

Spectroscopic Properties of Organic Photoconductors. II. Specular Reflection Spectra of Cationic Dye Films

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would reveal emission where theirs failed to do so. No emission was detected, out to about 11 000 Å, the wavelength limit of our equipment and plates.

The interpretation given by Beer and Longuet-Higgins for the failure to observe phosphorescence is that the lowest triplet level lies *above* the lowest excited singlet level, and that radiationless transition between these effectively quenches phosphorescence.

We prefer to interpret the failure to observe phosphorescence in the azulenes studied as simply a matter of wavelength difficulties. We believe it rather likely that the *lowest* triplet, corresponding to the visible ($S' \leftarrow S$) absorption band, may lie in the infrared at wavelengths longer than 12 000 Å.

It is evident that much of the discussion of the observed results on azulene emissions hinges on the role of the lowest several triplet states of azulene.

None of these have been found thus far, but it is highly desirable that information on this point should be actively sought.

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Spectroscopic Properties of Organic Photoconductors. II. Specular Reflection Spectra of Cationic Dye Films

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The specular reflectivity of solid dye films has been measured at 12° incidence, by means of a new device attached to the Beckman Quartz Spectrophotometer. The observed spectra are in general agreement with the results of dispersion theory.

THE brilliant metallic reflection colors of solid dyestuffs have been known for nearly a century. Christiansen, Kundt, Pfüger, and other early workers established their origin in the strong fluctuations in refractive index, associated with intense absorption bands. Pfüger¹ confirmed the Helmholtz theory of "anomalous" dispersion by comparing directly measured refractive indices and extinction coefficients of solid fuchsin and cyanine with values computed from Brewster's angle of reflection polarization. From these data, Wood² later computed a reflection spectrum for cyanine. Curiously, however, it appears that, with one exception,^{3,4} the specular reflection spectra of solid dyes have never been measured directly.

In the course of absorption measurements on solid films of some photoconductive dyes⁵ it became necessary to correct for the strong variation in reflectivity which

accompanies and distorts each absorption band. A simple device was built, which permits one to make concurrent transmission and specular reflection measurements on identical samples. The results are presented in the present communication.

EXPERIMENTAL

In order to obtain films of reproducible structural and photoelectric properties, it was necessary to deposit them inside evacuated 1×1 cm square Pyrex cuvettes. The details concerning sample preparation have already been presented (I). Reflection measurements were carried out in a device attached to the Beckman quartz spectrophotometer (Fig. 1). Monochromatic light from the exit slit, approximately collimated by a small quartz lens, is reflected from the aluminized first face of a 102° isosceles prism⁶ onto the sample cell, striking the latter at 12° from normal incidence. The light reflected from the dye on the inside of face "B" (Fig. 2) is returned to the aluminized second leg of the prism, and thence transmitted to the photometer. Unwanted light, reflected from the clear "front" window ("F") of the cell, falls on a blackened

* This work was supported by the Charles F. Kettering Foundation.

¹ A. Pfüger, Wied. Ann. **56**, 412 (1895); **65**, 173, 214, 225 (1898).

² R. W. Wood, *Physical Optics* (The MacMillan Company, New York, 1934), third edition, p. 512.

³ W. H. Taylor, Z. Krist. **91**, 450 (1935); J. Soc. Chem. Ind. **13**, 732 (1935).

⁴ Scott Anderson, J. Opt. Soc. Am. **39**, 49 (1949).

⁵ J. W. Weigl, J. Chem. Phys. **24**, 364 (1956)—hereafter referred to as "I."

⁶ Made to order by the Wm. Buchele Optical Company, 1309 Milburn Avenue, Toledo, Ohio.

