# PHOTOCHROMIC ANILS: SPECTROSCOPY AND MECHANISMS OF PHOTO- AND THERMAL REACTIONS

A Dissertation Presented to the Faculty of the Department of Chemistry College of Arts and Sciences University of Houston

In partial fulfillment of the Requirements for the Degree Doctor of Philosophy

> by Warren Frank Richey

> > 400802<sup>1967</sup>

### **ACKNOWLEDGEMENTS**

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The author wishes to express his most sincere appreciation to his wife, Karen, for her encouragement and understanding during these years of graduate study; to Dr. Ralph Becker for his counsel and assistance, but most of all for his insight into the sometimes bewildering workings of nature; to the United States Air Force, contract AF 33(615)-1733, for support, September 1965 to May 1966; to the National Aeronautics and Space Administration, Pre-doctoral Traineeship, for support, June 1966 to May 1967.

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### ABSTRACT

The photochromism and thermochromism of several salicylideneanilines and related compounds have been investigated. At room temperature or low temperature most salicylideneanilines exist almost exclusively in the enol form in solutions of hydrocarbon solvents. At low temperature in solutions of hydrogen bonding solvents or solutions in which strongly hydrogen bonding species are present, some of the anil molecules exist as the cis-keto tautomer. In the cases of the nitrosalicylideneanilines and 2-hydroxynaphthylideneaniline some cis-keto is produced at low temperatures even in solutions of hydrocarbon solvents. This phenomenon is attributed to the enhanced stability of the cis-keto tautomer.

In rigid solutions at low temperature excitation of the enol form of most salicylideneanilines produces a colored species via a cis-keto-like transition state. It is found that increased viscosity decreases the yield of the photo-product by increasing the potential energy barrier between the transition state and the photo-colored species. This photocolored species has a characteristic long wavelength absorption band which is different from either the absorption of the enol or the cisketo. This species is identified as a non-equilibrium form of the cisketo in which the C=C bond is twisted and the internal hydrogen bond broken in order to relieve the strain which the nitrogen acquires in the transition state. Warming the solution to decrease its viscosity results in the immediate conversion of this photo-colored species to the cis-keto. Further warming converts this cis-keto to enol.

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Under the proper conditions of temperature and viscosity the photo-colored species may be eradicated by irradiation into its absorption band. This process converts the photo-colored species to the enol through the transition state. No cis keto is produced.

Nitrosalicylideneanilines are not photochromic; 2-hydroxynaphthylideneaniline is photochromic, but in this case irradiation produces only more cis keto tautomer. This photo-produced cis keto may be eradicated by irradiation into the cis keto absorption band.

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I.

### INTRODUCTION

## A. Molecular Electronic Energy States: Absorption and Emission of Light

A consequence of the molecular orbital theory is that certain of the atomic orbitals of the atoms which bind together to form the molecule are combined in such a way as to produce molecular orbitals. The electrons originally in these atomic orbitals are assigned to the molecular orbitals in accordance with the Aufbau principle and the Pauli exclusion principle. That is, the electrons are placed such that the molecular orbitals of lowest energy are filled with two electrons each before any electron is assigned to an orbital of higher energy. Hund's rule applies for degenerate orbitals so that one electron is assigned to each degenerate molecular orbital before a second electron is placed in any one of them.

Each molecular orbital has a particular energy and wave function associated with it. Both are time independent and the Hamiltonian contains momentum and potential energy terms. If we borrow the idea from the theory of relativity that the energy of a body depends not only on its kinetic and potential energies but also on its rest mass and insert this energy term into the Hamiltonian, two independent orthogonal wave functions appear as solutions for each energy level.

By introducing the concept of an intrinsic angular momentum arising from the spinning motion of the electron about an axis through its center, the nature of the two wave functions may be explained. One corresponds to a system in which the intrinsic angular momentum has a component of +  $1/2 - \pi$  (where  $\pi = h/2\pi$ ), and the other has a component of -  $1/2 - \pi$ . Thus two electrons in the same molecular orbital will differ only in the intrinsic angular momentum component.

Most molecular orbital calculations use Hamiltonian operators that do not include the relativistic effects, and thus the resulting wave functions do not include spin. However the effects of spin may be introduced by multiplying the non-relativistic functions by functions  $\alpha$  and  $\beta$ which represent the possible spin states of the system.

Let us examine the case in which there are two molecular orbitals each containing one electron. The possible spin states of these two electrons are represented by the following functions:

 $\alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ 

The last two functions arise from the condition that the electrons are indistinguishable. The first three are symmetric to the interchange of electrons, whereas the fourth is antisymmetric. All are normalized and orthogonalized.

For this situation there are two possible spatial functions:

 $\int_{2}^{1} [\psi_{1}(1)\psi_{2}(2) + \psi_{1}(2)\psi_{2}(1)] \quad \text{where } \psi_{1} \text{ and } \psi_{2} \text{ refer}$   $\int_{2}^{1} [\psi_{1}(1)\psi_{2}(2) - \psi_{1}(2)\psi_{2}(1)] \quad \text{to the MO's involved}$ 

In order to obtain the complete wave function we must multiply the spatial functions by the spin functions. Further, in accordance with the Pauli principle the total wave function must be antisymmetric with respect to the exchange of electrons. Therefore a symmetric spatial function is multiplied by an antisymmetric spin function, and vice versa. The resulting wave functions are:

$$\begin{split} \Psi_{1} &= \frac{1}{\sqrt{2}} [\Psi_{1}(1)\Psi_{2}(2) + \Psi_{1}(2)\Psi_{2}(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ \Psi_{2} &= \frac{1}{\sqrt{2}} [\Psi_{1}(1)\Psi_{2}(2) - \Psi_{1}(2)\Psi_{2}(1)]\alpha(1)\alpha(2) \\ \Psi_{3} &= \frac{1}{\sqrt{2}} [\Psi_{1}(1)\Psi_{2}(2) - \Psi_{1}(2)\Psi_{2}(1)]\beta(1)\beta(2) \\ \Psi_{4} &= \frac{1}{\sqrt{2}} [\Psi_{1}(1)\Psi_{2}(2) - \Psi_{1}(2)\Psi_{2}(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{split}$$

Notice that the symmetric spatial function produces one state; this being known as a "singlet" state. On the other hand the antisymmetric spatial function is involved in three degenerate states which are collectively known as the "triplet" state.

Of these two states the triplet state will be lower in energy. The basis for this is that the antisymmetric spatial function vanishes if the electrons have identical spatial coordinates. Thus there is a very small probability that the electrons can approach one another in the triplet state. No such restriction occurs in the singlet state with the symmetric spatial function and therefore the energy of this state will include the repulsion energy generated by the approach of two like-charged particles. For almost all organic molecules the highest filled molecular orbital normally contains two electrons. Since the spatial wave functions of these electrons will be idential, the spin functions will be different (the spins are referred to as "paired"), and this will be a singlet state. Since it represents the minimum energy state of the molecule, it is known as the "ground state".

The energy differences between molecular orbitals corresponds to the energy of visible and ultraviolet radiation. The relationship is  $\Delta E = hv$ , where  $\Delta E$  is the energy difference, h is Planck's constant, and v is the frequency of the radiation. This provides the basis for absorption spectroscopy as each molecule will have a characteristic pattern of energy absorption depending on the complexity of the molecule and the nature of its MO's.

However, the presence of quanta of proper frequency for the transition of an electron to a higher energy state does not guarantee that the transition will occur. It has been shown that the probability of absorption between two electronic states, i (initial) and f (final), is given by

$$B_{if} = (8\pi^3 e^2/3h^2 c)G_f^{D}_{if}$$

where  $e_i$  is the charge of an electron, h Planck's constant, c the velocity of light,  $G_f$  the number of degenerate wave functions composing the state to which absorption can lead (in most cases unity), and  $D_{if}$  the dipole strength.

Thus the probability is directly proportional to the dipole strength,

$$D = \left[\int \Psi_{i} M \Psi_{f} d\tau\right]^{2}$$

where  $\Psi_{i}$  and  $\Psi_{f}$  are the total electronic wave functions of the initial and final states,  $d\tau$  represents the product of the volume elements in the coordinates of all the electrons, and M is the dipole-moment vector. M may be considered to represent a charge migration or displacement during the transition, and it is frequently called the transition moment.

Since the integral over all space of an odd function always vanishes identically, whereas the integral over all space of an even function generally does not, the transition moment integral above must be an even function in order for the dipole strength and in turn the probability of absorption to have any value. This requirement leads to certain selection rules for absorption.

