4,5-Dibromoöctanes.—Samples of the *dl* and *meso* isomers which were obtained from Professor Lucas[18] were used as the pure compounds in the rate determinations.

A large sample of the *dl*-dibromide was prepared from the *meso*-diacetate as described by Lucas and Gould.[18] The crude product (yield 85%) upon distillation through a Weston column had a rate constant $k_{\text{cor.}}$ of 0.0545 (pure compound 0.0604), indicating contaminants of relatively unreactive bromohydrins and/or bromoacetates (confirmed by lower refractive index, $n^{20}\text{D}$ 1.4921, 1.4982 for pure *dl*-dibromide). Upon four recrystallizations, the $k_{\text{cor.}}$ was 0.0613.

15.6 g. of this material was treated with a zinc-copper couple as described above for the *dl*-dibromohexane. The recovered olefin, b. p. 121–123.5° (yield 72%), was treated with bromine as above, and the dibromide product was distilled to give 7.9 g. of material boiling at 97.5–100° (9 mm.). The purity of this material has been discussed above.

Summary

Pure samples of the *meso*- and *dl*-dibromohexanes and octanes have been prepared from the pure diastereomeric glycols through their corresponding diacetates. A comparison of physical properties and rates of reaction with potassium iodide in 99% methanol before and after recrystallization indicates that little or no diastereomer formation is involved in the change glycol → diacetate → dibromide. A comparison of pure recrystallized dibromides with samples obtained by debromination with zinc followed by bromination of the resulting olefin indicates an increasing tendency toward stereomutation as the number of carbon atoms is increased from four to eight.

Los Angeles, California Received June 28, 1943

[Contribution from the Chemical Laboratory of the University of California]

The *y* Bands in Absorption Spectra

By Gilbert N. Lewis and Jacob Bigeleisen

It was first pointed out by Lewis and Calvin[1] that in a planar or nearly planar molecule there should be two types of absorption bands. In the one case, the *x* bands, the electronic oscillations characterizing the excited state have a certain direction in the molecule, and this direction may be called the main optical axis. In the other case, the *y* bands, the electronic vibrations of the excited state are in that direction in the plane perpendicular to that main axis.

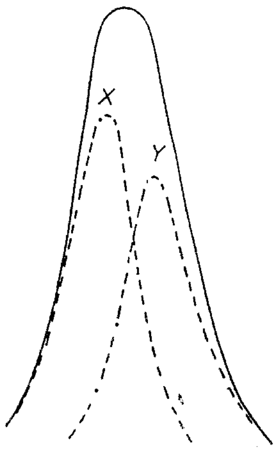
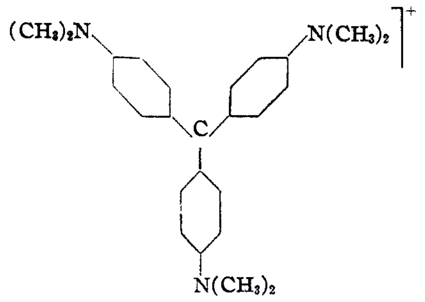
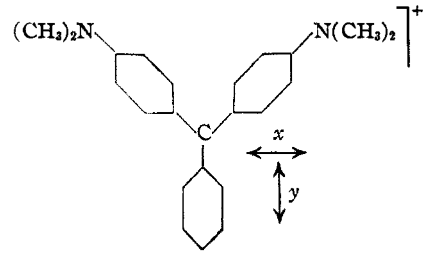


Fig. 1.—Hypothetical resolution of the band of a radially symmetrical molecule into an *x* and *y* band, when a slight dissymmetry is introduced.

If we could measure the polarizability of such a planar molecule in different directions, we should find a direction of maximum polarizability and, at right angles thereto, a direction of minimum polarizability. These two directions may be identified with the *x* and *y* axes of absorption. In a symmetrical molecule such as that of crystal violet (I) we have a degenerate case, in which the polarizability (except perhaps at very great field strength) is the same in all directions of the plane.[2] In such a case the *x* and *y* bands coincide.



I



II

If, in a symmetrical molecule, such as the A isomer of crystal violet, we make some minor chemical substitution so as to produce a slight dissymmetry, we should expect the absorption curve to be resolved into two neighboring *x* and *y* bands as indicated schematically in Fig. 1. If the dissymmetry is great, as in malachite green (II), where one of the auxochromes has been entirely removed, we may expect a wide separation and indeed, as was first shown by Hantzsch,[3] there are two bands[4] in the visible, one at 6250 Å. and another at 4230 Å.