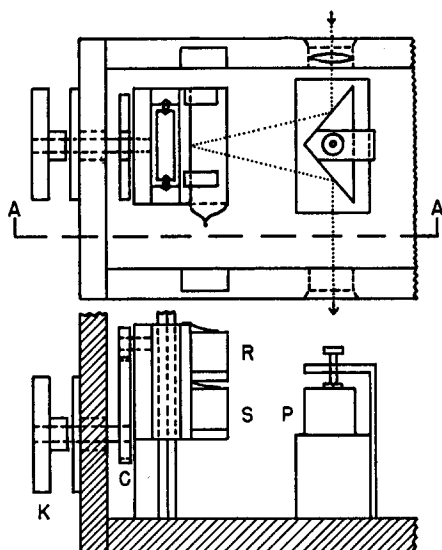


FIG. 1. Reflectometer attachment for Beckman Quartz Spectrophotometer. (a) Top view, indicating light path. (b) End view, cross section through $A-A$, with entrance wall not shown. P — 102° prism, R —sample, and S —standard cells, C —cam, operated by knob (K).

part of the prism, close to its apex. The sample is mounted above a standard cell on a carrier which may be alternately raised and lowered by means of a cam. The standard cell differs from the sample cuvette in that the inside of its back face ("B") has been aluminized. The height of the light beam is limited at the entrance window. Light losses are sufficiently low that the effective spectral band width for normal operation is only 10–30% greater than that used in transmission measurements of comparable sensitivity.

The standard cell is generally left in place on the carrier, but the position of each sample cell must be adjusted, prior to measurement, so that the light reflected from it falls on the same area on the phototube. For determination of the reflection at the *dye-glass* interface, sample and standard cells may be turned around, so as to let the light fall on the film through its glass backing, and moved 1.0 cm further from the prism. The prism must also be adjusted, so as to move the blackened area out of the reflected beam. The transmission of each sample was compared to that of a Pyrex blank, with the light entering through the front or back face of the cell, as desired.

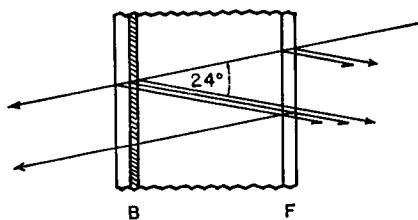


FIG. 2. Multiple reflections in sample cell. Dye is deposited on back face (B), front face (F) is clear glass.

CALCULATIONS

For our purposes, the reflectivity measured at 12° could be considered equal to that at normal incidence, which was encountered in absorption measurements.⁷ It was therefore possible to analyze the reflection and transmission data simultaneously, in terms of the following parameters⁸:

R_{of} , R_{ob} —ratio of light reflected from sample and standard (aluminized) cells, observed through front ("F") and back ("B") face, respectively.

T_{of} , T_{ob} —ratio of intensity transmitted through sample and standard (clear Pyrex) cells, measured with light incident through "F" and "B", respectively.

R_a , R_{ag} —absolute reflectivity of the standard aluminum surface, with light incident through "F" and "B", respectively; calibrated against a front-face aluminized mirror

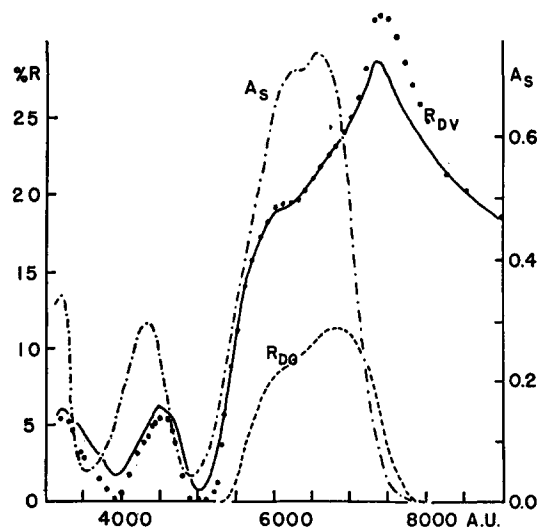


FIG. 3. Reflectivity of a thin, sublimed Malachite Green Film, at dye-vacuum (R_{dv}) and dye-glass (R_{dg}) interface. Round data points show R_f , the total film reflectivity seen from the front face. A_s is the absorbancy (or optical density) of this film.

R_g —reflectivity of a single glass-air interface, measured on a blackened half-cell ($=5.4\%$).

R_{gg} —combined reflectivity of both surfaces of a Pyrex window ($=8.5\%$).

R_{dv} —reflectivity of film at dye-vacuum interface.