A transition will not be allowed if the product  $\Psi_{i}\Psi_{f}$  does not belong to the same symmetry species as at least one of the spatial components of the dipole-moment vector M. This symmetry forbiddness may be alleviated by including in the transition moment integral the wave function of a molecular vibration of such a symmetry as to make the product  $\Psi_{i}M\Psi_{f}\Psi_{v}$ totally symmetric.

For a transition from the singlet ground state to a triplet excited state the following represents the transition moment integral

$$\int \Psi_{i} \alpha M \Psi_{f} \beta d\tau d\sigma = \int \Psi_{i} M \Psi_{f} d\tau \int \alpha \beta d\sigma$$

where  $d\sigma$  is the element of volume in the spin coordinates. Since the integrand  $\alpha\beta$  is odd the transition moment integral vanishes. The singlet to triplet transitions are strongly forbidden although the presence of

heavy atoms and paramagnetic species may produce some probability of absorption as a result of spin-orbit coupling.

Normally the absorption of light by an organic molecule involves going from the singlet ground state to a singlet excited state. The fate of this energy of excitation provides the basis for a study of emission spectroscopy. The following state diagrams will serve as a reference point for this discussion.



Since at room temperature and at lower temperatures most molecules exist in the lowest vibrational level of the ground state, the absorption of energy promotes them from this level to the various vibrational energy levels of the various excited electronic states. In almost all cases the molecule undergoes rapid vibrational deactivation, a radiationless transition known as internal conversion, to the lowest vibrational level of the first excited singlet. At this point the excitation energy may be dissipated in three ways. First, is the emission of radiation known as fluorescence. Second, if the ground state and first excited singlet state have isoenergetic vibrational levels, internal conversion to the ground state may occur. Ordinarily because of the large energy difference between  $S_0$  and  $S_1$  this is relatively unlikely. Third, the excited molecule may undergo a radiationless transition known as intersystem crossing to the manifold of triplet states. From the lowest triplet state, the molecule may be converted back to the ground state by the emission of radiation.known as phosphorescence. Also since the lowest triplet level lies closer in energy to the ground state than does the first excited singlet, there is an increased possibility of internal conversion to the ground state.

## B. <u>Previous Investigations Related to the Photochromism of the</u> <u>Salicylideneanilines</u>

Almost sixty years ago it was observed that when the pale yellow crystals of salicylidene-m-toliudene were exposed to sunlight they became orange. If then placed in the dark the yellow color returned (1). This reversible color change had been noticed for other types of compounds and had been designated phototropy or photochromism.

Several other compounds resulting from the condensation of salicylaldehyde and aniline (these compounds will henceforth be called anils) with various substituents on the rings were also found to exhibit the phenomenon of photochromism.(2). These early investigators theorized that the photochromic reactions were due to isomeric changes affecting the aggregation of molecules in solids rather than to monomolecular change.

De Goauck and Le Fevre (3) attempted to observe color changes resulting from irradiating fluid solutions of anils with ultraviolet light. This failed and they concluded that the photochromism of anils occurs only in the solid state.

In the case of the photochromic crystals no difference was found in the crystal lattice properties after irradiation. Also it was found that the substitution of a methyl group for the phenolic proton prevented photocoloration. On these bases they proposed that the color change was the result of an intermolecular proton transfer because of the molecules having a favorable lattice arrangement.

By far the most thorough and extensive investigation of the photochromism of anils was that of Cohen, Schmidt, and co-workers (4,5,6,7). A number of crystalline anils were prepared and their crystallographic properties determined (5). Several of these anils were found to exist in two crystalline forms, and in a few cases an anil in one crystalline form would be photochromic whereas in its other crystalline species it would not be photochromic, but thermochromic. This thermo chromic behavior involved the diminution of intensity of the long wave length absorption with a decrease in temperature.

The photo-coloration of the crystalline anils (5) was observable only between lower and upper temperature limits imposed by low yield and rapid fading, respectively. Irradiation at a temperature at which the yield was high followed by cooling to the lower temperature limit resulted in no loss of intensity of the photo-colored crystal. Thus, low temperature may inhibit photo-coloration, but did not affect the color once formed. It

was found that irradiation into the absorption band of the photo-colored form (5) caused eradication of this band. The efficiency of this eradication was temperature dependent in that it decreased markedly with decreasing temperature.

X-ray data indicated that the disappearance of the long wave length band with decreasing temperature for those thermochromic crystals resulted in little change in molecular shape and orientation. For one thermochromic anil, 5-chlorosalicylideneaniline, variation with temperature of the area under the long wave length absorption curve produced an energy difference of 1.76 kcal/mole between the high and low temperature forms.

The emission spectra of the crystalline anils (5) were also noted. Thermochromic anils emitted yellow at room temperature, but this emission became green at low temperatures. These emissions were apparently fluorescences as the lifetimes were less than the time-resolving power of their oscilloscope, i.e., less than a few microseconds. The photochromic anil crystals were not fluorescent above the lower temperature limit for photocoloration, and photo-coloration was not accompanied by fluorescence. However below this lower temperature limit fluorescence appeared which was similar to that observed for the thermochromic crystals at low temperature.

On the basis of the fact that neither photochromism or thermochromism were observed in the absence of the ortho-hydroxyl group, Cohen and Schmidt (4) proposed that the thermal color change is due to a quinoid-benzenoid tautomerism.



In the case of the molecular species responsible for the photoinduced color, they argued(4) that the necessity for the ortho-hydroxyl group and, except for the long wavelength absorption, the similarity of the spectra to those of the high temperature thermochromic crystals favor tautomerization to a quinoid state which is the trans-isomer of the high temperature thermochromic form.



The observation that the thermochromic crystals were not photochromic and vice versa was accounted for by the effect of differing crystal structures. Cohen and Schmidt (4) theorized that the plane-to-plane packing found in thermochromic crystals provided stabilization of the cis-keto form of the anil though dipole-dipole interaction. Also, this packing was responsible for the lack of photochromic properties in these crystals by sterically preventing the cis keto-trans keto isomerization.

The crystal structure of the photochromic anils was thought to be sufficiently open to allow the cis keto-trans keto isomerization, whereas the packing in these cases did not favor formation of cis keto. Finally this more open crystal structure was likened to the situation in rigid

solution for which they found that all the salicylideneanilines were photochromic.

In fluid solutions using polar solvents, a low intensity absorption band with maximum about 440 mm was noted (6). The intensity of this band was directly proportional to the electron donating tendency of the substituent para to the amino group on the aniline ring. No such band was observed in polar solutions of the anils of o-methoxy- and p-hydroxybenzaldehydes. In one case, the formation of this band in a methylcyclohexane-ligroin solution cooled to liquid air temperature was observed.

The principal conclusions which Cohen, Hirshberg, and Schmidt (6) derived from the study of rigid solutions of the salicylideneanilines were: (1) the photo-coloration in rigid solutions was confined to the anils of o-hydroxy-benzaldehydes; and (2) all salicylideneanilines were photoactive in rigid solutions.

In paraffin oil solution (6), it was possible to erase the photoinduced color by irradiation into the absorption band of the photo-colored species. A wavelength of 5460Å was noted to be most effective for erasure purposes. However, no further erasure occurred when absorption in that region had disappeared even if the absorption at the maximum (4800Å) was still appreciable (6).

No luminescence from these solutions was observed at room temperature (6). At low temperature those anils in rigid ethanol-methanol-ether solutions luminesced yellow on irradiation with light of 3000-4000Å. This luminescence became blue-green as irradiation proceeded. In rigid methylcylohexane-

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ligroin, most of the anils emitted yellow to green with the luminescence moving to longer wavelengths with decreasing intensity during irradiation. In paraffin oil the emission was yellow to green with little or no change observed on prolonged irradiation.

Finally the photochromic and thermochromic properties of the anils of l-hydroxy-2-naphthaldehyde and 2-hydroxy-l-naphthaldehyde were investigated both in the crystal form and in rigid solutions (7). Also, the effect of solvent on the room temperature absorption spectra and the effect of temperature on solutions in non-polar solvents were noted.

Several of the crystalline hydroxynapthylidene anilines showed the same thermochromic properties observed in the salicylideneanilines in which the absorption intensity of the long wave length band decreased with decreasing temperature. None of these crystalline anils were found to be photochromic. These anils showed solvent effects similar to those observed for some of the salicylideneanilines. In cases, however, the long wavelength band with maximum between 4400 and 4800Å was present even in hydrocarbon solvents, but increased in intensity in a polar solvent. It was noted that the intensity increase depended not only upon the dielectric constant of the solvent but also on its bonding ability.

