TECHNICAL REPORT
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A REVIEW OF PHOTOCHROMISM IN TRIPHENYLMETHANE DERIVATIVES AND RELATED COMPOUNDS

by

Richard N. Macnair

January 1967

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

U.S. ARMY MATERIEL COMMAND

CLOTHING AND ORGANIC MATERIALS DIVISION
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FOREWORD

This report is a literature review of photochromic triphenylmethane derivatives and was prepared under the Flashblindness Protection Research Project 1C024401A349, Task 05, of the Materials Research Branch, Clothing and Organic Materials Division, U. S. Army Natick Laboratories, Natick, Mass. The search and data collection were conducted by Dr. Richard N. Macnair largely during 1965 as one of the initial but continuing phases of the in-house research program on organic photochromic compounds. The report covers the literature up to and including January, 1966.

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ABSTRACT

A comprehensive review of photochromism in triphenylmethane derivatives and some related compounds is presented. Most of the individual compounds reported to be photochromic as well as some of those reported as non-photochromic are mentioned. Compounds were included only if the conditions under which the observations were made were reasonably well described. In preparing the review, little attention was given to the degree of photochromism reported since very little quantitative data were available. Physical properties of the compounds and/or their solutions which appear to be related to photochromism are discussed, including conductivity, dielectric constant and dipole moment. Among other topics discussed are mechanisms and kinetic studies.

A REVIEW OF PHOTOCHROMISM IN TRIPHENYLMETHANE DERIVATIVES AND RELATED COMPOUNDS

I. INTRODUCTION

Interest in photochromism as an ultimate means of flashblindness protection has prompted research on organic photochromic compounds. Numerous classes of organic compounds are known to exhibit photochromy but some are more deeply colored than others and are therefore of greater interest for this application. High on the list of deeply colored photochromic compounds are some triphenylmethane derivatives. Investigations of these derivatives have indicated that their quantum efficiencies are very high and the observed color changes occur very rapidly during a flash of light.

Several publications covering the general subject area of photochromy (or photochromism) briefly discuss triphenylmethane photochromism (see Chalkley[1] (1929), Brown[2] (1959), Brown and Shaw[3] (1961), Dessauer and Paris[4] (1962), Luck and Sand[5] (1964), and Exelby and Grinter[6] (1964)). This report presents a more comprehensive treatment of triphenylmethane photochromism than has appeared thus far, reviewing the literature through January, 1966.

The terms photochromism and photochromy will be used throughout this review to mean a reversible change of color brought about by incident light. Many articles in the literature refer to this phenomenon also as phototropy or phototropism.

II. PHOTOCHROMIC SOLUTIONS

Photochromism in triphenylmethanes has so far been observed only in "solution". For this report, the term solution will include gels, plasticized resins and similar materials. Known photochromic solutions of triphenylmethane derivatives and related compounds are shown in Tables IA, IB, II, III, and IV. The solutions were prepared either with the solid leuco forms of the compounds or in situ with the colored forms and the reagent specified, e.g., potassium cyanide or sodium bisulfite. The structures of the compounds are shown in Appendix A, in alphabetical order according to the nomenclature used in the literature.

III. NEGATIVE PHOTOCHROMIC SOLUTIONS

Negative photochromy is the light-induced phenomena observed when materials change reversibly from colored to colorless under the influence of light. Thus, the color of negative photochromic triphenylmethane solutions fades or disappears when the solutions are irradiated with ultraviolet light and returns when the light is removed. This phenomenon has been reported for solutions prepared with the chlorides of Crystal Violet, Fuchsin and Malachite Green in methyl cellosolve containing thiourea and concentrated hydrochloric acid.(15)

IV. NON-PHOTOCHROMIC SOLUTIONS

The compounds in Tables I - IV indicate the wide variety of photochromic triphenylmethane solutions which can be prepared, but one should not conclude that triphenylmethane derivatives are universally photochromic since the leucocyanide solutions in Table V were reported non-photochromic. The Victoria Blue B solution in Table V was reported to exhibit fluorescence instead of photochromy.

V. PHYSICAL-ORGANIC PARAMETERS

A. General. Numerous physical-organic studies have been made on solutions of triphenylmethane derivatives in an effort to elucidate the phenomenon of photochromy. The results of some of these studies have been contradictory and many problems need further investigation.

TABLE IA

PHOTOCHROMIC CYANIDE SOLUTIONS

Compound	Solvent Code Letter									
Auramine			B,G							A
Benzaurine					C					
Brilliant Blue		H								
Brilliant Green		A,H,J	A,B,G				A			A,B,G,M,N
Crystal Violet		H	A,B,G,N						A	A,B,G,M,N
Doebner's Violet		H								
Hexa(hydroxyethyl)-pararosaniline		H								
Malachite Green		H	A,B,G	A,D,F			A	I	A	A,B,G,M,N
Methyl Violet	A,K					D,E,G				
New Green		H								
New Magenta		A								
New Red		A								
New Yellow		H								
Pararosaniline		A,H	A,B,G,N						A	A,B,G,M,N
Phenolphthalein					C					
Victoria Blue R								L		
Reference No.*	7	8	9	10	11	12	13	14	17	18

Solvent Code: A. Ethanol. B. Diethyl ether. C. Water or aqueous alcohol with KCN. D. Ethylene chloride (dichloroethane). E. Ethanol-water, methanol, methanol-water, acetone, acetone-water, benzene-methanol, carbon tetrachloride-methanol, cyclohexane-methanol, chloroform, chloroform-methanol. F. Ethylidene dichloride, cyclohexane-ethylidene dichloride, cyclohexane-ethylene dichloride. G. Benzene. H. Dimethyl sulfoxide, aqueous and non-aqueous. I. Acetone or methyl cellosolve. J. Ethyl cellosolve, monoglyme, diglyme. K. Ethanol-benzene. L. Hydroxy solvents acidified with HCl. M. Chloroform. N. Ethanol with KCN.

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*See Section VII

TABLE IB

PHOTOCHROMIC CYANIDE SOLUTIONS CONTINUED

Compound	Solvent Code Letter	
Acid Blue 22	N,O	
Acid Blue 93	N	
Acid Green 3	N,O	
Acid Green 9	N,O	
Acid Violet 17	N,O	
Acid Violet 19	N,O	
Crystal Violet	L,M	
Malachite Green	K	
Malachite Green Derivatives[*]		P
Reference No. (See Section VII)	15	16

Solvent Code: K. Three-to-one "solutions" of cellulose acetate with the following plasticizer mixtures: (1) Polyethylene Glycol 600[+]/butyl stearate (5/1), (2) Ethylene glycol phenyl ether[±]/butyl stearate (5/1), (3) Polyethylene Glycol 600[+]/butyl acetoxy stearate (5/1), and (4) Ethylene glycol phenyl ether[±]/butyl acetoxy stearate (5/1). L. Cellulose acetate with Polyethylene Glycol 600[+] plasticizer (3/1) or with ethylene glycol phenyl ether[±] plasticizer (3/1). M. Solutions of cellulose acetate in 2-methoxy ethanol, and polyvinyl alcohol in aqueous alcohol; films cast from these solutions and containing some residual solvent. N. Dimethyl sulfoxide with methanolic KCN. O. Methyl Cellosolve with methanolic KCN. P. Solvents having dielectric constant greater than 4.5, containing polyvinyl butyral.

---

[*] These derivatives have a CN, OH, OCH_3 or SO_3H group on the amine unsubstituted ring and methyl groups in various ring positions.

[+] Allied Chemical Company, Nitrogen Division.

[±] Dow Chemical Company as Dowanol I (Now Dowanol EP).

TABLE II

PHOTOCHROMIC CARBINOL SOLUTIONS

Compound	Solvent Code Letter				
Benzaurine		B,C			
Crystal Violet	A,I		H		A,I,J,K
Malachite Green	A,I				A,I,J,K
Malachite Green Derivatives*				G	
Pararosaniline			D,E,F		
Phenolphthalein		B,C			
Reference No. (See Section VII)	9	11	15	16	18

Solvent Code: A. Ethanol with KOH. B. Water with or without KOH. C. Aqueous alcohol with KOH. D. Water with $NaHSO_3$. E. Methyl cellosolve with methanolic KCN. F. Dimethyl sulfoxide with methanolic KCN. G. Solvents having dielectric constant greater than 4.5, containing polyvinyl butyral. H. Solutions of cellulose acetate-butyrate with 2-methoxy ethanol, and vinyl acetate with methanol; films cast from these solutions and containing some residual solvent. I. Benzene. J. Ether or chloroform. K. Ethanol.

---

*These derivatives have a CN, OH, OCH_3, or SO_3H group on the amine unsubstituted ring and methyl groups in various ring positions.

TABLE III

PHOTOCHROMIC SULFITE SOLUTIONS

Compound	Solvent Code Letter					
Acid Blue 22		F				
Acid Fuchsin						E,F,G
Acid Green 3		F				
Acid Green 5		F				
Acid Green 9		F				
Acid Violet 17		F				
Acid Violet 19		F				
Basic Fuchsin						F
Brilliant Green	A,J*					
Crystal Violet			A			
Fuchsin		F				F
Magenta (Rosaniline)			A			
Malachite Green		C,D	A	B	B	I
Methyl Violet			A			
New Fuchsin		F				F
Pararosaniline	A**	F				F
Rosaniline Red					B	
Sevron Green B***						E,F,H
Reference No. (See Section VII)	9	15	19	20	21	22

*Sulfate of Brilliant Green Leucosulfite

**Hydrochloride of Pararosaniline Leucosulfite

***Proprietary product of du Pont

TABLE III (Cont'd)

Solvent Code: A. Water containing SO_2. B. Water containing bisulfite and papain. C. Polyvinyl alcohol with dimethyl sulfoxide (5/1). D. Solutions of Vinyl acetate/vinyl alcohol copolymer in alcohol-acetone; Polyvinyl alcohol in water; Polyvinyl pyrrolidone in water; Methyl vinyl ether-maleic acid copolymer in water; films cast from these solutions and containing some residual solvent. E. Methanol-water containing ammonium bisulfite and urease. F. Water or aqueous methanol containing bisulfite. G. Methanol-water containing ammonium bisulfite alone or with sodium dithionite. H. Methanol-water containing ammonium bisulfite and glucose oxidase. I. Methanol-dioxane with aqueous ammonium bisulfite. J. Benzene.

TABLE IV

PHOTOCHROMIC ACETATE, AMINE BASE*, CHLORIDE AND SULFATE SOLUTIONS

Compound	Solvent Code Letter		
Crystal Violet amine base	D,E,F		
Crystal Violet chloride		A,B,C	
Fuchsin chloride		A,B,C	
Malachite Green amine base	E		
Methyl Green chloride		A,B,C	
New Fuchsin chloride		A,B,C	
New Solid Green chloride		A,B,C	
Pararosaniline acetate		A,B,C	A
Pararosaniline sulfate		A,B,C	
Reference No. (See Section VII)	9	15	22

Solvent Code: A. Water with $NaHSO_3$. B. Methyl cellosolve with methanolic KCN. C. Dimethyl sulfoxide with methanolic KCN. D. Benzene. E. Ethanol with ammonia. F. Ethyl ether.