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[1] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[2] This would not be quite true of the B isomer found by Lewis, Magel and Lipkin, This Journal, **64**, 1774 (1942).

[3] Hantzsch, *Ber.*, **52**, 509 (1919).

[4] Foerster, *Z. Elektrochem.*, **45**, 548 (1939), quoting also the earlier work of Eistert, "Tautomerie und Mesomerie," Ferdinand Enke, Stuttgart, 1938, concluded that malachite green should have two bands for the one of crystal violet. However, these authors considered only the energy and not the orientation of the excitations.

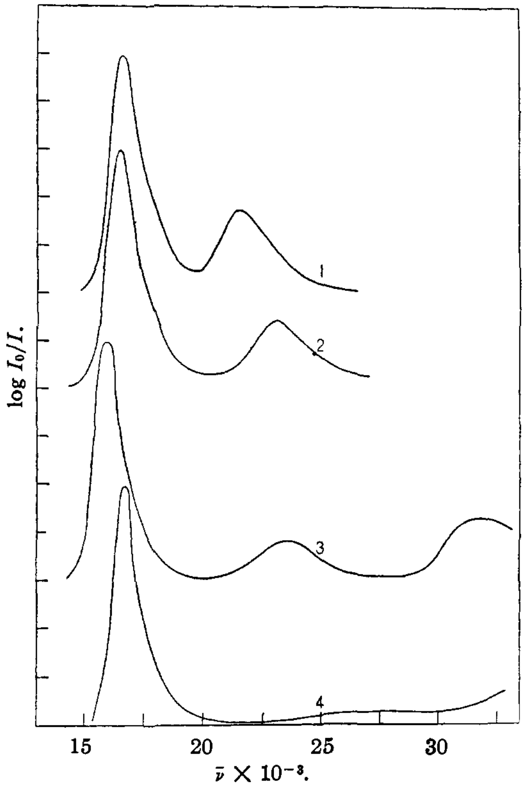

Fig. 2.—x and y bands of (1) *p*-methoxymalachite green, (2) *p*-methylmalachite green, (3) malachite green (identical with curve for acid green), (4) the ion of Michler's hydrol. All are at room temperature; (1), (2), (3) in ethanol; (4) in glacial acetic acid.

We have redetermined the absorption curves of several dyes of the malachite green type shown in Fig. 2. Curve 1 is for *p*-methoxy-malachite green. Here the methoxy group approaches the dimethylamino group in auxochrome character and the second band is high and not so far displaced from the first band as in the other cases. Curve 2 is for *p*-methyl-malachite green. The methyl group is known to have a small positive (basic) auxochrome effect. Curve 3 is for malachite green itself. It is also, identically within the limits of measurement, the curve for acid green (Colour Index No. 666) in which each pair of methyls in malachite green is replaced by an ethyl and a *para* sulfonated benzyl. Finally in curve 4 we have the ion of Michler's hydrol in which the whole unsubstituted phenyl group of malachite green is replaced by a hydrogen. In this case the scope of oscillation in the y direction is greatly limited; the second band is weak and has gone into the ultraviolet, at about 27 or 28 × 10^3 cm.$^{-1}$.

If we replace the phenyl of malachite green with α-naphthyl or with β-naphthyl, we again obtain the prominent second bands shown in the two curves of Fig. 3. That the second band is about twice as high in the β as in the α compound may be attributed partly to the greater extension in the y direction of the former molecule and partly to its nearer approch to coplanarity.

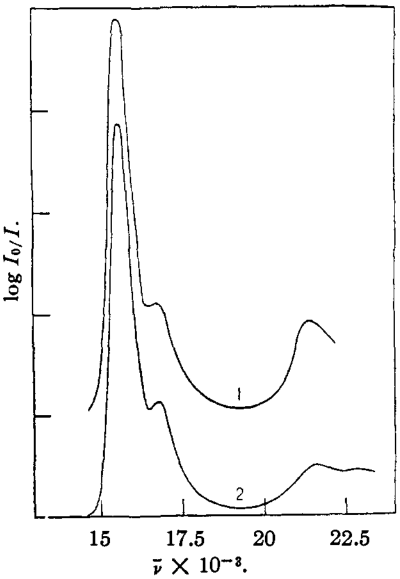

Fig. 3.—x and y bands of malachite green in which the unsubstituted phenyl group is replaced by (1) β-naphthyl, (2) α-naphthyl, in 95% ethanol at about 110°K.

