from 4 to 11 times the total surface area of the drops that carried the material. This suggests that the drops carry a compressed film when they leave the surf zone.

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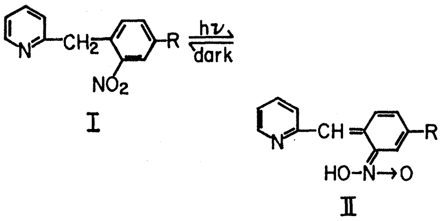
13. A. H. Woodcock, D. C. Blanchard, C. G. H. Rooth, *ibid.*, p. 159. I have calculated that the efficiency of collection of the wire at the windspeeds that were observed, 2 to 4 m/sec, exceeded 70 percent for drops greater than 4 μ in radius. It was only about 5 percent for drops of 1-μ radius. But this is of little concern since about 98 percent of the mass of the droplet spectrum is in drops greater than 4 μ in radius. These drops were estimated to be in concentrations of the order of 100 per cubic centimeter.
14. This is contribution No. 1523 from the Woods Hole Oceanographic Institution. The work was supported by ONR contract Nonr 4035 and, in part, by NSF grant GP 2296.

17 August 1964

Photoisomerism: A Colorless Photoinduced Intermediate of o-Nitrobenzylpyridine

Abstract. *Exposure to light of* o-*nitrobenzylpyridines at −185°C yields a long-lived colorless intermediate which is converted to a colored isomer on warming.*

Recently several investigators have reported on the photochromic behavior of substituted nitrobenzylpyridines (I) (*1*) and related compounds (*2*) having in common a nitro group ortho to an R_3CH group. When these compounds are exposed to light a colored isomer is formed, with a lifetime that depends upon structure and physical state. The formation of the colored isomer (II) has been interpreted as a tautomeric shift, I ⇌ II:



I

II

During studies on the photochromic behavior of these compounds incorporated in solid plastic matrices, we observed upon irradiation at −185°C that the usual color formation did not occur; but when the plastic discs were allowed to warm somewhat in the dark the colored isomer did develop. When the disc was recooled at this point, bleaching did not occur. On further warming, but at a temperature still below room temperature, the color slowly faded and the original colorless disc remained.

These observations provide evidence for the formation of a long-lived, colorless, photoinduced species at −185°C, which then changes to the colored isomer II on warming; on further standing it reverts to the original colorless form I.

The following experiments were designed to show the existence of the colorless intermediate. The photochromic compounds, 2-(2,4-dinitrobenzyl)-pyridine and 2-(2-nitro-4-cyanobenzyl)pyridine, were prepared (*1*) and purified by repeated crystallization from ethanol. A mixture of diethyl ether, isopentane, and absolute ethanol (EPA) (5 : 5 : 2 by volume) at room temperature was used as the solvent; this gave an optically clear glass at −185°C. A concentration of $2.64 \times 10^{-4}M$ 2-(2-nitro-4-cyanobenzyl)pyridine was used in the EPA glass.

Polymethyl methacrylate (PMMA) discs were prepared by polymerizing methyl methacrylate monomer containing the photochromic compound in solution. The discs contained 0.050 mole of the dinitro compound per liter, or 0.054 mole of the cyano-derivative per liter.

Potassium bromide discs were prepared by grinding 0.30 g of spectroscopic grade KBr with 0.24 mg of 2-(2,4-dinitrobenzyl)pyridine and pressing in the usual manner.

Dinitrobenzyl pyridine was incorporated in polyvinyl alcohol (PVA) by adding an alcohol solution of the pyridine derivative to an aqueous solution of polyvinyl alcohol and filtering through a fine sintered-glass filter. The clear filtrate was evaporated on a quartz disc, and a clear film was obtained.

Irradiations were performed in a cryostat (*3*). The sample discs were mounted as windows on a 2.5-cm sample cell against a reference disc of similar material but which contained no photochromic compound. All exposures were made at −185°C except when otherwise stated. The samples were exposed to an unfiltered quartz mercury lamp (*4*) for 5-second periods, followed by 15-second dark periods to minimize heating (Figs. 1 and 2).

After exposure, the cryostat was quickly transferred to the sample compartment of a spectrophotometer (*5*), and the absorption spectra were measured. The temperature of the sample disc was then slowly raised, and development of the colored isomer was recorded continuously at its wavelength maximum. Measurements of temperature were made by a copper-constantan thermocouple inserted in a well drilled into the disc. The spectrum was recorded (Figs. 1 and 2) when the color intensity reached a maximum; further warming resulted in a gradual discharge of the color.

The absorption spectra of 2-(2,4-dinitrobenzyl)pyridine incorporated in polyvinyl alcohol before and after color formation is shown in Fig. 1. When the irradiated sample was gradually warmed, a band developed at 585 mμ and reached a maximum intensity at −91°C, as shown in the third curve. No fading of color was measurable at this temperature during a 2-hour period, probably because of the extremely slow rate of the back reaction. However, at temperatures above −91°C the band at 585 mμ began to fade.

In Fig. 2, the colored forms are shown in the visible region for 2-(2,4-dinitrobenzyl)pyridine in KBr and in

Table 1. Absorption maxima of colored form of irradiated benzylpyridine derivatives.