---

*The amine bases may not be photochromic in the present definition of the term because the color changes they exhibit may not be reversible. Very few triphenylmethane amine base reactions have been reported in the literature.

TABLE V

NON-PHOTOCHROMIC CYANIDE SOLUTIONS

Solvent	Compound	Reference*
Benzene	Brilliant Green	13
	Crystal Violet	13,17
	Malachite Green	13,17
	Victoria Blue	9
Carbon Tetrachloride	Methyl Violet	12
Cyclohexane	Malachite Green	10,24
	Methyl Violet	12
Ethanol	New Orange	8
	Victoria Blue	18
	Victoria Blue B	24
Ether	Victoria Blue	9
Neutral Solutions (general)	Victoria Blue R	14

*The reference numbers correspond with the references in Section VII .

B. Conductivity. Lifschitz and Joffe(18) measured the conductivity of Malachite Green, Brilliant Green, Crystal Violet and Pararosaniline leucocyanides in absolute ethanol before and after irradiation with a mercury-quartz lamp and/or an iron-nickel arc lamp. They observed that the conductivities of Malachite Green and Brilliant Green leucocyanide solutions increased markedly when the solutions were irradiated and decreased to their original values after irradiation ceased. This is shown for Malachite Green in Table 1, Appendix B. In contrast, the conductivities of Crystal Violet and Pararosaniline leucocyanide solutions increased when irradiated but did not return to their original values when irradiation ceased. This is illustrated by the data in Tables 2 and 3 in Appendix B.

Malachite Green and Crystal Violet carbinol solutions slowly increased in conductivity without irradiation, i.e., while being stored in the dark. However, illumination of these two solutions with a mercury arc lamp produced a sharp increase in conductivity which fell off somewhat after a period of darkness storage.

These conductivity changes apparently occurred in direct proportion to visual color changes, but no quantitative simultaneous measurements of absorption and conductivity on the same triphenylmethane solution have appeared in the literature. However, some other data are discussed.(18) For example, Victoria Blue leucocyanide in an alcoholic solution became colored and showed a steadily increasing specific conductance while in the light. This conductance did not fall off in the dark nor did the color fade. Again it was not specified whether or not the conductivity was highest when the optical density was greatest.

De Gaouck and Le Fevre(13) re-examined the conductivity of alcoholic Malachite Green and Brilliant Green leucocyanide solutions. They found that the conductivities did not return to the original values after the solutions were irradiated and stored in the dark as Lifschitz and Joffe reported, but fell to a level somewhat higher than the original. They attributed this discrepancy to the presence of a small amount of water in the alcohol which, by hydrolysis of the leucocyanide, formed hydrogen cyanide. The initial exposure and darkness treatment established a new conductivity level to which the solutions returned in periods of darkness between subsequent exposures to light. Figure 1 illustrates this point.

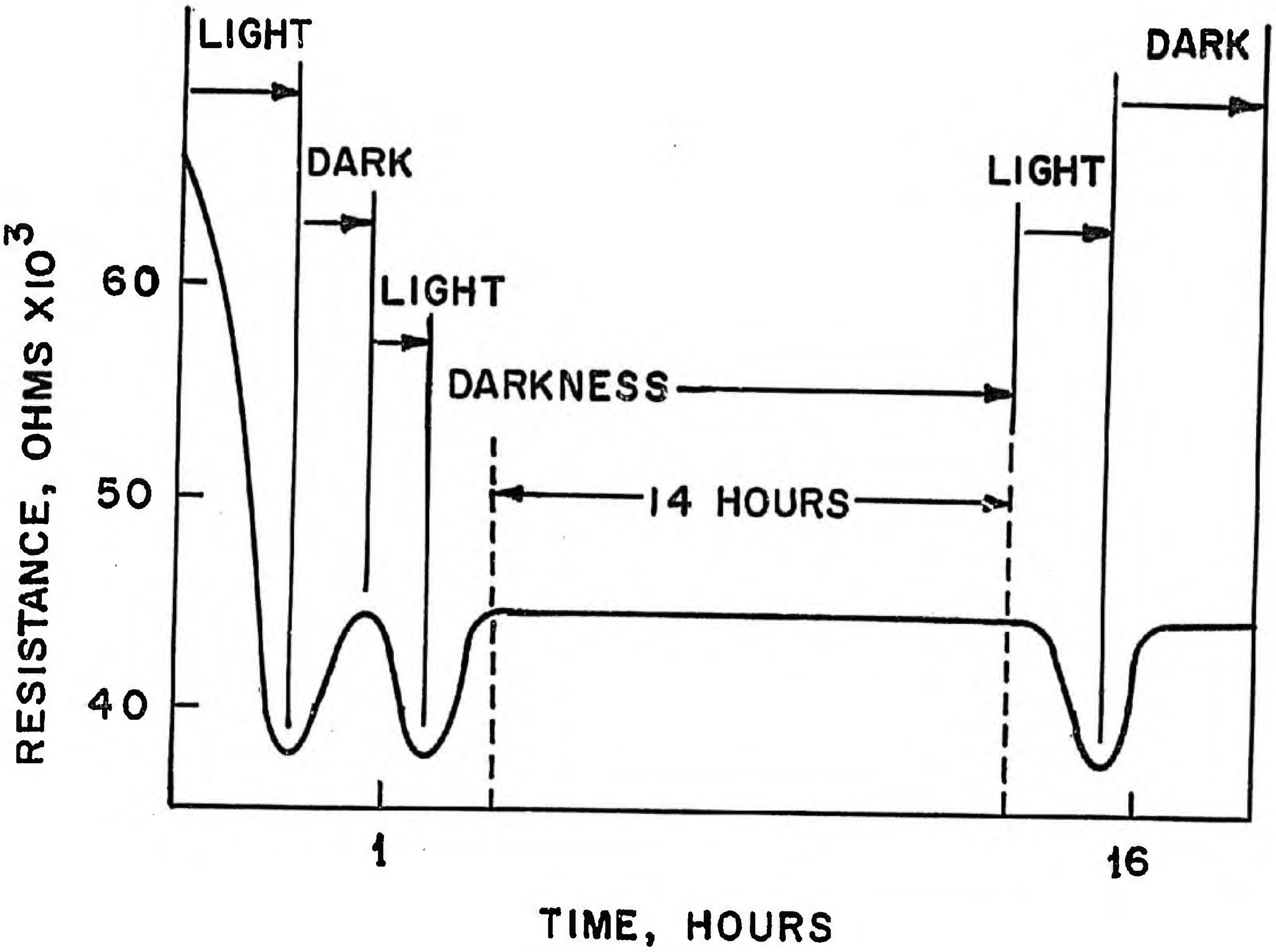


Figure 1. Resistance of Malachite Green Leucocyanide Solution in Ethanol as A Function of Time

C. Exciting Radiations. Holmes[19] studied the radiations producing photochromism in the triphenylmethane sulfonic acids. These compounds are activated by radiation in the 220-330 mμ range and, as expected, conform to the Grotthus-Draper Law which says that only those wavelengths which are absorbed by a system are effective in producing a chemical change. In general, it has been found that the activating wavelengths for the triphenylmethane compounds are in the near ultraviolet spectral region. The intensity of the radiations affects the velocity of the reaction as one can see by comparing ultraviolet lamp and photographic flash bulb irradiation of identical solutions. However, the intensity of the source does not affect the quantum yield of the reaction.

D. Quantum Yield. The quantum yield for the photochromic reaction has been determined by numerous authors and is apparently about unity in ethanol throughout the spectral absorption region of the leucotriphenylmethane compounds. Weyde et al. (24) studied Crystal Violet leucocyanide, Holmes (19) reported on Malachite Green, Harris and Kaminsky (25) studied both compounds, and Calvert and Rechen (26) confirmed Harris and Kaminsky's findings. Recently, Sporer (23), in a study of Malachite Green and N, N', N''-Tris-(2-hydroxyethyl)-pararosaniline leucocyanides, reported a quantum yield of almost 1.0 for dye formation in ethanol for each compound but only 0.25 in water for the latter.

E. Temperature. The effect of temperature on the photochromic reaction was discussed by Luck and Sand[5] who also described thermochromic effects in triphenylmethanes. Generally, the forward color-forming reaction in triphenylmethanes is affected very little by changes in temperature whereas the reverse bleaching reaction is accelerated with increases and decelerated with decreases in temperature. This is true, for example, of Crystal Violet and other leucocyanides in alcohol solution. Barring other factors in these cases, if the rate of the light-induced forward reaction equals the rate of the heat-induced reverse reaction, no photochromy will be observed. However, reverse photoreactions independent of temperature and back reactions dependent only on bleaching agent concentration can also give the same effect.

Although thermochromy is a separate phenomenon and is the subject of a recent review by Day (27), it appears to be closely related to photochromy. For example, the colored forms of a given system produced by heat may be the same as those produced by light as was shown by Hirshberg and Fisher (28) for a series of spiropyrans. These authors concluded that compounds which do not show thermochromy, but are photochromic, require more energy for color formation than can be obtained with heat. Parafuchsin (Pararosaniline), sulfite in aqueous solution shows a strong thermochromic effect (5), increasing in optical density from 0 to 2.8 with an increase in temperature from 20 to 80°C (19). Thermochromic responses have also been observed in aqueous bisulfite solutions of Crystal Violet, Methyl Green, Fuchsin, New Fuchsin, Acid Blue 22 and Acid Violet 19 as well as viscous aqueous methyl cellulose solutions of Methyl Green (15). These systems were also reported photochromic. It is not known whether these observations were made with sealed or unsealed vessels. This is important because temperature has an adverse effect on the photochromy of unsealed bisulfite solutions of triphenylmethane derivatives. Dreyer and Harries (15) reported that the heating process evolved SO_2 gas and formed a non-photochromic leuco base. In a closed vessel the loss of SO_2 is prevented and no change in photochromism is observed. Very brief heating periods will not affect the photochromic capability in open vessels as long as there is excess bisulfite or SO_2 present. This does not preclude the observance of the thermochromy in sealed vessels, however, since SO_2 gas may still be formed, but it does raise a question concerning fatigue with these thermochromic systems.

