PHOTOTROPY (OR PHOTOCHROMISM)

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I. INTRODUCTION

In 1899, Marckwald (108) observed that two different organic compounds, the anhydrous hydrochloride of benzo[*c*]-1,8-naphthyridine and 2,3,4,4-tetrachloro-1(4H)-naphthalenone, became colored when exposed to light and that they lost this light-induced coloration when placed in the dark. The term "phototropy" was introduced to designate this reversible color change induced by light. However, in view of the botanical connotation, photochromism (65) is also used to describe the phenomenon. Recent indexes of *Chemical Abstracts* give entries under both words.

These terms should be distinguished from thermochromism, the reversible dependence of color on temperature, which has recently been reviewed by Day (43).

Since the first discoveries, many other phototropic substances have been found, both organic and inorganic, some in solution and some in the solid state. In all cases atoms or molecules which are stable in two forms are involved which are capable of "switching" between two states representing different molecular or electronic configurations. The nature of the solvent has been found critical in the case of solutions, the reversible color change occurring only when the "switching" conditions are favorable. However, totally different mechanisms may be instrumental in different cases and no general theory is available to explain all phototropic reactions.

Previous reviews of this topic have been contributed by Stobbe (164) in 1920, by Chalkley (31) in 1929, and recently by Brown and Shaw (25). The present survey attempts to cover the literature to June 1964, and gives an organized list of phototropic compounds together with the properties, conditions, and theories involved.

In the tables which follow the plus sign indicates that

TABLE I

THE PHOTOTROPIC ANILS

	Aldehyde					
Aromatic amine	Salicyl-	5-Bromo-salicyl- (18)	3,5-Dibromo-salicyl- (17)	*p*-Hydroxy-benz- (148)	2-Hydroxy-3-me-thoxybenz- (152)	*o*-Nitrobenz-
m-Aminobenzoic acid	+(165)	–	–	0	–	0(147)
p-Aminobenzoic acid	+^{a}(151, 152)	0	–	0	–	0(147)
p-Aminobiphenyl	—	–	–	–	–	+(14)
o-Aminocinnamic acid	+(54)	–	–	–	–	–
p-Aminoethyl benzoate	+(54)	–	–	–	–	–
Aniline	+(26, 152)	0	0	0	0	0(147)
o-Anisidine	+^{a}(152)	0	–	+	0	0(14, 147)
p-Anisidine	+(146, 152)	0	–	0	0	0(14, 147)
m-Bromoaniline	+(152)	–	–	0	0	0(147)
o-Bromoaniline	+(152)	0	–	0	0	0(147)
p-Bromoaniline	+(18, 152)	+	0	+	0	0(147)
m-Chloroaniline	0(151)	0	–	0	0	+(147)
o-Chloroaniline	+(151, 152)	0	–	0	0	+(147)
p-Chloroaniline	0(151)	0	–	0	0	0(147)
α-Naphthylamine	0(150, 151)	+	0	0	–	0(14, 147)
β-Naphthylamine	+^{a}(151)	0	0	0	0	0(14, 147)
m-Nitroaniline	–	–	–	–	–	+(14)
o-Nitroaniline	–	–	–	–	–	+(14)
p-Nitroaniline	–	–	–	–	–	+(14)
p-Phenetidine	–	–	0	–	–	+(14)
m-Phenylenediamine	+^{a}(152)	–	0	–	–	0(147)
m-Toluidine	+^{a}(26, 150, 151, 152)	0(151)	–	0	0	0(147)
o-Toluidine	+(152)	–	–	–	0	–
p-Toluidine	+(18)	0	0	0	0	0(14, 147)
2,4-Xylidine	0(150)	0	–	+	0	+(147)
2,5-Xylidine	0(150)	0	–	0	+(146)	0(147)
3,4-Xylidine	+(151, 152)	–	–	0	0	0(147)

[a] Magnetic susceptibility determined (9).

the substance is phototropic The zero denotes that the substance has been examined but is not phototropic. A dash means that no data can be found.

II. ORGANIC COMPOUNDS

A. ANILS

The condensation products of aldehydes and primary amines are known as anils or Schiff bases and have the general formula R—CH=N—R′ in which R and R′ are organic radicals. More than 300 anils have been examined and, although the majority were found to be thermochromic, only a few are phototropic. These are colorless or light yellow crystals in the dark and are dark yellow or brownish red in sunlight. Anils which exhibit phototropy are indicated in Table I.

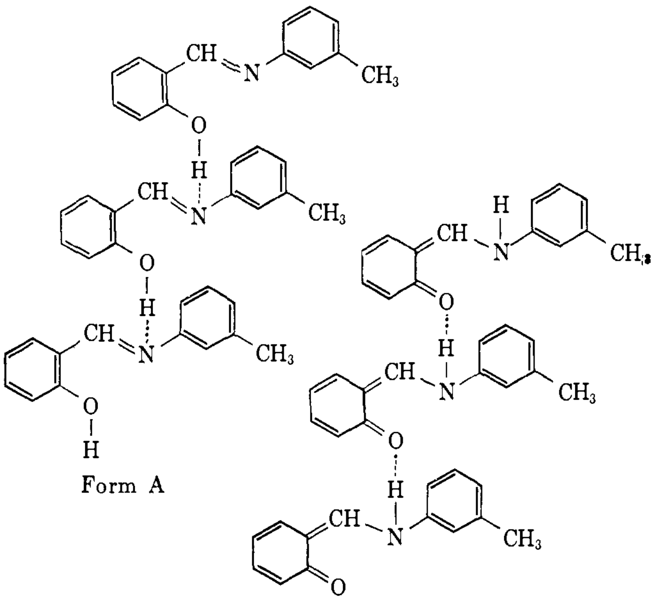
There is a great variation in the time required for the reversible change due to light or darkness. With 5-bromosalicylidene-α-naphthylamine there is a discernible darkening of the crystals on exposure to sunlight for as short an interval as 5 min., and this fades to the original pale yellow color after the compound is kept in the dark for an hour. However, salicylidene-β-naphthylamine requires an exposure to sunlight for an hour to change from yellow to red, and the compound does not change back to the yellow color unless kept in the dark for some weeks. After a number of cycles, some of the anils rapidly fatigue, although salicylidene-*m*-toluidine appears to retain its photosensitive properties for at least several months.

The magnetic susceptibility of the anils marked with superscript *a* in Table I have been determined (9). They showed no change after exposure. In the case of salicylidene-*m*-phenylenediamine the two crystal forms were investigated, both being phototropic. The magnetic susceptibility of the needle-like crystals remained at -4.195×10^{-7} e.m.u. per g. and that of the plate-like crystals remained at -4.782×10^{-7} e.m.u. per g.

Pleochroism is exhibited by the anils (165), and the color change takes place only where the light falls on the crystal.