As the temperature of solutions of the naphthylideneanilines was lowered to the range -80° to -120°C a change in the absorption spectrum was observed similar to that noticed upon going from a non-polar solvent to a polar solvent at room temperature. This effect was also noticed in some salicylideneanilines to a slight extent. At temperatures near that of liquid air, rigid solutions of the naphthylideneanilines were unaffected

by irradiation with light. In paraffin oil at -75°C irradiation caused a deepening of the present color to occur. In the case of naphthylidene-p-hydroxyaniline at -75°C the low temperature, long wavelength band reached its maximum and was unaffected by irradiation.

Finally the anils of 2-hydroxy-3-naphthaldehyde and 2-methoxy-1naphthaldehyde were investigated in a similar manner (7). These anils were not significantly affected by the polarity of the solvent nor did they show the temperature effects noted for the other naphthylidene anilines. Also irradiation of rigid solutions did not produce any new absorption in the visible region.

Dudek and Dudek (8) have provided strong evidence for the identity of the molecular species of the anils which is responsible for the appearance of the long wavelength absorption band in solutions of hydrogen bonding solvents. In a study of the keto-enol equilibria of  $N^{15}$ - substituted anilides they used the  $N^{15}$ -H spin coupling as a measure of the residence time of the proton on nitrogen. In the case of salicylideneaniline there was no  $N^{15}$ -H coupling observed in chloroform solution; thus, the proton was on the oxygen (enol). In alcohol a  $N^{15}$ -H coupling appeared. in conjunction with the long wavelength absorption band indicating that this band was the result of the formation of the cis-keto tautomer. Since the  $N^{15}$ -H spin coupling was directly proportional to the amount of cis keto tautomer present, by comparing the variation of the observed  $N^{15}$ -H spin coupling and the absorption band intensities with solvent, these bands were assigned to the two tautomers. Also, since the concentration of the tautomers could be calculated from the observed coupling, the extinction

coefficients for each tautomer were calculated from the observed intensities of its absorption bands.

It was found (8) that even in a carbon tetrachloride solution of 2-hydroxynaphthylideneaniline, about 15% of this anil was in the keto form at room temperature. In the case of this anil as well as the salicylideneanilines, the amount of keto tautomer as evidenced by the  $N^{15}$ -H spin coupling, increased as the temperature decreased for all solvents.

From a plot of the natural logarithm of the enol-keto equilibrium constant versus the reciprocal of temperature, enthalpy values for various solvents were obtained for naphthylideneaniline. The combination of these enthalpy values with the equilibrium constants indicated that the hydrogen bonding ability of the solvent produced a greater effect on the equilibrium than did the polarity.

Ledbetter (9) also investigated the formation of the new long wavelength absorption band in alcoholic and acidic solvents. Isobestic points in the cyclohexane-ethanol system demonstrated two absorbing species. In addition to the anils of o-hydroxybenzaldehyde, this phenomenon was also observed for the anils of p-hydroxybenzaldehyde, but for none of the other anils of substituted anilines and benzaldehydes.

To occur, the process required a hydrogen bonding solvent and the intensity of the long wavelength band was proportional to the acidity of the solvents. This combined with the previous observations caused Ledbetter (9) to theorize that there was an enol-keto tautomerism occuring and that the hydrogen bonding to the solvent provided a basis for hydrogen

transfer to the imine nitrogen. Also, it was proposed that the stability of the keto tautomer was increased through intermolcular hydrogen bonding with the solvent.

Anderson and Wettermark (10) have studied the effects of flashing ethanol solutions of salicylideneaniline at room temperature. Two differences in the absorption spectrum were observed. One was a new long wavelength absorption band with onset near 560 m $\mu$  and intensity maximum near 470 m $\mu$ . The species responsible for this absorption had a half life of the order of one millisecond. The other was a decreased absorption at wavelengths below 400 m $\mu$ . The species responsible for this decrease had a half life of approximately one second. These two transformations were postulated to be due to proton transfer to the imine nitrogen and cis-trans isomerization about the <u>carbon-nitrogen double bond</u> of the enolrespectively. This latter statement resulted from the observation that for the anils of p-hydroxybenzaldehyde and benzaldehyde, there was only one transient species which had the characteristics of the long-lived species observed for salicylideneaniline.

An investigation of the dipole moments of 20 salicylaldehyde anils in benzene indicated that the enol form was present exclusively (11). However certain discrepancies were noted for the 5-nitrosalicylaldehyde anils. The same investigators also performed a study of the electronic and vibrational spectra of both some salicylideneanilines and some hydroxy naphthylideneanilines (12). They rejected the possibility that the formation of the long wavelength absorption band in hydrogen bonding solvents

was the result of the production of the keto form of the anil. Instead, it was proposed that this band was an  $n \rightarrow \pi^*$  absorption for which a hydrogen bonding solvent increased the energy of the transition. This decrease in energy difference was postulated to result in more mixing of the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  states which in turn would produce a more intense  $n \rightarrow \pi^*$ transition.

The emission spectra of the anils has been studied and interpreted from the point of view of a quasi-aromatic ring resulting from the intramolecular hydrogen bonding (13). Photochromismwas explained on the basis of proton transfer from the oxygen to the nitrogen with retention of the quasi-aromatic ring, the cis keto tautomer of the anil. Fluorescence spectra were obtained for several anils in hexane at 77°K before and after irradiation to produce the colored form. The fluorescence before irradiation was assumed to be that of the enol whereas that after irradiation was assumed to be of the cis-keto. For 2-hydrokynaphthylideneaniline no change in the fluorescence spectrum was observed as a result of irradiation.

The photo-produced cis-keto anil was assumed to be formed in the excited state by passing over the potential energy barrier between enol and cis keto via an excited vibronic state of the enol (13). The reverse reaction

### cis keto → enol

was assumed to occur either by the action of light via an excited state or thermally.

Differences in the fluorescence spectra as well as a decreased photocoloration in going from a hydrocarbon solvent to a proton donating sol-

vent were observed. These effects were explained as the result of distortion of the quasi-aromatic ring by the hydrogen bond properties of the solvent.

Several articles have appeared concerning the electronic absorption spectra of the salicylideneanilines (12,14,15,16). Brocklehurst (14) in a study of benzylideneaniline showed that the molecule was not entirely planar and that the lone pair of electrons on nitrogen interfered to a certain extent with the  $\pi$  conjugation through the molecule. He also assigned the band with maximum intensity about 256 mµ as arising from the benzal portion of the molecule.

For the anils of o-hydroxyaldehydes, Minkin, <u>et al.</u> (12), found four bands and designated them  $E_1$ ,  $E_2$ , K, and R. The first three were presumed to be  $\pi \rightarrow \pi^*$  transitions. The  $E_1$  band was supposed to be a perturbed benzene transition  $A_{1g} B_{1u}$  having its origin in the amine ring. The longer-wavelength  $E_2$  bond represented a transition involving the hydroxygroup and the  $\pi$  electrons of the C=N bond. The K band denoted electron transfer along the whole chain of conjugated bonds. The R band was assigned to be an  $n \rightarrow \pi^*$  transition.

The assignment of these bands by Nurmukhametov, <u>et al</u>. (15), was in agreement with that presented above. Since the intensity of the K band was dependent on the conjugation between the aromatic rings of the anils, this intensity was used to calculate the angle of rotation of the N-phenyl ring for several anils.

On the basis of HMO calculations carried out for salicylideneaniline and some related compounds Chatterjee and Douglas (16) proposed that the

absorption band in the region  $315-350 \text{ m}\mu$  might be considered to be caused by a transition to an excited state of the quinoid type. This would involve a charge separation in which oxygen acquired a formal positive charge and nitrogen acquired a formal negative charge. II.

# EXPERIMENTAL

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#### **EXPERIMENTAL**

#### A. Preparation of Anils

Generally the syntheses followed that described in earlier work (1). A .OIM portion of either the aldehyde or the aniline (the solid in those cases where one was solid and one was liquid) was dissolved in methanol (most often 10-20 ml) and heated slightly. To this solution on equimolar quantity of the other reactant was added, and the solution was allowed to cool. In most cases the crystalline anil came out of solution<sup>-</sup> as the temperature approached that of the room, in other cases the crystalline anil was obtained by means of an ice bath.

The crystals were filtered by the use of vacuum filtration and washed with cold methanol. After they had been allowed to dry the crystals were dissolved and recrystallized. In most cases either methanol or benzene was used as the solvent for this process although occasionally petroleum ether was used. After recrystallization the anils were dried and stored in a dessicator in the dark.

