THE *CIS-TRANS* ISOMERIZATION OF CONJUGATED COMPOUNDS

GEORGE M. WYMAN

Quartermaster Research and Development Center, Natick, Massachusetts

Received February 14, 1955

CONTENTS

I. INTRODUCTION

The interconversion of the *cis* and *trans* isomers of organic compounds has been known to chemists almost ever since the discovery of geometrical isomerism, and recent reviews on *cis-trans* isomerism have contained brief discussions on the interconversion of such isomers (26, 88). While the *cis* and *trans* isomers of organic compounds containing isolated double bonds are usually quite stable and relatively drastic conditions are required to bring about isomerization, the interconversion of the geometrical isomers of conjugated compounds occurs more readily, and in the case of some highly conjugated compounds precautions are actually necessary in order to prevent isomerization (10, 48). During the last two decades the application of new physical techniques, spectroscopy and chromatography in particular, has permitted the study of the *cis-trans* isomerization of conjugated molecules (and sometimes the actual isolation and characterization of the isomers) that had previously gone unnoticed (52, 119).

It is the purpose of this article to review the literature dealing with this field, with particular emphasis on developments during the last twenty years. The scope of the review will encompass compounds in which the double bond (about which there is *cis-trans* isomerization) is conjugated with at least one other carbon–carbon double bond or with an aromatic ring. In addition, the few notable exceptions among the conjugated unsaturated compounds that do not exhibit *cis-trans* isomerization (e.g., indigo dyes and some hydroxyazo compounds) will also be discussed. In conclusion, an attempt will be made to correlate the many isolated experimental facts in the hope of arriving at a simple, unified picture concerning the *cis-trans* isomerization of conjugated compounds.

II. GENERAL MECHANISM OF THE ISOMERIZATION REACTION

Because of the tetrahedral structure of carbon and nitrogen, a double bond between any two atoms of these elements is usually pictured as two tetrahedra sharing one edge in common. Purely from a geometric viewpoint, this model predicts the existence of *cis* and *trans* isomers in (*a*) olefinic compounds having different substituents on each carbon, (*b*) azomethines having different substituents on the carbon atom, and (*c*) all azo compounds. These isomers differ in their physical properties (e.g., melting point, boiling point, absorption spectra, etc.) and, usually, in their relative stabilities. In general, both isomers of simple organic olefins are quite stable, suggesting that there is a considerable energy barrier that must be overcome before isomerization can occur. This energy barrier decreases with increasing conjugation in the olefin (26), probably because in such conjugated molecules the double bond acquires increasing single-bond character (99).

In common with other chemical reactions, the rate of *cis-trans* isomerization may be increased by raising the temperature or by the addition of a suitable catalyst. In addition, isomerization may also be brought about by irradiation with ultraviolet (or sometimes visible) light. In contrast with the thermal and catalytic isomerizations, the photochemical reaction tends to produce the less stable isomers.

The thermal *cis-trans* isomerization of a number of organic compounds has been studied by kinetic methods. It was observed that these reactions could be readily divided into two classes on the basis of their kinetic behavior: (*1*) reactions having a frequency factor of approximately 10^{11} and an activation energy (pz and E_a, respectively, in the Arrhenius equation) of about 45 kcal.;

$$k = pze^{-E_a/RT} \tag{1}$$

and (*2*) reactions having an unusually low frequency factor of approximately 10^4 and an activation energy of about 25 kcal. (67). It has been proposed that this indicates that the thermal isomerization may occur by one of two distinct mechanisms: (*1*) a rotation about the double bond without any change in the multiplicity of the electronic state of the molecule or (*2*) a rotation during which the molecule goes through a triplet state (85). The reaction may take place by either of these mechanisms, or by a combination of the two (18). In any event the product of the reaction is the more stable isomer.

Although the mechanism of the catalytic isomerization reaction is not fully understood, it probably involves the loosening of the double bond by the formation of some sort of an addition complex between substrate and catalyst (83, 93). A large number of substances of different types have been found to catalyze the reaction, and the product of the catalytic isomerization is also the more stable isomer.

Photochemical isomerization must take place by an entirely different mechanism, since the product is usually the less stable isomer. It is also clear that isomerization cannot occur through a common electronically excited state in which there is free rotation about the double bond, because in that event the unstable form should have its first absorption band at longer wave lengths than the stable isomer, the converse of which is usually true (10, 77, 119). Therefore, there have to be two separate excited states, one corresponding to each configuration. The energy difference between the two excited states must be of the same order of magnitude as that which exists between the two isomers in the ground state.

A mechanism for the photochemical *cis-trans* isomerization of stilbene has been proposed from a study of the rate of the reaction and the fluorescence of the two isomers (77) and on the basis of the results of earlier work on the photochemical isomerization of α,β-unsaturated acids (94). Since stilbene may be considered to be the prototype of conjugated olefins, the photochemical isomerization of these compounds probably occurs by some similar mechanism.

The energy diagram in figure 1 shows the various energy levels which have been proposed for the two isomers of stilbene. T_0 represents the lowest level of the *trans* molecule, while C_0, some 10 kcal. higher, shows the energy level of the *cis* isomer in its lowest state. The height of the potential energy barrier of the thermal isomerization reaction (approximately 42 kcal. for stilbene and 20–50 kcal. for other conjugated olefins) is indicated by the dotted line R on the diagram. The lines T_0, T_1, . . . etc. show the principal energy levels with respect to longitudinal vibrations along the double bond. Corresponding levels in the excited state are shown by $^*T_0$, $^*T_1$, . . . etc. When a molecule of *trans*-stilbene absorbs light at room temperature it goes from T_0 to one of the several energy levels in the excited state ($^*T_0$, $^*T_1$, . . . etc.), thus giving rise to the absorption spectrum. $^*T_x$ is the energy level to which *trans*-stilbene molecules are raised upon excitation by light of 2537 Å. wave length. From here some of them will

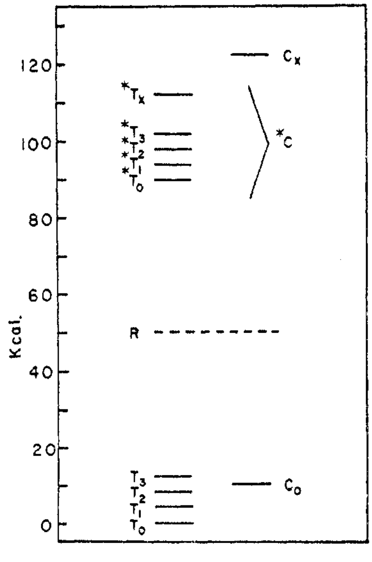


FIG. 1. Energy diagram of stilbene

rapidly fall to the $*T_0$ level without losing their *trans* configuration and will drop further, by fluorescence, to one of the ground states T_0, T_1, . . . etc. without any change in their configuration. However, a number of the excited *trans* molecules in the $*T_x$ state will not fluoresce, but will exchange their electronic energy for rotational and vibrational energy instead.

The behavior of the *cis* molecules is different, because they do not fluoresce. In the excited state there are no discrete energy levels, only a broad continuum of states. Excited *cis* molecules will exchange their electronic energy for vibrational and rotational energy. In this manner those of the excited *trans* molecules that were not deactivated by fluoresence and all of the excited *cis* molecules will acquire enough torsional energy to lose their identities as *cis* and *trans* isomers. From this "no man's land" they eventually fall by loss of energy to the ground state, some of them becoming *cis* and the remainder *trans* molecules in the process (77). It has been postulated that it is because of the large amount of energy possessed by these molecules that the isomers of highest potential energy are preferentially formed during the deactivation process (94).

Inasmuch as geometrical isomers frequently differ considerably in their absorption spectra, it is often possible to use the photochemical isomerization process for the selective preparation of one of the isomers: e.g., irradiation with light of a wave-length range which is absorbed by only one form, which then isomerizes, while at the same time the desired product is not being exposed to any radiation which it would absorb and thus cause the reversal of the process.

Since the absorption bands of organic compounds shift towards longer wave lengths and increase in intensity with increasing conjugation in the molecule (9), the photochemical isomerization process assumes particular importance for conjugated unsaturated compounds. Thus, it is not unexpected that, while it is necessary to subject a non-conjugated olefin to intense ultraviolet irradiation in order to bring about photochemical isomerization, a highly conjugated unsaturated compound may undergo isomerization even in ordinary diffuse daylight (10, 48).

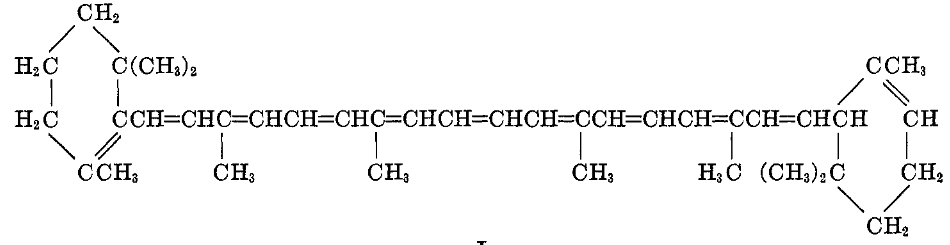
III. Isomerization about Carbon–Carbon Double Bonds

A. ALIPHATIC POLYENES

Most of the work that has been reported in the literature to date concerning the stereochemistry of aliphatic polyenes has dealt with the carotenoids. This is a group of plant pigments (red, yellow, orange, or violet) that consist of molecules comprising conjugated chains of about eight isoprene units between two more fully or partially hydrogenated terminal groups. These end groups may either be saturated or unsaturated hydrocarbon radicals or, alternatively, contain alcohol, aldehyde, keto, or acid groups. Carotenoids have been found to undergo *cis-trans* isomerization of all three types, i.e., thermal, catalytic, and photochemical. While it has been easy enough to observe the isomerization of these compounds by spectrophotometric methods and even to separate the several forms by chromatographic adsorption, the assignment of the configuration of the various isomers has been greatly complicated by the large number of double bonds about which *cis-trans* isomerism is possible. In general, a shift in the wave length of the absorption band to longer wave lengths and an increase in its intensity indicates a *cis* → *trans* change about one or more of the double bonds, while the appearance of a weak new band in the near ultraviolet is characteristic of a change to a multiple *cis* configuration.

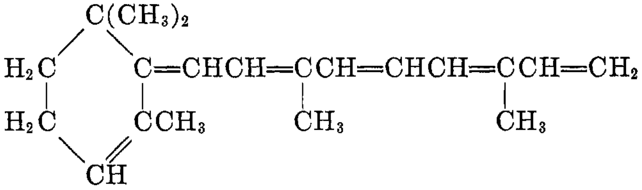
The early work in this field was reviewed a decade ago (120); therefore this review will be confined to developments that have occurred since that time. There also have been two more recent reviews touching only on the highlights of the research in this field (99, 122). For a detailed discussion of the problems and techniques involved and for generalizations concerning the effects of heat, light, and catalysts as disclosed during the early work in this field, the reader is referred to these review articles.