R_{dg} —reflectivity of film at dye-glass interface.

R_f —reflectivity of film, viewed through the front face (mainly due to R_{dv}).

R_w —reflectivity of entrance window and monochromator ($=5\%$).

T_c —transmittance of Pyrex standard cell, measured vs air path (at $\lambda > 3500$ A, losses are due to reflection only).

T_d —internal transmittancy of the dye film, fully

⁷ I. Šimon, J. Opt. Soc. Am. 41, 336 (1951).

⁸ Subscripts o , f , b , a , g , d , v , and w refer to: observed, front, back, aluminum, glass, dye, vacuum, and window, respectively.

corrected for reflection losses (i.e., the fraction of light entering the film which emerges on the opposite side).

A_s —the absorbancy, or optical density, of the dye, ($A_s = -\log_{10} T_d$).

Figure 2 shows the rays considered in the calculations, except for the contribution from R_m .⁹ Only first- and second-order reflections are considered. Strong's data for aluminum¹⁰ were used to calibrate the standard reflection cell. Minor variations of R_g and R_{gg} with wavelength were neglected.

To a first approximation,

$$\begin{aligned} R_f &= R_{of}R_a - T_{of}^2 R_{gg}(1 - R_{of}R_a), \\ T_{df} &= 1.02T_0(1 - R_f)^{-1}(1 + R_fR_g)^{-1}(1 + R_fR_{gg} + R_fR_w)^{-1}, \\ T_{db} &= T_bT_c(1 - R_{ob}R_{ag} - \frac{1}{2}R_{gg})^{-1}(1 + R_{ob}R_{ag}R_w)^{-1}. \end{aligned}$$

One may calculate the separate reflectivities of the vacuum and glass interfaces of the dye by two, quickly

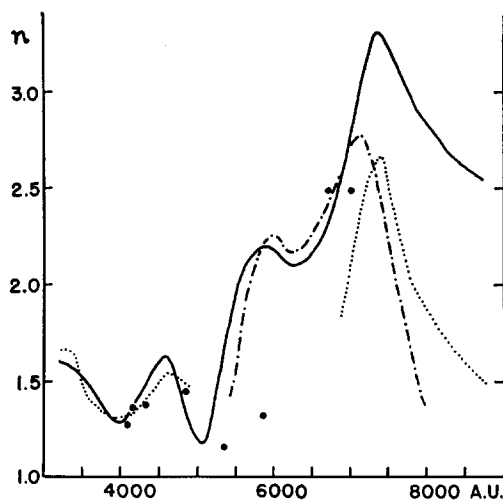


FIG. 4. Refractive index of Malachite Green: — calculated from R_{DV} of thin film (Fig. 3); - - - - - from R_{DG} of the same film; ····· from R_{DV} of a thicker film; • large dots represent data points of Pflüger.¹

converging, successive approximations:

$$\begin{aligned} R_{dv} &= R_{vd} = R_{of}R_a - R_{dg}T_d^2(1 - R_{dv})^2 \\ &\quad - R_gT_d^2(1 - R_{dv})^2(1 - R_{dg})^2, \\ R_{dg} &= R_{gd} = (1 - R_g)^{-2}(R_{ob}R_{ag} - R_g) - (1 - R_g)^2(1 - R_{dg})^2 \\ &\quad \times [R_{dv}T_d^2 - \frac{1}{2}(1 - R_{dv})^2T_d^2R_{gg}]. \end{aligned}$$

The evaluation of these quantities as a function of wavelength (every 20–100 Å), while still tedious, was greatly simplified by graphing the correction factors as functions of T_0 and R_0 . The general scheme of calculations was shown to be correct by the fact that the corrected absorbancy of the films went to zero at the absorption edge, and by the good agreement (within 1–4%) between T_{df} and T_{db} , calculated from independent measurements through the front and back faces

⁹ The exit slit jaws were blackened; the remaining reflection originated mainly at the plano-convex lens in the entrance window, mounted so that the convex side faced the sample.

¹⁰ John Strong, *Procedures in Experimental Physics* (Prentice-Hall, Inc., New York, 1938), p. 375.