Lindemann (101) showed that salicylidene-*m*-toluidine is converted from the light yellow crystals into the orange-red unstable form by irradiation with light of wave length 365 mμ. If the phototropic crystals are dissolved after exposure, the color disappears immediately and the resulting solution is identical with the nonexposed. Such solutions are nonphototropic.

de Gaouck and Le Fèvre (55) studied spectrophotometrically and dielectrically various anils in benzene, carbon tetrachloride, and chloroform solutions and detected no change when the solution was illuminated as compared with when it was kept in the dark. It was concluded that the phototropic change was suppressed by the presence of the solvent and that the change can only take place in the solid state. As no crystallographic property appeared to be changed, it was proposed that the change was due to a mutual interaction of the hydroxyl hydrogen of one molecule with the nitrogen atom of another (forms A and B).



Form A

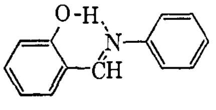
Form B

de Gaouck and Le Fèvre considered the whole solid to be a "hybrid" between the states represented by A and B, in which the molecules are imagined to be oriented as in the diagram. Form A would be yellow and form B would be colored red to yellow. The heat of formation of covalent links in B is 15 kcal. mole^{-1} greater than A, and photoactivation will correspond to an increase in the amount of form B. Modern nomenclature would designate A and B as tautomers not hybrids. Form B, the colored form, is a distinct species different from A. In the crystal the molecules are either A or B but not hybrids. If the hydroxyl hydrogen is blocked by methylation it is found that the phototropy is destroyed, a result which would be expected according to this theory.

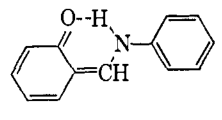
Cohen and Schmidt (39) consider the *o*-hydroxyl group to be of great importance in both phototropic and thermochromic behavior. Each particular anil crystal modification is either phototropic or thermochromic, but not both. Their earlier work (38) showed that in rigid glassy solutions all anils derived from salicylaldehyde and substituted salicylaldehydes are photochromic, whether or not they are so in the crystal form. The authors suggest that phototropy is a property of the isolated anil molecule in an arbitrary rigid matrix and phototropic crystals are a subgroup of this general case. The effect of the crystal structure is twofold: (a) it enables the photochemical *cis–trans* isomerism to occur in the phototropic, but not in the thermochromic series, and (b) it brings about stabilization of the *cis*-quinoid species in the thermochromic lattices (see structures I, II, and III).

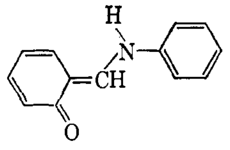
In thermochromic anil crystals the molecules are essentially planar and packed plane-to-plane at about 3.4 Å. spacing while displaced relative to one another along the length of the molecule, providing stabilization of the *cis*-quinone through dipole–dipole interaction. This, it is suggested, is responsible for lack of photochromic properties by preventing *cis–trans* isomerism. In phototropic crystals the structure is sufficiently open to allow the isomerization, while the packing is not of the right type for the dipole–dipole interaction to lead to the stabilization of the *cis*-quinone.

Cohen and Schmidt consider that the requirements for a phototropic system are: (1) a noncolored form I, (2) a colored form II geometrically very similar to I but of higher energy and readily converted into it, and (3) a colored form III geometrically different from II and requiring appreciable activation energy to allow conversion into II.



I, benzenoid





II, *cis*-quinoid III, *trans*-quinoid

(The *cis,trans* labeling is based on the relative positions of H, attached to N, and O)

More recent work (36, 37, 40) confirmed earlier results that there was no change in infrared spectra and X-ray diffraction pattern after irradiation, that photo- and thermochromism are mutually exclusive, and that there must be an hydroxyl group *ortho* to the aldehyde grouping. It is concluded that the phenomenon of phototropy is largely topochemically dominated since no correlation exists between photosensitivity and the chemical nature of the ring substituents and since polymorphic forms of a given anil differ markedly in light sensitivity.

B. HYDRAZONES

Hydrazones can be formed by the condensation of a hydrazine with an aldehyde, ketone, or α-diketone. The hydrazones which are phototropic in their solid state are listed in Table II. A typical structure is benzaldehyde phenylhydrazone.

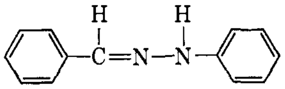


TABLE II

THE PHOTOTROPIC HYDRAZONES

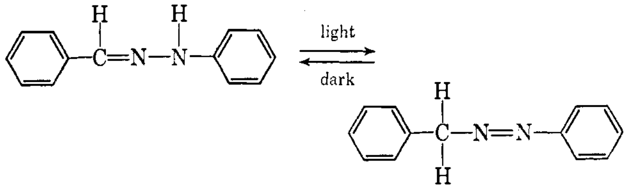
Aldehyde, ketone, or α-diketone	Hydrazine Anisyl- (131)	*p*-Bromo-phenyl- (62)	*m*-Chloro-phenyl- (63)	*p*-Chloro-phenyl- (63)	β-Naphthyl-	Phenyl-	*m*-Tolyl- (125)	*p*-Tolyl- (126)	3,4-Xylyl- (127)	3,5-Xylyl- (128)
o-Aminobenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
Anisaldehyde	0	0	+	0	+(126)	+^{a}(122)	0	0	+	0
Benzaldehyde	+	+^{a}	+	+	+(122, 126)	+^{a}(11, 122)	+	+^{a}	+	–
5-Bromosalicylaldehyde	–	–	–	–	–	+(2)	–	–	–	–
Cinnamaldehyde	+	+^{a}	+	+	+^{a}(126)	+^{a}(125)	+	+^{a}	0	+
Cuminaldehyde	+	+	+	+	+(126)	+(162, 165)	+	+	+	–
p-(Decyloxy)benzaldehyde	–	–	–	–	–	+(24)	–	–	–	–
Diethyl (dimethyl) oxalate	–	–	–	–	–	+(165)	–	–	–	–
2,4-Dihydroxybenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
p-Dimethylaminobenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
2-Furaldehyde	–	–	–	–	+(140)	0(140)	–	+(140)	–	–
m-Hydroxybenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
p-Hydroxybenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
9-Ketofluorene-4-carbonic acid ethyl ester	–	–	–	–	–	+(165)	–	–	–	–
m-Methoxybenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
o-Methoxybenzaldehyde	–	–	–	–	+(165)	–	–	–	–	–
5-Methyl-1-(3,4-methylenedioxyphenyl)-1-hexen-3-one	–	–	–	–	–	+(60, 111)	–	–	–	–
p-(Nonyloxy)benzaldehyde	–	–	–	–	–	+(24)	–	–	–	–
1-Phenyl-2-methyl-1-buten-3-one	–	–	–	–	–	+(60)	–	–	–	–
1-Phenyl-1-hexen-3-one	–	–	–	–	–	+(60, 111)	–	–	–	–
1-Phenyl-1-penten-3-one	–	–	–	–	–	+(60, 111)	–	–	–	–
Piperonal	+	0	+	0	+^{a}(165)	0(125)	+	+^{a}	+	0
Salicylaldehyde	0	+	+	0	0(127)	–	–	–	+	–
m-Tolualdehyde	–	–	–	–	+(165)	–	–	–	–	–
o-Tolualdehyde	–	–	–	–	+(165)	–	–	–	–	–
p-Tolualdehyde	0	0	+	+	+(127)	+(125)	0	0	+	0
Vanillin	+	0	–	0	+^{a}(127)	–	–	0	0	–
Veratraldehyde	–	–	–	–	+(165)	–	–	–	–	–

^{a} Magnetic susceptibility determined (9).

