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Supplementary Material Available: Tables of atom coordinates, thermal parameters, and mean planes (7 pages); calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

Rediscovery of Photochromic Osazones: Photochromism and Molecular Structure of Mesoxaldehyde 1-Allyl-1-phenyl-2-phenylosazone[1]

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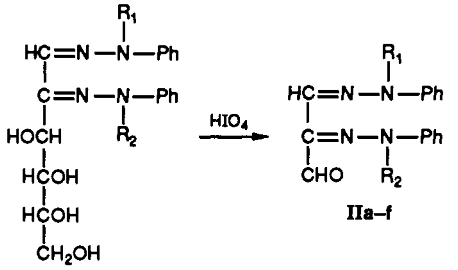
Abstract: A new photochromic family of osazones has been rediscovered. Mesoxaldehyde 1-allyl-1-phenyl-2-phenylosazone (IId) is photochromic both in solution and in the solid state. A pale yellow solution of IId changes to an orange solution when exposed to light. The exposed solution reverts to its original color with the addition of either acid or base. The decoloration is an acid–base-catalyzed reaction with clean first-order kinetics. The three-dimensional molecular structure of the unexposed crystal was determined by the X-ray crystallography. The presence of a planar chelate ring has been confirmed for the structure of the osazone. A hydrogen-transfer tautomerism in the chelate is a possible mechanism for the osazone photochromism.

The recent rapid growth in the study of erasable, optically read, and written memories demands the development and reassessment of what is known about photochromic substances. Photochromic substances were extensively reviewed by Brown in 1971.[3] Although some classic osazones are known to be photochromic in the solid state,[4] there has been no study carried out on photochromism of the osazone derivatives since one of the authors (ST) reported on their "phototropy" in 1952.[5] Mesoxaldehyde derivatives of osazones (II, Scheme I), prepared at that time, have been preserved for 40 years. The present paper reports our reinvestigation of the photochromism and the crystal structure of one of these compounds, mesoxaldehyde 1-allyl-1-phenyl-2-phenylosazone (IId).

Experimental Section

Materials and Methods. The series II was synthesized from glucosazones (I) by oxidation with 3 molar equiv of periodic acid as shown in Scheme I. Synthesis and chemical data for all of II have been reported,[5] and some of them, IIc, IId, and IIf, are photochromic in the solid state. We focus on IId in the present paper. The photochromic properties and the molecular structure of some other derivatives will be reported elsewhere.[6] The melting point (112 °C) of IId has been reconfirmed. Dichloromethane was distilled from CaH_2. All other reagents were obtained commercially and used without further purification.

Scheme I



Ia–f **IIa–f**

	R_1	R_2
a	H	H
b	CH_3	CH_3
c	CH_3	H
d	$CH_2CH{=}CH_2$	H
e	C_2H_5	H
f	n-C_4H_9	H

A stock solution of IId in dichloromethane was prepared and stored in the dark. The sample solutions were prepared by using the stock solution and were adjusted from 20 to 100 μM in IId concentration in a 1-cm quartz cell. Irradiation was carried out with light from a 500-W xenon short arc Wacom lamp filtered by a Toshiba C-39A glass filter (transmission maximum 390 nm, 64%) on the sample solutions. The incident light intensity of 2×10^{16} quanta cm^{-2} s^{-1} was determined by potassium ferrioxalate actinometry. UV–vis spectra were recorded on a Shimadzu UV-2100 spectrometer.

X-ray Diffraction. Diffraction data were measured with graphite-monochromated Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. The θ–2θ scan technique was used with a variable scan rate. Crystal data are as follows: $C_{18}H_{18}N_4O$ fw = 306.4, monoclinic, a = 18.868 (4) Å, b = 5.350 (1) Å, c = 17.198 (2) Å, β = 108.54 (1)°, V = 1646.1 (77) Å^3, Z = 4, space group $P2_1/c$, ρ_{calcd} = 1.236 g/cm^3, 1177 observed data to 2θ = 50.0°, temperature = 20 ± 1 °C. The structure was solved and refined by using the SDP software package from Enraf-Nonius: R_1 = 0.094, R_2 = 0.087.

Results and Discussion

Photochromism of IId in Solution. When a pale yellow solution of IId (3.6×10^{-5} M) in dichloromethane was irradiated near its main absorption band (λ_{max} = 413 nm, ϵ = 20 100 M^{-1} cm^{-1}) at room temperature, the spectrum changed, and new absorption bands at longer wavelength (λ_{max} = 457 nm, ϵ = 19 000 M^{-1} cm^{-1}) appeared (Figure 1). The conversion to the colored form was completed within 2 min in dilute solution with clean isosbestic

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(1) The nomenclature in this paper is in accord with ref. 2, while the correction of the chemical structure of ref 5 has been made, cf.: Tejima, S. *J. Pharm. Soc. Jpn.* **1957**, *77*, 673.