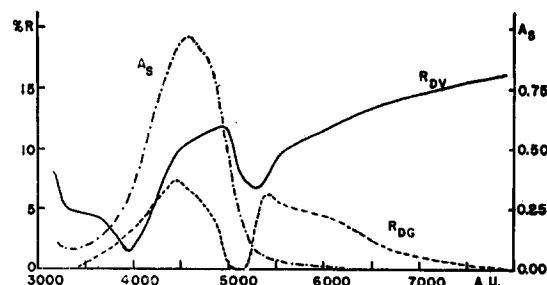


FIG. 5. Reflectivity and absorbancy of a sublimed tryptaflavin film.

of identical samples. R_{dv} and R_{dg} could be calculated separately only in the few cases where such concurrent measurements had been taken; however, as may be seen from Fig. 3, R_f may be considered to represent a good approximation to R_{dv} .

The refractive index was calculated from R_{dv} and R_{dg} and the extinction coefficients by the well-known formula:

$$R = [(n - n_0)^2 + \kappa_0^2] / [(n + n_0)^2 + \kappa_0^2],$$

where κ_0 is the (natural log) extinction coefficient per $\lambda/4\pi$, n is the real refractive index of the solid dye, and n_0 that of the adjacent medium (vacuum or glass).¹¹ From this follows:

$$n = n_0 \left(\frac{1+R}{1-R} \right) \pm \left\{ n_0^2 \left[\left(\frac{1+R}{1-R} \right)^2 - 1 \right] - \kappa_0^2 \right\}^{\frac{1}{2}}.$$

Only that solution in which the second term is positive has physical significance.

In order to evaluate κ_0 from the decadic molal extinction coefficients ϵ (see I), it was necessary to assume a density for the solid dye, there being no data available for the compounds of interest. For the chloride of malachite green it seemed reasonable to assume a molal volume of 0.35 l/mole, equal to that of crystal violet (I); this yielded a conversion factor $\kappa_0/\epsilon = 2.303\lambda/(0.35 \times 4\pi) = 0.525\lambda$ (for λ_{vac} in cm).

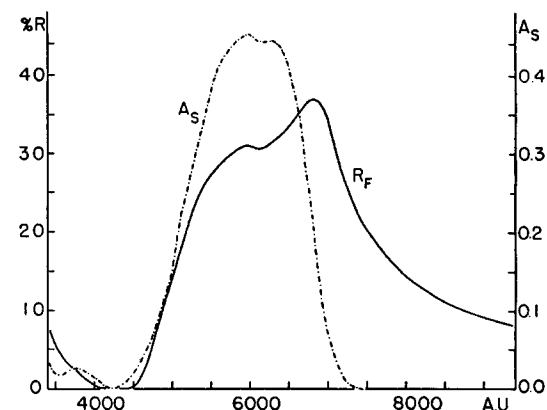


FIG. 6. Reflectivity and absorbancy of a crystal violet film, deposited from solution.

¹¹ For Pyrex glass 7740, $n_D \approx 1.474$, dispersion ≈ 67.0 (private communication, J. R. Bucher, Corning Glass Works, January 28, 1955).

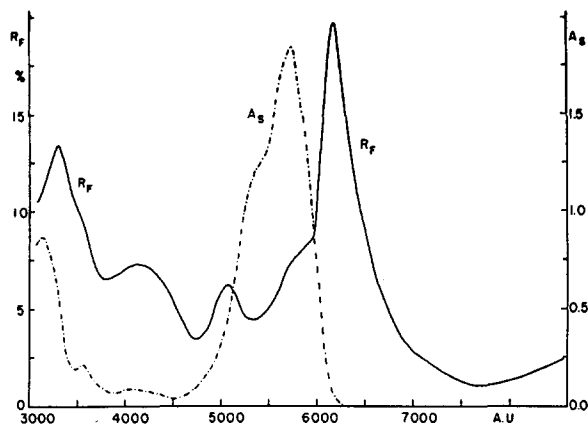


FIG. 7. Reflectivity and absorbance of a sublimed rhodamine B film.