F. Mechanisms. The nature of the environment has a real effect on photochromic reactions as can be inferred from the foregoing discussion. Lifschitz and co-workers (11, 17, 18, 29) proposed a mechanism for Malachite Green leucocyanide photochromy in ethanol wherein there is a reversible reaction between a colorless unionized and a colored ionized form which goes through a colorless ionized unisolable intermediate (transition state) as shown below.

$$\left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5CCN \ \underset{dark}{\overset{light}{\rightleftharpoons}}\ \left[\left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5C^+\ \ CN^-\right]$$

Colorless (un-ionized) Colorless (ionized)

$$\left[\left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5C^+\ \ CN^-\right] \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} \left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5C^+ + CN^-$$

Colorless (ionized) Colorless (ionized)

Harris, Kaminsky and Simard(30) showed evidence indicating that the above reaction is not reversible with water present but yields the colorless carbinol as in the following sequence of reactions.

$$\left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5CCN \xrightarrow{\text{light}} \left[\left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5CCN\right]$$

Colorless, undissociated
(leucocyanide)

Unstable intermediate

$$\downarrow$$

$$\left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5COH \xleftarrow{\text{water}} \left[(CH_3)_2\ NC_6H_4\right]_2\ C_6H_5C^+ + CN^-$$

Colorless, undissociated
(leucocarbinol)

Colored, dissociated

Harris et al. also assumed an unstable intermediate but showed no evidence for it. Their mechanism was supported, however, by Calvert and Rechen.(26) Germann and Gibson(31) contradicted it, stating that Malachite Green leucocyanide in ethanol containing only a limited amount of water neither reverses to the leucocyanide nor forms the leucocarbinol after the light source is removed but forms yet another substance. They could not identify this substance except as a colorless, light-sensitive material absorbing in the 350 mμ spectral region.

Although these mechanisms are reasonable and based on the experimental evidence, they present only a partial picture. The most nearly complete mechanistic explanations for the photochromic process that have appeared are those of Holmes(10) and Sporer.(23) Holmes showed that the final product of photochromism is the original leucocyanide, the carbinol or the ethyl ether of the triphenylmethane compound, depending upon the solvents and conditions of the reaction. If the KOH, KCN, or H_2O is present in the alcoholic reaction mixture before irradiation, the products are a mixture of carbinol and ethyl ether. In absolute alcohol the ether predominates. If the solution, either before or after irradiation, is saturated with HCN gas, the leuconitrile is the only product. Holmes used spectral techniques to show this and presented a mechanistic scheme in which the forward reactions are caused by light absorption and the reverse reactions are spontaneous thermal reactions. (MG stands for Malachite Green.)

$$\begin{tikzcd}
\mathrm{MGOH} \arrow[r, shift left, "r_1"] & \mathrm{MG}^+ \arrow[l, shift left, "r_4"] & + \arrow[d, shift left, "\mathrm{HCN}"] & \mathrm{OH}^- \\
\mathrm{MGCN} \arrow[r, shift left, "r_2"] & \mathrm{MG}^+ \arrow[l, shift left, "r_5"] & + \arrow[u, shift left, "\mathrm{HOH}"] \arrow[d, shift left, "\mathrm{C_2H_5OH}"] & \mathrm{CN}^- \\
\mathrm{MGOC_2H_5} \arrow[r, shift left, "r_3"] & \mathrm{MG}^+ \arrow[l, shift left, "r_6"] & + \arrow[u, shift left, "\mathrm{HCN}"] & \mathrm{OC_2H_5}^-
\end{tikzcd}$$

Holmes extended his studies of triphenylmethanes in an investigation of Malachite Green leucocyanide in solvents of low dielectric constant and proposed a free radical mechanism to explain his observations. The solvents used in this investigation were cyclohexane, ethylene dichloride, ethylidene dichloride and mixtures of these. Holmes noted that ionization occurs markedly when the solvent dielectric constant is 4.5 or greater and proposed a composite scheme including both free radicals and ions to explain photochromism in Malachite Green. This scheme is illustrated in Figure 2.

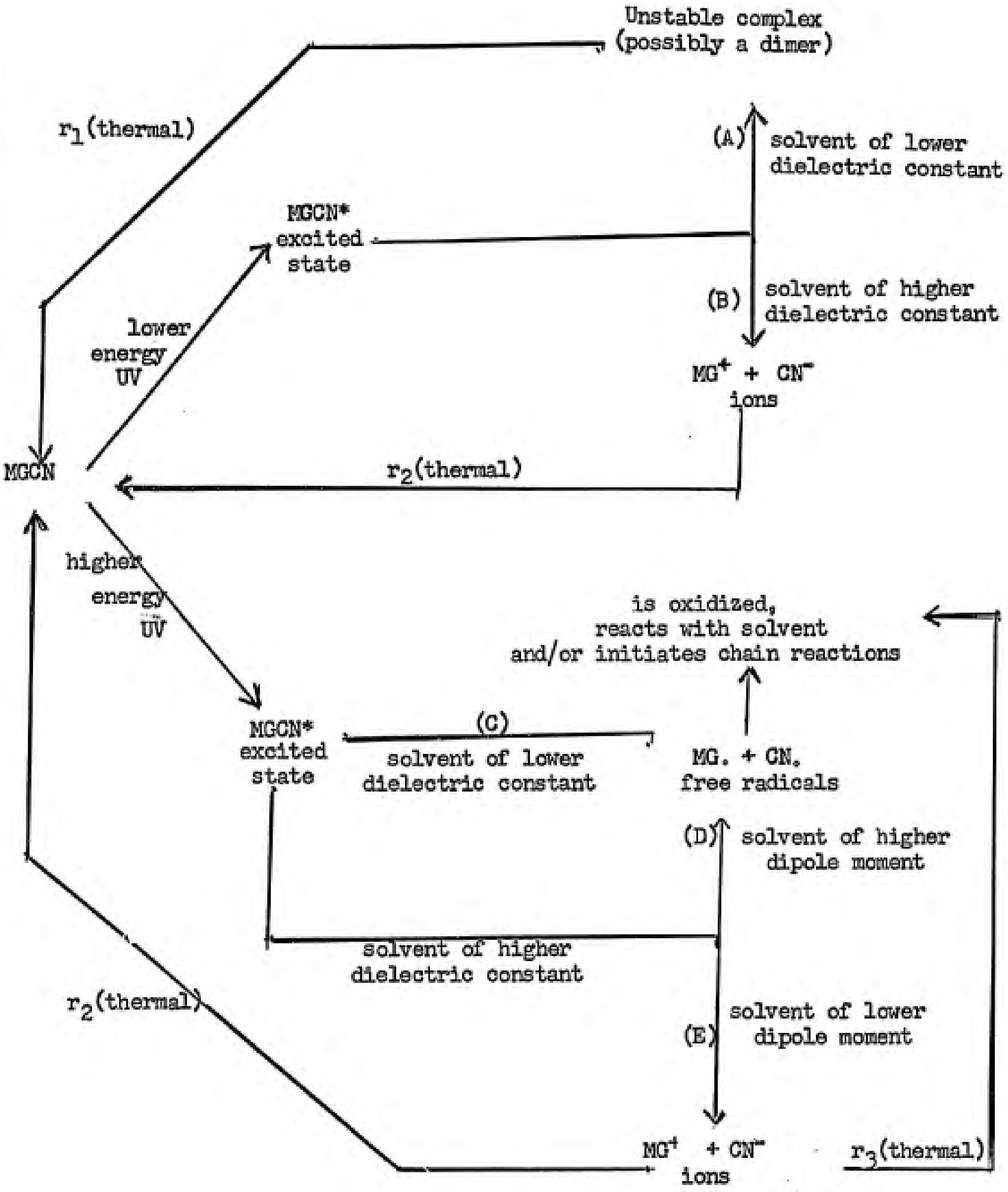


Figure 2. Scheme for Photochromism in Malachite Green Suggested by Holmes(10)

Sporer(23) investigated this further with Malachite Green, Crystal Violet, N,N',N"-Tris-(2-hydroxyethyl)-pararosaniline and Victoria Blue B leuconitrile solutions and reported two photoreactions occurring in most triphenylmethanes. The predominating reaction is photoionization to form the dye, but cleavage of groups on amine nitrogens also occurs, forming free radicals. The latter was indicated in polymerization experiments with vinyl chloride monomer, where a blueish-green polymer was produced during irradiation, and in electron spin resonance studies with dimethylaniline as a control. No triphenylmethyl radical was observed. Free radical formation occurs in solvents of both high and low dielectric constant in a quantum yield of about 2 percent, according to Sporer, but it is observed most easily in solvents of low dielectric constant. In solvents of high dielectric constant, the free radicals are masked by dye formation. Sporer also observed that free radicals were formed in the triplet state of photoexcited molecules but that dye formation occurred neither in the triplet state nor in the excited singlet state. He indicated that dye formation occurs when the molecule undergoes internal conversion from an excited state to the ionized state but he did not elucidate the pathway except to say that it occurs at some low energy level. A different photoreaction was observed in the irradiation of Victoria Blue B solutions where excitation energy is dissipated as fluorescence with no photochromy, except to a small degree when irradiation is carried out above room temperature.

A mechanism for photochromy in triphenylmethane dye-papain-bisulfite mixtures was postulated by Allinikov(21) during a study of various systems, including a parallel study of aqueous bisulfite-Malachite Green solutions with and without papain. He suggested that before photolization there may be a complex formed between the dye and enzyme which is followed by one or more other steps to the formation of colored dye cations during photolization. The enzyme may act as a cage to keep the ions close together after photolization, thus aiding the color-fading reaction. This system is attractive because it apparently resists the fatigue often suffered by dye solutions during a series of exposures to light.

G. Fatigue. Although fatigue is a common occurrence in many dye-solvent systems, the mechanism has not been studied directly in triphenylmethane compounds. However, Sporer's observation of substituent cleavage on the amine nitrogens forming free radicals indicates that unreactive photoproducts may be formed through secondary reactions. The presence of these photoproducts might readily explain the fatigue, observed by Weyde and Frankenburger(24), which occurred after very lengthy exposure of Crystal Violet in ethanol containing KCN. In this system a steady-state color was reached which then faded to yellow. Substituent cleavage may also explain Allinikov's observation of fatigue in aqueous bisulfite solutions of Malachite Green. However, according to Dreyer and Harries(15), fatigue of aqueous bisulfite solutions would be explained by the loss of sulfur dioxide if the systems were exposed to heat and SO_2 was allowed to escape from open or poorly sealed vessels. Dreyer and Harries postulated a reaction scheme for the formation of the leuco base and sulfur dioxide gas from the leucosulfonic acid using Malachite Green as a model but their equations are not balanced. This author suggests that hydrogen may have been formed during heating, causing reduction of the organic moiety as explained by the following equations:

$$\underset{\text{Leucosulfonic acid}}{\left[(CH_3)_2\,NC_6H_4\right]_2\,C_6H_5CSO_3H} \xrightleftharpoons{\text{heat}} \underset{\substack{\text{Colored species}\\\text{(resonance form)}}}{\left[\left[(CH_3)_2\,NC_6H_4\right]_2\,C_6H_5C\right]^+} \quad HSO_3^- \qquad (1)$$

$$NaSO_3H \quad + \quad H_2O \quad \xrightleftharpoons{\text{heat}} \quad NaSO_4H \quad + \quad H_2 \qquad (2)$$

$$\underset{\substack{\text{Colored species}\\\text{(carbonium ion form)}}}{\left[(CH_3)_2\,NC_6H_4\right]_2\,C_6H_5C^+} \quad HSO_3^- \quad + \quad H_2 \quad \xrightleftharpoons{\text{heat}} \quad \underset{\text{Leuco base}}{\left[(CH_3)_2\,NC_6H_4\right]_2\,C_6H_5CH} \qquad (3)$$

$$+ \quad SO_2 \quad + \quad H_2O$$

This scheme could be corroborated by the detection of excessive amounts of sulfate ion because reaction (2) does not occur unless there is a reducible substance present, in this case the organic moiety.