(2) (a) Mester, L.; Major, A. *J. Am. Chem. Soc.* **1957**, *79*, 3232. (b) Chapman, O. L.; King, R. W.; Welstead, W. J., Jr.; Murphy, T. J. *J. Am. Chem. Soc.* **1964**, *86*, 4968.

(3) Brown, G. H. In *Techniques of Chemistry, Vol. III, Photochromism*; Brown, G. H., Ed.; Wiley-Interscience: New York, 1971; p 1. (See, also, other chapters in this book.)

(4) References cited: Exelby, R.; Grinter, R. *Chem. Rev.* **1965**, *65*, 247.

(5) Akiya, S.; Tejima, S. *J. Pharm. Soc. Jpn.* **1952**, *72*, 1574, 1577, 1580; *Chem. Abstr.* **1953**, *47*, 9275g.

(6) A preliminary account was presented at the 110th Annual Meeting of the Pharmaceutical Society of Japan: Hatano, K.; Uno, T.; Kato, K.; Takeda, T.; Chiba, T.; Tejima, S. Abstract 21C 10-00, Sapporo, Japan, 1990.

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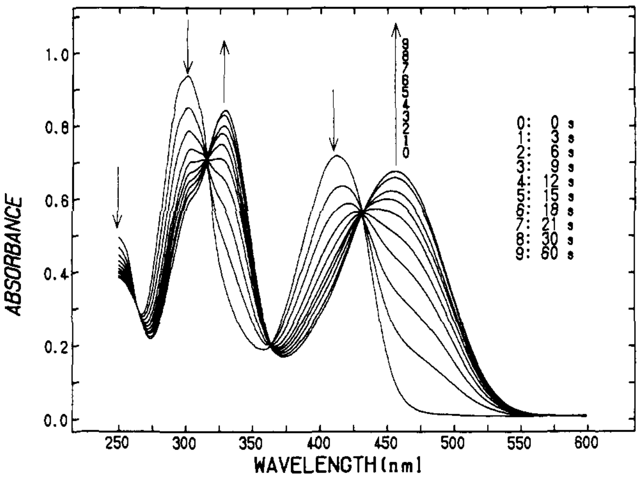


Figure 1. Absorption spectra of IId in CH_2Cl_2 (3.6×10^{-5} M) showing photochromic conversion. Irradiation times from 0 to 60 s displayed.

points during the photolysis by the incident continuous UV light. The colored form was stable in the dark at room temperature. More than 90% of the colored form usually remained after a day. The quantum yield was about 0.2 for this photochemical conversion, and there was no competing reaction of significance. Therefore, the conversion to the colored form is essentially quantitative in dilute solution. With the addition of triethylamine (2.3×10^{-4} M) to the colored solution, the spectrum returned to its original form with a half-life of 6.9 min at 20 °C. With use of this mixture, several photochromic on–off cycles could be accomplished without significant loss of the substrate and triethylamine; i.e., after 10 cycles of light-on (2 min) and bleaching (30 min), the same steady-state concentration of the colored form and the same bleaching rate as those of the first cycle were observed within the experimental error. Thus, there are no "yo-yo" effects[7] in several photochromic cycles of the IId–triethylamine system. Thus the reversible photochromism of IId *in solution* is first observed. The addition of dichloroacetic acid (1.3×10^{-4} M) into the colored solution also accelerated the decoloration (half-life = ca. 4 min). It has been observed that the decoloration of IId is a thermal process with clean first-order kinetics and is catalyzed by either acids or bases. A complete systematic and comparative analysis of the reaction kinetics of the photochromic osazones in solution is in progress along with the characterization of the colored species.[6]

The Solid State Behavior and Description of the Crystal Structure. IId is photochromic in the solid state. In order to obtain mechanistic insight about the solid-state photochromism, the molecular structure of IId has been determined by X-ray crystallography. During the X-ray data collection in the dark, exposure to Mo Kα radiation for about 50 h did not cause any apparent color change of the crystal. After the data collection, the crystal was exposed to sunlight for 30 min. The color changed to red.[8] Although the red crystal kept its color for weeks in the dark at room temperature, the original color was recovered when it was heated at 90 °C for 1 day. Thus, the photochromic property and the insensitivity to X-ray radiation in the solid state is confirmed.