Two methods were used to establish purity, the melting point and thin layer chromatography. The thin layer chromatography ultized strips of alumina or silica gel on glass plates. The anil was dissolved in ethyl ether and one drop of this solution was used to spot the strip at one end. After the ether had evaporated, the glass plate containing the spotted strip was placed in a dish at an angle such that the spotted end was submerged in an eluting solution, usually chloroform or a chloroform-methanol mixture. This elutant was allowed to saturate the strip to a point near

its upper end. The point of greatest advance of the elutant was marked, and the plate removed from the dish to permit the elutant to evaporate. When this was accomplished the plate was placed in a covered dish containing iodine crystals.

The iodine crystals stained the areas on the strip occupied by organic compounds. One spot on the strip at a position other than the origin in addition to no spot at the origin was taken as a sign of purity. In some cases using chloroform as a elutant and an alumina strip a persistant spot at the origin was noted. This spot disappeared when a 10% methanol solution was prepared and used as the elutant. Apparently some decomposition of the anil on the alumina occurred which was prevented by the presence of the more polar methanol. This spotting at the origin was never noticed when silica gel was used as the strip.

Note in Table I that the melting points for 5-nitro-salicylidene-2, 4-dimethylaniline and for 3-nitrosalicylideneaniline differ significantly from those obtained by Osipov, Minkin, and Kogan (11). Since the TLC analysis indicated that these compounds were pure and the NMR analysis indicated that the structures of the molecules were those expected, samples of these compounds were sent to Huffman Laboratories, Inc., Wheatridge, Colorado, for C, H, N analysis. The values found as compared to the values expected were for 3-nitrosalicylideneaniline:

	found	expected
carbon	64.73	64.45
hydrogen	4.36	4.16
nitrogen	11.54	11.56

# TABLE I

# ANILS PREPARED FOR THIS INVESTIGATION

Anil	Observed m.p.,°C	Litera m.p.,	ture C		
Salicylideneaniline	50-50.5	51	(5)		
5-Chlorosalicylideneaniline	110	110	(5)		
Salicylidene-4-chloroaniline	103-104	104	(5)		
Salicylidene-4-bromoaniline	109-109.5	109	(5)	-	
Salicylidene-4-iodoaniline	131.5-132				
5-Chlorosalicylidene-4-chloroaniline	151				
5-Chlorosalicylidene-4-bromoaniline	167.5-168				
Salicylidene-2-chloroaniline	82.5-83.5	83	(5)		
5-Bromosalicylideneaniline	122.5	122.5	(5),	120.5	(11)
5-Nitrosalicylideneaniline	135-136	133	(11)		
2-Hydroxynaphthylideneaniline	92-93	94	(11)		
Salicylidene-2,4-dimethylaniline	37.5-38	36	(11)		
Salicylidene-2,5-dichloroaniline	109-110				•
Salicylidene-o-toluidene	47-47.5				
5-Bromosalicylidene-o-toluidene	86.5-87	86.5	(5)		
Salicylidene-4-nitioaniline	162-163				
Salicylidene-2-bromoaniline	86-87	87	(5)		
2-Hydroxynaphthylidene-4-bromoaniline	167-168				
5-Nitrosalicylidene-2,4-dimethylaniline	150.5-181	168	(11)	~	
3-Nitrosalicylidene-aniline	137-138	159	(11)		
p-Hydroxybenzylideneaniline	198.5-199.5				

for 5-nitrosalicylidene-2,4-dimethylaniline:

	found	expected
carbon hvdrogen	66.68 5.16	66.65 5.22
nitrogen	10.25	10.36

Thus, it was judged that the melting points which were obtained in this investigation were the true ones for the anils involved.

## B. Absorption Studies

The absorption spectra of the anils which were studied were obtained on a Cary Model 15 Recording Spectrophotometer. This is a doublebeam, prism instrument designed for automatic recording of absorption spectra in the wavelength region of 1850Å to 8000Å.

The principal solvent used was 3-methylpentane although in some cases EPA (a mixture of isopentane, ethanol, ethyl ether in the proportion 5:2:5) and 2-methyltetrahydrofuran were used. All three of these solvents form rigid glasses at 77°K, however that of 3-methylpentane is by far the most stable. Special care was taken to eliminate water in all these solvents and hydrogen bonding species in the 3-methylpentane. Water causes cloudy glasses, and certain strongly hydrogen bonding compounds, partic-. ularly acids, in 3-methylpentane have an effect on the anils at low temperature which will be discussed later. The purification of 3-methylpentane and 2-methyltetrahydrofuran involved distillation over sodium and passage through an alumina column before making up solution. The EPA was purchased from the American Instrument Co., Silver Spring, Maryland. Solutions were made from as fresh EPA as possible in order to avoid the presence of peroxides. In addition, 2-methylpentane and a 1:1 isononane-isooctane mixture were used as solvents in the viscosity studies. These were passed through an alumina column before use to remove any hydrogen bonding impurities.

The absorption spectra were obtained by placing the anil solutions in long stemmed suprasil cells of rectangular shape with pathlengths of  $\cdot 2 \text{ mm}$  and 10 mm. The concentrations were generally between 5 x  $10^{-4}$  M and 8 x  $10^{-5}$  M. The cells were placed into dewars with flat suprasil windows. Most room temperature absorption spectra were made using the cell inside the dewar so that the same number of reflecting surfaces would be involved in both room temperature and low temperature spectra.

Generally two temperatures below that of the room were used, -196°C and -75°C. The lower temperature was attained by filling the dewar with liquid nitrogen and placing the solution filled cell into this medium. Serious problems with bubbling in the liquid nitrogen were avoided by plunging a copper wire into the dewar and stirring a number of times, or, better, by bubbling a stream of helium gas into the bottom of the dewar for a few seconds.

A temperature of -75°C was obtained by filling the dewar with isohexane and lowering the temperature by the addition of dry ice. The cell was placed into this medium and the temperature maintained by the addition of more dry ice. A collar around the stem of the cell prevented the dry ice from falling to the bottom of the dewar causing bubbling through the analyzing beam of the spectrophotometer.

In a few cases a temperature of -100°C was produced and maintained for a few minutes by the addition of liquid nitrogen to the isohexane in the dewar. A serious drawback to this method is that the addition of liquid nitrogen to the isohexane results in the vaporization of the nitrogen which in turn may carry some of the isohexane over the sides of the dewar. In the presence of a hot lamp this represents a considerable fire hazard.

#### C. Irradiation

Photocoloration was found to occur only in rigid solutions of the anils at low temperatures. Therefore, the solutions were irradiated while at low temperature inside the dewar. The excitation sources used were either a 1 KW xenon lamp or a 150 W Hg lamp. The latter was preferred because of its superior output in the ultraviolet, the region of anil absorption. Irradiation times varied from 5 to 60 minutes depending on the temperature and solvent. At -75°C some fading was observed after the removal of the irradiation source, but at -196°C no fading occurred so long as the temperature was maintained.

### D. Emission Studies

All emission spectra were taken at low temperature, either -196°C or -75°C. In most cases the emission was that occurring from the front surface of the sample cell containing the rigid solution of the anil. The apparatus consisted of an Englehard-Hanovia 1 KW AC xenon compact arc lamp as an exciting source; a Bausch and Lomb grating exciting monochromator;
an Aminco grating analyzing monochromator; an EMI9558B photomultiplier-, the output of which was channeled into a power supply-amplifier then into a Houston Instrument x-y recorder. This set-up is diagrammed below.



To obtain an emission spectrum a wavelength of excitation was chosen by means of the exciting monocromator. The sample cell was placed at the focal point of the exciting lens and adjusted so that most reflection passed back into the exciting monochromator. The analyzing lens was placed so that the emission from the sample would be focussed on the entrance slit of the analyzing monochromator. A motor inside the analyzing monochromator scanned the region of the spectrum desired, and a potentiometer attached to the scanning mechanism drove the X component of the recorder.

Once the emission of a particular compound had been obtained then an excitation spectrum could be made. This spectrumwas produced by setting the analyzing monochrometer at some wavelength at which emission is known to occur. Then the intensity of the emission at this wavelength was recorded as a function of the wavelength of the exciting radiation. The wavelength of excitation was varied by means of the exciting mono-

chromator, the drive of which was connected to a potentiometer which controlls the x-axis on the recorder. The resulting spectrum was usually very similar to the absorption spectrum.