Finally we were fortunate enough to obtain through the kindness of Professor T. D. Stewart two substances that we thought should give the small separation of x and y bands represented in Fig. 1. These were like crystal violet except that a pair of methyls was replaced by a pair of ethyls or a pair of *n*-propyls. Both of these substances, like crystal violet, showed the A and B bands,[5] but the A band was resolved into two. This result seemed sufficiently important to make sure that it was not due to some impurity. Therefore the diethyl compound was subjected to very thorough fractionation by the method of Lewis, Magel and Lipkin.[5] The purified substance was dissolved in a mixture of ether, isopentane and alcohol (EPA) and the absorption was measured at about 110°K., where the solvent is not sufficiently rigid to show the absorption of the phosphorescent state.[5] The curve is given in Fig. 4 and the resolution[6] of the main band into an x band at 16,660 cm.$^{-1}$ and a y band at 17,200 cm.$^{-1}$ almost reproduces Fig. 1 which had been drawn before these experiments were made.

We have sufficiently demonstrated that the absorption band of a symmetrical planar molecule is resolved into two bands by any substitution that produces dissymmetry, and that the maxima of these bands are more widely separated, the greater the optical dissymmetry. It remains now to show that these are actually x and y bands

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(5) Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

(6) Since the diethylamino is a slightly stronger basic auxochrome than dimethylamino, we conclude that the x axis is the one joining diethylamino and central carbon.

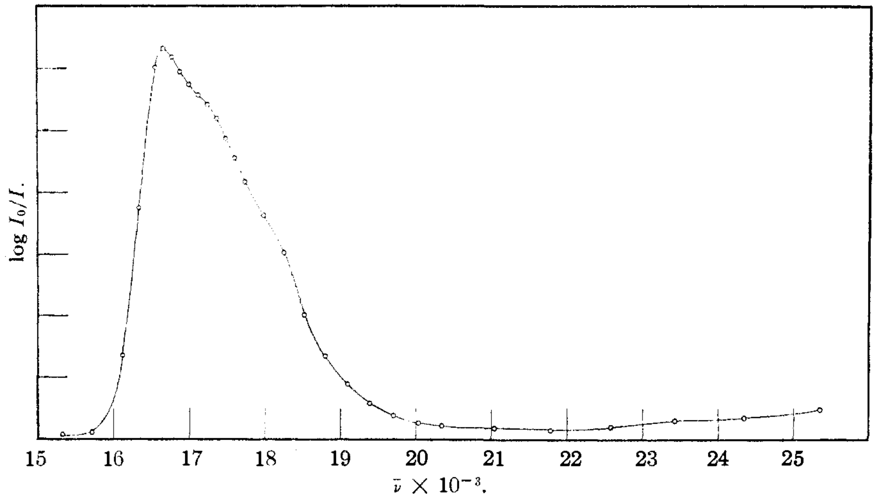


Fig. 4.—Showing the rudimentary separation of x and y bands when two neighboring methyls of crystal violet are replaced by ethyls; in EPA at about 110°K.

corresponding to electronic oscillations at right angles to each other.

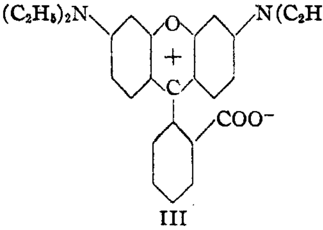
The Polarization of Absorption Bands in Oriented Molecules.—In studying the orientation of molecules produced photochemically in rigid solvents[7] we dealt only with x bands. Suppose, however, that we have a substance with both an x and a y band. In the case of normal orientation such a substance, when produced by vertically polarized light, would have its x axes predominantly oriented in the vertical direction. The substance would show a maximum of absorption with vertically polarized light. The y axes will now lie chiefly in the horizontal plane. They should therefore give maximum absorption with horizontally polarized light. Since, however, a molecule with its x axis vertical is as likely to have its y axis in the direction of the beam, as normal thereto, the polarization will be less for this band. Using the same mathematical methods as before[7] we find that the maximum obtainable orientation ratio, under the circumstances named, is 3 to 1 for the x band and 1 to 2 for the y band.