H. Kinetics. The kinetic studies which have been reported for photochromic triphenylmethanes to date are primarily qualitative in nature for the forward reaction and primarily quantitative in nature for the back reaction. The forward reaction was investigated by

Holmes(19) who presented qualitative data showing that Pararosaniline sulfite solutions change color intensity rapidly for the first few minutes of continuous irradiation, then level off, and gradually decrease in intensity after about five minutes of continuous irradiation. Additional qualitative data on the forward reaction were given by Ariga(32) for Malachite Green carbinol solution. In this case the color change was found to be directly proportional to the incident light intensity and independent of temperature and alkali concentration. No quantitative data are available on the rate of the forward reaction except for the limited data provided by Allinikov(21) and Kropp and Moore(20) who indicated that the response time for maximum color formation of Malachite Green with or without enzyme was equal to the rise (to peak intensity) time of their flash lamps, i.e., 10-25 microseconds.

Kinetic studies of the reverse reaction were made by Brown, Adisesh, and Taylor(7) with Methyl Violet and cyanide ion in aqueous ethanol solution and some preliminary data were obtained in ethanolbenzene solution. These authors observed a decrease in the second order rate constant as cyanide ion concentration was increased and explained it with an ion-pair mechanism. They derived equations based on a specific ion-pair, resulting in the equation:

$$k_{\text{obsd.}} = k^*K/(K\left[CN^-\right] + 1)$$

where k obsd. and k* are observed and corrected rate constants and K is the association constant for ion-pair formation. They also observed that both ion-pair formation and reaction rate increase with a decrease in the dielectric constant of the solvent. Rate constants and association constants at 25, 35, and 43.5°C as well as values for several thermodynamic functions were presented.

Similar second order data were obtained by A.D. Little, Inc.(8) (ADL), using Brilliant Green leucocyanide in ethanol solution. ADL indicated that the fading rate is dependent on the concentration of both the triphenylmethane and cyanide ions. The rate is further controllable by the proper choice of anion since experiments showed that the fading rate is also proportional to the basicity (pK_{A^-}) of the anion. ADL warned, however, of the possibility of obtaining a basicity-sensitivity (basicity-efficiency) effect. Additional fading rate data were obtained for eight triphenylmethane leucocyanides, including N,N,N',N',N",N",-Hexa-(2-hydroxyethyl)-pararosaniline, Brilliant Green, Pararosaniline, Crystal Violet, New Green, Malachite Green, Brilliant Blue, New Yellow, and Doebner's Violet in aqueous dimethyl sulfoxide.

I. Spectral Studies. Optical density, luminous density and ultraviolet spectral data have been presented by numerous authors for specific compounds. The most extensive density and spectral data were presented by ADL(8), for the leuco and colored forms of 17 triphenylmethane derivatives. In addition to individual compounds, ADL studied mixtures. The best of these, a mixture of Pararosaniline, Brilliant Green and N,N,N',N',N",N"-hexa-(2-hydroxyethyl)-pararosaniline leuconitriles in aqueous dimethyl sulfoxide, had an attainable luminous density of 2.2. Dependency of luminous density on environmental factors such as solvent composition is indicated by the ADL data, showing a decrease in luminous density from 2.2 to 1.95 with incorporation of ethanol into this solution in place of some of the dimethyl sulfoxide. This change was accompanied by a decrease in the fading rate, indicating a possible relationship between fading rate and sensitivity (efficiency).

Allinikov(21) reported, for Malachite Green, a maximum optical density of 2.5 in aqueous bisulfite alone and 2.0 in aqueous bisulfite with papain. No specific visible wavelength was given for these measurements. Direct comparisons of these data cannot be made because the ADL data are luminous densities whereas the Allinikov data are optical densities and the activation energies used to achieve these densities are not reported.

J. Synthesis. Synthesis data have been presented by nearly all authors for specific compounds under study but it is not within the scope of this review to discuss all the compounds. However, two sources of synthetic data are especially worthy of mention. 1) Tobin et al.(14) reported an improved method for preparation of leuconitriles in which dimethyl sulfoxide was used as the reaction medium in place of water. This eliminated the necessity for tedious recrystallization steps because the leuco product is soluble in the reaction medium and will not precipitate with occlusions as it does from water. 2) The A.D. Little, Inc. report(8) contains syntheses of 19 triphenylmethane derivatives. Some of these are complete syntheses while others are preparations of leuco compounds from the colored chlorides.

VI. CONCLUSIONS AND RECOMMENDATIONS

Photochromism has been observed to varying degrees in a large number of triphenylmethane compounds having relatively broad variations in ring substituents. But it must be clear to the reader by now that although a large amount of high quality work has been performed with a few of these compounds, photochromism in triphenylmethanes is still not thoroughly understood. The mechanisms discussed are still postulations and although the evidence supporting the postulations is convincing, no fundamental photochemical pathway has been determined except in vague terms. On the basis of the evidence accumulated to date it appears that photoionization and/or free radical formation are involved in the mechanism which differs according to the experimental conditions.

As is usual in research, many more questions have been raised than have been answered and new avenues for experimentation have been suggested. All the areas studied so far have room for further work. Typical questions raised are: why is the quantum yield approximately unity in ethanol but only a quarter of this in water, another hydroxylic solvent; why is the forward reaction in bisulfite solutions markedly affected by temperature and the back reaction much less affected, if at all, whereas the opposite is true in cyanide and most other anion solutions; and why do some compounds fluoresce at "lower" temperatures and exhibit photochromism at "higher" temperatures? Numerous experiments can and presumably will be devised to answer these questions. Other work suggested by studying past research efforts are:

1. Measurement of conductivity during flash photolyses for comparison with conductivity data obtained under other conditions of equivalent total irradiance.

2. Quantitative correlation of conductivity changes with the optical density of the irradiated solutions.

3. Study of the fatigue mechanism in bisulfite solutions in open vs. closed containers.

4. Study of the photochromic mechanism in terms of electronic transitions between the colorless state and the observed ionic and/or free radical colored state.

5. Quantitative measurement of the rates of the forward reaction at various levels of irradiance both during flash and constant irradiation photolysis.

6. Measurement of quantum yield data in hydroxylic solvents other than water and alcohol, for example, glycols.

VII. References

1. Chalkley, L., Jr., "Phototropy," Chem. Revs. 6, 217(1929).

2. Brown, G. H., "Phototropy, a literature review," WADC Technical Report 59-436, Contract AF33(616)-5469, Aerospace Medical Laboratory, Wright Air Development Center, Air Research and Development Command, USAF, Wright-Patterson AFB, Ohio, AD 234,009, Unclassified, 1959.

3. Brown, G. H., and Shaw, W. G., "Phototropism," Rev. Pure and Appl. Chem. 11, 2(1961).

4. Dessauer, R., and Paris, J. P., "Photochromism," in Advances in Photochemistry, Vol. 1, Interscience Publishers, 1963, p275.

5. Luck, W., and Sand, H., "The phenomenon of phototropy," Angew. Chem. Internat. Edit. 3(8), 570(1964).

6. Exelby, R., and Grinter, R., "Phototropy (or Photochromism)," Chem. Revs. 65, 247-260(1964).

7. Brown, G. H., Adisesh, S. R., and Taylor, J. E., "Kinetic studies of phototropic reactions, 1. Evidence for an ion-pair intermediate in the reaction of methyl violet with cyanide ion," J. Phys. Chem. 66, 2426(1962).

8. Little, A. D., Inc., Cambridge, Mass., "Research on photochromic compounds for flashblindness protection," Final Report, Subcontract to Edgerton, Germeshausen and Grier, Inc., Bedford, Mass., Contract N62269-2717, U. S. Naval Air Development Center, Johnsville, Pennsylvania (1965).

9. Joffe, C. L., Dissertation, Zurich, 1961.

10. Holmes, E. O., "The phototropy of malachite green leucocyanide in ethyl alcohol, cyclohexane, ethylene dichloride, and ethylidene dichloride, and some mixtures of them," J. Phys. Chem. 61, 434(1957).

11. Lifschitz, J., "Photochemical rearrangements in the triphenylmethane series, III," Ber. 58B, 2434(1925).

12. Brown, G. H., "Kinetic studies of phototropic reactions of triphenylmethane leuconitriles," Tech. Docum. Rept. AMRL-TDR-62-84, Contract AF33(616)-7636, Wright-Patterson AFB, Ohio(1962).

13. de Gaouck, V., and LeFevre, R. J. W., "Phototropy of anils and phototropy of solns. of the leucocyanides of malachite and brilliant greens," J. Chem. Soc. 1939, 1457.

14. Tobin, D., Katzakian, A., and Chisholm, M., "Preparation and study of leucocyanides of triarylmethane dyes," Radiobiology Dept., U. S. Army Medical Laboratory, Fort Knox, Kentucky, Report No. 292, Project No. 6-59-08-012, Subtask USAMRL S-2, MEDEA, Submitted 16 January 1957, AD 139,060, Unclassified.

15. Dreyer, J. F., and Harries, R. W., "Development of a means to provide protection against flashblindness effects of nuclear weapons," Polacoat, Inc., Blue Ash, Ohio, Final Report, Contract DA19-129-AMC-112(N) OI9080, Hdqtrs., QMREC, U. S. Army Natick Laboratories, Natick, Mass., to be published.

16. Gautron, L., "Phototropic materials," Fr. Pat. 1,356,450, March 27, 1964, to Compagnie de Saint-Gobain (C. A. 61, p5910e).

17. Lifschitz, J., and Joffe, C. L., "Photochemical transformations in the triphenylmethane series," Preliminary communication, Ber. 52B, 1919(1919).

18. Lifschitz, J., and Joffe, C. L., "Photochemical transformations in the triphenylmethane series and photoconcentration chains," Z. Physik. Chem. 97, 426(1921).

19. Holmes, E. O., "Photochemical activity of triphenylmethane sulfonic acids," J. Am. Chem. Soc. 44, 1002(1922).

20. Kropp, J. L., and Moore, R. S., "Research on phototropic dye-enzyme systems," Space Technology Laboratories, Inc., Redondo Beach, California, Progress Report, Contract AF-33(657)-11708, Aeronautical Systems Division, Wright-Patterson AFB, Ohio (24 April 1964), AD 448,773, Unclassified.

