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PHOTOCHROMIC CHELATING AGENTS

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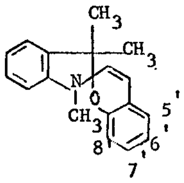
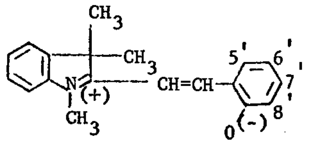
A recent communication described the synthesis and some properties of a photochromic spiropyran containing an 8-quinolinol chelating center.(1) We have also prepared some photochromic spiropyrans containing chelating functions and wish to record our preliminary work with these materials.

Spiropyrans with certain structural features are known to undergo reversible changes between colorless and colored forms with the application of either heat or light. The colorless "closed" form has the structure of a spiropyran, I, and the colored "open" form has the structural features of a merocyanine dye, II.(2)



I

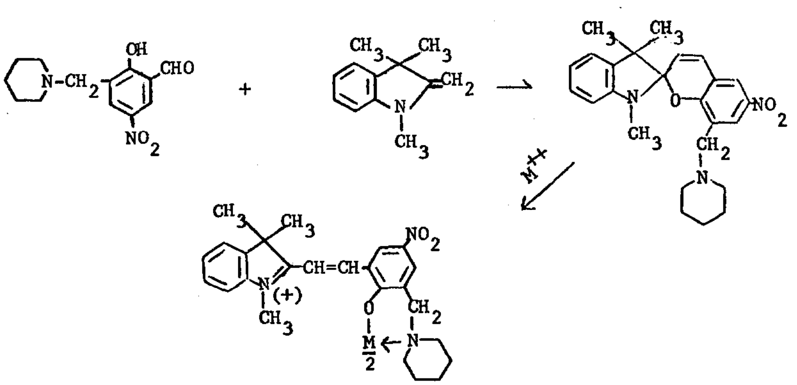


II

The position of the equilibrium is dependent upon both thermal and light exposure conditions. Another extremely important factor is the solvent polarity. In general non-polar solvents favor the closed colorless form while polar solvents favor the colored structure. The different colors one observes parallel the color-shifting of merocyanine dyes as a function of solvent polarity.(3)

In non-polar solvents such as benzene, the colored form which may be induced with exposure to ultraviolet light is readily reversed with the application of heat. In polar solvents such as ethanol, the opposite is true and the colored form may be generated by the application of heat alone. Lastly the position of the equilibrium is very sensitive to changes in the chemical structure of the spiropyran.(4) For example some compounds are only photochromic at very low temperatures in a particular solvent while analogues may be photochromic at room temperature in the same solvent. Conversely, changes in solvent polarities with one particular spiropyran may change the position of the equilibrium to the extent of rendering the compound inactive, it being either totally in the colored or uncolored form over a wide temperature range as well as over a wide range of light exposures.

Although the structure assigned to colored form II is only one possible isomer as well as being a resonance form (the other being a keto-amine form), the possibility of introducing a substituent such as an amino function, in the 8'-position, capable of forming a more stable colored form in the presence of metal ions, was considered. The model compound for our work was the very reactive 3-chloromethyl-5-nitrosalicylaldehyde.(5) This compound was chosen because the chloromethyl group enables one to easily prepare derivatives containing amino, hydroxyl or ether functions and the presence of the nitro group is well known for its ability to promote photochromism in spiropyrans. Thus condensation of a derivative of this compound, such as the piperidine product, with 1,3,3-trimethyl-2-methylene indoline yields a spiropyran with the chelating function in the 8'-position and a nitro group in the 6'-position.



Spiropyrans prepared from the chloromethyl intermediate were the piperidinomethyl (m.p. 154°), ethoxymethyl (m.p. 112-113°) and hydroxymethyl (m.p. 187-188°) derivatives substituted in the 8'-position. Satisfactory analyses were obtained for these compounds.

The piperidinomethyl compound was both photochromic and thermochromic in many solvents. It undergoes ready complexing with metal ions such as zinc, cobalt or cupric ion in solvents such as acetone-alcohol mixtures to yield orange or red solutions. The formation of this color is accelerated by both heat and light. Thus a solution at -40°C when treated with zinc or cobalt ion takes many minutes to change color. Irradiation of a second sample at -40° for 15 seconds with ultraviolet light readily produces the orange color when treated with metal ions. A control spiropyran without any 8'- substituent did not show the same behavior although this material can also form metal complexes of some sort. This behavior then is in keeping with the idea that the presence of the chelating function in the 8'-position leads to the formation of a colored complex which requires that the merocyanine form be generated. The rate of this process then will be related to the many interacting variables previously mentioned which control the amount of merocyanine form present, such as temperature, solvent polarity, chemical structure and ambient light. The presence of the metal ion simply adds a new factor favoring the formation of a chelated colored form.

In the case of the 8'-hydroxymethyl derivative some interesting observations were made. This compound could be prepared as either a white or a dark purple solid. In solvents such as ethanol or acetone it is not photochromic and exists in the colored form as a purple solution. In toluene it is colorless and photochromic. When cobalt ion is added to the ethanol solution, an orange complex initially forms; the color fades to colorless but it may be regenerated with heat but not light. In the case of zinc ion, a wine complex initially forms which fades with the application of heat but regenerates upon exposure to ultraviolet light. Thus we find that it is apparently possible to create complexes which can render materials photochromic or thermochromic in solvents in which they originally were not.

Because of the many interacting variables in this type system, careful measurements must be made to remove some obvious ambiguities. However the behavior noted thus far is in keeping with the notion of photochromic chelating agents.

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