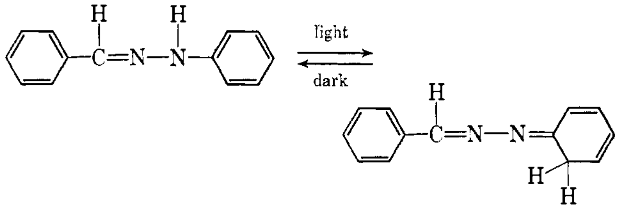
This substance fatigues quickly and loses its phototropic property after a long exposure, but if the crystals are broken in a mortar, the phototropy is regained (32). The crystals also show pleochroism (124).

Magnetic susceptibility determinations on hydrazones marked with a superscript *a* in Table II revealed no change before and after exposure (9).

The phototropy of benzaldehyde phenylhydrazone has been explained as due to isomeric change (32)



but the isomer has been synthesized and found stable (54). Graziani and Bovini (64) postulated the hydrogen transfer



but this cannot be supported as there is no change in the magnetic susceptibility. Gheorghiu (57) considered that as light absorption is produced by easily excited π-electrons in unsaturated compounds, the phototropy results from the ability of these electrons to assume

TABLE III

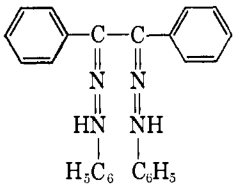
THE PHOTOTROPIC OSAZONES

Diketone	Hydrazine Diphenyl- (132)	Methyl phenyl- (132)	α-Naphthyl- (123)	β-Naphthyl-	Phenyl- (10, 12)	*m*-Tolyl- (130)	*o*-Tolyl- (129, 130)	*p*-Tolyl- (129, 130)	2,4-Xylyl- (123)
Benzil	0	0	0	+β(129)	0	+β	+β	+β	+
Anisil (4,4′-dimethoxybenzil)	0	0	+	+β(130)	+	+β	0β	+β	+
Cuminil (4,4′-diisopropylbenzil)	–	–	–	–	+β	–	–	–	0
Piperil (3,4,3′,4′-bis(methylene-dioxy)benzil)	–	0	+	+β(129)	+	+β	+β	+β	+

different positions. Substituents in the benzene ring capable of resonance favor phototropy, while nonresonating substituents tend to subdue it.

C. OSAZONES

The phototropic osazones are listed in Table III. They are formed by the condensation of the hydrazine with the diketone. The typical osazone structure is benzil phenylosazone.



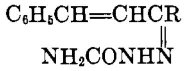
The osazones occur in stereoisomeric forms and where the modification studied is specified this is indicated in the table by α or β. They are reported phototropic only in the solid state.

D. SEMICARBAZONES

The phototropic semicarbazones, formed as the condensation products of semicarbazides with aldehydes and ketones, are listed in Table IV. Where specified the stereoisomeric form studied is indicated in the table.

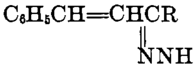
Some of the semicarbazones possess very interesting phototropic properties. Cinnamaldehyde semicarbazone is a white solid when freshly prepared, and its color does not change if it is kept in the dark or kept exposed to light. If, however, after exposure to sunlight it is placed in the dark the compound becomes yellow. Subsequent exposure of this yellow form to light brings back the colorless form. If either the yellow or the colorless form is recrystallized, colorless crystals are formed (184). The semicarbazones of *o*-methoxycinnamaldehyde, *m*-methoxycinnamaldehyde, and *p*-methoxycinnamaldehyde as well as the phenylsemicarbazones of *o*-methoxycinnamaldehyde and *p*-methoxycinnamaldehyde all exhibit this peculiar behavior to light (72). The absorption spectrum of cinnamaldehyde semicarbazone shows a maximum at 280 mμ (184).

Gheorghiu (60) concluded that the ethylenic ketones which give phototropic semicarbazones also give phenylhydrazones which are sensitive to light and in general those of the form ArCH═CHCOR′ give phototropic derivatives, whereas those of the form ArCH═C(R)-COCH$_3$ do not (Ar = aryl; R, R′ = alkyl). The formulas for nonphototropic and phototropic semicarbazones may be, respectively



$$C_6H_5CH{=}CH\underset{\underset{NH_2CONHN}{\|}}{C}R$$

and



$$C_6H_5CH{=}CH\underset{\underset{NNHCONH_2}{\|}}{C}R$$

TABLE IV

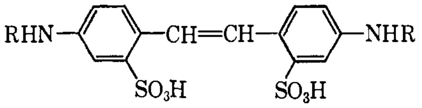
THE PHOTOTROPIC SEMICARBAZONES

Aldehyde or ketone	Carbazone Semi-	Carbazone Thiosemi-	Carbazone Phenylsemi-
Chalcone	+αγ(73)	—	+αγ(74)
Cinnamaldehyde	+(182, 184)	+(72)	—
1-(3,4-Dimethoxyphenyl)-1-buten-3-one	+(46)	—	—
1-(4-Hydroxyphenyl)-2-methyl-1-buten-3-one	—	+(56)	—
1-(2-Hydroxyphenyl)-1-penten-3-one	—	—	+(56)
1-(4-Isopropylphenyl)-1-hexen-3-one	—	+(56)	+(56)
1-(4-Isopropylphenyl)-1-penten-3-one	—	+(56)	+(56)
m-Methoxycinnamaldehyde	+(72)	—	0(72)
o-Methoxycinnamaldehyde	+(72)	+(72)	+(72)
p-Methoxycinnamaldehyde	+(72)	—	+(72)
1-(4-Methoxyphenyl)-2-ethyl-1-buten-3-one	—	+(56)	0(56)
1-(2-Methoxyphenyl)-2-methyl-1-buten-3-one	—	+(56)	—
1-(4-Methoxyphenyl)-5-methyl-1-hexen-3-one	+(58, 59)	—	—
1-(2-Methoxyphenyl)-4-methyl-1-penten-3-one	—	+(56)	—
1-(4-Methoxyphenyl)-1-penten-3-one	+(58, 59)	—	—
1-(3,4-Methylenedioxyphenyl)-1-hexen-3-one	—	—	+(56)
1-(3,4-Methylenedioxyphenyl)-5-methyl-1-hexen-3-one	+γ(60, 111)	—	+δ(60, 111)
1-(3,4-Methylenedioxyphenyl)-4-methyl-1-penten-3-one	—	+(56)	—
1-(3,4-Methylenedioxyphenyl)-1-penten-3-one	—	+(56)	+(56)
1-(1-Naphthyl)-1-hexen-3-one	+(61, 111)	—	—
1-(1-Naphthyl)-5-methyl-1-hexen-3-one	+(61, 111)	—	—
2-Nitrochalcone	+(111)	—	—
3-Nitrochalcone	+(111)	—	—
1-Phenyl-1-buten-3-one	—	+(56)	+(56)
1-Phenyl-1-penten-3-one	+(58, 59)	—	—

Substituents in the benzene ring capable of resonance favor phototropy, while nonresonating substituents tend to subdue it. Thus the semicarbazone of *o*-CH_3O-$C_6H_4CH{=}CCH_3COCH_3$ is more phototropic than the semicarbazone of $C_6H_5CH{=}CCH_3COCH_3$, while that of *p*-(*i*-C_3H_7)$C_6H_4CH{=}CCH_3COCH_3$ is almost entirely insensitive to light (57).