The *cis-trans* isomerization of α-carotene (I) was reinvestigated by Nash and Zscheile (92); their results confirmed the findings of Zechmeister and Polgar concerning the structure of this pigment (120, 130). Axerophthene (II), a recently discovered carotenoid, was found to undergo photochemical and catalytic isomerization in a manner typical of all-*trans* carotenoids (90). The isomerization behavior of *cis*-antheraxanthine (III), a pigment isolated from the blossoms



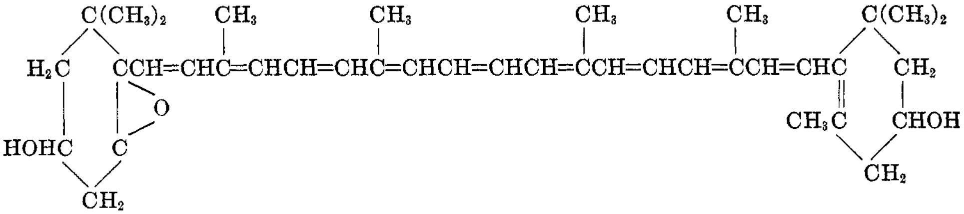
I

α-Carotene



II

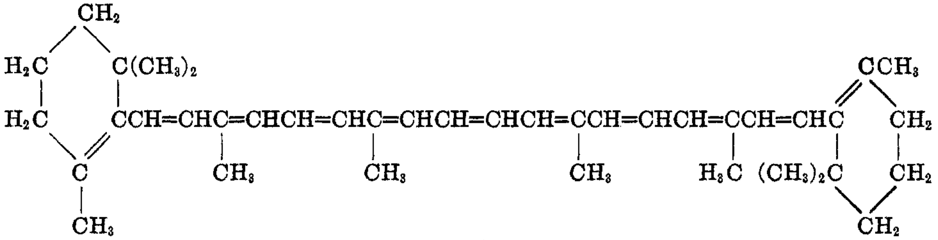
Axerophthene



III

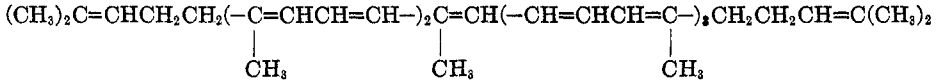
Antheraxanthine

of lily plants, was found to be typical of carotenoids containing several *cis* double bonds (111). The slow *trans* → *cis* isomerization of β-carotene (IV) and of lycopene (V) adsorbed on alumina or titanium oxide from petroleum ether solutions has been reported to occur even at room temperature (91). Six poly-*cis* lycopenes have been discovered that contained most of their double bonds in the *cis* configuration (127). Addition of traces of iodine to solutions of these compounds resulted in an increase in the intensities of the main absorption bands, accompanied by a shift to longer wave lengths and the appearance of fine structure (as shown in figure 2), which was characteristic of *cis* → *trans* isomerization about one or more of the double bonds (126). Other carotenoids (natural and synthetic) that have been reported to exhibit both catalytic and photochemical isomerization include retinene (VI) (63) and the dehydrogenation products of β-carotene (IV) (131), phytoene and phytofluene (123). (The structures of the two latter carotenoids have not been fully elucidated to date.)



IV

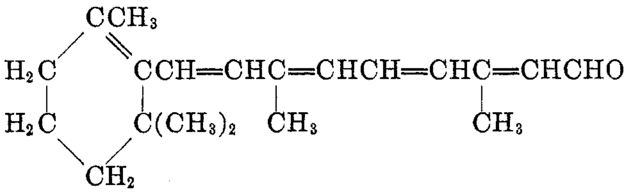
β-Carotene



$$(CH_3)_2C{=}CHCH_2CH_2(-\underset{CH_3}{C}{=}CHCH{=}CH-)_2\underset{CH_3}{C}{=}CH(-CH{=}CHCH{=}\underset{CH_3}{C}-)_2CH_2CH_2CH{=}C(CH_3)_2$$

V

Lycopene



VI

Retinene

Recently the synthesis of several of the sterically hindered *cis* isomers of a large number of carotenoid-like aliphatic polyenes containing two to five conjugated double bonds in isoprenoid structures has been reported. While the dienes were found to be inert to photochemical, thermal, or catalytic isomerization, the tetraenes and pentaenes were readily stereoisomerized upon the addi-

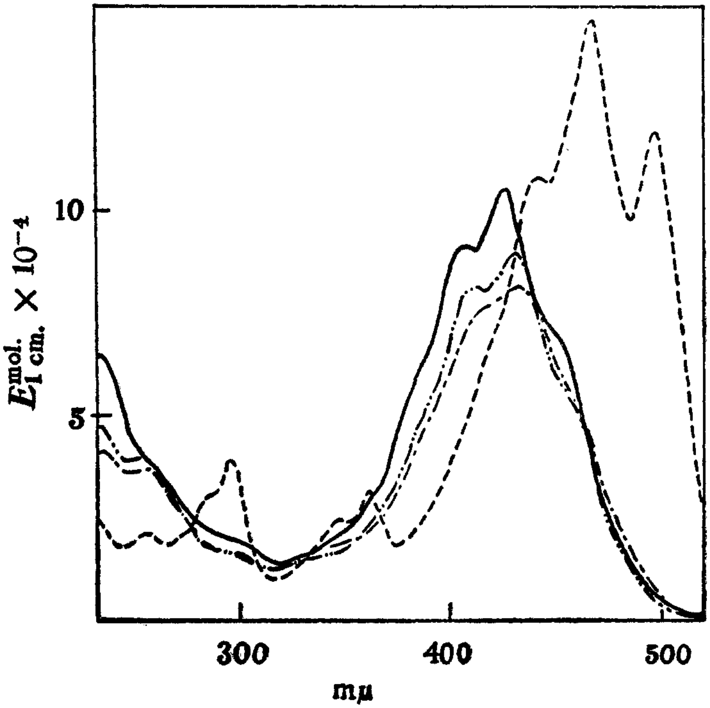


FIG. 2. Molecular extinction curves of fresh solutions of three different poly-*cis*-lycopenes in hexane. The dashed curve (- - -), characteristic of an all-*trans* carotenoid, is obtained after iodine catalysis in light of one of the poly-*cis* isomers (—··—··—).

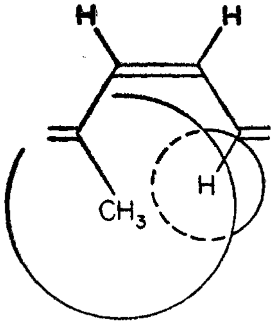


FIG. 3. Steric hindrance caused by a methyl group in the position alpha to a *cis* double bond in a conjugated polyene.

tion of iodine (95, 96). Among the compounds prepared in that investigation were a number of *cis*-polyenes possessing *cis* configurations about the double bonds that are once removed from the carbons holding the methyl groups. It had been recognized some time ago that this structure, which involves considerable steric hindrance (*cf.* figure 3), would be relatively unstable with respect to a *trans* configuration (97, 99). It is of interest to note that even these sterically hindered compounds were found to be stable enough not to undergo spontaneous isomerization at room temperature.

The *cis-trans* isomerization of a few miscellaneous aliphatic compounds possessing conjugated double bonds has also been described in the literature. Thus the dimethyl ester of corticrocin (VII) has been reported to undergo *trans* → *cis*

$$\mathrm{HOOCCH{=}CHCH{=}CHCH{=}CHCOOH}$$

VII

Corticrocin

isomerization (as shown by increased absorption in the ultraviolet region) when irradiated with light from an incandescent lamp (32, 106). The *cis-trans* isomerization of cinnamalazine (VIII) and of phenylpentadienalazine (IX) has

$$\mathrm{C_6H_5CH{=}CHCH{=}NN{=}CHCH{=}CHC_6H_5}$$

VIII

Cinnamalazine

$$\mathrm{C_6H_5CH{=}CHCH{=}CHCH{=}NN{=}CHCH{=}CHCH{=}CHC_6H_5}$$

IX

Phenylpentadienalazine

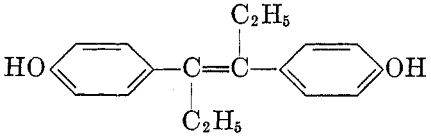
recently been investigated, using spectroscopic and chromatographic techniques (28). The stable (all-*trans*) form of each of these compounds was observed to undergo isomerization progressively to two *cis* isomers (*cis*-I and *cis*-II) when irradiated with sunlight or an incandescent lamp. Both *cis* forms may be converted thermally, catalytically, or photochemically to an equilibrium mixture that is rich in the all-*trans* compounds. The *cis*-II isomers were found to be relatively inert to thermal isomerization. The addition of a small amount of iodine, however, brought about a spectacular increase in the rate of the thermal isomerization of the *cis*-II compounds, while leaving the isomerization of the *cis*-I forms unaffected. Since this inertness to iodine catalysis set the *cis*-I compounds apart from *cis*-carotenoids, it was considered probable that these compounds possessed a *cis* configuration about one of the carbon–nitrogen double bonds, while the *cis*-II isomers were assigned a structure involving a *cis* configuration about one of the carbon–carbon double bonds.

B. AROMATIC COMPOUNDS

1. *Aromatic olefins*

The *cis-trans* isomerization of stilbene and other aromatic olefins has been extensively investigated. The preparation of the two geometrical isomers of stilbene and some of the early work on their interconversion has recently been reviewed (121). The thermal *cis-trans* isomerization of stilbene (66), *p*-methoxystilbene, *p*-nitrostilbene, *p*-methoxy-*p*′-nitrostilbene (18), and β-cyanostyrene (68) has been studied by kinetic methods. The results indicate that while the isomerization of stilbene and of β-cyanostyrene occurs without a change in the multiplicity of the electronic state of the molecule, *p*-amino-*p*′-nitrostilbene probably goes through a triplet state during the reaction (87). The isomerization of the three other compounds is likely to occur by a combination of these two mechanisms.

The catalytic isomerization of *cis*-stilbene may be brought about by the action of boron trifluoride (101) or of bromine atoms produced by the photolysis (65) or the oxidation of hydrogen bromide (113), but not by hydrogen bromide *per se.* The *cis-trans* isomerization of the *o*-amino- and *o*-nitrostilbenes has been brought about by heating these compounds in quinoline or nitrobenzene solutions in the presence of a trace of iodine (103). The isomerization of 5,5′-dibromo-2,2′-dimethoxystilbene and of 5,5′-dicyano-2,2′-dimethoxystilbene has also been reported to occur under similar conditions (1). An equilibrium mixture of the two isomers was obtained from the biologically important diethylstilbestrol (X) by heating either isomer with alcoholic hydrogen chloride (86). The catalytic *cis-trans* isomerization of 2,2′,4,4′,6,6′-hexaisopropylstilbene was observed when a solution of this compound in ethanol was shaken with a platinum catalyst in an atmosphere of hydrogen (42). Changes in the spectra of aqueous solutions of *p*-amino-*p*′-nitrostilbene hydrochloride with increasing acidity have also been attributed to *cis-trans* isomerization (20).

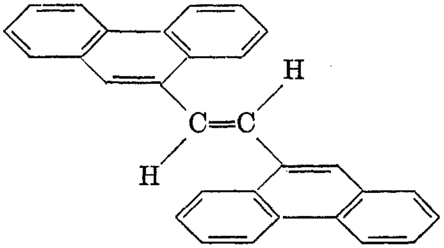


X

Diethylstilbestrol

The photochemical isomerization of stilbene was first studied by Smakula (107). He reported that, upon irradiation with monochromatic light of 313 mμ wave length, *trans*-stilbene was completely converted to the *cis* isomer and that the reaction occurred even at liquid-air temperatures. The quantum efficiency of the process was stated to be 1.00 when radiation of this wave length was employed, and lower when light of shorter wave lengths was used. (At 313 mμ the absorption of the *trans* isomer is approximately eight times more intense than that of the *cis* form (19, 77).) The yield of 1.00 claimed by Smakula was questioned by Lewis, Magel, and Lipkin (77) on the basis of the observed fluorescence of the *trans* isomer, and also because of the reverse reaction that they found to occur to an appreciable extent. They determined the quantum efficiency of the *trans* → *cis* isomerization process to be 0.68, when the 2537 Å. line of mercury was used as the light source. The same reaction was recently reinvestigated by Hausser, who also used radiation of 313 mμ wave length to bring about the reaction. She reported a value slightly lower than unity (0.9) for the quantum efficiency of the process (53, 54). The photochemical isomerization reaction followed by the chromatographic separation of the isomers has also been utilized for the preparation of the *cis* forms of stilbene, *p*-nitrostilbene, *p*-amino-*p*′-nitrostilbene, and *p*-methoxy-*p*′-nitrostilbene (19). The partial isomerization of *trans*-α-nitrostilbene in alcohol under the influence of sunlight and its reversal by heating the solution in darkness has also been reported (36). During a study of the carcinogenic properties of *p*-aminostilbene and its derivatives it was observed that the absorption curves of *p*-dimethylaminostilbene and of a number of its alkyl- and halogen-substituted derivatives showed appreciable changes in their absorption spectra when solutions of these compounds were allowed to stand in the light (48). In order to test this effect, solutions of 2,5-dimethyl-4′-(dimethylamino)stilbene in alcohol, cyclohexane, and benzene were exposed to radiation of a mercury arc, in the presence of oxygen and also in an inert atmosphere. In all experiments the first absorption band was found to shift rapidly to shorter wave lengths and to decrease in intensity as a result of the irradiation. These photochemical changes, similar to the behavior reported for stilbene itself (77), were ascribed to *trans* → *cis* isomerization.