A continuous light source was required for the excitation spectrum because any lines present from the lamp would show up on the spectrum. For the most part the xenon lamp was quite satisfactory although it has a series of lines in the region 450-500 mµ. In order to obtain an excitation spectrum in this region, a 150 w tungsten source with a built-in parabolic reflector which gives a continuum and the equivalent of approximately 500 w was used. III.

# RESULTS AND DISCUSSION

#### **RESULTS AND DISCUSSION**

#### A. Salicylideneaniline

### 1. Absorption Studies

The room temperature absorption spectrum of salicylideneaniline in 3-methylpentane shows a long wavelength onset near 400 mµ [see Figure 1]. The first band is of Franck-Condon allowed shape and shows intensity maxima at 340, 316 and 300 mµ, whereas the second band has a single maximum at 266 mµ. Upon lowering the temperature to 77°K the spectral shape remains the same with a slight red shift of each maximum [see Figure 1]. No absorption is noticed at longer wavelengths as the temperature is lowered. It has been shown that at room temperature in a hydrocarbon solvent salicylideneaniline exists almost exclusively in the enol form (8,9). Thus this absorption spectrum is that of the enol tautomer. Upon irradiation a large, structured absorption band appears which has a long wavelength onset near 565 mµ[see Figure 1]. The maximum intensity for this band occurs at 469 mµ. The band which was formerly that of longest wavelength undergoes a lessening of intensity and a change in shape; this is also the fate of the other, shorter wavelength band.

If the previously irradiated, orange rigid solution at 77°K is allowed to warm about 10 to 15°, the 3-methylpentane rigid glass begins to soften. A change in the color of the solution from orange to yellow accompanies this softening. If after the entire solution is allowed to become yellow and the temperature is suddenly returned to 77°K, this yellow color remains. The absorption responsible for this color has a

long wavelength onset near 530 m $\mu$  and an intensity maximum at 465 m $\mu$  [see Figure 4]. If irradiation is selectively directed into this new absorption band by the use of narrow band pass filters, it is found that no change in the shape of the absorption spectrum is observed and no absorption appears at longer wavelengths.

A 2-methylpentane solution may be allowed to warm from -196° to a point just above the softening point of the rigid solution, a temperature in the region of -150 to -170°. If this solution is irradiated for 3 minutes, a yellow color appears. Recooling the solution to -196° prevents the color from fading while an absorption spectrum is obtained. This spectrum indicates that the molecular species produced upon irradiation under these conditions is identical to that formed upon warming the previously irradiated rigid solution. An explanation of this process and identification of this species will be deferred until some generalizations can be made on the basis of all the evidence acquired in this investigation.

### 2. Emission Studies

The emission spectrum obtained by excitation of the enol species present before irradiation (8,9) shows a short wavelength onset near 490 mµ with intensity maxima at 518 and 546 mµ. There is a gap of 4590 cm<sup>-1</sup> between the onset of the enol absorption and the onset of emission [see Figure 2]. Normally one would assume this emission to be a phosphorescence

on the basis of this large offset of emission from absorption. However, previous investigators (4,13) have assigned this emission to be a fluorescence, and we find that it will not pass through a phosphoroscope. Thus, this emission is originating from a molecular species which is not that which was excited. In the following discussions this species will be referred to as the transition state, and the identification of this species will be made later on the basis of evidence obtained for all the molecules studied.

The excitation spectrum when corrected for drop off in lamp intensity with decreasing wavelength and change in monochromator efficiency with wavelength shows a very close resemblance to the absorption spectrum of the enol form at 77°K. Also of interest is the fact that the relative quantum efficiencies of the peaks in the excitation spectrum [see Figure 2], have quantum yields of one relative to that at some particular wavelength. It has been noticed for photochromic compounds as the chromenes (17) and spiropyrans (18), that the relative intensities of the shorter wavelength structure in the excitation spectra are much less than the o-o band or for a band corresponding to that near the onset of absorption. This phenomenon has been interpreted (17) on the basis that excitation into the higher vibrational or electronic energy levels results in a competition between photochemistry and internal conversion. Excitation to the lower energy levels results primarily in emission because there are less levels from which competition can occur.

The absence of such an effect in the excitation spectrum of the enol form of salicylideneaniline indicates that photochemistry, which in this

case is the formation of the transition state from which the observed emission occurs, proceeds from the o vibrational level of the first excited state of the enol. Moreover, since no emission is observed from the zero and any other vibrational level of the enol excited state, the rate constant for photochemistry must be at least 100 times faster than the rate constant for fluorescence. Thus,  $k_{pc}$ , the rate constant for photochemistry, would be of the order of  $10^{10} \text{sec}^{-1}$ .

Since the relative intensities of the excitation spectra indicate that the excited state enol is converted completely to the transition state, the production of the photo colored species must take place from the transition state. In this case the rate constant for production of the photocolored form would have to compete with that of fluorescence. Experimentally it is observed that the production of the colored form is accompanied by intense emission, and the time required to reach a photostationary state may be as long as 30 minutes. Thus, the reaction

transition state  $\rightarrow$  photo-colored species

must have a rate constant which is approximately equal to that for emission,  $k_{pc} \sim 10^8 \text{sec}^{-1}$ .

The emission spectrum of the photo-colored species shows a short wavelength onset near 515  $m_{\mu}$  with intensity maxima at 550, 565, 580, and 610  $m_{\mu}$  [see Figure 3]. This emission is judged to be a fluorescence because of its overlap with the absorption. Scanning to longer wavelengths reveals no further emission, indicating that there is no detectable phosphorescence from this species. Excitation throughout the long

wavelength absorption band produces the same emission. This means that only one final molecular species, the photo-colored product, is produced by irradiation.

The excitation spectrum indicates a long wavelength onset near 560-570 mµ [see Figure 3]. The intensity maxima occur at 510, 500, and 480 mµ. Generally the spectral shape conforms to that of the long wavelength absorption although the structure noted in the absorption does not show up as well in the excitation spectrum. Also the excitation spectrum is not corrected for diminution of lamp intensity and monochrometer efficiency with decreasing wavelength.

Finally, the emission spectrum of the molecular species produced by warming a solution of photo-colored product is presented [see Figure 5]. The short wavelength onset occurs near 495 m $\mu$  with intensity maxima at 534 and 560 m $\mu$ . This emission is also assigned so a fluorescence on the basis of its overlap with the absorption and excitation spectra of this species. It will be noted that the spectral shape and position of this emission is very similar to that obtained from excitation of the unirradiated solution at 77°K. The excitation spectrum of this species shows a long wavelength absorption onset near 540 m $\mu$  with an intensity maximum near 475 m $\mu$  [see Figure 5]. Again no correction was made for lamp intensity or monochrometer efficiency.

SALICYLIDENEANILINE: COMPARISON OF ABSORPTION SPECTRA BEFORE AND AFTER IRRADIATION, 3MP SOLUTION

- (a) Absorption spectrum, room temp.
- (b) Absorption spectrum, 77°K, before irradiation
- (c) Absorption spectrum, 77°K, after 20 min. irradiation



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wavelength,  $\mathtt{m} \mu$ 

SALICYLIDENEANILINE: EMISSION SPECTRUM OBTAINED FROM EXCITATION . IN ENOL ABSORPTION BANDS; EXCITATION SPECTRUM OF THIS EMISSION, UN-CORRECTED AND CORRECTED FOR LAMP INTENSITY AND MONOCHROMATOR EFFICIENCY (NUMBERS ABOVE CORRECTED EXCITATION SPECTRUM ARE QUANTUM EFFICIENCIES)

- (a) Emission spectrum
- (b) Uncorrected excitation spectrum
- (c) Corrected excitation spectrum



wavelength,  $m_{\mu}$ 

SALICYLIDENEANILINE: EMISSION AND EXCITATION SPECTRA OF PHOTO-COLORED SPECIES, 3MP SOLUTION, 77°K

(a) Emission spectrum

(b) Excitation spectrum



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SALICYLIDENEANILINE: COMPARISON OF ABSORPTION SPECTRA OF CIS KETO AND PHOTO-COLORED SPECIES, 3MP SOLUTION, 77°K

- (a) Absorption of photo-colored species
- (b) Absorption of cis keto produced by warming previously irradiated solution



SALICYLIDENEANILINE: EMISSION AND EXCITATION SPECTRA OF CIS KETO PRODUCED BY

WARMING PREVIOUSLY IRRADIATED SOLUTION, 3MP,  $77^{\circ}K$ 

(a) Emission spectrum

(b) Excitation spectrum



#### B. 5-Bromosalicylidene-o-toluidene

#### 1. Absorption Studies

The absorption spectrum of 5-bromosalicylidene-o-toluidene in EPA solution at room temperature shows a long wavelength onset near 410 m<sub>µ</sub> with the first absorption band consisting of intensity maxima at 351, 329, and 313 m<sub>µ</sub> with a Franck-Condon allowed shape. The second absorption band consists of a single peak with maximum at 267 m<sub>µ</sub> [see Figure 6]. At 77°K in rigid EPA solution the spectrum retains the shape observed at room temperature with a general sharpening of the vibrational fine structure. At the lower temperature the intensity maxima for the first band occur at 354, 328, and 312 m<sub>µ</sub>, whereas that for the second band occurs at 274 m<sub>µ</sub>.