Matrix	Absorption (mμ)			
	λ₁	λ₂	λ₃	λ₄
		NO_2		
PMMA	567			
PVA	585	260		
KBr	610			
		C≡N		
PMMA	580	450	405	
EPA	590	450	405	225

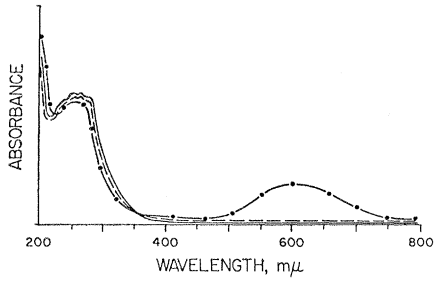


Fig. 1. Ultraviolet and visible absorption spectra of 2-(2,4-dinitrobenzyl)pyridine in PVA: spectrum at −185°C before irradiation, —; spectrum at −185°C after irradiation for 120 seconds at −185°C, - - -; spectrum of colored form at −91°C after irradiation for 120 seconds at −185°C, -•-•.

polymethyl methacrylate, and for 2-(2-nitro-4-cyanobenzyl)pyridine in polymethyl methacrylate. Maximum intensity of the colored form developed at −47°C for either compound in polymethyl methacrylate.

The stability of the colorless intermediate was shown by an experiment in which a polymethyl methacrylate disc containing dinitrobenzylpyridine was irradiated in a liquid-nitrogen bath and maintained at this temperature overnight (16 hours). When it was allowed to warm, a blue color developed showing that the colorless intermediate had a long lifetime at liquid-nitrogen temperature (Table 1). Included in Table 1 are the data for 2-(2-nitro-4-cyanobenzyl)pyridine in EPA glass, in which an intermediate was also formed.

We believe that reaction I → II proceeds only by way of the intermediate, but that the fading reaction occurs by way of II → I directly. Since the intermediate is formed photochemically, it must exist at room temperature. However, its conversion to the colored form is so fast at room temperature that we have not been able to measure the reaction in solid or solution by means of flash photolysis.

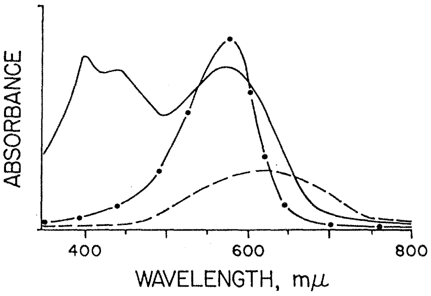


Fig. 2. Visible absorption spectra of: 2-(2,4-dinitrobenzyl)pyridine in PMMA at −47°C after irradiation for 30 seconds at −185°C (-•-•) and in KBr at 15°C after irradiation for 40 seconds at −185°C (- - -); 2-(2-nitro-4-cyanobenzyl)pyridine in PMMA at −47°C after irradiation for 30 seconds at −185°C (—).

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10 August 1964

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Thermochemical Etching Reveals Domain Structure in Magnetite

Abstract. *Single crystals of magnetite were prepared for study of the magnetic domain structure by etching in a molten mixture of boron oxide and lead oxide. The domain pattern on a (110) surface shows 71°, 109°, and 180° Bloch walls. The intensity of remanent magnetization is much less than the saturation value.*

Magnetite, the principal magnetic mineral, has long defied investigation of its magnetic domain structure. Crystals, both natural and synthetic, rarely have the surface perfection necessary for direct observation of the domain form. The electrical conductivity, which is low relative to that of the ferromagnetic metals, hinders the use of electrolytic polishing (*1*). The opacity precludes using the Faraday effect in thin sections as has been done on ferrimagnetic garnets and some ferrites.

Remeika in 1962 proposed that a strain-free surface on ferrites and some other crystals could be prepared by etching in a mixture of boron and lead oxides (1:10 by weight) (*2*). This etchant is suitable for revealing the magnetic domain structure of magnetite (Fe_3O_4). The etched surface can be treated with a colloidal suspension of Fe_3O_4, the so-called Bitter technique (*3*), and the domain boundaries or Bloch walls can be observed through a reflected-light microscope.

The magnetite crystal form is commonly the octahedron. The naturally occurring {111} faces do not contain an easy direction of magnetization, and hence their domain boundary patterns are complicated by the occurrence of "closure domains"—domains which form at some oblique angle to both the surface and to the interior directions of magnetization. [A study of these closure domains was made by Sugiura (*4*), who inferred that the internal domain structure of magnetite was similar to that of nickel.]

To study the internal domain structure of magnetite, natural crystals were cut into triangular prisms having {110} planes for sides and length parallel to a [[111]] direction. Saw abrasion was removed by polishing each prism with 000 emery. The application of the Bitter technique at this stage revealed only a set of closely spaced lines, the effect of residual surface strain.

One of the prisms, with sides 2 mm long and 1.5 mm wide, was then placed in a platinum crucible with about 0.1 g of etchant per square millimeter of crystal surface. The crucible was heated to 650°C for 10 minutes, a period sufficient to remove the strain induced by polishing, a layer about 30 μ thick. The crucible was agitated constantly to eliminate localized attack on the crystal. If the etching was carried out at too high a temperature, etch pits developed rapidly, especially at sites of inhomogeneity in the crystal.

After the required time, the crucible was removed from the heat and cooled in air to room temperature. The solidified etchant, a yellow glass, was removed from the surface of the crystal by dissolving the entire mass in warm $3N$ nitric acid; the freed crystal was then washed in hot distilled water.

In order to ascertain whether any changes in the lattice structure or composition of the crystal occurred during the etching process, Debye-Scherrer x-ray patterns were made before and after etching. FeK radiation was used with both a Straumanis-type cylindri-