Among the aromatic monoölefins of higher molecular weight *trans*-*sym*-di-*p*-toluylethylene was similarly reported to undergo isomerization to the *cis* form when irradiated in dilute acetone solution with light of 4047 Å. wave length (87). The shifts observed in the ultraviolet absorption spectrum of *sym*-di(9-phenanthryl)ethylene (XI) upon irradiation with ultraviolet light (as shown in



XI

sym-Di(9-phenanthryl)ethylene

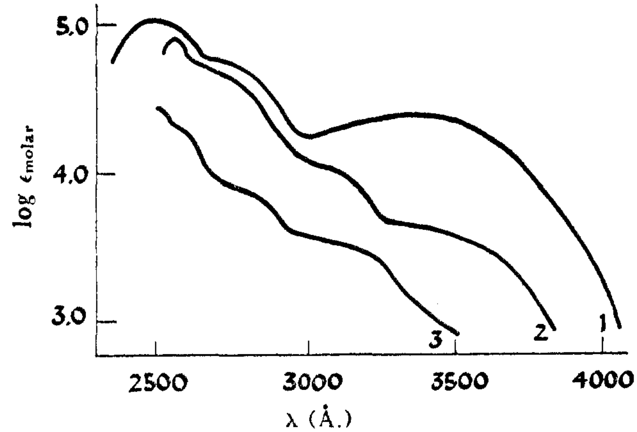


FIG. 4. Absorption spectrum of *sym*-di(9-phenanthryl)ethylene (XI): curve 1, original substance; curve 2, after irradiation for 1 hr.; curve 3, after irradiation for 2 hr.

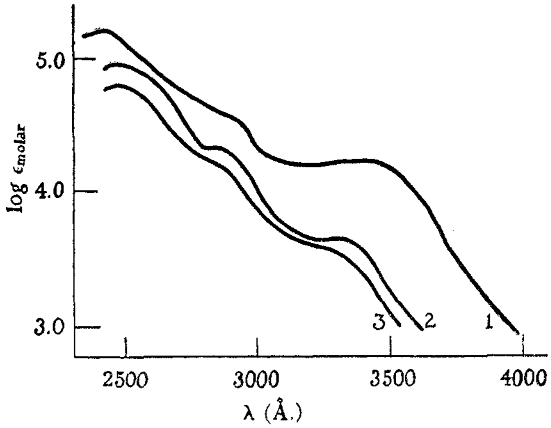
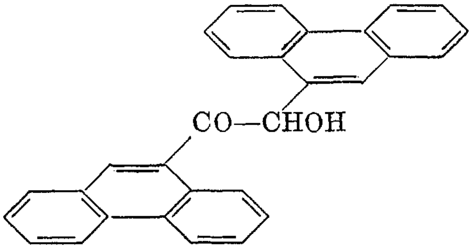
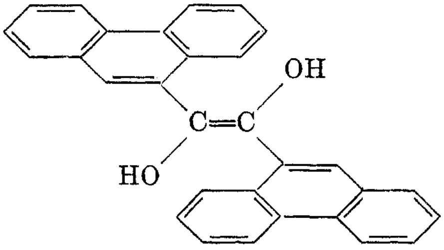


FIG. 5. Absorption spectrum of 9,9′-phenanthroin (XII): curve 1, original substance; curve 2, after irradiation for 1 hr.; curve 3, after irradiation for 2 hr.

figure 4) also have been attributed to *trans* → *cis* isomerization when it was found that the spectra of the symmetrical compounds, tetra(9-phenanthryl)-ethylene and tetraphenylethylene, failed to show such changes even after prolonged irradiation (57). Since the spectrum of 9,9′-phenanthroin (XII) also exhibited such changes (*cf.* figure 5), it was concluded that this latter compound had to exist exclusively in the enediol structure (XIIb) rather than as a tautomeric mixture, as had previously been suggested (64). It should be noted that the *trans* compound showed the stronger fluorescence, as had also been reported for the stilbenes (77).



XIIa



XIIb

XII

9,9′-Phenanthroin

The *cis-trans* isomerization of the simplest conjugated aromatic diolefin, 1-phenyl-1,3-butadiene, has been investigated, using spectroscopic techniques (46, 47). It was observed that irradiation of the *trans* form in ethanol solution by sunlight or by ultraviolet radiation caused conversion to the *cis* isomer in good yield. In contrast with piperylene (37), the catalytic *trans* → *cis* isomerization of this compound could not be brought about by heating it with a trace of iodine.

The photochemical *cis-trans* isomerization of 1,4-diphenylbutadiene was first described by Straus, who noted the effect of sunlight on one of the labile isomers

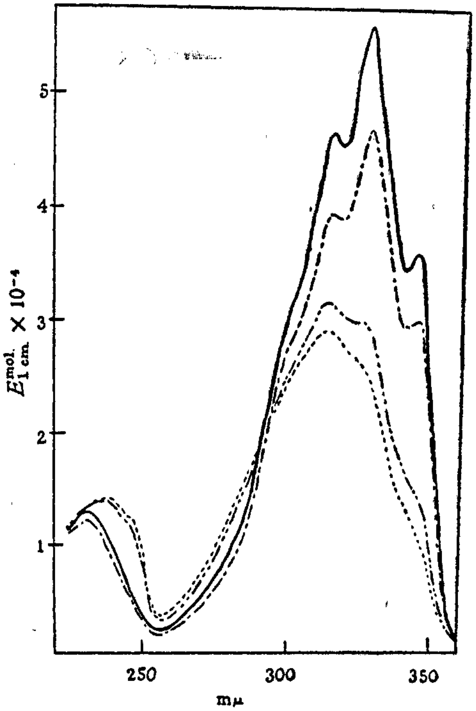


FIG. 6

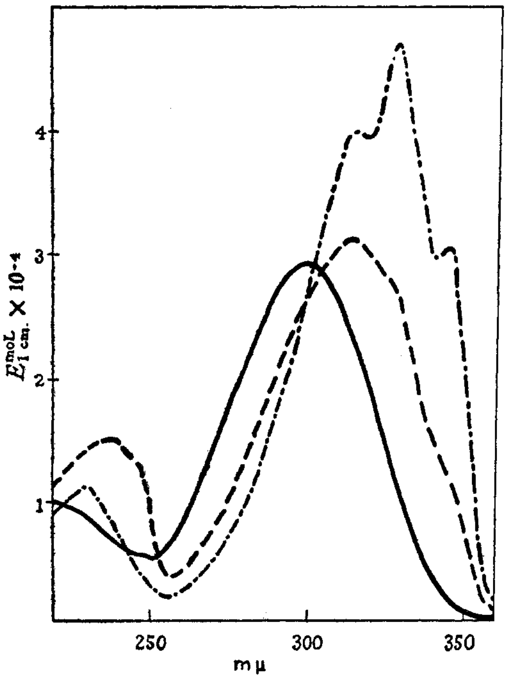


FIG. 7

FIG. 6. Molecular extinction curve of *trans-trans*-1,4-diphenylbutadiene in hexane and its shift toward the curve of the *cis-trans* form during exposure to sunshine: ——, fresh solution; —··—··—, after 1 min; – – –, after 10 min. of insolation; –·–·–, after iodine catalysis at the end of 10 min. of insolation.

FIG. 7. Molecular extinction curve of *cis-cis*-1,4-diphenylbutadiene in hexane and its shift toward the curve of the *cis-trans* form during exposure to sunshine: ——, fresh solution; – – –, after 10 min. of insolation; –·–·–, after iodine catalysis at the end of 10 min. of insolation.

obtained from the hydrogenation of diphenyldiacetylene (110). The all-*trans* isomer of 1,4-diphenylbutadiene has been reported to undergo partial *trans* → *cis* isomerization under the influence of sunlight or upon irradiation by an incandescent lamp (105). Solutions thus enriched with respect to the *cis* isomers are readily isomerized to the all-*trans* form by the addition of a trace of iodine. Further studies disclosed that both the all-*trans* and the all-*cis* forms in hexane solutions were converted to the *cis-trans* form under the influence of sunlight; however, the addition of a trace of iodine (in the presence of light) brought about reversal to the all-*trans* form (100), as shown in figures 6 and 7. Light from an incandescent lamp was also found to be effective in bringing about the isomerization. It was shown spectrophotometrically that the reverse reaction was a stepwise one; i.e., the all-*cis* compound was first almost completely converted to the *cis-trans* form before that isomer was further rearranged to the all-*trans* compound. In the solid phase the crystalline *cis-trans* form appeared to be stable, but oils containing the two *cis* isomers showed a tendency to rearrange and deposit crystals of the all-*trans* isomer (100).

A study of a number of ring-substituted 1,4-diphenylbutadienes (in alcohol or dioxane solutions) disclosed that the all-*trans* isomers of each of these compounds were stereoisomerized by ultraviolet radiation (58). It was also noted that in each instance the all-*trans* isomers exhibited the most intense fluorescence (59). The catalytic conversion of the *cis-trans* isomer of 1-phenyl-4-(2-nitrophenyl)butadiene to the all-*trans* compound has been carried out by heating it with a trace of iodine in nitrobenzene solution (2).

The existence of five of the six possible spatial configurations has been observed during a study of the stereoisomerism of 1,6-diphenylhexatriene, utilizing spectrophotometric and chromatographic techniques (78). In a manner resembling the behavior of diphenylbutadiene, the all-*trans* form was observed to undergo rearrangement toward partial *cis* structure under the influence of sunlight, and reversal of the reaction was found to occur upon the addition of a catalytic amount of iodine in the presence of light (78). During the catalytic *cis* → *trans* isomerization reaction it could be shown that it was the sterically most hindered double bonds which first rearranged their configuration.

The stereochemistry of 1,8-diphenyloctatetraene was studied by Zechmeister and LeRosen (124, 125) and by Zechmeister and Pinckard, using spectrophotometric and chromatographic techniques (129). Partial isomerization to mixtures containing varying amounts of three different *cis* forms was brought about by irradiation with sunlight or from an incandescent lamp, by the addition of iodine, or by the heating of crystals of the all-*trans* form above their melting point. Some of the *cis* forms that were produced in this manner were believed to possess *cis* configuration about the first double bond and were therefore sterically hindered. The photochemical isomerization of the all-*trans* isomer of 1,8-diphenyloctatetraene has also been observed by Hirshberg, Bergmann, and Bergmann (58).

The synthesis of some of the *cis* isomers of a number of α,ω-diarylpolyenes containing seven, nine, and eleven conjugated double bonds has also been described in the literature (44). It was found that these compounds were readily isomerized to the all-*trans* forms by the catalytic action of iodine in daylight. It is noteworthy that their dehydrogenation products (in which some of the conjugation has been destroyed by the formation of adjacent double bonds) are not susceptible to catalytic or photochemical isomerization.