E. STILBENE DERIVATIVES

Stobbe and Mallison (166) found a number of phototropic derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid (IV, R = H). The phototropic crystals are derived from the original aminostilbene acid by sub-


IV

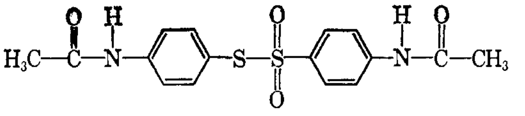
stituting the group -COR for one of the hydrogen atoms of each of the amino groups. The reversible color changes of all the derivatives are from colorless or yellow in the dark to pink in the light.

The phototropic acids are: (1) 4,4′-diformamido-2,2′-stilbenedisulfonic acid (IV, R = HCO); (2) 4,4′-diacetamido-2,2′-stilbenedisulfonic acid (IV, R = CH_3CO) and its sodium, potassium, barium, strontium, calcium, magnesium, and lead salts; (3) diformamido-*p,p′*-diaminodibenzoyl-4,4′-diaminostilbene-2,2′-disulfonic acid (IV, R = HCO-NH-*p*-C_6H_4-CO-); (4) diacetamido-*p,p′*-diaminodibenzoyl-4,4′-diaminostilbene-2,-2′-disulfonic acid (IV, R = CH_3CO-NH-*p*-C_6H_4-CO-); (5) diacetamido-*p,p′*-diaminodibenzoyl-*p,p′*-diaminodibenzoyl-4,4′-diaminostilbene-2,2′-disulfonic acid (IV, R = CH_3CO-NH-*p*-C_6H_4-CO-NH-*p*-C_6H_4-CO-).

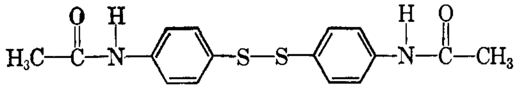
The phototropic mechanism suggested by Stobbe (166) is that on exposure to light the stilbene derivatives take up oxygen to form a colored organic oxide which may be a peroxide, an ethylene oxide, or an amine oxide.

F. THIOSULFONATES (DISULFOXIDES)

Acetanilide-*p*-thiosulfonate is phototropic when



mixed with about 0.1% of acetanilide *p*-disulfide (7, 34)



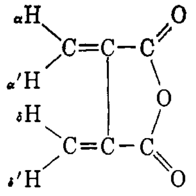
Exposure to light produces a reversible change from colorless crystals to yellow ones.

Perfectly pure acetanilide-*p*-thiosulfonate is not phototropic. The disulfide must be in solid solution in the crystals of the thiosulfonate in order to exhibit phototropy (simple mechanical mixing is not sufficient) and the disulfide must be in the proper concentration. Other phenyl disulfides containining amino groups, or substituted amino groups, *para* to the sulfur atoms may replace the acetanilide disulfide. However, the corresponding *meta* and *ortho* compounds are not phototropic.

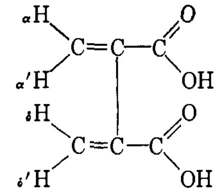
The following substances, which probably contain traces of disulfide, are also phototropic: 1-acetylaminonaphthyl-4-thiosulfonate, 2-acetylaminotolyl-5-thiosulfonate, and 4-acetylaminophenyl-*p*-chlorobenzenethiosulfonate.

G. FULGIDES

The fulgides (substituted succinic anhydrides) are obtained by substitution of the lettered hydrogen atoms in the acid anhydride



It is also possible to prepare the free acids



the salts, and esters of the acids. As four hydrogen atoms can be substituted by organic radicals and as certain substituted fulgides may exhibit *cis–trans* isomerism, it will be seen that the possible derivatives of the parent substance are quite large in number.

The fulgides have been studied by Stobbe (162, 163, 165) and Hänel (67) and Table V lists some which are phototropic. The anhydrous sodium salt of α,δ-diphenylfulgic acid was found to be nonphototropic, but the salt with water of crystallization proved to be phototropic.

The fulgides have initially a yellow to red color and the effect of light is to deepen the color. The fulgic acids and their derivatives are white or light yellow and also darken on exposure. Stobbe suggested that some listed as nonphototropic may show a change of absorption in the ultraviolet.

Stobbe (161, 162) believed a colored isomer is formed, the fulgide being converted into a stereoisomeric form which reverts to the original on standing in the dark.

H. DYE DERIVATIVES

1. Aromatic Azo Compounds

The phototropic behavior of some azo dyes in solution (20, 21, 70, 159) has been carefully investigated because of their wide use in industry. The changes induced in the absorption spectra of aminoazo dyes in benzene solution by irradiation from a tungsten lamp were found to be reversible and dependent on the structure of the dyes concerned. In general, derivatives of *p*-aminoazobenzene were most strongly phototropic, those of *p*-hydroxyazobenzene less phototropic. α-Naphthylazobenzene dyes were found to be weakly phototropic; *o*-hydroxyazobenzene and its derivatives showed phototropism only under the influence of ultraviolet light.

TABLE V

THE PHOTOTROPIC FULGIDES (67, 162, 163, 165)

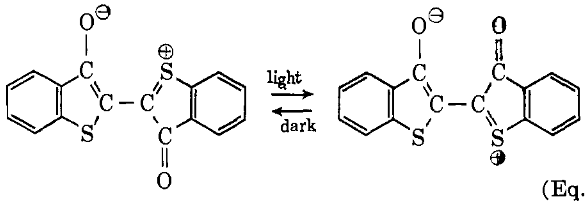
	Fulgide	Fulgic acid	Na salt	Ba salt	Acid ester Na salt	K salt	Me ester	Ca salt
α-Anisyl-δ,δ′-diphenyl-	0	+	–	–	–	–	–	–
α-Anisyl-δ-phenyl-	+	–	0	0	–	–	–	–
α-(*p*-Chlorophenyl)-δ,δ′-diphenyl-	+	+	–	–	+	–	–	–
α-Cumyl-δ,δ′-diphenyl-	+	0	+	+	–	–	–	–
α,δ-Dianisyl-	+	–	–	–	–	–	–	–
α,δ-Dicumyl-	+	–	–	–	–	–	–	–
α,δ-Dicumyliso-	+	–	–	–	–	–	–	–
α,δ-Difuryl-	+	–	–	–	–	–	–	–
α,α′-Diphenyl-δ,δ′-dimethyl-	+	0	–	–	–	–	–	–
α,δ-Diphenyl-δ′-methyl-	+	–	–	–	–	–	–	–
α,δ-Diphenyl-	+	+	+	–	–	–	–	–
α,δ-Distyryl-	+	–	–	–	–	–	–	–
α,δ-Diveratryl-	+	+	–	–	–	–	–	–
α-(*o*-Ethoxyphenyl)-δ,δ′-diphenyl-	+	0	–	–	–	–	–	–
α-Furyl-δ,δ′-diphenyl-	+	–	–	–	–	–	–	–
α-(*o*-Methoxyphenyl)-δ,δ′-diphenyl-	+	+	+	–	–	–	+	–
α-(*p*-Methoxyphenyl)-δ,δ′-diphenyl-	+	–	–	–	–	–	–	–
α-(*o*-Nitrophenyl)-δ,δ′-diphenyl-	+	+	+	–	–	–	–	–
α-(*p*-Nitrophenyl)-δ,δ′-diphenyl-	+	+	+	–	–	–	–	–
α-Piperonyl-δ,δ′-dimethyl-	+	0	–	–	–	–	–	–
α-Piperonyl-δ,δ′-diphenyl-	+	0	–	–	–	–	–	–
α-Piperonyl-δ-phenyl-	+	–	–	–	–	–	–	–
α-Styryl-δ,δ′-diphenyl-	+	–	–	–	–	–	–	–
Tetraphenyl-	+	–	–	–	–	–	–	–
α-(*p*-Tolyl)-δ,δ′-diphenyl-	+	+	+	–	–	–	–	–
α,α′,δ-Triphenyl-	–	+	+	0	–	–	–	+
α,δ,δ′-Triphenyl-	+	–	–	–	–	–	–	–
α-Veratryl-δ,δ′-diphenyl-	+	+	+	0	–	0	–	–