In the actual illumination of malachite green leuco cyanide the highest orientation ratio obtained was 1.22 for the x band. Making the simplifying assumption that a small part of the molecules are oriented according to theory and the remainder are randomly oriented, the orientation of 1.22 for the x band would correspond to an orientation of 0.91 for the y band.

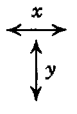
Using this sample we attempted to measure the polarization of the y band at 4200 Å., although we had no apparatus for accurate work in this region. Instead of the ratio 0.91, we found 1.00 ± 0.03, in other words no polarization. We found, however, that in addition to the malachite green ion another colored substance is produced by the light, which may be the positive ion obtained from the leuco cyanide merely by the ejection of an electron. It is evident from the absorption curve that this yellow substance makes a substantial contribution to the absorption at 4200 Å. If its absorption is polarized like the x band of malachite green its polarization would neutralize that of the y band.

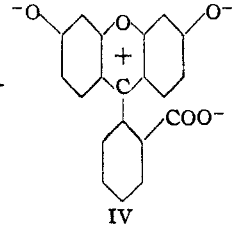
In any case the results show that the band at 4200 Å. cannot be another x band. These experiments were discontinued when we found another much simpler and more powerful method of proving that the band at 4200 Å. is a y band.

Measurement of the Polarization of Fluorescence.—Since the phenomenon was first found by Weigert,[8] it frequently has been observed that when a fluorescent substance, in so viscous a solvent that the molecules have not much chance of turning during the lifetime of the fluorescent state, is irradiated by polarized light, it reëmits light polarized in the same sense. However, Wawilow[9] found that when certain dyes were irradiated by light in the near ultraviolet they showed the same fluorescence bands but now the fluorescent light was polarized in a direction perpendicular to that of the exciting light. This remarkable phenomenon was given a simple explanation by Lewis and Calvin.[1] To answer some objections that have privately been made to that explanation we have redetermined the absorption spectra of two of Wawilow's dyes, the sodium salts of rhodamine B and fluorescein, with formulas and x and y axes as below.



III





IV

Our absorption curves are given in Figs. 5 and 6. In each case the x band with its subsidiary vibrational bands extends through the visible region.[10] It is followed by the y band, at 28,160

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[7] Lewis and Bigeleisen, THIS JOURNAL, 65, 520 (1943).

[8] Weigert, *Physik. Z.*, 23, 232 (1922).

[9] Wawilow, *Z. Physik*, 58, 690 (1929).

[10] The band in rhodamine B with maximum at about 24×10^3 cm.$^{-1}$ seems a little high for a subsidiary vibrational band. We thought it might be due to an impurity, but it is not. It was found

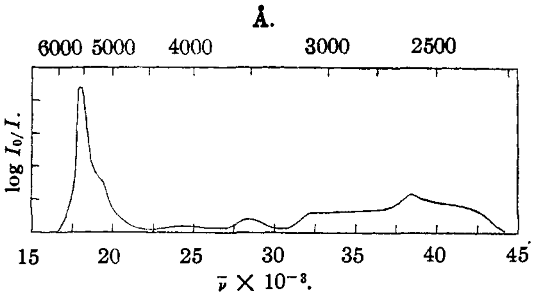

Fig. 5.—Absorption by rhodamine B in dilute aqueous alkali at room temperature.

cm.$^{-1}$ (3550 Å.) for rhodamine B, and 30,800 cm.$^{-1}$ (3250 Å.) for fluorescein. Now Wawilow found the maximum negative polarization in these two cases, respectively, at 3200 Å. and 3000 Å., namely, at the extreme right of the two y bands.

However, Wawilow would not have claimed any high accuracy for his results. For rhodamine B at 3660 Å. where his curve would show a small positive polarization, the more accurate work of Pheofilov and Sveshnikov[11] showed a negative polarization, higher than the maximum obtained by Wawilow. We may conclude that the maximum of negative polarization nearly coincides with maximum absorption in the supposed y bands.[12]

Let us look at formula III with the accompanying arrows, and imagine it to represent an actual molecule of rhodamine B lying in the plane of the paper. If now we consider a beam of light of 5550 Å., normal to the paper, and polarized along x, an excited state will be produced with an additional energy of 51.5 kcal. and with electronic oscillations in the x direction. When this excited molecule reëmits by fluorescence the light will again be polarized along x.

