confirms the presence of a plasma torus resembling in many respects the 1979 Voyager picture. These observations extend the Voyager snapshot in time, and a number of important regularities have been seen. Earth-based observations can bridge the gap between Voyager and future spacecraft measurements. The planned tour of the Jovian system by the Galileo spacecraft in 1989–1990 will provide a unique opportunity to carry out extensive ground-based measurements in conjunction with an Io flyby and a yearlong spacecraft presence in the nebula.

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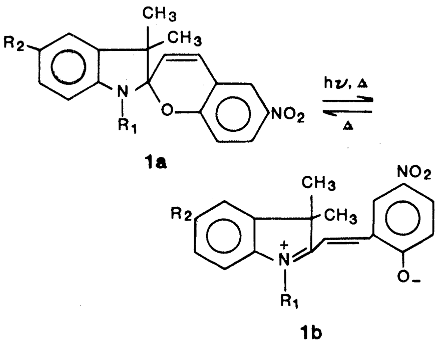
16 April 1984; accepted 16 July 1984

Photocontraction of Liquid Spiropyran-Merocyanine Films

Abstract. *Amorphous films of a photochromic spiropyran containing a mesogenic group melt, when exposed to heat together with irradiation, to yield a red fluid. This fluid contains aggregates of merocyanine molecules and exhibits marked contraction under light illumination. The mechanism of the photocontraction is dependent upon a specialized microstructure, which may be termed a "quasi-liquid."*

The reversible transformation of spiropyrans, **1a**, into merocyanine dyes, **1b**, determines the photo- and thermochromic properties of these compounds (*1*). This transformation is also responsible for the formation by these compounds of a variety of assemblies (*2–6*), based on the capability of the merocyanine dyes to give tightly bound giant molecular aggregates (*7*). These aggregates are molecular stacks of two types: H-aggregates, which exhibit an absorption that is blue-shifted relative to that of the nonaggregated dye, and J-aggregates, which exhibit a red-shifted absorption. The J- and H-aggregates have, respectively, parallel and antiparallel arrangements of the molecular dipoles in a stack.



1a

1b

One of the reported molecular assemblies is the "quasi-crystal" formed on photochromic conversion of spiropyrans into merocyanines in an electrostatic field. This consists of highly dipolar assemblies of molecular stacks of the J-type, covered by amorphous envelopes and forming submicron-sized globules aligned along the field (*2–4*). Polyvinyl macromolecules with spiropyran side groups give other types of assemblies with intra- and intermolecular stacking of merocyanine side groups in H-aggregates (*5, 6*).

Recently (*8*) we reported a new type of spiropyran-merocyanine assembly, termed quasi-liquid crystals, obtained from spiropyrans containing mesogenic groups (R_2 = –N=CHPhCOOPhX; X = $-OCH_3$, $-OC_6H_{13}$, –CN, where Ph is phenyl). These materials exhibit some features of conventional liquid crystals (birefringence and response to an electric field) but have completely different structure.

In a search for quasi-liquid crystals we synthesized spiropyran compounds **2** of the general formula **1a**, where R_1 = $-(CH_2)_6OOCPhOOCPhX$ and R_2 = –H. These T-shaped molecules, in contrast to the rod-like ones that form quasi-liquid crystals, do not exhibit mesophase properties. However, the melt of one of them, that with X = –CN, reveals a very unusual and intriguing photocontraction effect. This melt, produced by the irradiation and heating of amorphous films of the material, contracts markedly under irradiation.

The synthesis of spiropyrans **2** was from spiropyrans **1**, having R_1 = $-C_6H_{12}OH$ and R_2 = –H (*9, 10*), by direct esterification with acids XPhCOOPhCOOH (*11, 12*). The materials were purified by flash chromatography (*13*), the yields being about 60 percent. Yellow crystals of **2a** (X = –CN) and **2b** (X = $-OCH_3$) melt at 120° to 121°C and 118° to 119°C, respectively, to form fluids that are blue because of the presence of some merocyanine molecules formed spontaneously from the spiropyrans (*1*).

The amorphous films were obtained by fast evaporation of the solvent from a solution of the spiropyran in benzene on a glass surface, with subsequent removal of the residual solvent under vacuum. The grease-like films prepared in this way are metastable, and crystallization occurs after several hours (*8*).