21. Allinikov, S., "Phototropic enzyme-dye complexes," Nature 205, 492(1965).

22. Brake, J. M., Kropp, J. L., and Moore, R. S., "Research on phototropic dye-enzyme systems," TRW Systems (formerly TRW/Space Technology Labs), Redondo Beach, California, Informal Progress Report, Contract AF33(657)-11708, Aeronautical Systems Division, Wright-Patterson AFB, Ohio (15 October to 15 July, 1965), AD 472,101, Unclassified.

23. Sporer, A. H., "Photoionization of triarylmethyl leuconitriles," Trans. Faraday Soc. 57, 983(1961).

24. Weyde, E., and Frankenburger, W., "Measurement of ultra-violet radiation, esp. of the physiologically active ultra-violet (which produces erythema) by means of the photochem. formation of triphenylmethane dyestuffs from the leuco compounds," Trans. Faraday Soc. 27, 561(1931); Weyde, E., Frankenburger, W., and Zimmerman, W., "Method of measurement for small intensities of ultraviolet light," Naturwissenschaften 18, 206 (1930); Weyde, E., Robl, R., and Zimmerman, W., German Patent 489,471(June 10, 1927).

25. Harris, L., and Kaminsky, J., "Actinometer for the ultraviolet region - test of the Einstein equivalence law," J. Am. Chem. Soc. 57, 1151-4(1935).

26. Calvert, J., and Rechen, H.J.L., "Precision actinometry at low light intensities with MGCN," J. Am. Chem. Soc. 74, 2101 (1952).

27. Day, J. H., "Thermochromism," Chem. Revs. 63, 65(1963).

28. Hirschberg, Y., and Fischer, E., "Photochromism and reversible multiple internal transitions in some spiropyrans at low temperatures," Part I, J. Chem. Soc. 1954, 297; Part II, ibid. 3129.

29. Lifschitz, I., and Girbes, G., "Color, molecular weight and electrolytic character of triphenylmethane derivs.," Ber. 61B, 1463(1928).

30. Harris, L., Kaminsky, J., and Simard, R. G., "Absorption spectrum of malachite green leucocyanide - dark reaction after photolysis," J. Am. Chem. Soc. 57, 1154(1935).

31. Germann, F. E. E., and Gibson, C. L., "Reactions of the leucocyanides of the triphenylmethanes, 1. Dark reaction following the photolysis of malachite green leucocyanide," J. Am. Chem. Soc. 62, 110(1940).

32. Ariga, T., "Photochem reactions of coloring matters, 1. Reversible photochem reaction of malachite green," Bull. Chem. Soc. Japan 2, 65(1927).

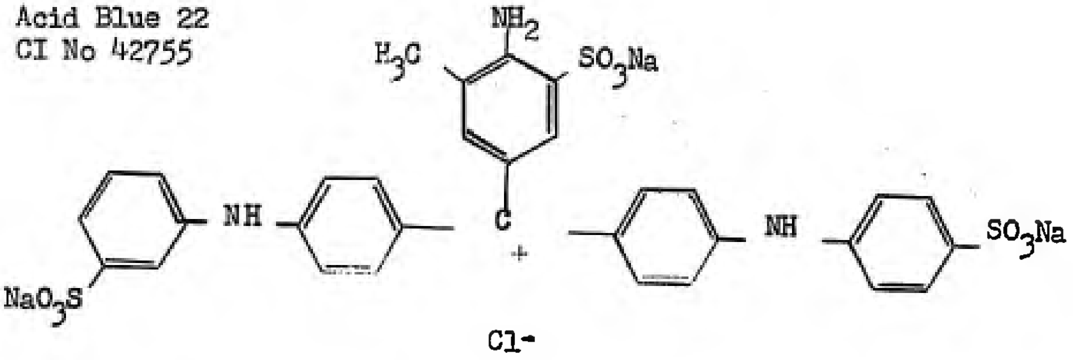
APPENDIXES

APPENDIX A

STRUCTURE OF TRIPHENYLMETHANE DERIVATIVES AND RELATED COMPOUNDS*

*All compounds are presented as the chloride (colored, from which the various leuco forms, i.e., cyanide, carbinol, etc., can be prepared.

Acid Blue 22
CI No 42755



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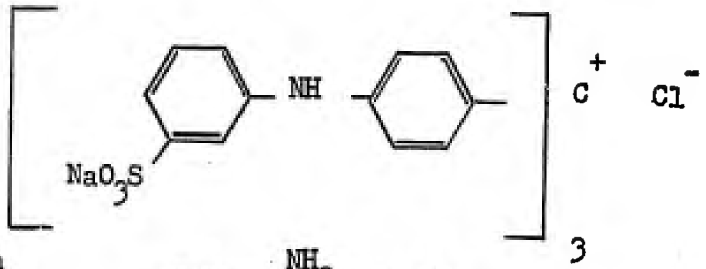
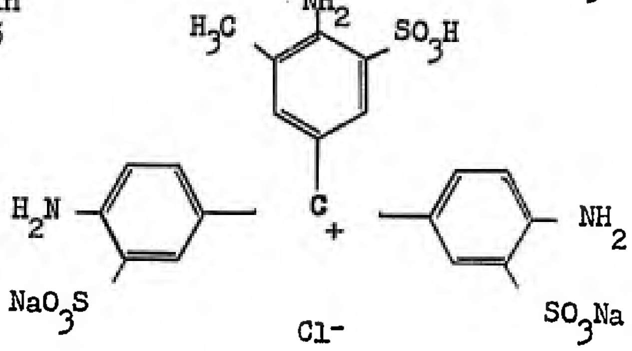
C.I. No 42780



Acid Fuchsin
CI No 42685



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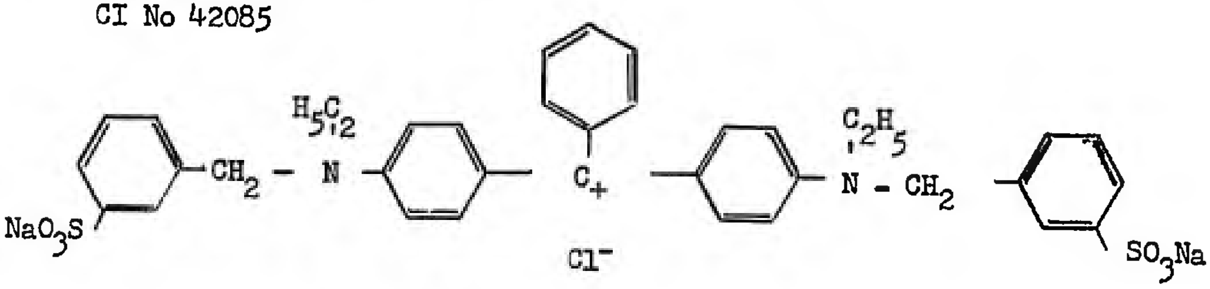

Acid Green 5
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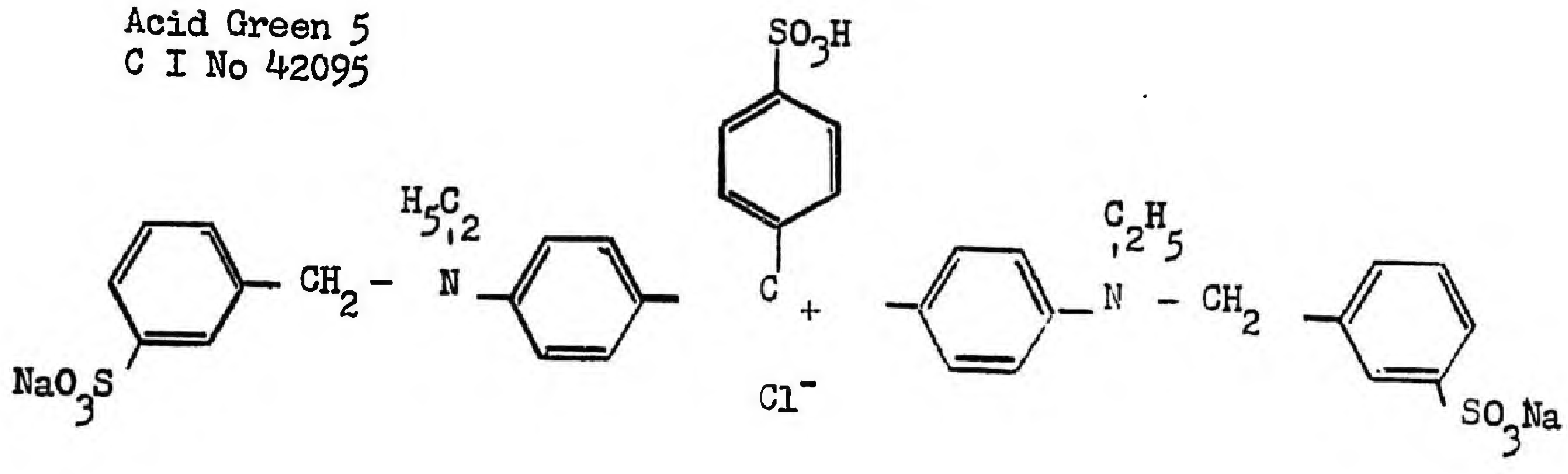