Suppose again the light is of 3550 Å. and polarized in the y direction. The molecule will now be excited by 80.6 kcal. with electronic oscillations along the y axis. We assume that before this excited molecule has time to reëmit its normal fluorescence it suffers partial quenching to reach the first excited state, losing 80.6 minus 51.5 kcal. In this process the y oscillations will change to x oscillations, and it is this process that is responsible for the Wawilow effect. The molecule will now reëmit the same fluorescence as in the preceding case but the polarization of the light will be perpendicular to that of the exciting light.

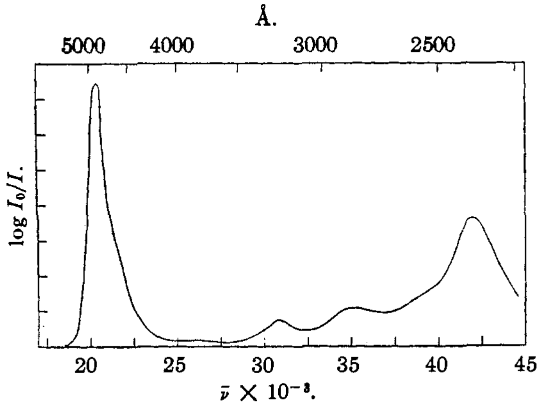

Fig. 6.—Absorption by fluorescein in dilute aqueous alkali at room temperature.

It is known that in the normal case of dyes, when exciting and fluorescent light are polarized in the same direction, the maximum obtainable polarization is $^1/_2$. On the other hand, in the case of abnormal or "negative" polarization, we find from the identical mathematics[13] used in our previous paper[7] the maximum amount of negative polarization is $^1/_3$.

In order to apply such methods to the study of the y bands of malachite green and similar dyes, we have improved the methods of detecting and measuring small degrees of polarization as described in the experimental section. With this new apparatus we have studied the fluorescence of malachite green in 95% ethanol over liquid air, the temperature being about 115°K. A brilliant red fluorescence is obtained with a maximum at 14,900 cm.$^{-1}$ (6720 Å.).

When the illumination is with the yellow light of the sodium arc and we view from the back of the cell toward the source, with red filters which let through only the fluorescent light, a large positive polarization is found. Also illuminating with

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with several independent samples and in the almost identical spectrum of the ethyl ester, rhodamine 3B extra. Further study of rhodamine 3B extra in 95% ethanol shows that the x absorption at 24×10^3 cm.$^{-1}$ increases with respect to the main band about twofold from 290 to 110°K. If this is due to isomerism, the second isomer has about 0.2 kcal. less energy. Such isomerism could only mean that in a molecule of the xanthene type the two linked benzene rings are not quite coplanar.

(11) Pheofilov and Sveshnikov, *J. Phys.* (U. S. S. R.), **3**, 493 (1940).

(12) We refer of course to a pure y band. It is evident from Fig. 5 that at 3660 Å. there may be some overlapping of the subsidiary x band and the y band. Since, as we shall see, the x axes are more oriented than the y axes, there should at this point be some considerable positive polarization to cut down the observed negative polarization. Our calculation shows that the ratio obtained by Pheofilov and Sveshnikov[11] between the negative polarization at 3660 Å. and the positive polarization at 5460 Å. can be interpreted quantitatively if we assume that the tail of the x band is responsible for 15% of the absorption at 3660 Å.

(13) The mathematical results may be summarized as follows. When, under ideal conditions, randomly distributed molecules are excited by light polarized in the X directions, of the frequency of the x band, the system will behave as though there were three excited molecules with axes in the X direction to one in the Y and one in the Z directions. Two molecules that have their x axes in one direction behave as though their two y axes were along each of the two perpendicular directions. Thus in the same orientation just considered it is as though there were two molecules with y axes along Z, two along Y, to one along X.

In considering extinction coefficients, orientation has been ignored. Thus Wizinger, "Organische Farbstoffe." Ferd. Dummler's Verlag, Berlin, 1933, draws some chemical conclusions from the fact that $\epsilon_{max.}$ for malachite green is only $^4/_5$ that of crystal violet. But crystal violet molecules randomly distributed have twice as many opportunities for favorable orientation. If we had a molecule of malachite green and one of crystal violet, each in the optimum orientation with respect to the light polarization, malachite green would show the higher absorption probability in the ratio of 8/5.

ultraviolet light at about 32×10^3 cm.$^{-1}$ where we see a third band, which we consider (see paper just following) as a second order *x* band, we also obtained positive polarization.