The films were prepared between two cover glasses that were separated by spacers of aluminum foil and clamped together. For studies of the thermal behavior of the films, these "sandwiches" were placed on the hot stage of a polarizing microscope (Wild M8). When the films were heated at about 85°C, they were transformed to a fluid that was blue like the melts from the crystals.

Irradiation (nonfiltered light with an intensity of 10^{-6} to 10^{-7} einstein cm^{-1} sec^{-1} from an Osram HBO 200 mercury lamp) of the blue melt films of spiropyrans **2a** above 85°C produces red spots or stripes that disappear in the dark. However, if an amorphous film is irradiated during slow heating from room temperature to about 60° to 70°C, it acquires a uniform, stable, cherry-red color. This color does not disappear even at temperatures higher than 85°C. (In some cases several tiny spiropyran crystals appeared during preparation or storage of the amorphous films; irradiation led to the transformation of these crystals to cherry-red, birefringent, probably merocyanine, crystals that disappeared at temperatures higher than 85°C.)

The photocontraction effect occurs when a red fluid film is irradiated at temperatures in the range 85° to 150°C. Holes are formed in the middle of the film (Fig. 1). The net area of the film is reduced by 10 to 20 percent, depending on the film thickness and light intensity. The thicker the film, the less pronounced the effect. Since the spacing between the cover glasses is fixed, the percentage contraction in the volume of the film is equal to the percentage decrease in basal area.

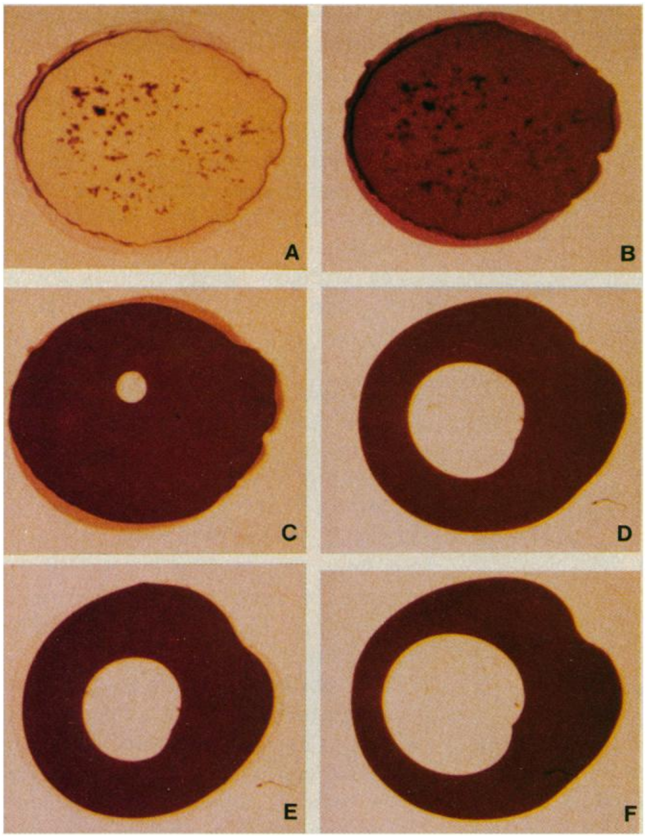


Fig. 1. Formation and contraction of the red melt film. (A) Amorphous film after evaporation of solvent at room temperature; thickness (distance between glass slides), 15 μm (×65). A number of spiropyran crystals can be seen. (B) Initial formation of the red phase, room temperature, 1 minute of irradiation. (C and D) Photocontraction during about 1 minute of irradiation, 85°C. (E) Healing of the hole in the dark, after 5 minutes. (F) Repeated photocontraction (14 percent), 3 minutes of irradiation.