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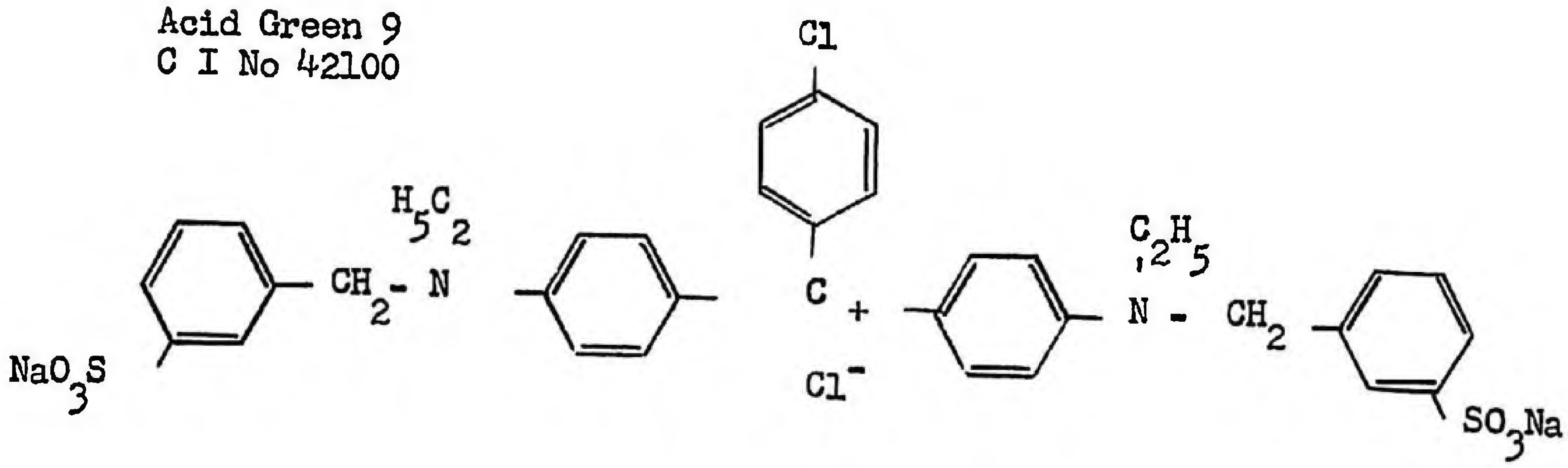
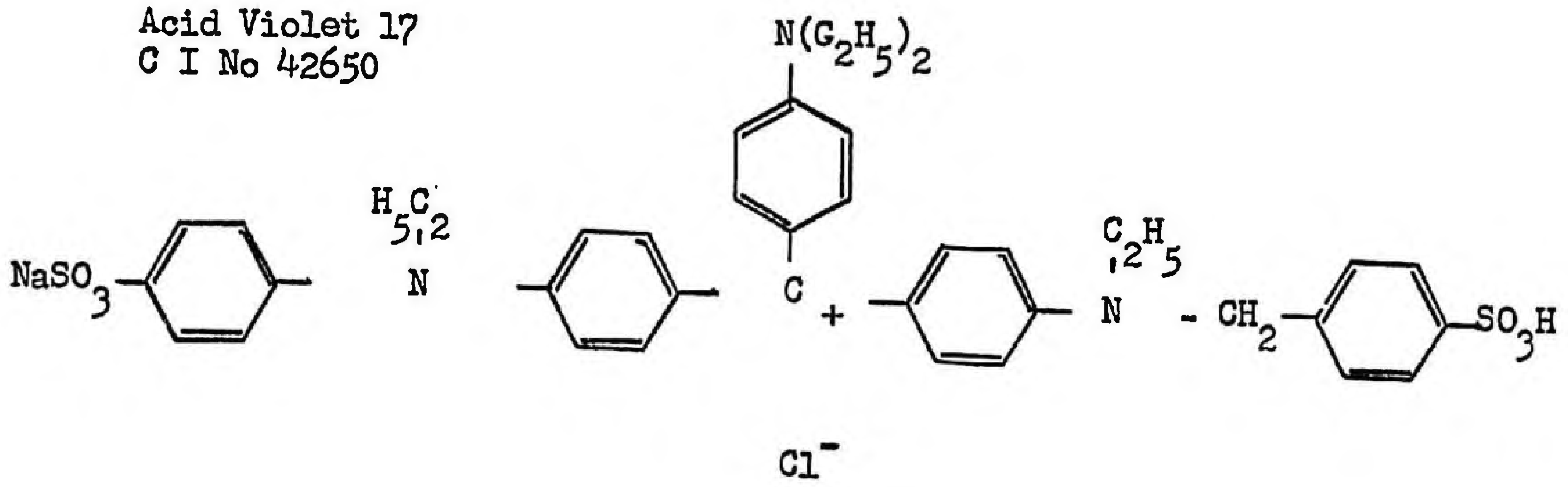
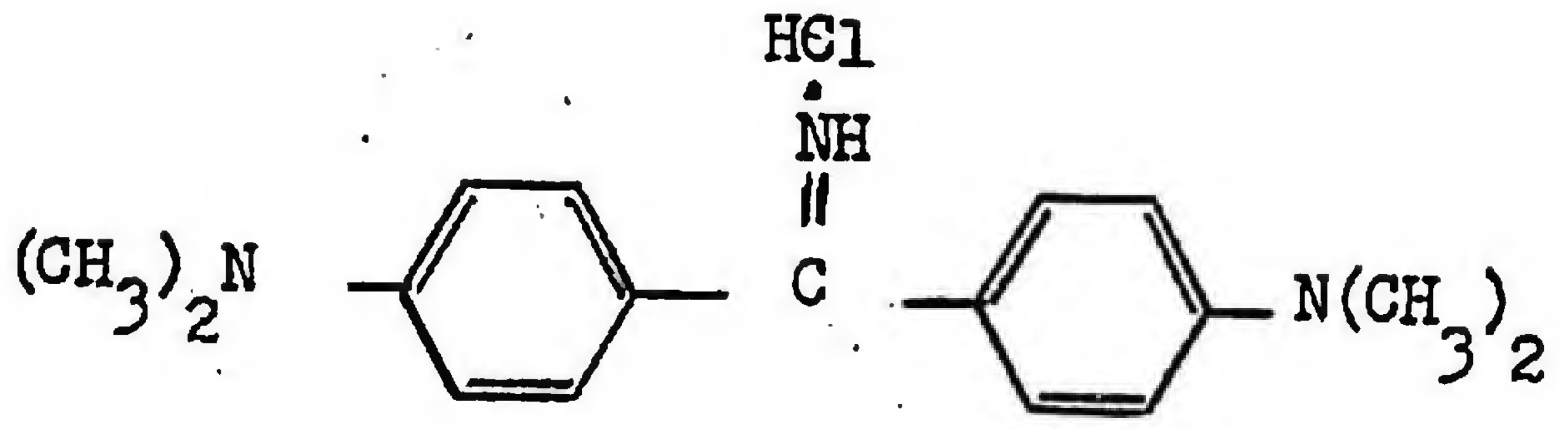