Irradiation into the low temperature absorption band results in the appearance of an orange color for the solution. The absorption band responsible for this coloration has a long wavelength onset near 560 mµ with an intensity maximum at 470 mµ (8). The shape of the former long wavelength absorption band changes appreciably and possesses a maximum at 334 mµ. Also the absorption peak at 274 undergoes a large diminution in intensity and becomes a shoulder on a shorter wavelength absorption.

It has been shown that in a strongly hydrogen bonding 2,2,2-trifluoroethanol solution (8,9) the anil exists primarily as the cis-keto tautomer (8,9). The room temperature absorption spectrum of this solution shows a long wavelength onset near 510 m $\mu$  with an intensity maximum at 442 m $\mu$ . The second band has an intensity maximum at 325 m $\mu$  [see Figure 8], whereas the third band peaks at 263 m $\mu$ . It was discovered that the addition of one drop of an organic acid such as acetic or propionic acid to a 3-methylpentane solution would produce an absorption spectrum at 77°K very similar to that of a trifluoroethanol solution at room temperature [see Figure 7]. At room temperature this acid-3-methylpentane solution has an absorption spectrum essentially identical to that of the 3-methylpentane solution alone. On this basis it is possible to conclude that at room temperature in this solvent the anil exists exclusively in the enol form; however, lowering the temperature to 77°K shifts the equilibrium to produce some cis-keto tautomer.

If the acid-3-methylpentane solution is irradiated selectively into the long wavelength absorption band at 77°K, it is found that no absorption appears at longer wavelength and, in fact, no change in intensity or shape occurs in the spectrum after irradiation [see Figure 9]. However when irradiation is conducted into the entire absorption spectrum, a new long wavelength absorption appears with onset near 570 mµ. If the long wavelength low temperature absorption present before irradiation is subtracted from this the resultant band is identical to that observed after the irradiation of a 3-methylpentane solution.

This evidence indicates that the molecular species formed upon irradiation is not the cis-keto anil. Also, it is not possible to produce this species photolytically from the cis-keto tautomer. Upon warming a previously irradiated 3-methylpentane solution from 77°K to the softening point of the rigid glass, the color of the solution changes from orange to yellow. The spectrum of this yellow solution shows a long wavelength onset near 530 mµ with a maximum intensity of the long wavelength

band at 465 mµ [see Figure 8]. The overall shape of this spectrum closely resembles that obtained for the 2,2,2-trifluoroethanol solution although the long wavelength band of the former is red shifted in comparison to the latter. On the basis of this similarity of spectra, we conclude that the yellow species is the cis-keto tautomer. If the temperature is allowed to return to that of the room, the yellow color disappears and the absorption spectrum is that of the enol. Thus, the thermal back reaction involves going from the photo-colored form to the cis-keto tautomer then back to the enol.

### 2. Emission Studies

The emission spectrum of 5-bromosalicylidene-o-toluidene in 3methylpentane at 77°K shows a short wavelength onset near 490 m $\mu$  with intensity maxima at 523 and 550 m $\mu$  [see Figure 6]. Comparison of this emission spectrum with the absorption spectrum acquired under identical environmental conditions shows that the short wavelength onset of emission and the long wavelength onset of absorption are separated by 800Å or 3980 cm<sup>-1</sup>. As was mentioned in the previous case, other investigations have indicated that this emission is a fluorescence, and that we find the lifetime of this emission to be too short to pass through the phosphoroscope.

Thus since the absorption under the above conditions is due to the enol tautomer (8), and the emission is offset from the absorption in energy but is not phosphorescence, then the conclusion is the same as that for salicylideneaniline. That is, the emitting species is not the enol tautomer, but a transition state.

The 3-methylpentane solution to which a small quantity of propionic acid has been added shows two spearate emissions [see Figure 7]. Excitation into the new long wavelength absorption band produces an emission with short wavelength onset near 480 m $\mu$  with intensity maxima at 515 and 530 m $\mu$ . Excitation at shorter wavelengths into the absorption present before the addition of the acid produces an emission identical to that found for the 3-methylpentane solution alone. Since the long wavelength absorption is due solely to the cis-keto tautomer (8.9), the first emission is identified as that of the cis-keto. On the other hand the second emission is the same as that observed when a 3-methylpentane solution of 5-bromosalicylidene-o-toluidene is excited and therefore, is the emission originating from the transition state. Since this cis-keto emission overlaps the cis-keto absorption and excitation spectra, it is assigned as fluorescence. The close similarity between the spectral shape and energy of these two emissions should be noted.

A third emission is found after the irradiation of a 3-methylpentane solution at 77°K [see Figure 10]. It has a short wavelength onset near  $m_{\mu}$  with intensity maxima at 558 and 597  $m_{\mu}$ , and is assigned to be a fluorescence on the basis of its overlap with the absorption of the photocolored species. The excitation spectrum obtained from this emission indicates a long wavelength onset near 560  $m_{\mu}$  and maxima at 530, 495, and 480  $m_{\mu}$ . Although it lacks the structure of the long wavelength photoproduced absorption band, this excitation spectrum is quite similar in band shape and position. The short wavelength side of the excitation tails off more rapidly than the absorption because the excitation spectrum

is not corrected for the diminution of lamp intensity in that wavelength region. In addition, excitation thoughout the photo-produced absorption band results in the same emission. No cis-keto emission is observed. Thus, it is evident that irradiation of the enol produces no cis-keto but does result in the formation of a molecular species other than the cis-keto.

The emission from the molecular species responsible for the yellow color obtained upon warming the previously irradiated solution to the softening point of the rigid glass consists of a short wavelength onset near 495 m<sub>µ</sub> with intensity maxima at [see Figure 10] 537 and 565 m<sub>µ</sub>. The excitation spectrum from this emission shows a long wavelength onset near 525 m<sub>µ</sub> with a maximum at 475 m<sub>µ</sub>. Comparison of this emission with that of the cis-keto tautomer produced at low temperature in an acid-3methylpentane mixture shows that they are very similar in band shape. The emission of the yellow species produced on warming is red shifted, as predicted by solvation theory for a polar solute and a non-polar solvent.

The emission from this yellow species also resembles that obtained from exciting the enol. However, the excitation spectrum shows that the emission of this species results from excitation in a region in which the enol has no absorption. Thus, it is certain that this yellow color produced upon warming a previously irradiated rigid solution is the result of the formation of the cis keto anil in a thermal back reaction.

5-BROMOSALICYLIDENEANILINE: COMPARISON OF ENOL ABSORPTION WITH THE EMISSION OBTAINED UPON EXCITATION IN THE ENOL BANDS, 77°K

- (a) Absorption spectrum
- (b) Emission spectrum



5-BROMOSALICYLIDENEANILINE: COMPARISON OF CIS KETO ABSORPTION IN ACID-3-METHYLPENTANE SOLUTION WITH THAT IN 2,2,2-TRIFLUOROETHANOL, AND COMPARISON OF CIS KETO EMISSION WITH THAT OF TRANSITION STATE

- (a) Absorption spectrum, acid-3methylpentane solution, 77°K
- (b) Absorption spectrum, 2,2,2trifluoroethanol solution, room temp.
- (c) Cis keto emission ( $\lambda_{ex}$ =430 mµ) 77°K in acid 3-methylpentane solution
- (d) Transition state emission ( $\lambda_{ex}$ =350 mµ) 77°K in acid 3-methylpentane solution



### 5-BROMOSALICYLIDENEANILINE: COMPARISON OF

#### ABSORPTION SPECTRA OF CIS KETO AND

### PHOTO-COLORED SPECIES

- (a) Absorption of photo-colored species, 3MP solution, 77°K
- (b) Absorption of cis keto produced upon warming previously irradiated solution, 3MP solution, 77°K
- (c) Absorption of cis keto produced in 2,2,2-trifluoroethanol solution, room temp.