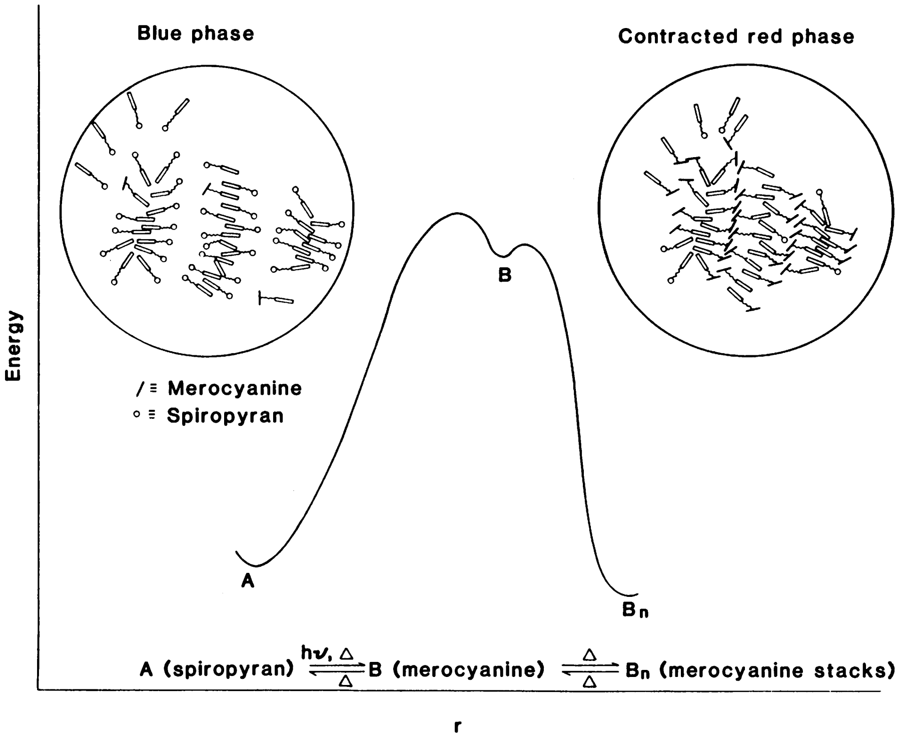


Fig. 2. Scheme of interconversions in the spiropyran-merocyanine melts.

On subsequent standing in the dark, the holes are healed while the outer perimeter decreases slightly, with a resulting net expansion of the film. The growth and healing of the holes lag after, respectively, the start and shut-off of the illumination. These lags on illumination by chopped light, at temperatures of 120° to 130°C, produce an effect that is reminiscent of the pulsation of unicellular organisms. However, after a number of such cycles the rates of contraction and expansion of a given film slow down, and eventually no volume changes are detected in finite observation times. The same behavior of the red melt was observed on a hydrophobic surface, prepared by treatment of a cover glass with a solution of trichloroctadecylsilane in bicyclohexyl.

Spiropyran **2b** and spiropyrans **1** with $R_1 = -C_6H_{12}OH$ and $R_1 = -C_6H_{12}O$-$COC(CH_3) = CH_2$ (*6*) form only blue melts and do not exhibit photocontraction. The melts of **2a** become rigid on fast cooling to room temperature, with preservation of color.

We obtained Debye-Scherrer patterns (Philips NR D1703 camera, Joyce MK IIIC automatic recording microdensitometer), using materials packed in capillaries of 0.5 mm inside diameter. These patterns for the cooled blue and red phases of **2a** show one diffuse halo with maximum intensity corresponding to an interplanar spacing d of ~5 Å. Crystals of **2a** give a typical crystalline diffraction pattern, the intense reflections corresponding to d = 9.61, 7.12, 5.24 (most intense), 4.46, and 3.54 Å.

The absorption spectra of the cooled blue (nonirradiated) and red (irradiated) films show that irradiation leads to a hypsochromic shift (from 590 to 550 nm) and to substantial enhancement of the absorbance. Separated merocyanine molecules in spiropyran solution and polymers have an absorption band with maximum at 590 nm; a band with maximum at 550 nm is typical of H-stacks (*5*, *14*). Thus, we conclude that the red melt contains H-stacked merocyanine. The fact that only the red melt exhibits photocontraction suggests that the presence of these stacks in the melt is essential for this effect.

The absorption spectra allow us to estimate roughly the merocyanine/spiropyran ratio in the films. The extinction coefficient of **2a** at the absorption maximum in benzene solution is 2×10^4 liter $mole^{-1}$ cm^{-1}, and for merocyanine we assume this coefficient to be 4×10^4 in both the blue and red phases (*1*). This gives a ratio for the red film before contraction approximately four times that for the blue one (30 and 7 percent, respectively).

The concentration of the merocyanine molecules in the blue fluid films is determined by the thermal spiropyran-merocyanine equilibrium. Irradiation of these films at temperatures higher than 85°C does not increase the concentration of the merocyanine molecules, because of the fast thermal back reaction (*1*). The low concentration of merocyanine makes formation of stacks improbable.