Acid Violet 17
C I No 42650



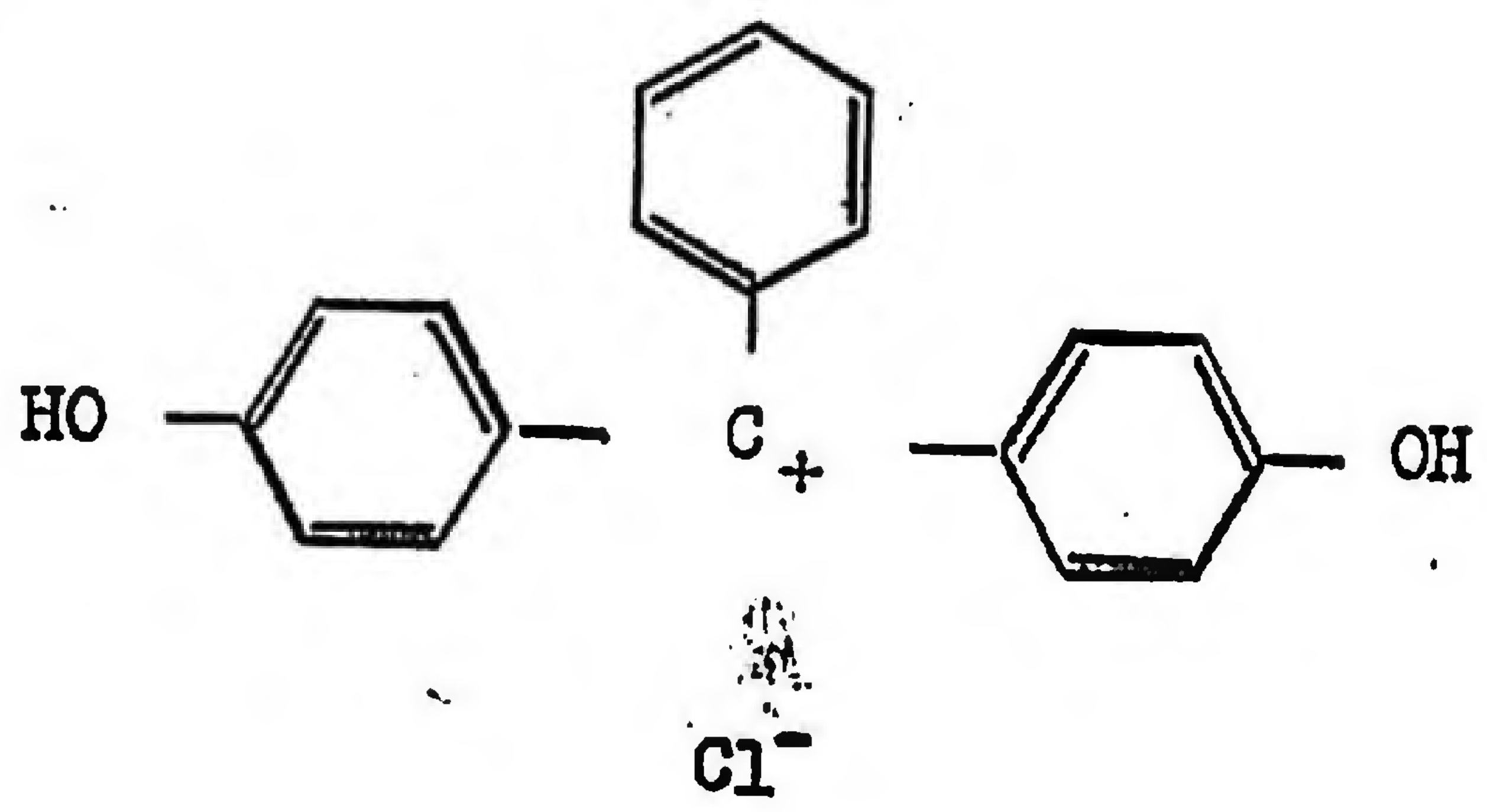
Acid Violet 19 See Acid Fuchsin

Auramine

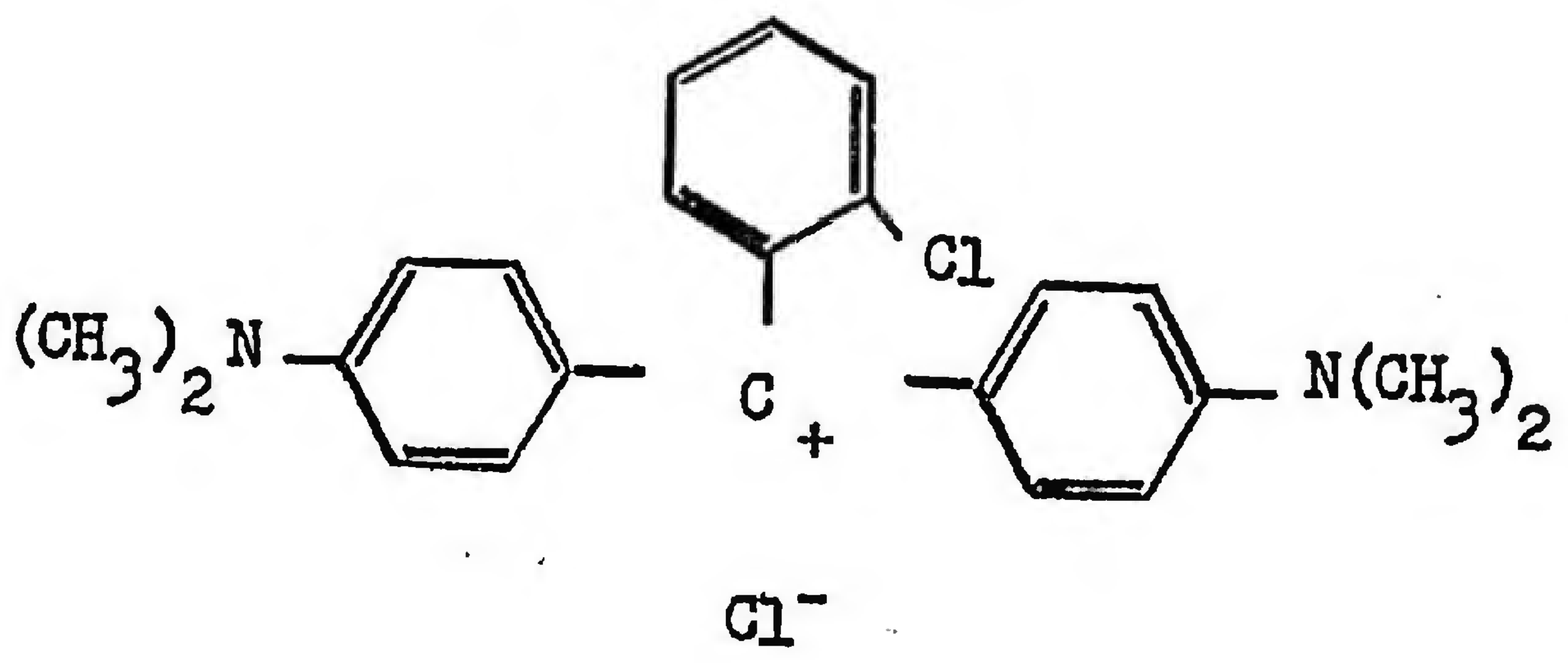


Basic Fuchsin See Fuchsin

Benzaurine



Brilliant Blue (New Solid Green)
C I No 42025



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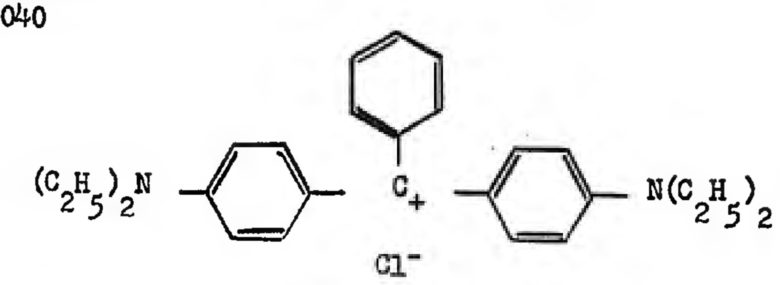
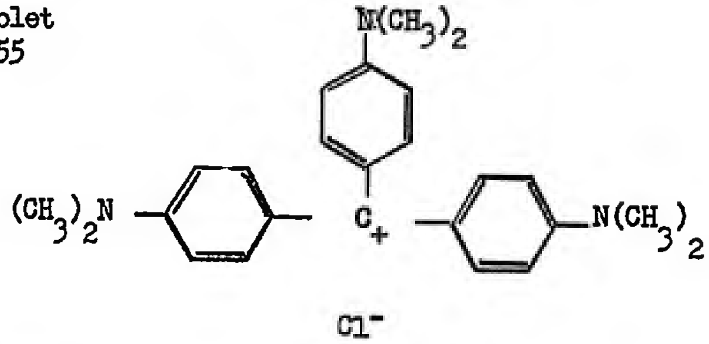
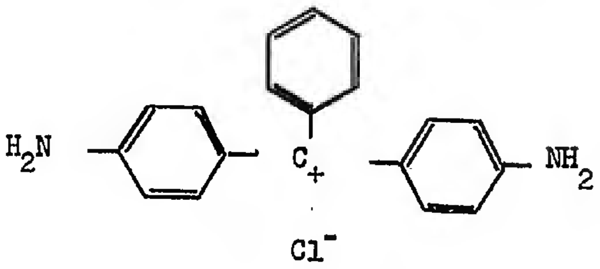
C I No 42040



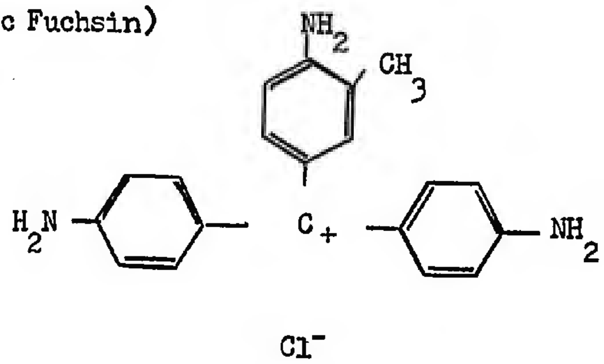
Crystal Violet
C I No 42555



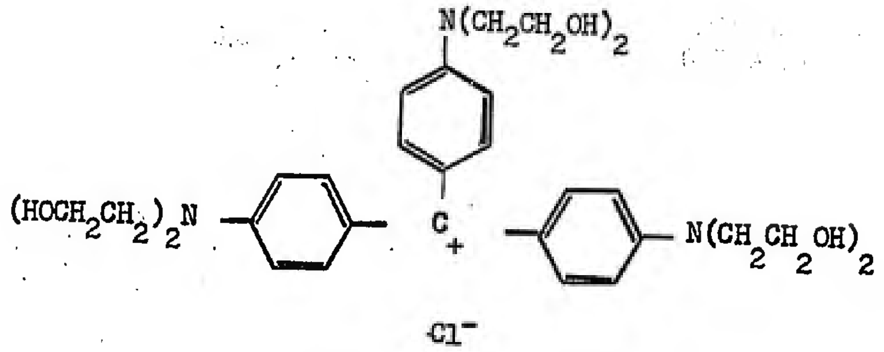
Doebner's Violet



Fuchsin (Basic Fuchsin)
C I No 42510

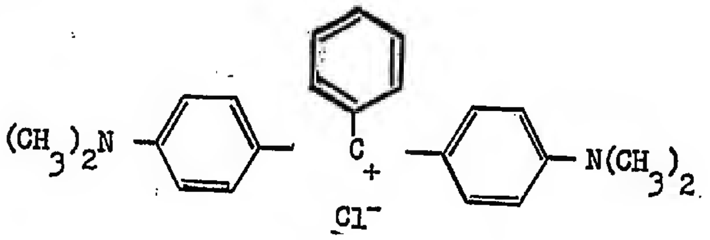


N-Hexa(2-hydroxyethyl) Pararosaniline

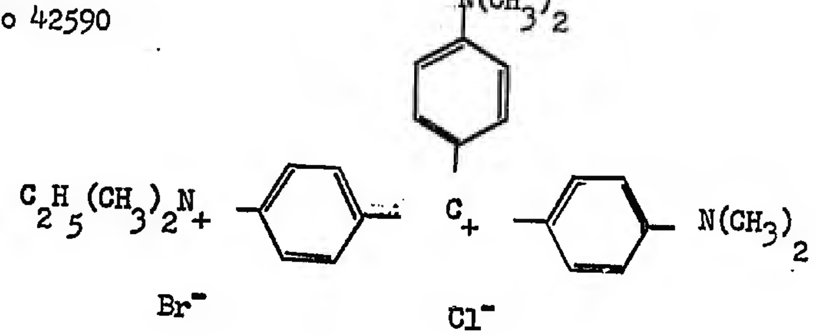


Hydroxyethylated Pararosaniline See N,N',N" - Tris-(2-hydroxyethyl)-pararosaniline

Malachite Green
C I No 42000



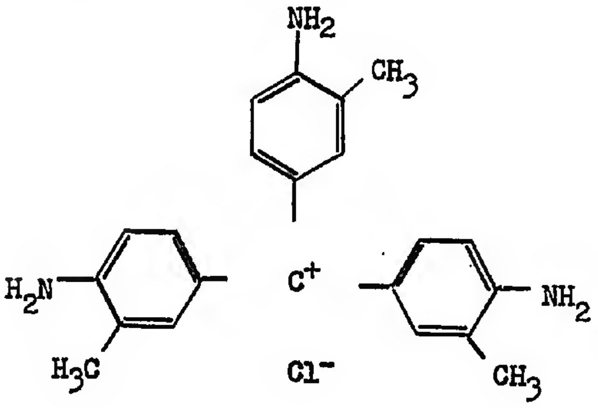
Methyl Green
C I No 42590



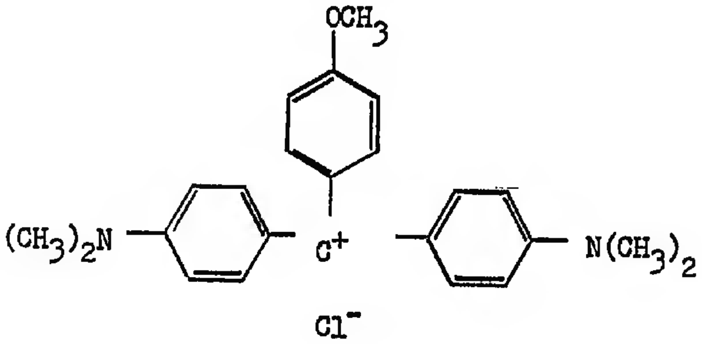
Methyl Violet
C I No 42535

Mixture of methylated Pararosanilines - all stages

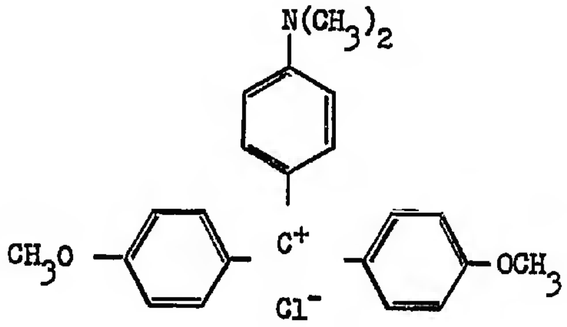
New Fuchsin
C I No 42520



New Green*

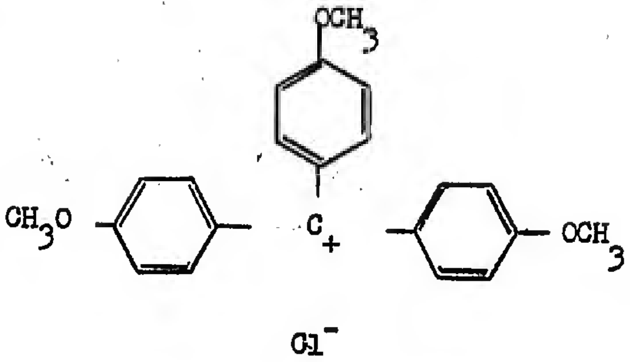


New Magenta*

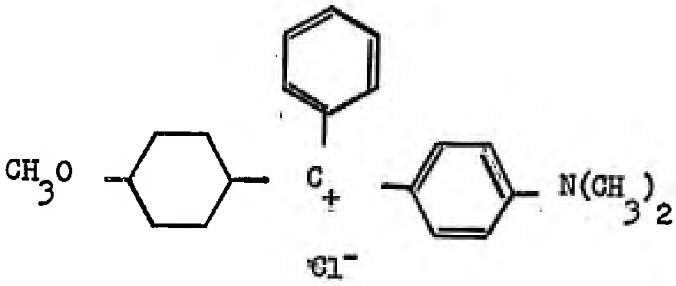


*Name used by A. D. Little, Inc.