# 5-BROMOSALICYLIDENEANILINE: COMPARISON OF ABSORPTION SPECTRA

### AFTER IRRADIATION INTO CIS KETO ABSORPTION AND

### AFTER IRRADIATION INTO ENOL ABSORPTION

- (a) Acid-3-methylpentane solution, 77°K, long wavelength absorption
- (b) After 45 min. irradiation of acid-3-methylpentane solution at 77°K into long wavelength band (a)
- (c) After 45 min. irradiation of 3-methylpentane solution at 77°K into entire region of absorption



# 5-BROMOSALICYLIDENEANILINE: COMPARISON OF EMISSION AND EXCITATION SPECTRA OF CIS KETO AND PHOTO-COLORED SPECIES

- (a) Emission of photo-colored species
- (b) Excitation spectrum of photo-colored species  $\lambda_{mon} = 561 \text{ m}\mu$
- (c) Emission of cis keto produced by warming irradiation solution
- (d) Excitation spectrum of cis keto emission  $\lambda_{mon.}$  = 530  $m\mu$



### C. Salicylidene-o-toluidene

#### 1. Absorption Studies

A 3-methylpentane solution of salicylidene-o-toluidene at 77°K has an absorption spectrum which shows a long wavelength onset near 400 m $_{\mu}$ . [see Figure 11]. The first band shows maxima at 345, 325, and 308 m $_{\mu}$ , and the second band shows a single maximum at 273 m $_{\mu}$ .

Irradiation into this enol absorption band produces an orange color in the rigid solution. A new, long wavelength absorption band responsible for this coloration appears with long wavelength onset near 565 m $\mu$  and an intensity maximum at 468 m $\mu$  [see Figure 13]. This band shows resolved vibrational structure and is quite broad. Irradiation causes corresponding changes to occur in the region of previous absorption. In the place of the band originally at longest wavelength a new band appears with a intensity maximum at 317 m $\mu$ . Also the peak originally at 273 m $\mu$  either disappears or is shifted beneath a strong absorption at shorter wavelengths.

Warming the solution to the softening point of the rigid glass causes the orange color to disappear and a yellow color to take its place. If the temperature of the solution is returned to 77°K, the yellow color thus produced remains. The absorption spectrum obtained under these conditions shows a long wavelength onset near 520 m $\mu$  with an intensity maximum at 443 m $\mu$  for the long wavelength band. The second band has a maximum at 325 m $\mu$ , and the third band reappears with a maximum at 262 m $\mu$  [see Figure 13]. Continued warming causes the absorption spectrum to revert to that of the enol.

In a 2,2,2-trifluoroethanol solution at room temperature the anil exists primarily as the cis-keto tautomer (8,9). The absorption spectrum consists of a long wavelength onset near 500 m $\mu$  and three bands with maxima at 426, 322, and 266 m $\mu$  respectively [see Figure 15]. If this spectrum is compared with that obtained of the yellow species the close similarity is immediately evident. The only major difference is the red shift of the long wavelength band in the 3-methylpentane solution. Thus as for the previous cases discussed the thermal back reaction involves going from the photo-colored species to the cis-keto tautomer to the enol tautomer.

It is found that a small quantity of propionic acid added to the 3-methylpentane solution results in a long wavelength band at 77°K similar to that observed for the trifluoroethanol solution thus indicating that some cis-keto is formed. This cis-keto band has more structure than does the latter and has an intensity maximum at 429 mµ [see Figure 12]. Irradiation into this band produces no further coloration and no absorption at longer wavelengths. However irradiation into those absorption bands at shorter wavelengths results in an orange color and an absorption spectrum which is a superposition of that present before irradiation and that observed after irradiation of a 3-methylpentane solution alone. Thus, as for the anils previously discussed, production of the photo-colored species results from excitation of the enol tautomer, but not from excitation of the cis-keto tautomer. Finally, irradiation into the long wavelength portion of the photo-produced absorption at 77°K causes no erasure of this band.

#### 2. Emission Studies

The emission spectrum of salicylidene-o-toluidene at 77°K in 3methylpentane solution shows a short wavelength onset near 480 m<sub>µ</sub> with intensity maxima at 519 and 545 m<sub>µ</sub> [see Figure 11]. The significant point associated with this emission as mentioned before is the fact that although it is a fluorescence, it is offset from the absorption spectrum by about 4170 cm<sup>-1</sup>. Thus, it is evident that the molecular species responsible for the emission is not that which absorbs the light originally, but a transition state.

This offset of emission is graphically demonstrated in the excitation spectrum [see Figure 11]. It onsets near 400  $m_{\mu}$  and generally shows the same features as the absorption spectrum. A much greater correspondence to the absorption spectrum may be obtained if the correction is made for the decrease in lamp output and monochromator efficiency with decreasing wavelength.

Excitation of the 3-methylpentane solution at 77°K to which a small quantity of propionic acid has been added results in two emissions. If 345 m<sub>µ</sub> is used for excitation, the emission is identical to that observed above. Excitation with 430 m<sub>µ</sub> light produces an emission of similar band shape but with onset near 465 m<sub>µ</sub> and maxima at 507 and 530 m<sub>µ</sub>. As for the 5-bromosalicylidene-o-toluidene case, excitation at longer wavelengths produces the cis-keto emission whereas excitation at shorter wavelengths produces the emission from the transition state. As mentioned previously for salicylideneaniline and 5-bromosalicylidene-o-toluidene similarity of
shape and position of these spectra indicates that the transition state must be very similar to the cis-keto tautomer.

If the excitation spectrum of this latter emission is obtained by monitoring at 488 m<sub>µ</sub>, the principal features notes are onset near 480 m<sub>µ</sub>, first band maximum at 430 m<sub>µ</sub>, and second band maximum at 325 m<sub>µ</sub>. A comparison of this excitation spectrum with the absorption spectrum of salicylidene-o-toluidene in trifluoroethanol shows that they are almost identical, and thus the emission is assigned as that of the cis-keto tautomer.

On the other hand the excitation spectrum obtained by monitoring the emission at 590  $m\mu$  is practically identical to that obtained for the 3-methylpentane solution alone. Thus, both enol and cis-keto anil exist in an acid-3-methylpentane mixture at 77°K.

The emission spectrum of the photo-colored form produced by irradiating a 3-methylpentane solution at 77°K consists of onset near 490 m<sub>µ</sub> with maxima at 560 m<sub>µ</sub> and 589 m<sub>µ</sub> [see Figure 14]. Excitation throughout the long wavelength absorption band attributable to the photocolored form shows the same emission. No cis-keto emission is observed when the excitation is in the region of its long wavelength absorption thus indicating that no cis-keto anil is formed by irradiation of the enol, and that the photo-colored form is not the cis-keto tautomer.

The excitation spectrum of this emission shows a close similarity to the long wavelength absorption of the photo-colored form except for the decrease in intensity on the short wavelength side due to decrease in lamp output. The long wavelength onset is near 560 mµ with maximum intensity at 470 mµ [see Figure 14].

SALICYLIDENE-O-TOLUIDENE: SPECTRA OF

ENOL TAUTOMER, 3MP SOLUTION, 77°K

- (a) Absorption spectrum
- (b) Emission spectrum,  $\lambda_{ex}$  = 360 m $\mu$
- (c) Excitation spectrum,  $\lambda_{mon.}$  = 520 m $\mu$



wavelength,  $m_{\mu}$ 

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SALICYLIDENE-O-TOLUIDENE: SPECTRA OF CIS KETO TAUTOMER PRODUCED AT 77°K IN ACID-3-METHYLPENTANE SOLUTION

- (a) Absorption spectrum
- (b) Emission spectrum,  $\lambda_{ex}$  = 430 m $_{\mu}$
- (c) Excitation spectrum,  $\lambda_{mon.}$  = 500 m $\mu$



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## SALICYLIDENE-O-TOLUIDENE: COMPARISON OF

ABSORPTION SPECTRA OF PHOTO-COLORED SPECIES AND CIS KETO SPECIES

- (a) 3MP solution, 77°K; photo-colored species
- (b) 3MP solution, 77°K; cis keto anil produced upon warming previously irradiated solution



wavelength,  $m_{\mu}$ 

# SALICYLIDENE-O-TOLUIDENE: SPECTRA OF PHOTO-COLORED SPECIES

- (a) 3MP solution, 77°K, emission spectrum
- (b) 3MP solution, 77°K, excitation spectrum



### SALICYLIDENE-O-TOLUIDENE: CIS KETO SPECTRA

- (a) 3MP solution, 77°K; absorption spectrum of cis keto tautomer produced upon warming previously irradiated solution.
- (b) 3MP solution, 77°K; emission spectrum of cis keto
- (c) 3MP solution, 77°K; excitation spectrum of (b)
- (d) 2,2,2-Trifluoroethanol solution, room temp., absorption spectrum of cis keto tautomer produced in strongly Hbonding solvent



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The emission spectrum of the yellow species produced by warming the orange photo-colored solution to the softening point of the rigid glass consists of an onset near 480 m $\mu$  with intensity maxima at 523 and 559 m $\mu$  [see Figure 15]. Except for a red shift which may be explained on the basis of solvent-solute effects, this emission is identical to that of the cis-keto anil present in an acid-3-methylpentane mixture at 77°K.

