols. To verify this, we have undertaken AM1 calculations, which have been shown to yield results in agreement with experiment for benzocyclobutenol to *o*-xylylenol transformation.[27] The results of these AM1 calculations (QCMP 137, MOPAC6/PC)[28] show that the hydrogen-bonded (*E*)-enols of **1b** and **1c** are more stable by 2.32 and 3.49 kcal/mol than their corresponding cyclobutenols, respectively (Scheme 2).

Scheme 2. AM1 Calculated Enthalpies of Reaction



Similar calculations for **2b** show that its (*E*)-enol is less stable by 7.76 kcal/mol than the corresponding cyclobutenol. Presumably, a similar difference in energies prevails in the solid state as well, resulting in the former undergoing thermal rapid cyclization to the more stable cyclobutenol. Our attempts to observe the red color arising from the formation of the enols on irradiation at ca. −80 °C were not successful. It is worth adding that steric congestion in trialkyl-substituted phenyl ketones, e.g., 2,4,6-triethylbenzophenone, has been known to enhance cyclization of the intermediate dienols.[6,29]

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(17) Colorless solid: IR (KBr) cm^{-1} 3286, 2923, 1439, 1140, 1059; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 3H), 2.82 (d, J = 14 Hz, 1H), 3.41 (dd, J = 14 Hz, 1H), 3.79 (s, 3H), 5.12 (d, J = 3 Hz), 6.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 41.53, 56.46, 68.6, 102.8, 112.8, 133.7, 138.8, 143.5, 156.8.

(18) Bromophenyl ketones are known to undergo photoinduced C−Br bond cleavage; see: Wagner, P. J.; Sedon, J. H.; Gudmundsdottir, A. *J. Am. Chem. Soc.* **1996**, *118*, 746. Although this process may be competitive in **1b** and **2b**, we believe that the recombination of the radicals to the precursor aldehydes would be faster in the solid matrix.

(19) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

(20) Ito, Y. *Synthesis* **1998**, 401.

(21) Scheffer, J. R.; Pokkuluri, P. R. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991; Chapter 5, p 185.

(22) The solution-state photochemistry of simple *o*-tolualdehyde is marked by the formation of a variety of products; see: Findlay, D. M.; Tchir, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 514. Arnold, B. J.; Mellows, S. M.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 401.

(23) The detailed crystal structure analyses of **1b** and **1c** will be reported elsewhere.

(24) The geometrical parameters for γ-hydrogen abstraction (Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885) calculated from X-ray structural parameters fall in the range generally observed. Thus, the γ-hydrogen abstraction, the primary event, is facile for both **1b** and **2b**.

(25) Ito, Y.; Kawatsuki, N.; Giri, B. P.; Yoshida, M.; Matsuura, T. *J. Org. Chem.* **1985**, *50*, 2893.

(26) Ito, Y.; Kano, G.; Nakamura, N. *J. Org. Chem.* **1998**, *63*, 5643.

(27) Coll, G.; Costa, A.; Deya, P. M.; Flexas, F.; Rotger, C.; Saa, J. M. *J. Org. Chem.* **1992**, *57*, 6222.

(28) Dewar, M. J. S.; Zeobish, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3092.

(29) Kitaura, Y.; Matsuura, T. *Tetrahedron* **1971**, *27*, 1597.

AM1 calculations predict the (*E*)-enol to be less stable than the cyclobutenol for **2b** as well as **2c**. However, the (*E*)-enol of **2c** is relatively more stable by 3.39 kcal/mol than that of **2b**. Evidently, the cyano-substitution leads to stabilization of the (*E*)-enol relative to the corresponding cyclobutenol. The observation of photochromism in **2c** suggests that the crystal lattice effects must outweigh the marginal energy difference (4.37 kcal/mol) in the energies of the enol and the cyclobutenol. Otherwise, the photochromism would not be observed.

In summary, we have demonstrated solid-state photochromism in carbonyl compounds through a simple design of substrates. It is shown that *o*-anisaldehydes capable of stabilizing (*E*)-enols through intramolecular hydrogen bonding exhibit reversible photochromism. The stabilization appears to be so pronounced that the enols are remarkably persistent for hours to permit spectral characterization. Such a long lifetime of the *o*-xylylenols is unprecedented. That the photobehavior of substrates devoid of any mechanism to stabilize the photoenols can be at variance is seen from the reactivity of *p*-anisaldehyde **2b**, which cyclizes to cyclobutenol **7b**. AM1 calculations show that cyano-substitution in **2c** leads to stabilization of its (*E*)-enol as compared to that of **2b**. The observation of photochromism in **2c** suggests that its crystal lattice effects outweigh the unfavorable marginal difference in the energies of enol and cyclobutenol in favor of the former.

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Supporting Information Available: Photolysis procedure, a perspective view of the molecular structures of **2b**, tables of crystallographic data, atomic coordinates, and isotropic and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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