New Orange*

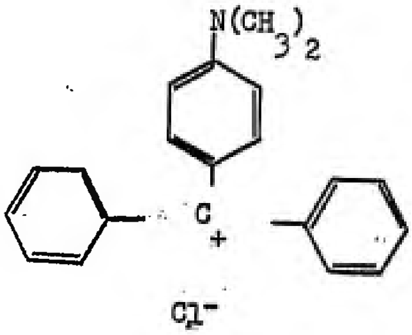


New Red*
C I Natural Red 7



New Solid Green See Brilliant Blue

New Yellow*



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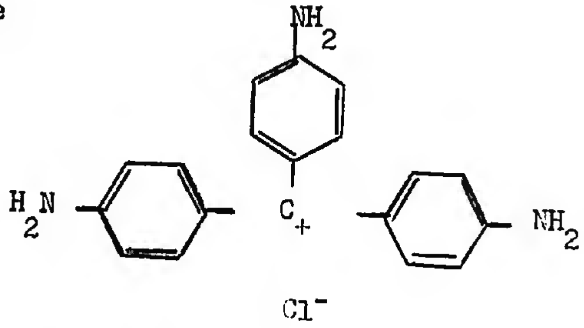
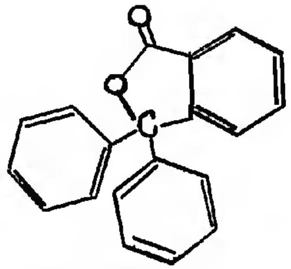
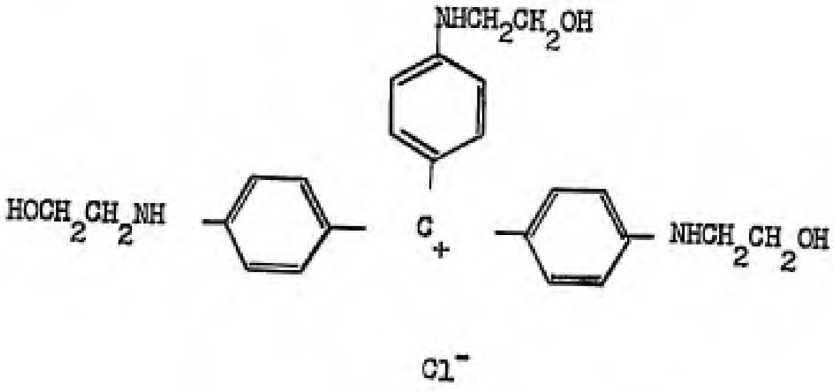
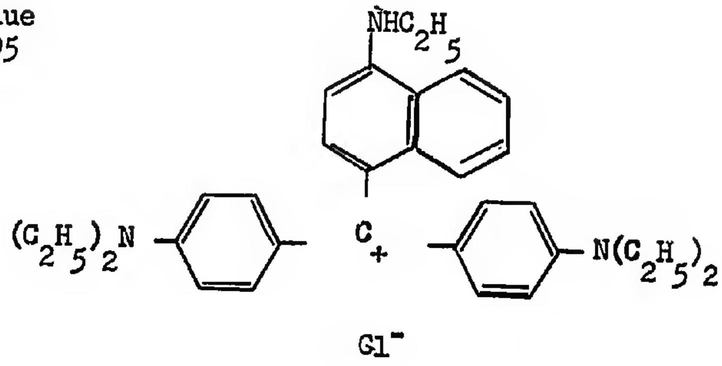
*Name used by A. D. Little, Inc.

Pararosaniline C I No 42500	
Phenolphthalein	
Rosaniline	See Fuchsin
Rosaniline Red	See Fuchsin
Sevron Green B C I Basic Green 3 No CI Number	Proprietary compound of DuPont-exact structure not revealed. Intimated to be a close relative of Victoria Green B[22], a derivative of Malachite Green.

N,N'N"- Tris(2-hydroxyethyl) pararosaniline



Victoria Blue
C I No 42595



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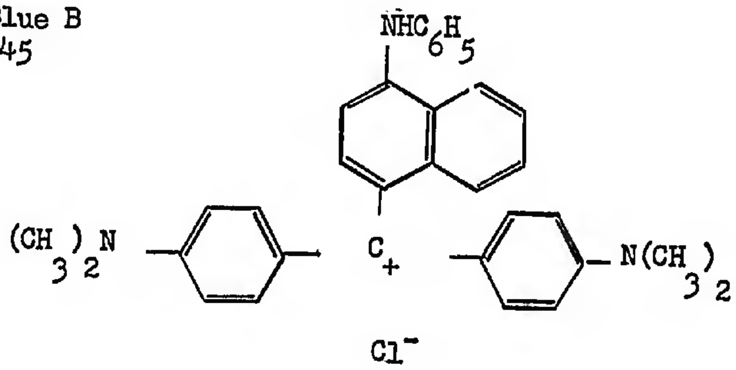

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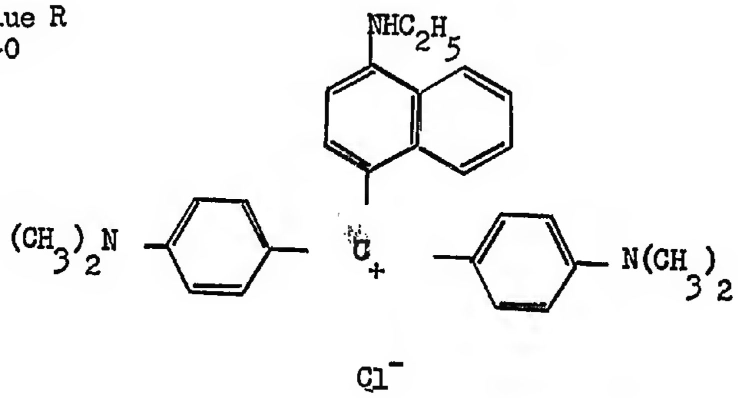

APPENDIX B

TABLES OF CONDUCTIVITY DATA FOR SELECTED TRIPHENYLMETHANE COMPOUNDS

TABLE 1

SPECIFIC CONDUCTIVITY OF A SOLUTION OF MALACHITE GREEN CYANIDE(18)

Temperature: 25°C Solvent: Absolute Ethyl Alcohol

Concentration of Solution: 0.001N Light Source: Mercury Quartz Lamp

Conditions	Specific Conductance (k) x 10^7 (ohm^{-1} cm^{-1})
Original solution	3.5
After illumination for 2 hours	35
In the dark:	
after 2 minutes	31
after 5 minutes	27
after 41 minutes	14
after 46 minutes	13
after 51 minutes	12
after 2 hours 49 minutes	6
after 5 hours	4
after 23 hours 45 minutes	3
after 30 hours 22 minutes	3
after 51 hours 15 minutes	3

TABLE 2

SPECIFIC CONDUCTIVITY OF PARAROSANILINE CYANIDE(9,18)

Temperature:* 25°C

Concentration 0.001N

Solvent: Absolute Ethanol**

Light Source: Iron-nickel Arc Lamp

Conditions	Specific Conductance (k) (ohm^{-1} cm^{-1})
After illumination for 1 hour	18
After illumination, 1-3/4 hours	27
After illumination, 2 hours	41
In the dark after 19 hours	37.5
After additional illumination, 20 minutes	48.5
After additional illumination, 45 minutes	53
After additional illumination, 1-1/2 hours	72.5
In the dark for an additional 66 hours	51
After additional illumination for 1-1/4 hours	70.5
After additional illumination for 2-3/4 hours	100
In the dark for an additional 18 hours	68
After additional illumination for 3/4 hour	82.5
After additional illumination for 3-1/4 hours	86.5
After additional illumination for 4-3/4 hours	91
After an additional 106 days in the dark	52.5

---

*Illuminations were carried out at 12°C, conductivity measurements were made at 25°C

**Alcohol conductivity was 3×10^{-7} to 7×10^{-7} ohm^{-1} cm^{-1}

TABLE 3

SPECIFIC CONDUCTIVITY OF A SOLUTION OF CRYSTAL VIOLET CYANIDE(18)

Temperature: 25°C. Solvent: Absolute Ethyl Alcohol

Concentration of Solution: 0.0002N Light Source: Mercury Quartz Lamp

Conditions	Specific Conductance (k) x 10^7 (ohm^{-1} cm^{-1})
Original solution, in dark	Nearly 0
After illumination for 2 hours	27.5
In the dark for 1-1/2 hours	25
After additional illumination for 4-1/2 hours with an iron-nickel arc lamp	36
After additional illumination for 8-1/2 hours with an iron nickel arc lamp	39.5
In the dark for 66 hours	38
After additional illumination for 12-1/2 hours with an iron-nickel arc lamp	43.5
In the dark for 18 hours	42.5
After additional illumination for 19 hours with an iron-nickel arc lamp	43

TABLE 3 (Cont'd)

SPECIFIC CONDUCTIVITY OF A SOLUTION OF

CRYSTAL VIOLET CYANIDE(18)

Conditions	Specific Conductance (k) x 10^7 (ohm^{-1} cm^{-1})
After additional illumination for 22 hours with an iron-nickel arc lamp	46.5
In the dark for 20 days	24
After additional illumination for 20 hours with an iron-nickel arc lamp and 1-1/2 hours with a mercury quartz lamp	42
In the dark for 20 hours	31
After additional illumination for 22 hours with an iron-nickel arc lamp and 6-1/2 hours with a mercury quartz lamp	56

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13. ABSTRACT

A comprehensive review of photochromism in triphenylmethane derivatives and some related compounds is presented. Most of the individual compounds reported to be photochromic as well as some of those reported as non-photochromic are mentioned. Compounds were included only if the conditions under which the observations were made were reasonably well described. In preparing the review little attention was given to the degree of photochromism reported since very little quantitative data are available. Physical properties of the compounds and/or their solutions which appear to be related to photochromism are discussed including conductivity, dielectric constant and dipole moment. Among other topics discussed are mechanisms and kinetic studies.

14.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Conductivity	6					
Temperature	6					
Fatigue	6					
Physical properties	6		8			
Organic properties	6		8			
Solutions	6,9		9			
Photochromism	7		8			
Triphenylmethane	9		9			
Chemical compounds	9		9			
Dynamics			8			
Spectroscopy			8			
Mechanism			8			
Eyeglasses	4		4			
Protection	4		4			
Flashblindness	4		4			
Literature review	0		0			

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