On the other hand, high concentrations of merocyanines and H-stacks are formed on irradiation and slow heating of a film from room temperature. This is probably determined by two factors: (i) the lower rate of thermal conversion of merocyanine to spiropyran at the lower temperature and (ii) the retardation of this reaction due to the organization of the merocyanines in the stacks. Very significant stabilization of transient merocyanines in H-stacks has been demonstrated in our recent studies (*6, 14, 15*). The thermal conversion of the stacked merocyanines to spiropyrans proceeds only at the ends of the stacks.

We believe that the red melt is a complex liquid system in which there are present spiropyran molecules, H-stacks, and separated merocyanine molecules, all interconvertible to one another (Fig. 2). Irradiation of this melt leads to an increase in the concentration of separated merocyanine molecules, and these have a good chance of joining the H-stacks already formed on irradiation at low temperature. This growth of the stacks inhibits the thermal back-conversion to spiropyran. Formation of the high-density stacks from loosely arranged bulky spiropyran molecules must lead to contraction of the fluid. The healing of the holes in the dark is determined by the tendency of the fluid to acquire a minimum surface and by the expansion of the films. The expansion is connected, apparently, with destruction of large stacks due to the thermal merocyanine-spiropyran conversion. Both photocontraction and the thermal expansion are controlled by processes occurring at the stack ends. Therefore, the rates of both the direct and back reactions are inversely proportional to the length of the stacks at a given merocyanine/spiropyran ratio. Long irradiation should bring about the accumulation of long stacks at the expense of short ones. This may provide an explanation for the decay of the effect on repetitive contraction-expansion cycles. Growth of the stack length must increase melt viscosity, which may also contribute to the decay of the photocontraction.

The x-ray diffraction patterns of the cooled red and blue melts show that in both cases we are dealing with noncrystalline materials. The patterns do not allow us to decide unambiguously whether **2a** preserves some remnant order after melting. The order, if any, must be poorer than in liquid crystals. Even in the case of liquid crystals, the x-ray diffraction patterns are not always distinguishable from those of the isotropic phases (*16*).

Substitution of the mesogenic group in spiropyrans **1** by other groups [$-C_6H_{12}OH$,$-C_6H_{12}OCOC(CH_3) = CH_2$] and even slight modification of the mesogenic group (methoxy instead of cyano group) lead to disappearance of the photocontraction effect. This points to the importance of this moiety. Further, a value of $d \sim 5$ Å, deduced from the halo in the x-ray pattern, is typical of the intermolecular distance in nematics having molecular structures similar to that of our mesogenic group (*16*). One may assume that mesogenic groups provide head-to-head positioning of the spiropyran moieties, which facilitates formation of merocyanine stacks (Fig. 2).

An interesting feature of the photocontraction is the formation of holes inside the film, with no decrease or a slight increase of the perimeter. The light that converts spiropyran to merocyanine penetrates only a very thin layer of the film (for example, the absorbance of a red film 10 μm thick is more than 10). Therefore, in order to achieve high conversions of spiropyran to merocyanine, there must occur some sort of convective flow that allows exposure to light of the material originally in the lower layers, leading to the formation of holes inside the film.

The suggested mechanism is a preliminary attempt to explain an astonishing phenomenon, the marked contraction of a liquid on illumination with light. Such an effect will occur only in a system having very special microstructure, which may appropriately be termed a "quasi-liquid."

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15 March 1984; accepted 18 July 1984

Temporal Variability of the Antarctic Circumpolar Current Observed from Satellite Altimetry

Abstract. *Sea level measurements by the Seasat altimeter were used to study the temporal variability of the Antarctic Circumpolar Current between July and October 1978. Large-scale zonal coherence in the cross-stream sea level difference was observed, indicating a general increase in the surface geostrophic velocity of the current around the Southern Ocean. The result demonstrates the power of satellite altimetry to monitor the variability of large-scale ocean currents.*

Recent observations (*1, 2*) have revealed that there are substantial temporal variations in the mass transport of the Antarctic Circumpolar Current (ACC). The magnitude of the variation (peak-to-peak range) has been estimated to be 40 sverdrups (1 Sv = 10^9 kg/sec), about 30 percent of the mean transport. ACC transport variations of this magnitude have profound effects on the circulation of the world's oceans, which are important determinants of the global climate (*3*).

Because synoptic global observations of the ACC are lacking, very little is known about the spatial structure of its temporal variability. For example, what is the zonal scale of the variability? Does