The results (20) are consistent with the idea that these dye solutions contain the *cis* and *trans* isomers in equilibrium with each other. Irradiation causes partial isomerization to the unstable *cis* isomer and subsequent standing in the dark results in reversal to the stable form. The accumulation of substituents in the *ortho* positions of *p*-hydroxyazobenzene inhibits the resonance, and additional stabilization of the *trans* isomer can be produced by hydrogen bonding in *o*-hydroxyazobenzene and its derivatives (76).

Absorption spectra for some azo dyes in ethyl alcohol solution and in acetyl cellulose film have been obtained (113). The phototropic behavior of 4-(*p*-dimethylaminobenzeneazo)phenylmercuric acetate dissolved in dimethylformamide has been shown to be due to photoinduced *trans–cis* isomerism (83).

2. Thioindigo Dyes

The light-induced color changes which occur in benzene and chloroform solutions have been attributed (22, 187) to the *cis–trans* equilibrium shown in Eq. 1. While the azo dyes were found to have very rapid recovery times, in the case of the thioindigo dyes the rate of return of the *cis* form to the *trans* form is so slow that it was possible to obtain a complete spectrum of solutions rich in the *cis* isomer.



(Eq. 1)

trans form *cis* form

3. Triphenylmethane Dye Derivatives

The cyanides, carbinols, and sulfites of various triphenylmethane derivatives have been found to be phototropic in solution. The solutions are colorless or faintly colored in the dark, but acquire the color of the parent dyestuff on exposure to light.

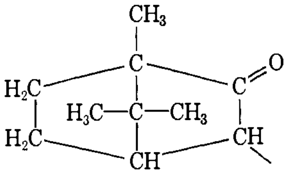
Solutions which are known to be phototropic include: *Cyanides:* auramine, brilliant green, crystal violet, methyl violet (23), malachite green, and pararosaniline in ethanol (97) or ethyl ether (86); benzaurine cyanide and phenolphthalein cyanide in water, or aqueous alcohol containing KCN (98). *Carbinols:* malachite green and crystal violet in ethyl alcohol with KOH (97, 99); benzaurinecarbinol and phenolphthaleincarbinol in water or aqueous alcohol with KOH (98). *Sulfites:* crystal violet, malachite green, methyl violet, pararosaniline, (86, 99), and rosaniline in water containing sulfur dioxide (81).

The phototropy of malachite green leuco-cyanide has been ascribed to ionization induced by the illumination (55) and a colorless ionized intermediate has been postulated (97–99). de Gaouck and Le Fèvre (55) (unlike Joffé (86)) found no phototropy exhibited in benzene solutions, but in alcoholic solutions they confirmed the increase in electrical conductivity which accompanies illumination and color development. The colorless carbinol, not the original leuco-cyanide, has been proposed as the final product of the dark reaction (27, 69).

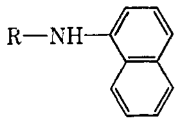
Holmes (82) has proposed that the triarylmethyl leuco-nitriles on excitation with ultraviolet light show phototropism by the formation of either a triarylmethyl radical or the corresponding dye depending upon the dipole moment and the dielectric constant of the solvent. Sporer (158) found that there are two photoreactions—dye formation and cleavage of substituents on the amine nitrogens. The cleavage was found to be most pronounced in solvents having a low dielectric constant. Cleavage was also found in solvents of high dielectric constant, but this process was masked by dye formation. The kinetics of the formation of the leuco-nitrile in ethanol have been studied and an ion-pair mechanism for the phototropy postulated (23).

I. CAMPHOR DERIVATIVES

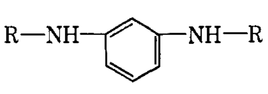
In all structural formulas in this section R is



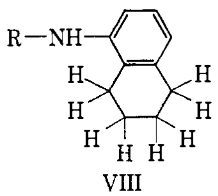
In chloroform solution 3-(1-naphthylamino)-*d*-camphor (V), 3-(*m*-phenylenebisamino)-*d*-camphor (VI), and 3-(5,6,7,8-tetrahydro-1-naphthylamino)-*d*-camphor (VII) are found to be phototropic (153). The phototropic change of 3-(1-naphthylamino)-*d*-camphor also occurs in bromoform, ethanol solution of iodoform, chloral alcoholate, and methylene iodide and is much less marked in carbon tetrachloride. It is inhibited by traces of sodium ethoxide and water. The solutions become green on exposure (154).



V

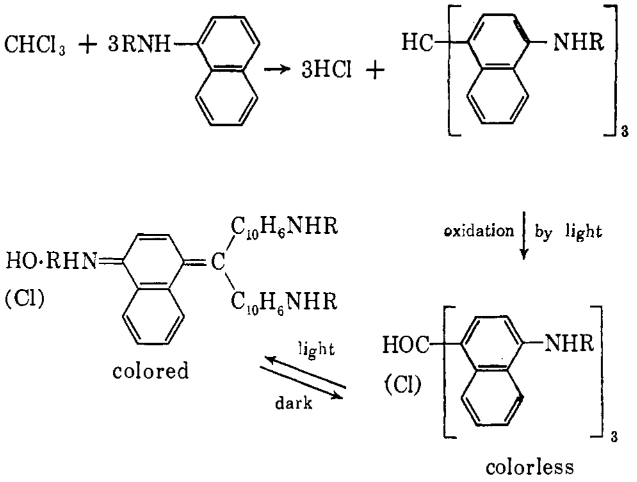


VI

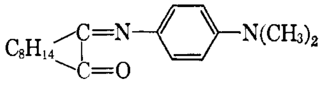


VIII

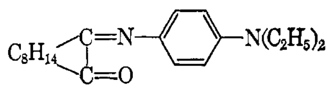
Singh and Bhaduri (154) found that the solutions of 3-(1-naphthylamino)-*d*-camphor become more acidic after exposure and that only those halogen-containing solvents which contain two or three atoms of halogen attached to the same carbon atom can bring about the phototropic change. The specific rotation was found to increase on exposure to sunlight. They proposed the dinaphthylmethane or trinaphthylmethane derivative is first formed with the liberation of the halogen acid, and the methane derivative is then oxidized to the carbinol or the chloride by the action of the light.