RESULTS AND DISCUSSION

Figures 3-8 show typical specular reflection curves for a number of solid cationic dyes, together with the absorption spectra of the films measured. The reflection spectra bear a strong qualitative resemblance to what was expected on the basis of simple dispersion theory, including, of course, the appearance of a separate reflection peak for every absorption band, and a broadening of those reflection peaks associated with broadened absorption bands (I). The difference between the reflectance of the dye-glass and dye-vacuum interfaces, due to the refractive index of the adjoining medium, is very similar to that computed by Wood² for cyanine *vs* air and quartz. The differences in surface color of films viewed through their front and back faces are readily accounted for. For example, the front face reflection of malachite green films is always copper-red; when observed through the glass backing, *thick* films are golden-yellow, due to R_{dg} alone. *Thin* films viewed through the back face, however, assume a copper color, because the light *internally* reflected at the front face ($R_{va}=R_{dv}$) is not absorbed within the film, but emerges, instead, from the glass face, still brighter than R_{dg} . Analogous effects may be observed on other dyes.

For pairs of equally thick sublimed films of a given dye, both the intensity and shape of reflection peaks are very similar. However, increasing the thickness appears to lower the reflectivity, and films deposited from solution show a broader short-wavelength shoulder. This variation appears to stem largely from partially oriented thin surface layers, and makes it rather hazardous to compute bulk properties, such as refractive index, from surface colors. Two additional sources of systematic error in the refractive index calculations are: an uncertainty in the positioning of the sample cell, amounting to perhaps 10% R , and possible errors in the molar extinction coefficients and densities of the films (I), both of which are required for a calculation of κ_0 .

Refractive index computations were actually carried out only for two films of one dye, malachite green.

Both vacuum and glass interface data were used for the thinner sample (Fig. 4). All things considered, the results are in fairly satisfactory agreement with each other and with a few old data of Pflüger.¹ However, direct measurements of the refractive index should, in general, be more meaningful than values determined from the reflectivity.

Visual examination under a metallographic microscope of high resolving power¹² showed *sublimed* films to reflect homogeneously, in natural and polarized light, to the limit of the resolving power of the microscope (1-2 wavelengths of light). Films deposited from solution, on the other hand, appeared like multicolored mosaics of microcrystals, one micron and greater in size; larger crystals were usually birefringent, as well as pleochroic. The over-all reflectivity of both types of film, then, represents an average of the reflection colors of the various crystal faces.

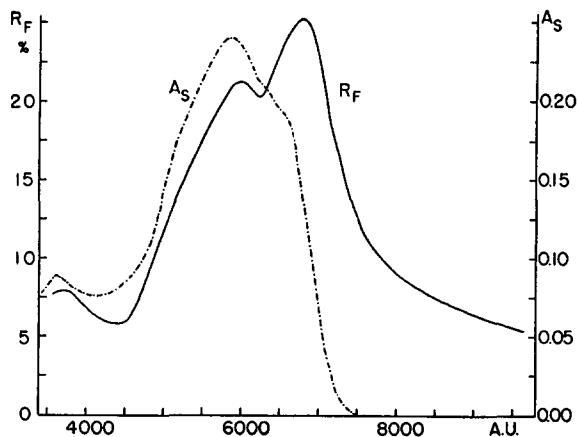


FIG. 8. Reflectivity and absorbance of a sublimed pinacyanole film.

Apparently the only dye whose reflection pleochroism has been related in detail to its crystal structure is methylene blue. Taylor³ first showed that single crystals of this compound exhibit an intense greenish-golden luster from the *ab* and *bc* faces, which contain the long (or "X") molecular axes, and only a weak violet sheen from the orthogonal *ac* face. Anderson⁴ later used these observations to determine the molecular orientation of thin methylene blue films, adsorbed on rubbed glass surfaces, and published semiquantitative reflection spectra for oriented films and single crystal faces. Unfortunately, the reflectance of our methylene blue films was too weak to permit comparison with Anderson's results. Here—as in the case of *absorption* spectra of solid dyes—more work with single crystals should be of great interest.

The author is indebted to Professor R. C. Nelson for a number of helpful discussions.

¹² We are indebted to Professor R. Speiser of the Department of Metallurgy for the use of a 500X (0.4 N.A.) Bausch and Lomb Metallograph.