2. Aromatic carbonyl compounds

The photochemical isomerization of benzalacetone and of ethyl styryl ketone was first studied by Baroni and Seifert (3). They observed that a lower melting and more intensely yellow modification was obtained when either of these ketones was exposed to ultraviolet radiation from a mercury arc and attributed this to partial *trans* → *cis* isomerization. The *trans* → *cis* isomerization of benzalacetone, along with that of cinnamonitrile, by ultraviolet radiation has also been carried out by v. Bree, who was unsuccessful, however, in attempting the photoconversion of *trans*-cinnamaldehyde (7). The partial *trans* → *cis* isomerization of benzalacetone by sunlight has also been reported recently, and the ultraviolet absorption spectra of the two isomers have been described in a qualitative manner (80). Semicarbazones and phenylhydrazones of benzalacetone and its derivatives have been obtained in two forms, depending on the configuration about the carbon–nitrogen double bond. The *anti* derivatives were found to undergo a reversible color change upon exposure to sunlight, suggesting isomerization about the carbon–carbon double bond, while the *syn*-phenylhydrazones were readily converted to pyrazolones (89).

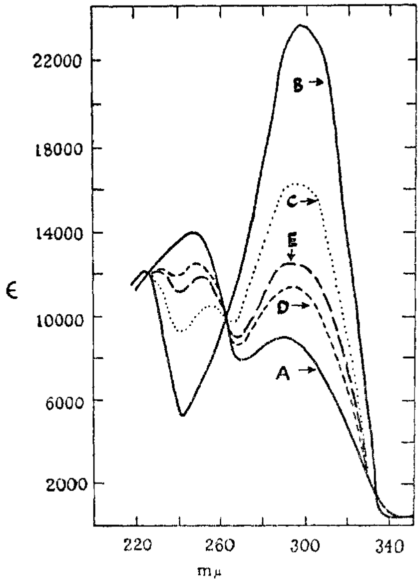


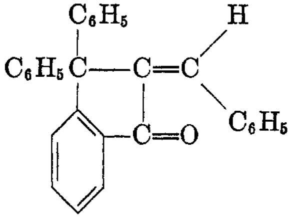
FIG. 8. Absorption spectra of benzalacetophenone. Curve A, *cis* isomer; curve B, *trans* isomer; curve C, *trans* isomer exposed to sunlight for 2 min.; curve D, *cis* isomer exposed to sunlight for 2 min.; curve E, either isomer exposed to sunlight for 12 min.

Although the phototropism of benzalacetophenone was first observed by Cromwell and Watson by spectrophotometric methods, they attributed this to a dimerization reaction (27) which had first been postulated twenty years earlier (109). The same reaction was subsequently studied by Lutz and Jordan by a similar technique, who attributed the change in the spectrum to *trans* → *cis* isomerization and succeeded in separating the *cis* isomer by fractional crystallization (81). They noted that the progress of the isomerization could be conveniently followed spectrophotometrically because of the differences in the absorption spectra of the two isomers, as shown in figure 8. The *cis-trans* isomerization of substituted α-aryl-substituted benzalacetophenones has also been studied using spectrophotometric techniques; their behavior was found to parallel that of the parent compound. From the shifts observed in the ultraviolet spectra upon the introduction of different substituents, it was concluded that in α-aryl-*p*-nitrobenzalacetophenone the nitro group was in conjugation with the α-phenyl group rather than the benzoyl group (6).

During a study of the relative stabilities of the *cis* and *trans* isomers of 1,2-dibenzoylethylene and some of its alkyl-, aryl-, and halogen-substituted derivatives, it was found that the labile forms were readily converted to the stable isomers by the action of acids, bases, or iodine. It was shown by spectroscopic methods that both the relative stabilities of the two isomers and the resonance between the several parts of these conjugated molecules were determined by steric considerations. While the *trans* isomer of 1,2-dibenzoylethylene was observed to be the stable one, the introduction of bulky substituents in the α-position was found to give rise to steric interference with coplanarity preferentially in the *trans* configuration; thus for a number of α-substituted derivatives the *cis* isomers were found to be the stable ones. The photochemical isomerization of these compounds has not been reported (69).

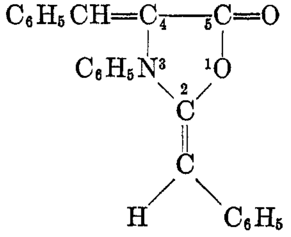
The geometrical isomerization of a number of α-aryl-substituted dibenzoylethylenes (1,2-dibenzoylstyrene and its derivatives) has also been investigated. In these compounds there is considerable steric hindrance in the *trans* configuration, owing to the bulky α-phenyl group; consequently, the *cis* isomers of these compounds are the stable ones. The unstable (*trans*) isomers are readily converted to the stable (*cis*) forms by heating and/or by the action of catalysts (e.g., hydrogen chloride), while exposure of the stable *cis* isomers to sunlight causes partial isomerization to the *trans* forms (4).

The *cis* and *trans* isomers of a number of ring-substituted derivatives of 2-benzylidene-3,3-diphenyl-1-hydrindone (XIII) have been synthesized and characterized. Partial interconversion was found to occur on treatment of either isomer with hot acetic acid, while the unstable (*cis*) compounds could be converted to the *trans* modifications by heating them to 160°C. (43). The isolation of a red and a yellow form of 2,4-dibenzylidene-3-phenyl-5-oxazolidone (XIV) has been ascribed to *cis-trans* isomerism about the double bond in the 4-position (70). Although the irradiation of each isomer with light of a wave-length range corresponding to its first absorption band failed to bring about the interconversion of the two forms, it did bring about changes in their absorption spectra. This suggested that under these conditions partial isomerization occurred about the double bond in the 2-position, giving rise to two additional isomers (118).



XIII

2-Benzylidene-3,3-diphenyl-1-hydrindone



XIV

2,4-Dibenzylidene-3-phenyl-5-oxazolidone

Among aromatic unsaturated acids and their derivatives the iodine-catalyzed *cis-trans* isomerization of cinnamic acid has been studied by kinetic methods.

The reaction was found to be first order with respect to the acid and one-half order with respect to iodine, suggesting a mechanism involving catalysis by iodine atoms. The energy of activation was found to be approximately 24 kcal. (30). These observations support the theory that had been previously proposed, suggesting that the halogen-catalyzed isomerization of unsaturated acids probably takes place through catalysis by halogen atoms (5). The thermal isomerization of methyl cinnamate has been reported to occur by a unimolecular reaction mechanism with an activation energy of approximately 24 kcal. Since this value is almost the same as the one obtained for stilbene (66), it suggests that both isomerizations probably occur by similar mechanisms involving the triplet state (67).

The photochemical isomerization of cinnamic acid has been studied using the 3130 Å. (114) and more recently both that and the 2537 Å. mercury line to cause the excitation (94). It was found that either isomer was converted to an equilibrium mixture by irradiation and that the position of the equilibrium was a function of the wave length of the light used and the absorption curve of the isomer that was being irradiated. It was on the basis of this investigation and the study of some simple unsaturated aliphatic acids that some of the theories concerning the mechanism of photochemical isomerization reactions (*cf.* Section II) were formulated (94).

The unstable *cis* isomers of β-benzoyl- and β-(4-bromobenzoyl)acrylic acids and of their methyl esters and amides have been prepared by exposing the corresponding *trans* compounds to sunlight in acetone or benzene solution. It was found that isomerization of the esters occurred most readily (82). The photochemical isomerization of β-styrenesulfonamide, *N*,*N*-dimethyl-β-styrenesulfonamide and methyl β-styrenesulfonate has also been carried out by irradiation from a mercury lamp for several days. Although the isomers were not separated and identified, it was observed that more soluble forms were obtained after irradiation (112).

3. Dyes

Since only a few classes of dyes possess carbon–carbon double bonds which may give rise to geometrical isomerism,[1] it may seem arbitrary to discuss them separately. However, dyes are known to exhibit anomalous physical and chemical properties, largely because our structural formulae are inadequate to describe systems possessing such a high degree of conjugation. Moreover, by definition, dyes show absorption in the visible region of the spectrum and their behavior with respect to photochemical isomerization is likely to be different from that of colorless conjugated compounds. It is on the basis of such considerations that it was decided to discuss the *cis-trans* isomerization of dyes separately.

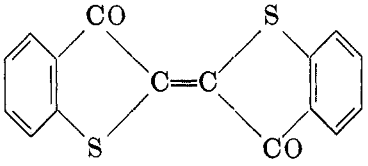
It has been known for a long time that dyes, in general, undergo chemical changes upon irradiation (115). It has also been shown that the spectra of some azo and thioindigo dyes show reversible changes under the impact of irradiation

---

[1] The important family of azo dyes possesses nitrogen–nitrogen double bonds and will be discussed below.

by visible light (108). It was not until recently, however, that systematic studies were undertaken to investigate the *cis-trans* isomerization of some of these compounds.

The *cis-trans* isomerization of thioindigo dyes (XV) is probably best understood at present (14, 119). It has been found that in solutions of these dyes in organic solvents an equilibrium exists between the *cis* and *trans* forms. The position of the equilibrium depends on the solvent, the temperature of the solution, and the illumination to which the solution has been exposed. Irradiation with light of a wave-length range corresponding to the first absorption band of the dye shifts the equilibrium toward the *cis* form, while irradiation with light of shorter wave lengths, or heating in the absence of light, causes a shift in the opposite direction (*cf.* figure 9). The separation of the geometrical isomers of



XV

Thioindigo

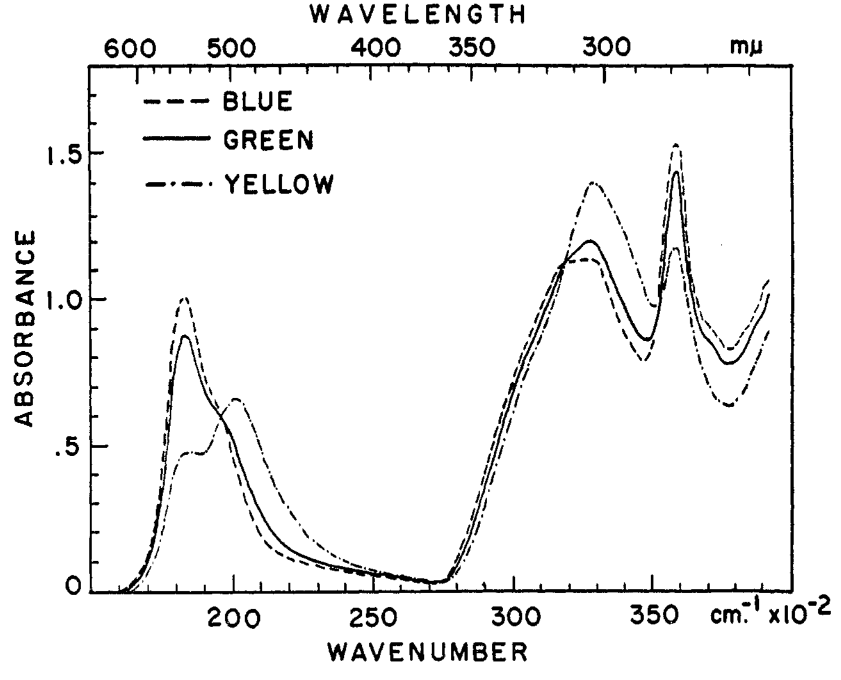


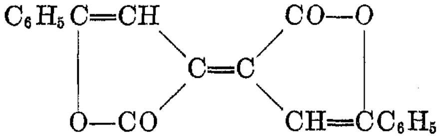
FIG. 9. Absorption spectra of thioindigo in chloroform after exposure to (*a*) blue light ($\lambda < 495$ mμ), (*b*) green light ($\lambda > 350$ mμ), (*c*) yellow light ($\lambda > 520$ mμ). Concentration, 10.1 mg./liter. Cell length, 2.00 cm.