In the solid state 3-(*p*-dimethylaminophenylimino)-camphor (VIII) and 3-(*p*-diethylaminophenylimino)-camphor (IX) are phototropic (156). The former crystals are yellow and become deep yellow with an orange tinge on exposure to light and the latter turn from a light orange to scarlet. The compounds were found to be diamagnetic, but become paramagnetic on exposure. This may be due to the formation of free radicals in which the molecules contain an odd number of electrons resulting in paramagnetism owing to the existence of resultant spin moment.



VIII



IX

o-NITROBENZYL DERIVATIVES

The solid 2-(2′,4′-dinitrobenzyl)pyridine is phototropic and has been studied extensively over the last two decades (35, 65, 92, 121, 145, 175), but it has been recently found that the color change can be brought about in solution by employing low temperatures (68). Other structurally related compounds such as 4-(2′,4′-dinitrobenzyl)pyridine have also been found phototropic in solution (116, 157).

TABLE VI

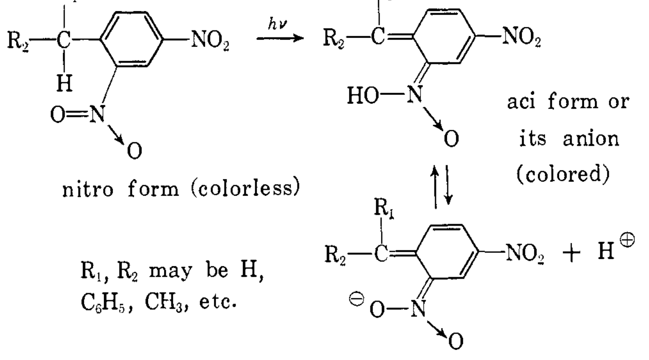
THE PHOTOTROPIC *o*-NITROBENZYL DERIVATIVES

	Color after exposure	Ref.
2-(2′,4′-Dinitrobenzyl)pyridine	Purple	109[a]
4-(2′,4′-Dinitrobenzyl)pyridine	Blue	109, 116
2-(2′,4′-Dinitrobenzyl)pyridine N-oxide	Pink	109
4-(2′,4′-Dinitrobenzyl)pyridine N-oxide	Pink	109
2,4,2′-Trinitrodiphenylmethane	Faint rose	109
2,4,4′-Trinitrodiphenylmethane	Blue	109
2,4,2′,4′-Tetranitrodiphenylmethane	Blue	109
2,4,2′,4′,2′′,4′′-Hexanitrotriphenylmethane	Blue	109
Ethyl bis(2,4-dinitrophenyl)acetate	Blue	109
Ammonium 2,4-dinitrophenylacetate	Green	109
Alkali metal salts of 2,4-dinitrophenylacetic acid	Green	109
2-(2′-Nitro-4′-carbomethoxybenzyl)-pyridine	Blue-green	13
2-(2′-Nitro-4′-carboethoxybenzyl)-pyridine	Blue-green	13
2-(2′-Nitro-4′-carbamylbenzyl)pyridine	Blue-green	13
2-(2′-Nitro-4′-carboxybenzyl)pyridine	Blue-green	13
3,3′-Dinitro-4,4′-bis(2-pyridylmethyl)-azoxybenzene	Blue-green	13
2-(2′,4′-Dinitro-α-hydroxybenzyl)-pyridine	Blue-green	13
4-(2′-Nitro-4′-cyanobenzyl)pyridine	Blue-green	13
2-(2′-Nitro-4′-cyanobenzyl)pyridine	—	157
2-(2′-Nitro-4′-aminobenzyl)pyridine	—	157
2,4-Dinitrobenzyl alcohol	Red-purple	157

[a] See also ref. 35, 65, 92, 121, 145, and 175.

Tschitschibabin proposed that the color change of crystalline 2-(2′,4′-dinitrobenzyl)pyridine was due to a hydrogen transfer from the methylene bridge to the nitrogen of the pyridine ring (175). More recent research on the solutions (68, 116) appears to show that the hydrogen transfers to the oxygen of the nitro group. No compound of the various nitrobenzyl derivatives was found to be phototropic which did not have a nitro group *ortho* to a benzyl hydrogen. The phototropic derivatives are shown in Table VI.

The hydrogen transfer produces a colored aci-quinoid structure in equilibrium with its anion (13)

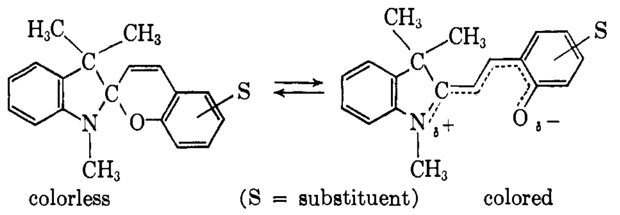


The rate of fading of the colored form varies greatly with the solvent, acidity, and temperature as well as the structure of the compound.

The phototropy of these compounds in monomolecular films has also recently been investigated (50, 51).

K. SPIRO COMPOUNDS

Chaudé and Rumpf (33) found that spirans in solution existed in two forms, which were in equilibrium.



The absorption of ultraviolet light shifts the equilibrium toward the colored form; visible light tends to make the change toward the colorless form (33, 110).

1,3,3-Trimethylindolinonaphthospiropyran is converted into the open merocyanine colored form when irradiated with ultraviolet light (75). When this colored modification is produced at low temperature (−160°), in the highly viscous glassy medium the spectrum is different from that of the colored modification produced at higher temperatures and then cooled. The authors propose the existence of several stereoisomers of the dye molecule each with different spectrum. Some of these stereoisomers would be more readily converted into the spiropyran than others by visible light.

Hirshberg and co-workers (78, 79) have investigated other spiro compounds. No spin resonance was observed for solutions (−120 to −60°) of bisspiro-2,2′-(5,6-benzopyran), 5,6-benzopyran-2-spiro-2′-(β-naphthopyran), and bisspiro-2,2′-(β-naphthopyran) after irradiation with ultraviolet light. It therefore appears that the colored species are not free radicals (80).

It was found that the thermal stability of the colored forms of the substituted 1,3,3-trimethylindolinobenzopyrylospirans varied with the substituent (8). The decay constants for the dark reaction were found to differ by a factor of more than one thousand with different substituents when in ethanol at 6°, as shown in Table VII.