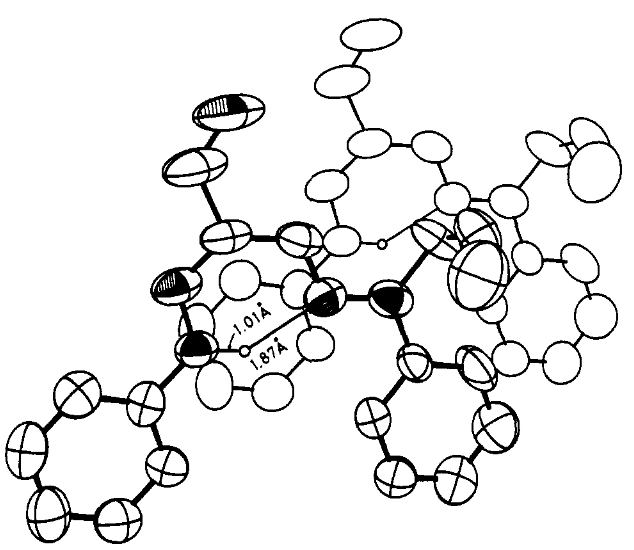
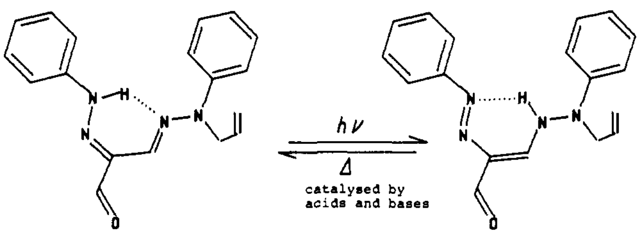


Figure 2. A perspective view of the IId molecule. Also shown is another stacking molecule; the heavy and open bonds are related by a translation along the *b* cell dimension (x, $y \pm 1$, z). Octant shaded ellipsoids are heteroatoms, and all thermal ellipsoids are 50% probability. All hydrogens are ommitted for clarity except for a chelating hydrogen which is shown as an arbitrary circle.

Scheme II



The molecular structure could be solved and refined routinely. Figure 2 shows, we believe, the first three-dimensional molecular structure for osazones.[9] The molecule exhibits an entirely flat osazone moiety and a coplanar conformation of the two phenyl rings. The major perpendicular deviations from the mean plane of 21 atoms (all the non-hydrogen atoms except for the vinyl group) are found to be 0.20 Å at the oxygen atom and −0.11 Å at the root carbon of the allyl group. The molecules stack parallel along the *b* cell dimension; this feature can also be outlined in the plot of two molecules. The distance between the two mean planes is 3.31 Å. An intramolecular hydrogen bond (bond distances using partially refined hydrogen are inserted in Figure 2) makes a chelate structure, which was first suggested by the Fiesers for the osazones.[10] The N–N bond length in the chelate ring, 1.313 (7) Å, is considerably shorter than the other N–N bond length, 1.35 (1) Å, suggesting a conjugated osazone chelate system. Atomic coordinates and individual bond lengths and bond angles are given in tables in the supplementary material.

The red exposed crystal diffracted as well as the unexposed one, but the essentially same structure as the original one was found from the diffraction data. Although the significance of the observed subtle differences in the structure factors of two forms is foregoing to be discussed here, an important point to be noted for the photochromism of IId in the solid state is as follows: The average depth of the colored layer on the crystal surface is estimated to be, at most, several micrometers thick, on the basis of the absorption coefficient and molar density in solution. This estimate corresponds to a small percent in the bulk of the small crystals used for the examination. It has experimentally been confirmed by dissolving the red crystals in CH_2Cl_2 for the spectroscopic quantitative analysis of the colored form. Therefore, the coloration of molecules in the crystal was limited to a short depth on the crystal surface with only a few thousand molecular layers. The generation of the colored form in the crystal is thought to occur near the surface but under the constraint of the original crystal lattice, i.e., the positions of the principal atoms in the

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(7) Bertelson, R. C. In *Techniques of Chemistry, Vol. III Photochromism*; Brown, G. H., Ed.; Wiley-Interscience: New York, 1971; p 130.

(8) The reflectance spectra of the powder sample dispersed in $BaSO_4$ were recorded on a Shimadzu UV-2100 spectrometer equipped with an integrating sphere assembly (ISR-260). The unexposed form showed an absorption maximum at about 425 nm in the visible, while the exposed form showed a shoulder absorption around 510 nm tailing nearly to 700 nm.