However, if we illuminate with blue light in the neighborhood of our band at 23,500 cm.$^{-1}$, we obtain the highest negative polarization that has yet been found, namely, -0.17, and in a similar experiment with the α-naphthyl compound -0.20. Both are to be compared with the theoretical maximum -0.33. Our values are subject to error, perhaps as great as ± 0.05. The accuracy could be improved with a more finished apparatus and greater number of readings. We could probably have obtained a higher negative polarization with more dilute solutions on account of the depolarizing effect of concentration demonstrated by Pheofilov and Sveshnikov.[11] Our results, however, are adequate for our purpose and show conclusively that the bands in question are *y* bands.

Experimental

Some of the dyes used were commercial samples carefully tested for purity. The bis-(*p*-dimethylamino-phenyl)-*p*-diethylamino-phenylchloromethane and the corresponding dipropyl compound, as well as the bis-(*p*-dimethylaminophenyl)-α- and β-naphthylchloromethanes, were prepared for us under the direction of Professor T. D. Stewart, to whom we wish to express our great obligation.

The absorption spectra at room temperature were determined with a Beckman quartz photoelectric spectrophotometer; those at low temperature with the spectrophotometer previously described.[14] The method of studying the orientation of the photochemical products of malachite green leuco cyanide have also been previously described,[7] except that the oriented absorption at 4200 Å. was determined directly by using a monochromator with Polaroid and a light sensitive cell.

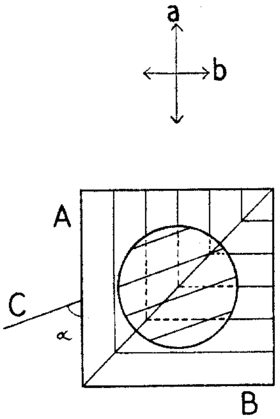

Fig. 7.—Illustrating a new method of viewing and measuring the degree of polarization of light.

An Improved Polariscope and Method of Measuring the Degree of Polarization.—In a preceding investigation[14] a Pfund plate was used as a polariscope. We find that a more effective one can be made simply by cutting a square of Polaroid along the diagonal, reversing one-half and mounting the square thus formed, with Canada balsam between two glass sheets. Such a square is illustrated in Fig. 7 with the lines A and the lines B showing the polarizing directions. It detects very slight polarization, as one-half appears darker than the other and the difference is enhanced by the eye, as in all instruments of the "half shadow" type. To determine quantitatively the degree of orientation we superpose another Polaroid plate which is turned until the light intensity is the same on both sides of the diagonal. If its polarizing direction is C, making the angle α with A, and if *a* and *b* represent the intensities of the incoming light polarized along A and B, respectively, then $a/b = \tan^2 \alpha$, and the degree of polarization is defined as

$$\frac{a-b}{a+b} = \frac{\tan^2 \alpha - 1}{\tan^2 \alpha + 1}$$

To isolate the region around 4200 Å., light from the high pressure mercury arc was passed through a copper sulfate filter and Corning filters no. 511 and 430. The fluorescent light was viewed through Wratten filters no. 25 and 35. For excitation in the *x* band at 5890 Å., light from a large sodium arc was passed through potassium dichromate solution and a solution of methylene blue in 3 *M* H_2SO_4 of such concentration that none of the neon lines in the sodium arc were visible when this filter combination was used in conjunction with the Wratten filters. For the ultraviolet excitation, light from the high pressure mercury arc was passed through a copper sulfate solution and then a thick Corning no. 586 filter.

Summary

When one of the three equivalent groups of crystal violet is replaced by a different group, the single absorption band is resolved into two bands, *x* and *y* bands. The separation is greater the more the new group differs, as an auxochrome, from the old.

It is shown that the electronic oscillations of the two excited states are perpendicular to each other. The negative fluorescent polarizations found by Wawilow in fluorescein and rhodamine-B are shown to be in accord with Lewis and Calvin's theory of this phenomenon.

The second band of malachite green is proved to be the *y* band by two methods. The first depends on the production of oriented molecules in a rigid solvent. The second, which was also applied to another similar dye, is the method of polarized fluorescence.

A new method of viewing and measuring small degrees of polarization is described.

BERKELEY, CALIFORNIA RECEIVED JULY 12, 1943

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[14] Lewis, Lipkin and Magel, THIS JOURNAL, **63**, 3005 (1941).