TABLE VII

DECAY CONSTANTS FOR THERMAL STABILITY OF SUBSTITUTED 1,3,3-TRIMETHYLINDOLINOBENZOPYRYLOSPIRANS (8)

Substituent(s)	Colored form	Decay constant, sec. $^{-1}$
6′-Nitro	Purple	4.28×10^{-5}
7′-Nitro	Orange	7.11×10^{-5}
7′-Chloro	Purple	1.26×10^{-3}
6′,8′-Dibromo	Blue	3.97×10^{-3}
6′-Nitro-8′-allyl	Purple	2.10×10^{-4}
6′-Nitro-8′-bromo	Purple	3.67×10^{-6}
6′-Nitro-8′-fluoro	Purple	6.33×10^{-6}
6′-Chloro-8′-nitro	Purple	2.27×10^{-5}
6′-Bromo-8′-nitro	Purple	1.70×10^{-5}
6′-Nitro-8′-methoxy	Dark blue	5.53×10^{-4}
6′-Methoxy-8′-nitro	Green	1.32×10^{-2}
5′-Nitro-8′-methoxy	Dark green	2.52×10^{-3}

L. CHLOROPHYLL

The phototropy of chlorophyll in an air-free solution of methanol has been investigated intermittently for about 25 years. It has been found (87, 105) that the extent of the steady state bleaching is proportional to the square root of the intensity of the absorbed light, inversely proportional to the square root of the concentration of the chlorophyll, and sensibly independent of the temperature. The reversible bleaching rate is decreased by dissolved oxygen, falling to a value of half its oxygen-free maximum at an oxygen concentration of 3×10^{-6} *M*. No reversible bleaching occurs in benzene or carbon tetrachloride (either dry or water saturated) but it is restored by 1% methanol (104).

The reversible formation of pairs of radicals detected by the use of steady, comparatively weak illumination is apparently preceded by efficient photochemical production of chlorophyll molecules in a metastable (presumably triplet) state (102). Using flashes of light with synchronized absorption measurements it has been found that during an intense flash up to 90% of chlorophyll in a 10^{-6} *M* solution can be present in the metastable state with a half-life of about 5×10^{-4} sec. (103, 134). The photochemical conversion of chlorophyll into its triplet state is at least as efficient in benzene as in methanol. This is in marked contrast to the steady state formation of the radicals which occurs detectably in methanol, acetone, etc., but not when benzene is the solvent. Since extensive conversion under flash illumination occurs in both polar and nonpolar solvents (102), it may be concluded that at least one intermediate is formed by an intramolecular process, rather than by a reaction in which the solvent participates (1, 100).

The photobleaching of chlorophyll has also been carried out in rigid solvents (88, 100).

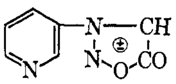
M. ANTHRONES

Investigation of solutions of dihydrodianthrone and its derivatives (77, 90, 91) showed that they were converted into a green biradical when irradiated at a low temperature (−78°). The reaction was reversed by heating. 1,3,6′,8′-Tetramethyldehydrodianthrone was converted in liquid solutions, but not solid solutions (89). It was concluded that the colored form is a biradical, and the coupling of the radicals occurs in such a manner that the planes of the radicals are at right angles to each other.

No electron spin resonance was observed (80) in a study of the colored products formed by irradiation with ultraviolet light of xanthylideneanthrone, 4,4′-methylanthrone, and 4,4′-methoxybianthrone, showing the absence of free radicals. The phototropy of xanthylideneanthrone has been attributed to steric isomerism (96).

N. SYDNONES

The sydnones, the chemistry of which has been recently reviewed (160), are a group of anhydro compounds which are neutral, highly crystalline, stable, and fairly soluble in most organic solvents including benzene. The most phototropic sydnone was found to be N-(3-pyridyl)sydnone (173)



On exposure of the solid to direct sunlight the colorless sample turned deep blue, becoming colorless again on heating to 80°, on standing overnight in the dark (174), or on application of an electric field (114). The two modifications gave identical infrared spectra (174), but the colored form showed electron spin resonance absorption (65). More recent work (115) suggests that two species, one colored and one paramagnetic, are formed on irradiation.

Cohen and Schmidt (39) have suggested that the phototropy of N-(3-pyridyl)sydnone is due to the separation of the molecule into a cation of unspecified structure and an electron which diffuses into the crystal lattice.

Other phototropic sydnones examined (114) were N-benzylsydnone, N-*p*-methylbenzylsydnone, N-3,4-dimethylbenzylsydnone, N-*p*-chlorobenzylsydnone, N,N′-ethylenebissydnone, and N,N′-tetramethylenebissydnone. In solution the various sydnones were not phototropic; however, nonreversible color formation did sometimes occur.

All the sydnones absorbed in the 312–322 mμ range and fatigued after repeated or prolonged exposure, probably owing to decomposition. This may be enhanced by the presence of impurities.

It was proposed (114) that the phototropy is due to the formation of a metastable intermediate and the material can undergo a change of color if the metastable state has more (or less) contributing resonance forms than the ground state of the molecule.

O. OTHER ORGANIC COMPOUNDS

Other organic compounds which have been found to be phototropic include: N-(5-bromosalicylidene)benzylamine (48), N-(5-methylsalicylidene)benzylamine (48), and N-(5-bromosalicylidene)methylamine (48) which turn from orange to red in sunlight; tetrachloro-1(2 or 4)-naphthalenone (49, 142, 164, 178) (turning colorless to amethyst), *o*-nitrobenzylideneisonicotinic acid hydrazide (112) (turning yellow to red), 2,3-epoxy-2-ethyl-3-phenyl-1-indanone (44), brucine salts of bromo- and chloronitromethionic acid (3) (turning white to violet), diphenacyldiphenylmethane (28, 29), 2,4,4,6-tetraphenyl-1,4-dihydropyridine (28, 29), 2,4,4,6-tetraphenyl-3,5-dibenzoyltetrahydropyran (28, 29), α-azoxynaphthalene (yellow modification) (41), *o*-nitrobenzylidenedesoxybenzoin (167), *p*-nitrobenzylidenedesoxybenzoin (167), *p*-aminobenzene derivatives (113), tetrabenzoylethylene (66), substituted 2-benzylidene-3-oxo-2,3-dihydrothionaphthenes (85, 117), neutral red (3-amino-6-dimethylamino-2-methylphenazine) (4), and fluorescent pigments with thiol compounds (53).

III. INORGANIC COMPOUNDS

A. OXIDES

The phototropy of two different crystalline forms of titanium dioxide known as anatase and rutile have been investigated together with anatase–rutile mixtures. Strong color changes were obtained when TiO_2 was contaminated with Fe_2O_3 (0.2% for optimum results) provided that some rutile was present (182, 183). Weyl and Förland (180) suggested that Fe^{3+} ions enter the rutile lattice where a neighboring pair, strongly deformed, may be separated by an oxygen vacancy. Fe^{4+} ions are formed owing to excited electrons leaving the Fe^{3+} ions to take up the position of the missing O^{2-} ion. The brown coloration on exposure was due to the grouping Fe^{4+} 2e Fe^{4+}. An electron transfer from Fe^{3+} to Ti^{4+} was considered (180, 181), giving colored Ti^{3+}. Rutile glazes were found phototropic (93, 133).

McTaggart and Bear (107) systematically investigated the effect of impurities on titanium dioxide. With pure anatase or pure rutile no phototropic effects were observed, but 0.01 to 0.5% of some metals and certain rare earths when incorporated with rutile gave rise to darkening of the host oxide in ultraviolet light. They suggested that the impurity is absorbed at the interfaces rather than that a true lattice phenomenon is involved and this is confirmed by the fact that moisture plays an important part in the color development. On irradiation oxygen is liberated from titanium dioxide, oxidizing the impurity ions to a higher valency state which is usually colored. When the radiation ceases, the higher valency form reverts again to the lower and this change may take a time varying from minutes to weeks.