(9) Two-dimensional structure: Bjamer, K.; Dahm, S.; Furberg, S.; Petersen, C. S. *Acta Chem. Scand.* **1963**, *17*, 559.

(10) Fieser, L. F.; Fieser, M. *Organic Chemistry*; D. C. Heath and Co.: Boston, MA, 1944; p 351.

colored form should be maintained to be similar with those in the original form.

Tautomeric Switch of the Photochromic Osazone. Given the crystal structure and the photochromic characteristics above, a currently proposed mechanism for IId is a proton transfer in the chelate ring. The tautomer formed with the proton transfer upon light irradiation, formally, has an azo–phenyl chromophore which is not formulated in the original form (Scheme II). The hypsochromic shift of the colored form relative to the original osazone could be interpreted as being due to a conjugated phenylazo system of the osazone, as has been similarly discussed from the spectra of a related osazone group of dehydro-L-ascorbic acid phenylosazone.[11] The aldehyde and the allyl (or alkyl) groups are reported to be essential for the manifestation of photochromism of the osazone derivatives;[5] those groups may be playing a vital role in stabilizing the colored tautomer. It is possibly a new mechanism for a chelate hydrogen acting as a simple "switch" of the photochromic cycles. We expect that the rediscovered class of photochromic osazones will be subjected to further study because of the simplicity of the mechanism and the potential usefulness in various applications.

Acknowledgment. We are greatly indebted to Professor W. R. Scheidt (Notre Dame) for helpful advice on some aspects of this paper.

Registry No. IId, 132127-03-8.

Supplementary Material Available: Figure S1 displaying the atom labeling scheme and tables of atomic coordinates, anisotropic temperature factors for non-hydrogen atoms, and individual bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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Mechanism of Thiazolidine Hydrolysis. Ring Opening and Hydrolysis of 1,3-Thiazolidine Derivatives of *p*-(Dimethylamino)cinnamaldehyde

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Abstract: The hydrolysis reactions of 2-(*p*-(dimethylamino)styryl)-1,3-thiazolidine and the corresponding *N*-butyl and *N*-phenyl derivatives in the pH range 1–12 proceed via the iminium ion intermediate formed in an equilibrium ring-opening reaction. Such an intermediate was detected spectrophotometrically (λ_{max} = 480–525 nm). The fast formation of the iminium ion in ring opening of the *N*-phenyl-1,3-thiazolidine could be monitored at pH 3–10. Ring opening involves a pH-independent reaction at pH >4, which proceeds 2.25-fold slower in D_2O than in H_2O, and hydronium ion catalysis at low pH. General acid catalysis in ring opening was observed with acetic acid buffers. Ring opening of the *N*-butylthiazolidine occurs 250-fold more rapidly than with the *N*-phenyl derivative. The plot of log k_0 vs pH for aldehyde formation from the *N*-butyl-substituted thiazolidine has five unit changes in slope. The hydrolysis reactions subsequent to ring opening proceed with (a) attack of OH^- on the zwitterion (ionized thiol group) at high pH, (b) attack of OH^- on the positively charged species (un-ionized thiol group) at pH <10 (or the kinetically equivalent attack of water on the zwitterion), (c) attack of water on the positively charged species at pH <5, and (d) attack of water on the protonated dipositive species at low pH. There is an apparent p*K* of 6.3 in the hydrolysis reactions (aldehyde formation) of the *N*-butyl-substituted thiazolidine, which is a complex constant governing the reversible ring opening and protonation. The stability of the iminium ion intermediate has great influence on the shape of the pH–rate constant profiles and the interpretation of the apparent p*K* values. The hydrolysis of 2-(*p*-(dimethylamino)phenyl)-*N*-acetyl-1,3-thiazolidine at 90 °C is pH independent from pH 1–4 and hydronium ion catalyzed at pH >4. The reaction involves rate-determining ring opening, which is due to the poor stabilization of the developing carbonium ion when there is an *N*-acetyl substituent.

The hydrolysis reactions of acetal analogues in which oxygen has been replaced by nitrogen or sulfur have been actively studied in our laboratory[1-10] and others,[11-17] because such reactions can have great utility in shedding light on the mechanisms of specific and general acid catalyzed processes. Also compounds of these general types have important biochemical counterparts. We have previously investigated the reactions of cyclic acetals and acetal analogues having a 5-membered ring such as 2-substituted 1,3-dioxolanes,[10,18-22] 1,3-oxathiolanes,[1,10] 1,3-oxazolidines,[4,5] and 1,3-imidazolidines,[6-9] i.e., O,O, O,S, O,N, and N,N derivatives.

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