TABLE 1

First absorption bands of thioindigo dyes

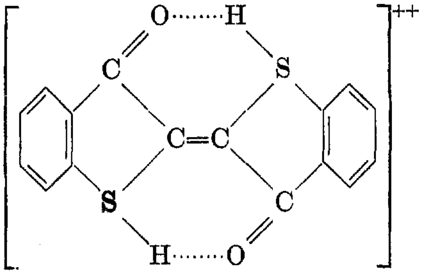
Substituent	In $CHCl_3$	In H_2SO_4
	mμ	mμ
None	546	640
5,5′-Dichloro-7,7′-dimethyl-	565	694
5,5′-Dichloro-4,4′,7,7′-tetramethyl-	574	709
5,5′,7,7′-Tetramethyl-	568	729
4,4′-Dimethyl-6,6′-dichloro-	540	671

two of these dyes was accomplished by chromatographic adsorption in the absence of light. Among other dyes possessing structures similar to that of thioindigo, Pechmann's dye (XVI) (8) has also been observed to undergo reversible photochemical isomerization in chloroform solution. In contrast with their behavior in organic solvents, thioindigo dyes were found not to undergo photochemical isomerization in concentrated sulfuric acid solution (15). The absence of phototropism, coupled with the observed strong bathochromic shifts in the position of the first absorption bands (as shown in table 1), suggested that in this medium each thioindigo dye exists in the form of a hydrogen-bonded complex possessing a *trans* configuration (XVII). The behavior of the hemi-thioindigoid dye Vat Scarlet G (XVIII) in organic solvents and also in sulfuric acid solution was found to parallel that of the thioindigo dyes.

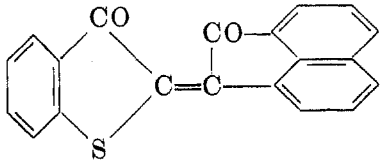


XVI

Pechmann's dye



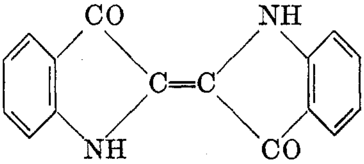
XVII



XVIII

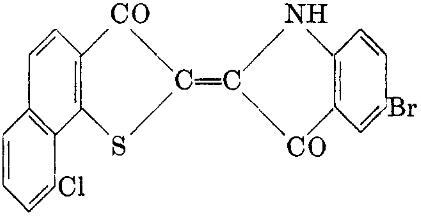
Vat Scarlet G

The possibility of the existence of *cis* and *trans* isomers of indigo (XIX) has intrigued organic chemists for a long time. Although derivatives of *cis*-indigo



XIX
Indigo

have been reported (102) and the appearance of a fleeting blue color during the oxidation of leucoindigo at low temperatures has been attributed to *cis*-indigo (55), the existence of this isomer has never been established beyond doubt. Attempts at bringing about the photochemical isomerization of indigo and several of its halogenated derivatives by irradiating them with light of a wave-length range corresponding to the first absorption band failed to disclose any change in the spectra (12), even when irradiation and measurement of the solution were carried out essentially simultaneously, utilizing a rotating shutter for this purpose (45). Since this latter technique had been found to be successful for obtaining qualitative evidence for the existence of some very unstable *cis*-azo dyes (see below), it appears that the *cis* isomers of indigo and its derivatives are too unstable (with respect to the corresponding *trans* isomers) to form. The high relative stability of *trans*-indigo is consistent with the hydrogen-bonded structure which had been proposed for this isomer (31, 84). It was conclusively proven that the difference between the behavior toward photochemical isomerization of indigo and thioindigo dyes was due to the existence of hydrogen bonding in the former, when it was shown that *N*,*N*′-diacetylindigo (which had no hydrogen atoms available for hydrogen-bond formation) acted very much like thioindigo dyes when irradiated with light of a wave-length range corresponding to its first absorption band (12), as shown in figure 10. A similar behavior is also exhibited by *N*,*N*′-dimethylindigo (118). It should be mentioned that the mixed indigo-thioindigo dye Solvat Grey BL Base (XX) also failed to undergo photochemical



XX
Solvat Grey BL Base

isomerization, indicating that the formation of just one hydrogen bond endows the *trans* form of dyes of this type with sufficient additional stability to make it impervious to photochemical isomerization.

There is only one report in the literature that suggests the existence of geo-

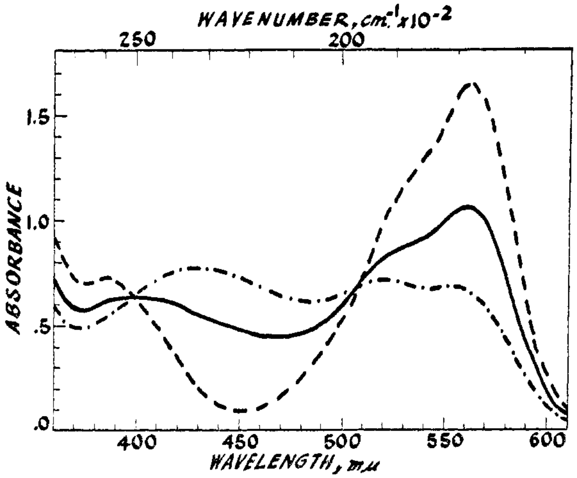
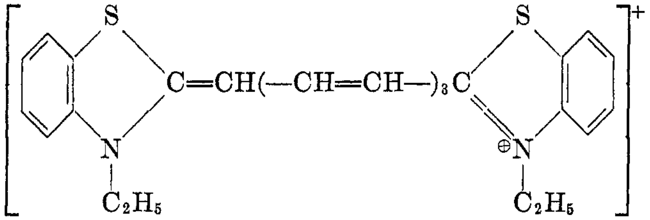
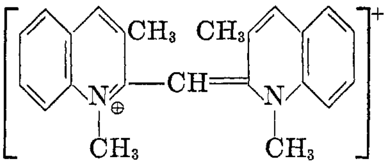


FIG. 10. Absorption spectra of N,N'-diacetylindigo in benzene after exposure to (*a*) blue light ($\lambda < 495$ mμ) (- - -), (*b*) green light ($\lambda > 350$ mμ) (——), (*c*) yellow light ($\lambda > 520$ mμ) (-·-·-). Concentration, 40.2 mg./liter. Cell length, 2.00 cm.

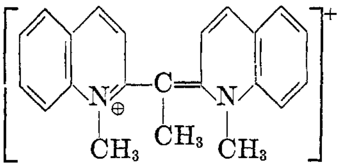
metrical isomers of a cyanine dye (128). In that work it was observed that when a solution of this dye (XXI) was subjected to chromatographic analysis, during the development of the chromatogram the dye separated into three zones. However, upon isolation of each of the zones it was found that they were spectrophotometrically identical. On the basis of these observations it was believed that three of the geometrical isomers were separated, but that isomerization to an equilibrium mixture had occurred before it was possible to identify each of the isomers. The attempted photochemical isomerization of two other cyanine dyes (XXII and XXIII) in chloroform solution, by the techniques that had been successful in the study of thioindigo and azo dyes, disclosed only an irreversible fading reaction (8). Phototropism was exhibited, however, by the chloroform



XXI



XXII



XXIII

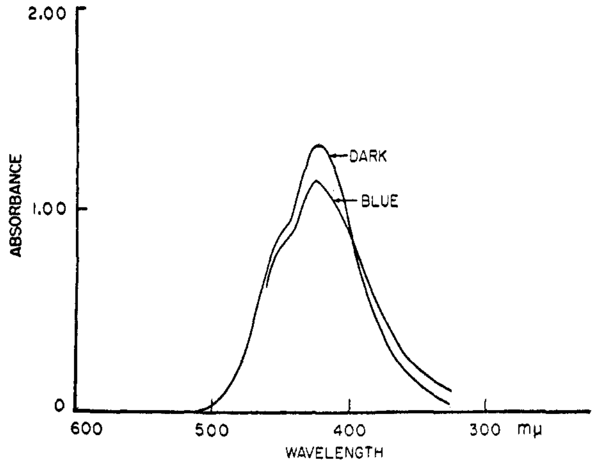
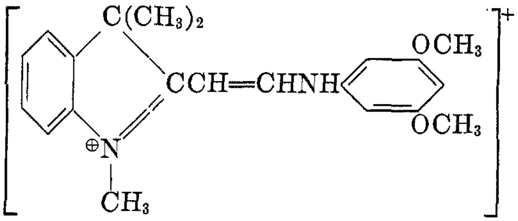


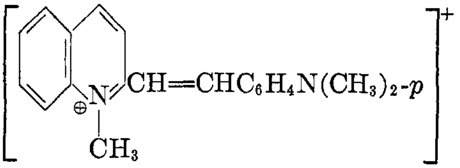
FIG. 11. Absorption spectra of Genacryl Yellow (XXIV) (*a*) on standing in darkness and (*b*) after exposure to blue light.

solutions of a number of other dyes containing but one carbon–carbon bond about which *cis-trans* isomerism was possible. Such behavior was shown by Genacryl Yellow (XXIV), Quinaldine Red (XXV), and a Rhodanine derivative (XXVI), as shown in figure 11 for XXIV (8).



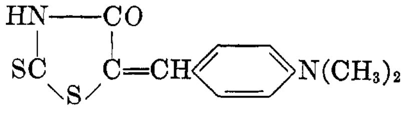
XXIV

Genacryl Yellow



XXV

Quinaldine Red



XXVI

It was recently reported that each of a number of colorless spiropyrans gave rise to several unstable colored modifications upon heating or irradiation (34

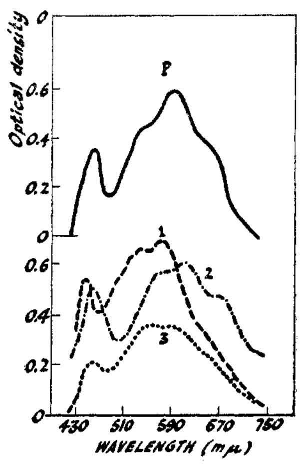


FIG. 12

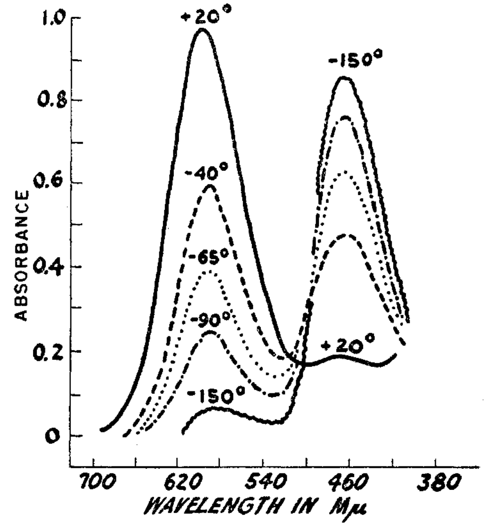
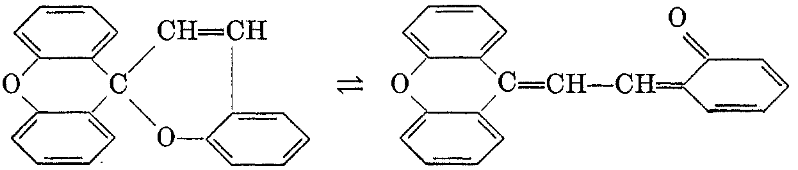


FIG. 13

FIG. 12. Absorption spectra of the spiropyran shown in equation 2. Curve 1, solution after 1 min. of irradiation at −183°C.; curve 2, solution 1 heated to −160°C. and recooled; curve 3, solution 2 heated to −100°C.; curve 4, solution in ethanol-methanol after 1 min. of irradiation at −160°C. (note the separate scale), not changed when heated to −100°C.

FIG. 13. Absorption spectrum, at several temperatures, of dye XXVIIIa in a mixture of ethanol and methanol. Concentration, 2 mg./liter.