TABLE VIII

PHOTOTROPY OF OXIDES CONTAINING IMPURITIES (6, 107)

Host oxide	Impurities Fe	Cr	Cu	Ni	V	Mn
TiO_2 (anatase)	0	0	0	0	0	0
TiO_2 (rutile)	+	+	+	+	0	+
Nb_2O_5	+	+	+	0	+	+
Al_2O_3	0	+	0	0	+	0
ZnO (from carbonate)	0	0	+	0	+	0
ZnO (from nitrate)	0	0	+	0	+	–
HfO_2	0	+	–	–	–	–
ThO_2	0	0	0	0	+	0
SnO_2	0	0	+	–	–	0
Ta_2O_5	0	0	+	–	–	0
ZrO_2	0	0	+	+	0	0
BeO	0	0	0	0	+	0
GeO_2	0	0	0	0	0	0
SiO_2	0	0	0	0	0	0
MgO	0	0	0	0	0	0

The same authors (6) have investigated other white host oxides (Table VIII). They found that in all cases the development of color was prevented by exclusion of moisture and oxygen. Fading in the dark took 12 to 24 hr., except chromium and vanadium contaminations which required several months. Heating to 100° caused rapid and complete removal of the darkening.

B. MERCURY COMPOUNDS

Phototropic mercury compounds are listed in Table IX. All become dark brown or black when exposed to light of wave length less than 5500 Å. and reversal can be obtained by exposure to red light or by heating (137). The photoelectric emission of a number of mercury compounds which show a high degree of phototropic activity has been measured (138).

The phototropy of $HgI_2 \cdot 2HgS$ has been explained as due to the formation of mercuric iodide and sulfide on exposure to sunlight, with recombination in the dark (136). However, magnetic susceptibility measurements have shown that the initially diamagnetic yellow powder becomes paramagnetic after blackening by sunlight, and X-ray diffraction reveals no change in crystal structure (169). It is supposed that electrons of I^- or S^{2-} ion are elevated to the conduction band by the light and leave positive holes in the crystal. The trapped unpaired electrons produce the paramagnetism. The

TABLE IX

THE PHOTOTROPIC MERCURY COMPOUNDS

	Color before exposure	Ref.
$Hg(Cl)CNO$	Pale brown	137
$Hg(Br)CNO$	Pale yellow	137
$Hg(I)CNO$	Golden yellow	137
$Hg(Cl)CNS$	White	54, 135
$Hg(Br)CNS$	White	54, 135
$Hg(I)CNS$	Orange-yellow	54, 135, 170
$Hg(Cl)CNSe$	Pale yellow	137
$Hg(Br)CNSe$	Yellow	137
$Hg(I)CNSe$	Orange	137
$Hg(HS)CNS$	Lemon yellow	176, 177
$Hg(HS)CNSe$	Pale brown	137
$HgCl_2 \cdot 2HgS$	White	170
$HgBr_2 \cdot 2HgS$	Pale yellow	45, 170
$HgI_2 \cdot 2HgS$	Orange yellow	45, 169, 170
$HgI \cdot 2HgS$	—	171
$HgI_2 \cdot Ag_2S$	Yellow	168
$HgCl_2 \cdot 2HgSe$	White	137
$HgBr_2 \cdot 2HgSe$	Pale yellow	137
$HgI_2 \cdot 2HgSe$	Pale brown	137
$Hg(SCN)_2 \cdot 2HgO$	Yellow	137
$Hg(SCN)_2 \cdot 2HgS$	Yellow green	137
$Hg(CNSe)_2 \cdot 2HgS$	Brown	137
$I{-}Hg{-}S{-}S{-}Hg{-}I$	—	139
$HgBrCl$	—	54, 135
$HgICl$	—	54, 135
$HgIBr$	—	54, 135

photosensitivity was increased by the addition of small amounts of foreign substances.

X-Ray diffraction investigations have also been made on phototropic mixtures of silver sulfide and mercuric iodide in various proportions (168). This forms a combined sulfide–iodide anion lattice with the cations in tetrahedral holes. Variations in the lattice constants with composition indicate solid solution formation and the properties of $HgI_2 \cdot Ag_2S$ are similar to $HgI_2 \cdot 2HgS$.

The mixture of mercurous and silver iodides produced by toning photographic images of silver with mercuric iodide is phototropic and has been explained as due to the formation of colloidal silver (152). Similar theories have been proposed (170) for $HgI_2 \cdot 2HgS$ and Hg(X)-CNS (where X is a halogen).

C. ALKALINE EARTH TITANATES AND SULFIDES

The occurrence of phototropy in barium, calcium, and strontium titanates but not in magnesium titanate illustrates the requirement of an appropriate crystal structure which is not present in the latter (106). An impurity must also be present such as Fe^{+3}, Zn^{+2}, V^{+5}, or Sb^{+5} which has ionic radius near, but not equal, to that of Ti^{+4} to distort the lattice and a valence other than four in order that electron transfer be possible. The phototropic effect increases with the amount of impurity.

Despite previous reports (172), the presence or absence of oxygen and moisture produced no difference in the color response.

Mourelo (118–120) investigated for a number of years the phototropy of alkaline earth sulfides and concluded that there must be traces of an active ingredient present such as manganese or bismuth before they would exhibit the effect.

D. ZINC SULFIDE

Phototropy was first observed in lithopone, but pure zinc sulfide itself is phototropic. The hydrated form only becomes photosensitive after being heated and when moist (47, 143). The sensitivity was found to increase with addition of zinc sulfate, ammonia, or formaldehyde (95).

It was suggested that the blackening attributed to the action of light was due to the formation of metallic zinc (30), and this was supported by the discovery that oxygen was required for the bleaching action. Others attribute the blackening to the formation of metallic zinc (19, 95).

E. COPPER COMPOUNDS

Copper(I) halides have been found to be phototropic (155). Investigation of the reversible blackening of Cu_2Cl_2 and Cu_2Br_2 revealed (71) that the phototropic effect occurred only if the salts were exposed in water or in a moist state and not with any other solvent. Above a temperature of 75° practically no spectral sensitivity was observed. It was concluded that metallic copper was formed in an unstable form

$$2Cu^+ + h\nu \rightarrow Cu^* + Cu^{+2}$$

A solution of 7 ml. of 1% *l*-(+)-ascorbic acid, 1.5 ml. of 45% acetic acid, and 25 ml. of 1% copper acetate was found to form a phototropic system (185). On exposure to light the color changed from light yellow to dark green, the pH value of the system decreased, and the electrical conductivity rose. The change took about 15 sec.; the recovery time was about 15 min. (186).

F. OTHER INORGANIC COMPOUNDS

Other inorganic compounds which have been found to be phototropic include: bismuth oxalate (141), lithium imide (42) (turning colorless to brown), pink hackmanite (93), and sodalite (84).

A solution of molybdenum trioxide in selenium oxychloride is light yellow becoming blue in sunlight (94).

An aqueous solution of potassium ferrocyanide with a little phenolphthalein is yellow turning red (5).

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