

to the fact that the fluorescence emission is caused by one of the tautomer forms of the dyestuff.

Owing to self-absorption an analysis of the emission bands could not be accomplished.

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About an Effect of Oriented Molecules on Polarized Light

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Introduction.

According to the investigations of P. Fröhlich and L. Szalay the dyestuff molecules are oriented in rigid gelatinous solution of acridine orange under illumination(1). If a part of the solution is preexcited by polarized light and after the preexcitation the phosphorescence emission is measured by weak polarized light, at the same time illuminating also the unexcited part of the preparation, the intensity of emission of the preexcited surface is greater or smaller than the intensity of emission of the unexcited surface. When the directions of polarization of preexciting and exciting lights are parallel, the preexcited surface has a more intensive phosphorescence emission than that of its surroundings; when they are perpendicular, the phosphorescence emission of the preexcited surface is smaller than that of its surroundings.

The effect is similar to that found by G. N. Lewis and his co-workers (2), according to which the absorption of dyestuffs, exposed to and measured by polarized light, depends on the direction of polarization of the measuring light. The absorption is great when the directions of polarization of exciting and measuring lights are parallel, and small if they are perpendicular.

Both effects may be explained by assuming the orientation of molecules. Planar molecules have two optical axes which are perpendicular. The molecule is excitable if its plane is perpendicular to the beam, and if, when excited with polarized light, one of its axes is parallel to the direction of polarization. During preexcitation the molecules are oriented until the plane of their optical axes is normal to the beam of light and one of their optical axes takes up a parallel position to the direction of polarization. Mischung was the first to prove that the absorption coefficient increases during excitation, this establishment indicates the existence of an orientation effect (3).

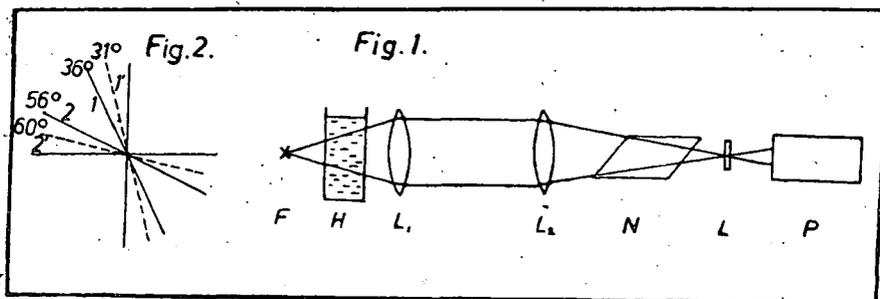
The phenomenon of saturation which means that the phosphorescence emission requires considerable time to reach its maximum during excitation is also interpretable by assuming the orientation of the molecules (4).

The preexciting effect proves that the oriented state due to irradiation persists in gelatinous solutions also after discontinuing the irradiation, consequently the molecules are permanently oriented in rigid gelatinous solutions.

The orientation effect is undoubtedly a phenomenon which is due to the reciprocal effects of light and dyestuff molecules caused by the influence of light on the molecules. It is obvious that the permanently oriented molecules must exert an influence on polarized light. This effect is described in the following paper.

Experimental.

It was demonstrated that oriented molecules influence the direction of the polarization of light. As was described above in a rigid gelatinous solution, the permanently oriented state may be caused by excitation with intense polarized light. The observations were made with a Cornu-polarimeter to ascertain the direction of polarized light after it had passed through the preexcited dyestuff solution. Considering that the measuring light itself also exerts an orientation effect on the molecules, its intensity must be very small as compared with the intensity of the preexciting light. Thus the intensity of the preexciting light had to be reduced by means of a glass-plate covered with lamp-black on using it as measuring light. Fig. 1. exhibits the measuring arrangement.



The source of light „F“ was a 5000 watt tungsten filament lamp. The light from passes through a circulating water cooler

(*H*) and two lenses (L_1 and L_2). The polarized light is produced by means of a nicol (*N*). The direction of polarization is measured with a polarimeter (*P*). The course of the measuring was as follows. The plate was illuminated 10 minutes with intense polarized light. This time is sufficient to induce permanent orientation. Subsequently the intensity of light was decreased by means of a glass-plate covered with lampblack. The direction of polarization was changed through rotating the nicol, and the angle of rotation was measured with the polarimeter. First the rotation angle was measured on removing the gelatine plate placed between the polarimeter and nicol, then the plate was put between the nicol and polarimeter, and the rotation angle measured again.

Results.

The first results disclosed that not only light exerts an orientating effect on the molecules, but that also the oriented molecules affect polarized light, the direction of polarization of the faint light after transmission through the solution rotates if the solution contains oriented molecules. Detailed investigations gave very interesting results. Hence it was obvious that the angle of rotation depends to a great extent on the difference between the direction of polarization of the orientating light and that of the weak measuring light. The results are summarized in Table I referring to a rigid gelatinous plate of 0.1 mm. The preparation contained acridine orange.

Table II.

Direction of polarization without plate	Direction of polarization after the introduction of the plate	angle of rotation
0°	0°	0°
18°	16°	2°
26°	23°	3°
36°	31°	5°
56°	56°	-4°
66°	69.5°	-3.5°
75°	76°	-1°
90°	90°	0°

The concentration of the dyestuff was $10^{-2.5}$ gr dyestuff/cm² dry gelatine. The measurements were made at room-temperature. The orientation was made with nicol at 0°, the light polarizing horizontally. Table I shows that the direction of polarization remains unchanged on passing through the plate if the weak polarized measuring light is also horizontally polarized. But if the direction of polarization of measuring light is changed, the preparation containing oriented molecules rotates to a certain degree the direction of polarization of the light passing through it. The direction of polarization will be rotated to a lesser extent after transmission through the dyed plate comprising oriented molecules, e. g. if the nicol is at 18° on the light passing through the plate it will be

reduced to 16° . In other words, the oriented molecules rotated the direction of polarization as if they wanted to change the direction back to that originally employed for orientation. This behaviour could, however, only be observed to an angle of 36° . At an angle of 56° a change in opposite direction took place. On introduction of the plate containing the oriented molecules at this angle the direction of polarization rotated towards the opposite direction. However, the molecules had no influence whatever on the direction of polarization if the measuring light polarized vertically (Fig. 2.).

The two perpendicular directions correspond to the horizontally and vertically polarized directions respectively. The plate rotates direction 1 of polarized light to direction 1', and direction 2 of polarized light to direction 2' respectively. The direction of the two perpendicularly polarized lights does not change when it passes through the plate.

Several plates of various concentration and thickness were investigated and similar results were always obtained. Since all examined preparations behaved essentially in the same manner, only differing in the angles of rotation, it does not seem necessary to enumerate further data.

It should further be noted that the method employed was unsuitable for the determination of the angle between 0° and 90° dividing the two directions of rotation. Therefore the change in the direction of polarization was simply observed by means of a Nicol. The well-known phenomenon, that the linearly polarized light becomes partially polarized on passing through the gelatine plate was observed. The rotation which was measured with the polarimeter is not the rotation of the plane of polarization, but that of the plane of the partial polarization.

Summary.

It was demonstrated by the aid of the preexciting effect that oriented molecules influence the direction of polarized light. One of the optical axes of the oriented molecules is parallel to the direction of the polarization of the exciting light, the other is perpendicular. If a weak polarized light is passed through a dyestuff solution which contains oriented molecules the direction of polarization will be rotated in the direction of the axis which is closer to the direction of polarization.

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