61, 62), as shown in figure 12 for XXVII. The formation of the colored modification was found to be a function of the temperature and of the solvent used. Although the mechanism of these changes in the absorption spectra is not fully understood at present, it was suggested that this behavior may be attributable to spiropyran–merocyanine tautomerism (as shown in equation 2 for a typical molecule), followed by the *cis-trans* isomerization of the merocyanine dye (61).

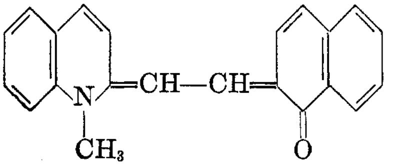


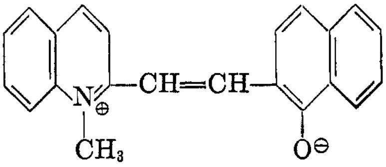
(2)

XXVIIa
Spiropyran

XXVIIb
Merocyanine

A study of the effect of temperature on four merocyanine dyes disclosed that the spectra of these compounds exhibit drastic changes upon heating, as shown in figure 13 for dye XXVIIIa. The gradual disappearance of an absorption band accompanied by the simultaneous appearance of a new band upon heating has been attributed to the formation of a new modification (60). This may well be due to *cis-trans* isomerization about one of the acyclic double bonds (if they

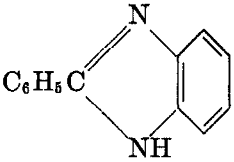

XXVIIIa


XXVIIIb

have sufficient double-bond character), or about the central bond, if the dye should exist principally in the dipolar structure XXVIIIb.

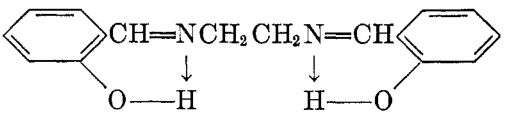
IV. Isomerization about Carbon–Nitrogen Double Bonds

The *cis-trans* isomerization of organic compounds containing a carbon–nitrogen double bond has been studied relatively little, although the existence of geometrical isomers in compounds of this type has been well known for a long time. Benzalaniline, the simplest aromatic compound containing a C═N bond, and some of its derivatives have been investigated, using dipole moment and ultraviolet spectroscopic techniques. Although these compounds were known to exist in two modifications, it was found that neither the absorption spectra nor the dipole moments showed changes when their solutions were exposed to radiation from a mercury arc. On this basis it was concluded that the two modifications must have been due to polymorphism and that the molecules existed exclusively in the *trans* configuration (29). This last conclusion was subsequently disputed by Wiegand and Merkel, who noted that the dipole moment of benzalaniline was intermediate between the two values expected for the *cis* and *trans* configurations. Moreover its ultraviolet spectrum was very different from that of 2-phenylbenzimidazole (XXIX), which is structurally very similar to *trans*-benzalaniline and which, consequently, would be expected to have a similar spectrum. On the basis of these observations, coupled with the reported absence of *cis* and *trans* isomers, they suggest a linear structure for this compound (116). Irradiation of benzalaniline with light of a wave-length range corresponding to its first absorption band and measurement of the absorption spectrum using the rotating-shutter technique have also failed to disclose any change (118).

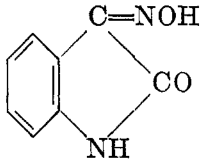

XXIX

2-Phenylbenzimidazole

The existence of hydrogen bonding has been postulated in the Schiff base (XXX) derived from ethylenediamine and salicylaldehyde on the basis of spectroscopic evidence, suggesting a *trans* configuration in compounds of this type (33). Benzaldehyde phenylhydrazone and isatin β-oxime (XXXI) failed to exhibit phototropism when irradiated with light from an incandescent lamp (8).



XXX



XXXI

Isatin β-oxime

The *cis-trans* isomerization about the carbon–nitrogen double bond in cinnamalazine (VIII) and in phenylpentadienealazine (IX) has already been discussed in the section on aliphatic polyenes (III,A).

V. Isomerization about Nitrogen–Nitrogen Double Bonds

The unstable *cis* isomer of azobenzene was first isolated and identified by Hartley by means of repeated fractional crystallizations of irradiated solutions of azobenzene (51, 52). In addition to the slow thermal isomerization reaction (yielding the stable form) under the influence of ultraviolet light there occurred a much faster photochemical reaction which caused isomerization to an equilibrium mixture containing 15–40 per cent of the *cis* isomer. The position of the photochemical equilibrium is dependent on the temperature and the nature of the solvent. The activation energy of the thermal isomerization reaction was reported to be 23 kcal. Shortly thereafter the *cis* isomers of azobenzene and of some of its alkyl-, nitro-, and halogen-substituted derivatives were isolated by the chromatographic analysis of their irradiated solutions (23, 24), and their absorption spectra were reported (25). Recently the kinetics of the thermal isomerization of azobenzene and of its *p*-methyl, *p*-chloro, *p*-bromo, *p*-nitro, and *p*-methoxy derivatives has been investigated. The results (E_a = about 23 kcal.; frequency factors, about 10^{11}) suggest a reaction path that does not entail a triplet state (74), i.e., one similar to that of stilbene.

Although the darkening of solutions of some of the 4-hydroxy- and 4-amino-substituted azobenzenes upon irradiation had been noted in these early investigations, suggesting *trans* → *cis* isomerization, the *cis* isomers appeared to be so short-lived that they could not be estimated photometrically (52), and during the attempted chromatographic analyses only an indefinite "tailing" and the appearance of subsidiary zones indicated their possible presence (24), but none could be definitely isolated. The absorption spectrum of 4-acetylamino-4′-dimethylaminoazobenzene has also been reported to undergo reversible changes upon irradiation from an incandescent lamp (108).

The development of a recording spectrophotometer for the ultraviolet and visible regions which utilizes a light beam of low intensity (22) and the invention of a rotating-shutter attachment for such a spectrophotometer, so as to allow for the periodic irradiation of the azo compound during the measurement (45), have recently permitted the study of the photochemical *trans* → *cis* isomerization of aminoazo and hydroxyazo compounds (10). In general, the spectra of 4-amino- and 4-hydroxyazobenzenes showed drastic changes upon exposure to light of a

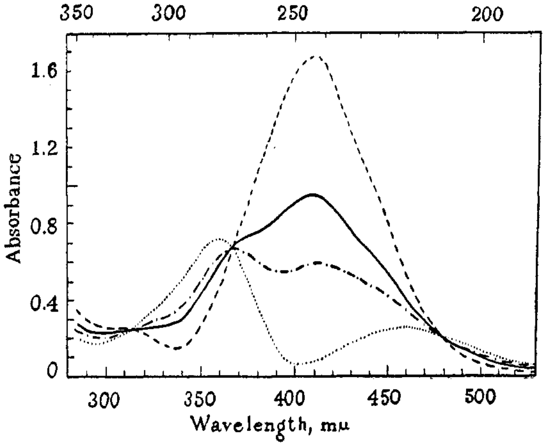


FIG. 14. Absorption spectra of 4-dimethylaminoazobenzene in benzene: – – –, after exposure to darkness; ——, after exposure to green light ($\lambda > 350$ mμ); –·–·–, after exposure to blue light ($\lambda < 495$ mμ); · · · · ·, calculated curve for *cis* isomer. Concentration, 6.7 mg./liter. Cell length, 2.00 cm.

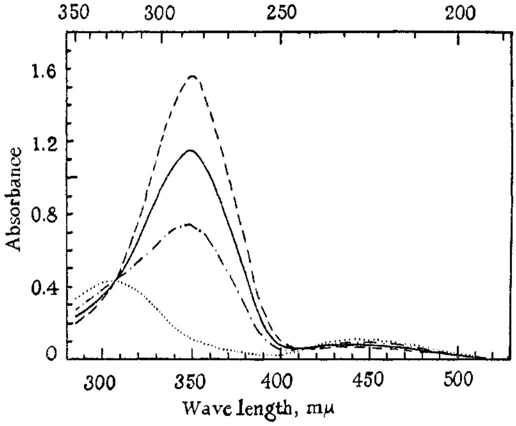


FIG. 15. Absorption spectra of 4-chloro-4′-hydroxyazobenzene: – – –, after exposure to darkness; ——, after exposure to green light ($\lambda > 350$ mμ); –·–·–, after exposure to blue light ($\lambda < 495$ mμ); · · · · ·, calculated curve for *cis* isomer. Concentration, 6.8 mg./liter. Cell length, 2.00 cm.

wave-length range corresponding to the wave length of the main absorption band. As a result of such irradiation the intensity of this absorption band was greatly diminished, and usually a new absorption band appeared at shorter wave lengths, as shown in figures 14 and 15. When the irradiation was discontinued, the solutions reverted to the original spectra within a few minutes. The extent of the change in the spectrum (probably a measure of the shift in equilibrium toward the *cis* form) was found to be a function of the structure of the compound and of the solvent used. In general, amino compounds were found to be more strongly phototropic than the hydroxy derivatives. From these data it was possible to calculate the approximate spectral absorption curves for the *cis* forms of some of these dyes. Solutions in non-polar hydrocarbon solvents showed the greatest changes in the spectra, while hydroxylic solvents seemed to suppress the phototropism (11). Thus the spectra of aqueous solutions of some typical water-soluble azo dyes did not show any changes upon irradiation by this technique. Azo dyes containing hydroxyl groups in the ortho position to the azo group were found to exhibit little or no phototropism under these conditions even in hydrocarbon solvents. Since it has been well-known that azo groups are prone to form hydrogen bonds (35, 56), this suppression of phototropism by hydroxylic solvents and by hydroxyl groups in the ortho position was attributed to hydrogen bonding (10, 11).

The behavior of 2,2′-azopyridine has been found to parallel that of azobenzene closely; exposure of this compound in benzene or cyclohexane solution to sunlight for several hours was found to cause changes in the absorption spectrum and the dipole moment (76). Since the irradiated solution had the greater dipole moment and the change was reversed on standing in darkness, this behavior was attributed to the existence of an equilibrium between *cis* and *trans* isomers. The isolation of the two isomers of 2,2′- and 3,3′-azopyridine was accomplished when the irradiated solutions of these compounds were subjected to chromatographic analysis. However, the same technique was found to be unsuccessful when applied to 4,4′-dimethyl-2,2′-azopyridine and to 5-bromo-2-phenylazopyridine (21). The *cis-trans* isomerization of azobenzene and of azobenzene-3,3′-disulfonic acid has been studied polarographically. The latter compound appeared to consist of an equal mixture of *cis* and *trans* isomers and the equilibrium could be shifted still further toward the *cis* form by ultraviolet irradiation (117).

Among the azo compounds containing more than one azo group, the photochemical isomerizations of *p*-bisbenzeneazobenzene, 4,4′-bisbenzeneazobiphenyl, and 4,4′-(bisbenzeneazo)azobenzene have been examined (24). Each of these compounds was found to undergo *trans* → *cis* isomerization under the influence of ultraviolet irradiation and the isomers could be separated chromatographically. All three possible isomers of the two bis-azo compounds were obtained in this manner, indicating that there was isomerization about each of the double bonds, and their absorption spectra determined. However, the various isomers of the tris-azo compound could not be successfully separated by this method. The photochemical isomerization of a number of 4,4′-diamino-substituted *p*-bisazobenzenes has also been studied, using the rotating-shutter technique. It was found that in these compounds, too, isomerization occurred about each of the double bonds (13).

In addition to azo compounds, the *cis-trans* isomerization of other types of organic compounds containing the —N=N— group has been reported in the literature. Thus the kinetics of the thermal *cis* → *trans* isomerization of benzene diazocyanide (XXXII) and of some of its halogen and nitro derivatives was

$$C_6H_5N{=}NCN$$

XXXII

Benzene diazocyanide

studied, utilizing the difference in the dipole moments of the two isomers for the measurements. The reaction was found to be unimolecular, with an energy of activation of 21–26 kcal. and frequency factors of 10^{12}–10^{15} for a large number of substituted benzene diazocyanides (17, 73, 75, 104), indicating that this reaction also occurs without a change in the multiplicity of the molecule. The photochemical isomerization of four aromatic hydrocarbon diazocyanide derivatives has also been examined. It was observed that the dipole moments of these compounds decreased upon exposure to sunlight; they were found to return to their original values after standing in darkness for several hours, thus demonstrating the reversibility of the reaction (72). From a spectrophotometric study of the thermal isomerization of *cis-p*-chlorobenzene diazocyanide in a variety of solvents it was concluded that the reaction occurred at a much faster rate in polar than in non-polar media (79).

The isolation of pairs of isomers from solutions containing aromatic diazonium salts and alkali sulfites was first attributed by Hantzsch to the *cis-trans* isomerism of the aryl diazosulfonates (XXXIII) produced in the reaction (49, 50).

$$\mathrm{ArN{=}NSO_3Na}$$

XXXIII

This contention has been subject to considerable debate in the literature when several investigators preferred to attribute the existence of the two forms to structural rather than geometrical isomerism. The history of this controversy was recently reviewed in detail by Freeman and Le Fèvre, who investigated the behavior of a number of substituted benzene diazosulfonates, using spectrophotometric techniques (38). They found that the spectral changes brought about by irradiating the solutions with ultraviolet light were partially reversed when the irradiated samples were allowed to stand in darkness for several hours, as shown in figure 16. Accordingly, they concluded that the several pairs of these compounds were indeed geometrical isomers and that the effect of irradiation involved a reversible *trans* → *cis* isomerization accompanied by some irreversible decomposition. A similar behavior was also observed for benzenediazocarboxamide (XXXIV) and its *p*-bromo- and *p*-nitro derivatives (*cf.* figure 17), indicating that the same reactions were occurring (41). Investigations of the photochemical *trans* → *cis* isomerization of a number of aromatic diazosulfones (XXXV) (40) and of some 1-aryl-3,3-dimethyltriazenes (XXXVI) (71), utilizing spectroscopic and dipole moment measurements, gave inconclusive results, owing to the extensive decomposition of the substrates.

$$\mathrm{C_6H_5N{=}NCONH_2} \qquad \mathrm{ArN{=}NSO_2R} \qquad \mathrm{ArN{=}NN(CH_3)_2}$$

XXXIV XXXV XXXVI

The thermal *cis-trans* isomerization of azoxybenzene and of *p,p'*-azoxytoluene in a variety of solvents has also been studied by spectrophotometric methods (79). Their isomerization was found to take place about fifty times faster than that of azobenzene; this was attributed to the weakening of the —N=N— double bond by the nitrogen–oxygen bond. The dipole moments and the ultra-

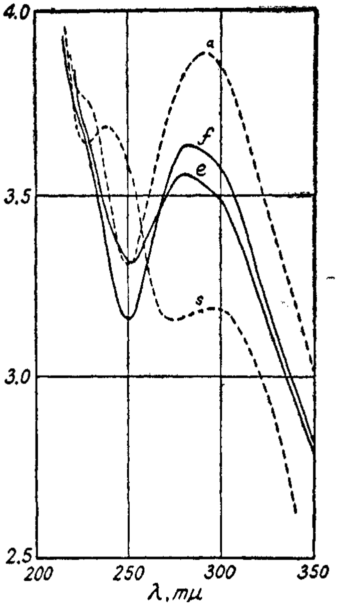


FIG. 16. Absorption spectra of *o*-chlorobenzenediazosulfonate in water. Curve *e*, after exposure to sunlight for 20 min.; curve *f*, on standing in darkness for 24 hr. after the treatment with sunlight. Curves *s* and *a* are for the *syn* and *anti* forms, respectively.

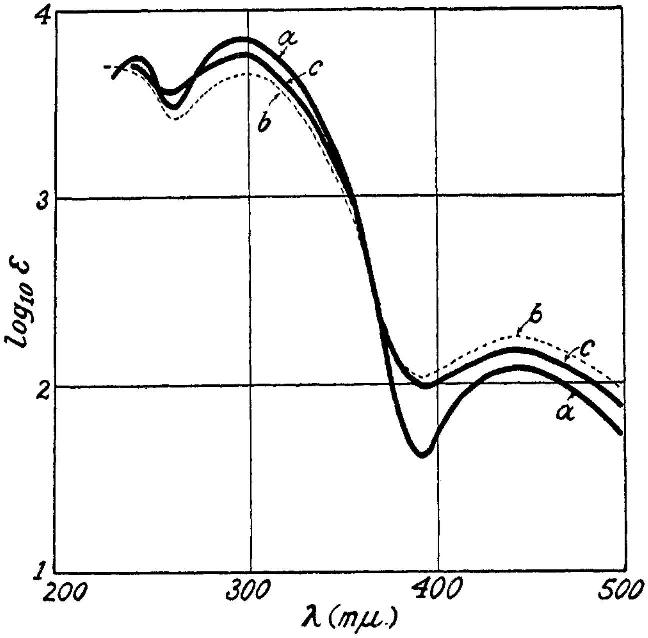


FIG. 17. Absorption spectra of *p*-bromobenzenecarboxamide: (*a*) before irradiation: (*b*) after irradiation; (*c*) solution from (*b*) after 24 hr. in the dark.

violet spectra of phenyl *p*-tolyl azoxysulfone and some of its *p'*-dialkylamino derivatives have been found to be unaffected by sunlight, indicating the absence of *cis-trans* isomerism in these compounds (39).

VI. Summary and Generalizations

Although the geometrical isomerization of literally hundreds of conjugated compounds has been reported, this still does not provide enough data for generalizations that are certain to stand up under the scrutiny of future investigators. While certain classes of conjugated unsaturated compounds (e.g., the carotenoids and aromatic unsaturated carbonyl compounds) have been rather fully investigated, a dearth of data is particularly evident concerning cyanine dyes and aromatic compounds containing carbon–nitrogen double bonds, where even the existence of geometrical isomers is still subject to considerable doubt. It is possible, however, to draw certain useful generalizations from the behavior of the other types of compounds discussed in this review and to make some surmises concerning these two classes for which insufficient data are available at present.

1. While *cis* and *trans* isomers of conjugated compounds are separate molecular species differing in their physical properties and (usually) stabilities, their interconversion may be brought about by any of the three methods discussed in Section II.
2. The ease of isomerization is a function of the solvent and increases with increasing conjugation in the molecule. Auxochromic groups conjugated with the double bond also increase the ease of isomerization.
3. Excitation of the stable isomer by radiation of a wave-length range corresponding to the wave length of its first absorption band causes the formation of the unstable isomer. Since increasing conjugation shifts the wave length of the absorption bands toward the visible region and at the same time increases their intensity, highly conjugated colored compounds will undergo partial isomerization even in diffuse daylight.
4. The unexpected absence of *cis-trans* isomerization under circumstances where structural features would require it indicates the selective stabilization of one of the isomers, usually by means of hydrogen bonding. Conversely, when intramolecular hydrogen bonding is possible in only one isomer, that isomer will probably be unusually stable with respect to the other and is usually not converted to the labile isomer even by irradiation.
5. The existence of unusually large steric hindrance in the labile isomer will also lead to the relative stabilization of the stable isomer. However, this does not seem to prevent the formation of the labile form, but exhibits itself in a fast thermal isomerization reaction.

These generalizations appear to be valid for all of the classes of conjugated organic compounds discussed in this review for which sufficient data are available. The very lack of data on the *cis-trans* isomerism of cyanine dyes and of benzalaniline derivatives strongly suggests that these two groups of compounds do not exist in two forms. A linear coplanar structure has, indeed, been proposed for benzalaniline (116), and with a single exception (dye XXI), the existence of *cis* and *trans* isomers of cyanine dyes has not been reported, in spite of the large volume of spectroscopic studies on dyes of this type (16). This suggests that in cyanine dyes the "double" bonds probably possess so much single-bond character as to be indistinguishable from the "single" bonds, thus resulting in a linear structure. It will be up to future investigations of structure to resolve the validity of these generalizations and surmises.

The author wishes to express his appreciation to Dr. R. S. Cahn for his permission to reproduce figures 12, 16, and 17, which appeared in the Journal of the Chemical Society; to Dr. C. A. Hutchison, Jr., for his consent to reproduce figure 13, originally published in the Journal of Chemical Physics; and to Dr. W. A. Noyes, Jr., for his cooperation in allowing the reproduction of figures 1–2, 4–10, and 14–15, all of which have appeared in the Journal of the American Chemical Society. The author is also indebted to Dr. W. R. Brode for providing some of his as yet unpublished results on the phototropism of dyes, including figure 11.

It is the author's privilege to express his gratitude to Miss Betty Hickey for her invaluable assistance in preparing the manuscript.

VII. REFERENCES

(1) ASHLEY, J. N., AND HARRIS, J. O.: J. Chem. Soc. **1946,** 567.
(2) BACHMAN, G. B., AND HOAGLIN, R. I.: J. Org. Chem. **8,** 300 (1943).
(3) BARONI, E., AND SEIFERT, H.: Naturwissenschaften **29,** 560 (1941).
(4) BAUER, C. R., AND LUTZ, R. E.: J. Am. Chem. Soc. **75,** 5997 (1953).
(5) BERTHOUD, A., AND URECH, C.: J. chim. phys. **27,** 291 (1930).
(6) BLACK, W. B., AND LUTZ, R. E.: J. Am. Chem. Soc. **75,** 5990 (1953).
(7) BREE, G. V.: Bull. soc. chim. Belges **57,** 71 (1948).
(8) BRODE, W. R.: In *Roger Adams Symposium Volume*. John Wiley and Sons, Inc., New York (1955).
(9) BRODE, W. R.: *Chemical Spectroscopy*, 2nd edition, p. 214. John Wiley and Sons, Inc., New York (1943).
(10) BRODE, W. R., GOULD, J. H., AND WYMAN, G. M.: J. Am. Chem. Soc. **74,** 4641 (1952).
(11) BRODE, W. R., GOULD, J. H., AND WYMAN, G. M.: J. Am. Chem. Soc. **75,** 1856 (1953).
(12) BRODE, W. R., PEARSON, E. G., AND WYMAN, G. M.: J. Am. Chem. Soc. **76,** 1034 (1954).
(13) BRODE, W. R., PEARSON, E. G., AND WYMAN, G. M.: Unpublished data.
(14) BRODE, W. R., AND WYMAN, G. M.: J. Research Natl. Bur. Standards **47,** 170 (1951).
(15) BRODE, W. R., AND WYMAN, G. M.: J. Am. Chem. Soc. **73,** 4267 (1951).
(16) *cf.* BROOKER, L. G. S.: In *Advances in Nuclear Chemistry and Theoretical Organic Chemistry*, pp. 98–132. Interscience Publishers, Inc., New York (1945).
(17) CALDERBANK, K. E., LE FÈVRE, R. J. W., AND NORTHCOTT, J.: Chemistry & Industry **1948,** 158.
(18) CALVIN, M., AND ALTER, H. W.: J. Chem. Phys. **19,** 768 (1951).
(19) CALVIN, M., AND ALTER, H. W.: J. Chem. Phys. **19,** 765 (1951).
(20) CALVIN, M., AND BUCKLES, R. E.: J. Am. Chem. Soc. **62,** 3324 (1940).
(21) CAMPBELL, N., HENDERSON, A. W., AND TAYLOR, D.: J. Chem. Soc. **1953,** 1281.
(22) CARY, H. H.: Rev. Sci. Instr. **17,** 558 (1946).
(23) COOK, A. H.: J. Chem. Soc. **1938,** 876.
(24) COOK, A. H., AND JONES, D. G.: J. Chem. Soc. **1939,** 1309.
(25) COOK, A. H., JONES, D. G., AND POLYA, J. B.: J. Chem. Soc. **1939,** 1315.

(26) Crombie, L.: Quart. Revs. (London) **6**, 106 (1952).
(27) Cromwell, N. H., and Watson, W. R.: J. Org. Chem. **14**, 411 (1949).
(28) Dale, J., and Zechmeister, L.: J. Am. Chem. Soc. **75**, 2379 (1953).
(29) de Gaouck, V., and Le Fèvre, R. J. W.: J. Chem. Soc. **1938**, 741.
(30) Dickinson, R. G., and Lotzkar, H.: J. Am. Chem. Soc. **59**, 472 (1937).
(31) Dokunikhin, N., and Levin, E.: Compt. rend. acad. sci. U.S.S.R. **35**, 110 (1942).
(32) Erdtman, H.: Acta Chem. Scand. **2**, 209 (1948).
(33) Ferguson, L. N., and Kelly, I.: J. Am. Chem. Soc. **73**, 3707 (1951).
(34) Fischer, E., and Hirshberg, Y.: J. Chem. Soc. **1952**, 4522.
(35) Flett, M. St. C.: J. Soc. Dyers & Colourists **68**, 59 (1952).
(36) Flürscheim, B., and Holmes, E. L.: J. Chem. Soc. **1932**, 1458.
(37) Frank, R. L., Emmick, R. D., and Johnson, R. S.: J. Am. Chem. Soc. **69**, 2313 (1947).
(38) Freeman, H. C., and Le Fèvre, R. J. W.: J. Chem. Soc. **1951**, 417.
(39) Freeman, H. C., Le Fèvre, R. J. W., Northcott, J., and Worth, C. V.: J. Chem. Soc. **1952**, 3384.
(40) Freeman, H. C., Le Fèvre, R. J. W., Northcott, J., and Youhotsky, I.: J. Chem. Soc. **1952**, 3381.
(41) Freeman, H. C., Le Fèvre, R. J. W., and Wilson, I. R.: J. Chem. Soc. **1951**, 1977.
(42) Fuson, R. C., and Horning, E. C.: J. Am. Chem. Soc. **62**, 2962 (1940).
(43) Gagnon, P. E., and Charette, L. P.: Can. J. Research **19B**, 275 (1941).
(44) Garbers, C. F., Engster, C. H., and Karrer, P.: Helv. Chim. Acta **35**, 1850 (1952).
(45) Gould, J. H., and Brode, W. R.: J. Opt. Soc. Amer. **42**, 380 (1952).
(46) Grummitt, O., and Christoph, F. J.: J. Am. Chem. Soc. **71**, 4157 (1949).
(47) Grummitt, O., and Christoph, F. J.: J. Am. Chem. Soc. **73**, 3479 (1951).
(48) Haddow, A., Harris, R. J. C., Kon, G. A. R., and Roe, E. M. F.: Phil. Trans. Roy. Soc. (London) **A241**, 167 (1948).
(49) Hantzsch, A.: Ber. **27**, 1702 (1894).
(50) Hantzsch, A.: Ber. **27**, 1726 (1894).
(51) Hartley, G. S.: Nature **140**, 281 (1937).
(52) Hartley, G. S.: J. Chem. Soc. **1938**, 633.
(53) Hausser, I.: Naturwissenschaften **36**, 315 (1949).
(54) Hausser, I.: Z. Naturforsch. **5a**, 56 (1950).
(55) Heller, G.: Ber. **77B**, 163 (1944).
(56) Hendricks, S. B., Wulf, O. R., Hilbert, G. E., and Liddel, U.: J. Am. Chem. Soc. **58**, 1955 (1936).
(57) Hirshberg, Y., and Bergmann, F.: J. Am. Chem. Soc. **72**, 5118 (1950).
(58) Hirshberg, Y., Bergmann, E., and Bergmann, F.: J. Am. Chem. Soc. **72**, 5120 (1950).
(59) Hirshberg, Y., Bergmann, E., and Bergmann, F.: J. Am. Chem. Soc. **72**, 5117 (1950).
(60) Hirshberg, Y., and Fischer, E.: J. Chem. Phys. **22**, 572 (1954).
(61) Hirshberg, Y., and Fischer, E.: J. Chem. Soc. **1954**, 3129.
(62) Hirshberg, Y., and Fischer, E.: J. Chem. Soc. **1954**, 297.
(63) Hubbard, R., Gregerman, R. I., and Wald, G.: J. Gen. Physiol. **36**, 415 (1953).
(64) Jones, R. N.: J. Am. Chem. Soc. **67**, 1956 (1945).
(65) Kharasch, M. S., Mansfield, J. V., and Mayo, F. R.: J. Am. Chem. Soc. **59**, 1155 (1937).
(66) Kistiakowsky, G. B., and Smith, W. R.: J. Am. Chem. Soc. **56**, 638 (1934).
(67) Kistiakowsky, G. B., and Smith, W. R.: J. Am. Chem. Soc. **57**, 269 (1935).
(68) Kistiakowsky, G. B., and Smith, W. R.: J. Am. Chem. Soc. **58**, 2428 (1936).
(69) Kuhn, L. P., Lutz, R. E., and Bauer, C. R.: J. Am. Chem. Soc. **72**, 5058 (1950).
(70) Larsen, S., and Bernstein, J.: J. Am. Chem. Soc. **72**, 4447 (1950).
(71) Le Fèvre, R. J. W., and Liddicoet, T.: J. Chem. Soc. **1951**, 2743.
(72) Le Fèvre, R. J. W., and Northcott, J.: J. Chem. Soc. **1949**, 333.
(73) Le Fèvre, R. J. W., and Northcott, J.: J. Chem. Soc. **1949**, 944.

(74) Le Fèvre, R. J. W., and Northcott, J.: J. Chem. Soc. **1953,** 867.
(75) Le Fèvre, R. J. W., and Vine, H.: J. Chem. Soc. **1938,** 431.
(76) Le Fèvre, R. J. W., and Worth, C. V.: J. Chem. Soc. **1951,** 1814.
(77) Lewis, G. N., Magel, T. T., and Lipkin, D.: J. Am. Chem. Soc. **62,** 2973 (1940).
(78) Lunde, K., and Zechmeister, L.: J. Am. Chem. Soc. **76,** 2308 (1954).
(79) Lunder, P., and Winkler, C. A.: Can. J. Chem. **30,** 679 (1952).
(80) Lutz, R. E., Bauer, C. R., and Jordan, R. H.: J. Am. Chem. Soc. **72,** 4300 (1950).
(81) Lutz, R. E., and Jordan, R. H.: J. Am. Chem. Soc. **72,** 4090 (1950).
(82) Lutz, R. E., and Scott, G. W.: J. Org. Chem. **13,** 284 (1948).
(83) McConnell, H.: J. Chem. Phys. **20,** 1043 (1952).
(84) Madelung, W., and Wilhelmi, O.: Ber. **57,** 237 (1929).
(85) Magee, J. L., Shand, Jr., W., and Eyring, H.: J. Am. Chem. Soc. **63,** 677 (1941).
(86) Malpress, F. H.: Nature **158,** 790 (1946).
(87) Martin, W. H.: Trans. Roy. Soc. Can., Sect. III, **34,** 35 (1940).
(88) Marvel, C. S.: In *Organic Chemistry,* edited by H. Gilman, 2nd edition, Vol. I, p. 453. John Wiley and Sons, Inc., New York (1943).
(89) Matei, V.: Ann. sci. univ. Jassy I, **29,** 17 (1943); Chem. Abstracts **42,** 3743 (1948).
(90) Meunier, M. P.: Compt. rend. **222,** 1528 (1946).
(91) Meunier, M. P., Jouannetou, J., and Zwingelstein, G.: Bull. soc. chim. biol. **33,** 1228 (1951).
(92) Nash, H. A., and Zscheile, F. P.: Arch. Biochem. **5,** 77 (1944).
(93) Olson, A. R.: J. Chem. Phys. **1,** 418 (1933).
(94) Olson, A. R., and Hudson, F. L.: J. Am. Chem. Soc. **55,** 1410 (1933).
(95) Oroshnik, W., Karmas, G., and Mebane, A. D.: J. Am. Chem. Soc. **74,** 295 (1952).
(96) Oroshnik, W., and Mebane, A. D.: J. Am. Chem. Soc. **76,** 5719 (1954).
(97) Pauling, L.: Fortschr. Chem. org. Naturstoffe **3,** 203 (1939).
(98) Pauling, L.: *The Nature of the Chemical Bond,* 2nd edition, p. 174. Cornell University Press, Ithaca, New York (1943).
(99) Pauling, L.: Helv. Chim. Acta **32,** 2241 (1949).
(100) Pinckard, J. H., Wille, B., and Zechmeister, L.: J. Am. Chem. Soc. **70,** 1938 (1948).
(101) Price, C. C., and Meister, M.: J. Am. Chem. Soc. **61,** 1595 (1939).
(102) Pummerer, R., and Fiesselmann, H.: Ann. **544,** 206 (1940).
(103) Ruggli, P., and Staub, A.: Helv. Chim. Acta **20,** 37 (1937).
(104) Saboor, M. A.: Indian J. Phys. **17,** 223 (1943).
(105) Sandoval, A., and Zechmeister, L.: J. Am. Chem. Soc. **69,** 553 (1947).
(106) Shaw, B. L., and Whiting, M. C.: J. Chem. Soc. **1954,** 3217.
(107) Smakula, Z.: Z. physik. Chem. **B25,** 90 (1934).
(108) Stearns, E. I.: J. Opt. Soc. Amer. **32,** 292 (1942).
(109) Stobbe, H., and Bremer, K.: J. prakt. Chem. **123,** 1 (1929).
(110) Straus, F.: Ann. **342,** 190 (1905).
(111) Tappi, G., and Karrer, P.: Helv. Chim. Acta **32,** 50 (1949).
(112) Terentev, A. P., Gracheva, R. A., and Sherbatova, Z. F.: Compt. rend. acad. sci. U.S.S.R. **84,** 975 (1952).
(113) Umsibara, Y., and Simamura, O.: Bull. Chem. Soc. Japan **14,** 323 (1939).
(114) Vaidya, B. K.: Proc. Roy. Soc. (London) **A129,** 299 (1930).
(115) *cf.* Venkataraman, K.: *The Chemistry of Synthetic Dyes,* Vol. 2, p. 1210. Academic Press, Inc., New York (1952).
(116) Wiegand, C., and Merkel, E.: Ann. **550,** 175 (1942).
(117) Winkel, A., and Siebert, H.: Ber. **74B,** 670 (1941).
(118) Wyman, G. M.: Unpublished data.
(119) Wyman, G. M., and Brode, W. R.: J. Am. Chem. Soc. **73,** 1487 (1951).
(120) Zechmeister, L.: Chem. Revs. **34,** 267 (1944).
(121) Zechmeister, L.: Chem. Revs. **34,** 335 (1944).
(122) Zechmeister, L.: Experientia **10,** 1 (1954).

(123) Zechmeister, L., and Koe, B. K.: J. Am. Chem. Soc. **76,** 2923 (1954).
(124) Zechmeister, L., and LeRosen, A. L.: J. Am. Chem. Soc. **64,** 2755 (1942).
(125) Zechmeister, L., and LeRosen, A. L.: Science **95,** 587 (1942).
(126) Zechmeister, L., LeRosen, A. L., Schroeder, W. A., Polgár, A., and Pauling, L.: J. Am. Chem. Soc. **65,** 1940 (1943).
(127) Zechmeister, L., and Pinckard, J. H.: J. Am. Chem. Soc. **69,** 1930 (1947).
(128) Zechmeister, L., and Pinckard, J. H.: Experientia **9,** 16 (1953).
(129) Zechmeister, L., and Pinckard, J. H.: J. Am. Chem. Soc. **76,** 4144 (1954).
(130) Zechmeister, L., and Polgar, A.: J. Am. Chem. Soc. **66,** 137 (1944).
(131) Zechmeister, L., and Wallcave, L.: J. Am. Chem. Soc. **75,** 4493 (1953).