The excitation spectrum of this emission onsets near 520  $m_{\mu}$  and peaks at 468  $m_{\mu}$ . The close similarity of this excitation spectrum to that of the cis-keto anil in the acid-3-methylpentane mixture along with the evidence provided by comparison of the emissions and absorptions confirm that the yellow species is the cis-keto tautomer. Thus, the photo-colored form produces the cis-keto anil as the solution warms and the rigid glass softens.

### D. Nitrosalicylideneanilines

Cohen and Schmidt (6) made the generalization that all of the anils of o-hydroxybenzaldehyde were photochromic. However three anils of nitrosubstituted salicylaldehyde were prepared, and none exhibits photochromic properties.

### 1. 5-nitrosalicylideneaniline

At room temperature a 3-methylpentane solution of 5-nitrosalicylideneamiline exhibits an absorption spectrum which consists of a long wavelength onset near 390 m<sub>µ</sub> with intensity maxima at 335, 300, and 263 m<sub>µ</sub> [see Figure 16].

If the temperature of this solution is lowered to  $77^{\circ}$ K (-196°C) the absorption spectrum undergoes marked change. A low intensity long wavelength band appears with onset near 490 mµ with maximum intensity near 445 mµ [see Figure 16]. Going to shorter wavelengths, maxima occur at 345, 305, and 275 mµ.

A trifluoroethanol solution at room temperature shows a long wavelength onset near 480 m $_{\mu}$  with maximum intensity of the first band occurring at 419 m $_{\mu}$  [see Figure 16]. The maxima of the second band occur at 346, 330, and 302 m $_{\mu}$ . This then is the specturm of the cis-keto tautomer (8,9). Comparing this spectrum with that taken at low temperature shows that lowering the temperature apparently results in the formation of some cis-keto tautomer although the enol is still the dominant species.

If the 3-methylpentane solution at 77°K is irradiated in the enol absorption band no new absorption at longer wavelengths develops. Indeed, the spectrum undergoes almost no change after 30 minutes irradiation. Thus, in addition to the complete absence of any new molecular species, there is apparently no net erasure or formation of the cis-keto tautomer.

At 77°K two emissions are noted for the 5-nitro-salicylideneaniline solution [see Figure 16]. Excitation with light of wavelength 440 mµ produces the keto emission which has an onset at 485 mµ and maxima at 515 and 532 mµ. Excitation at 350 mµ produces an emission which is predominantly that of the transition state. It has an onset at 475 mµ with maxima at 520 and 545 mµ.

### 2. 5-Nitrosalicylidene-2,4-dimethylaniline

The room temperature 3-methylpentane solution of 5-nitrosalicylidene-2,4-dimethylaniline has a long wavelength onset near 405 m $\mu$  with intensity maxima at 348, 335, 305, and 265 m $\mu$  [see Figure 17]. After lowering the temperature to 77°K the absorption spectrum shows a new long wavelength band of low intensity with onset near 500 m $\mu$  and maximum near 445 m $\mu$ . The shorter wavelength intensity maxima now occur at 385, 365, 348, 335, 305, and 270 m $\mu$ . Thus as in the previous case, the reduction in temperature favors the formation of a small amount of the cis-keto tautomer.

Also as before irradiation for 30 minutes with a 1 KW xenon lamp produces no new absorption at longer wavelengths and little change in the existing spectrum. Therefore this anil is not photochromic but is thermochromic.

### 3. 3-Nitrosalicylideneaniline

The room temperature absorption spectrum of 3-nitrosalicylideneaniline in 3-methylpentane solution has a long wavelength onset near 440 m $\mu$  with intensity maxima at 350, 317, 302, and 252 m $\mu$  [see Figure 18]. Lowering the temperature to 77°K produces the new long wavelength absorption noted previously for the anils of nitrosalicylaldehyde. For this anil it is much more intense with onset near 525 m $\mu$  and maximum at 460 m $\mu$ . Other intensity maxima at this temperature are at 365, 305, and 266 m $\mu$ .

In trifluoroethanol solution at room temperature the absorption spectrum of 3-nitrosalicylideneaniline shows an intense peak at long wave-

lengths with maximum intensity at 445 m $\mu$  [see Figure 18]. The second absorption is structured with maxima at 335, 315, 303, 285, and 260 m $\mu$ . Under these conditions the cis-keto tautomer is the predominant species, thus the spectrum is essentially that of the cis-keto anil. In a study of temperature dependence of the intensity of the long wavelength maximum it was found that the intensity decreases about 37% as the temperature is raised from -75°C to 45°C.

Also for this anil, irradiation for 30 minutes produces no change in the absorption spectrum. Thus 3-nitrosalicylideneaniline is not photochromic but is thermochromic.

In EPA solution the long wavelength band seen at 77°K in 3-methylpentane is present at room temperature. Lowering the temperature to 77°K increases the intensity of this band. As in the 3-methylpentane solution,irradiation produces no changes in the spectrum.

The emission spectrum of 3-nitrosalicylideneaniline in EPA at 77°K shows two distinct emissions [see Figure 19]. Excitation at 440 mµ into long wavelength cis-keto band results in an emission of the keto tautomer which has an onset at 465 mµ and a maximum at 497 mµ with a long wavelength shoulder near 520 mµ. Excitation with light of wavelength 360 mµ produces the transition state emission. It has an onset at 475 mµ and maxima at 510 and 540 mµ. Thus, in this case as the others in this group a considerable amount of enol species exists at 77°K and yet no formation of the photo-colored species is observed.

### 5-NITROSALICYLIDENEANILINE: 3MP SOLUTION

- (a) Room temperature absorption spectrum
- (b) Absorption spectrum, 77°K, before and after 30 min. irradiation
- (c) Transition state emission spectrum,  $\lambda_{ex} = 350 \text{ m}\mu$ , 77°K
- (d) Cis keto emission spectrum,  $\lambda_{ex} = 440 \text{ m}_{\mu}$ , 77°K
- (e) Room temp absorption spectrum, 2,2,2-trifluoroethanol
  solution



## 5-NITROSALICYLIDENE-2,4-DIMETHYLANILINE: ABSORPTION SPECTRA

- (a) Room temperature
- (b) 77°K, before and after 30 min. irradiation



## 3-NITROSALICYLIDENEANILINE: ABSORPTION SPECTRA

- (a) 3MP solution, room temp.
- (b) 3MP solution, 77°K, before and after irradiation
- (c) 2,2,2-trifluoroethanol solution, room temp.



3-NITROSALICYLIDENEANILINE: EMISSION SPECTRA EPA SOLUTION, 77°K

(a) Cis keto emission,  $\lambda_{ex}$  = 440 m $_{\mu}$ 

(b) Emission from transition state,  $\lambda_{ex}$  = 360  $m_{\mu}$ 



### E. Salicylidene-4-nitroaniline

In the last section it was noted that contrary to the generalization of Cohen and Schmidt that all anils of o-hydroxybenzaldehyde are photochromic (6), the anils of nitro-substituted salicylaldehydes are not photochromic. This inhibition of photochromism does not occur, however, when the nitro-group is substituted on the aniline ring, as in the case of salicylidene-4-nitroaniline.

At 77°K, the absorption spectrum shows an onset near 425  $m_{\mu}$  with maxima at 372, 335, 320, and 273  $m_{\mu}$  [see Figure 20]. Irradiation produces a new absorption band with onset near 590  $m_{\mu}$  and maxima near 515 and 490  $m_{\mu}$ , which is characteristic of the absorption of the photo-colored species of the other anils.

The emission spectrum before photo-conversion obtained by exciting with 380 m $\mu$  light shows an onset at 480 m $\mu$  with maxima at 541 and 575 m $\mu$ . This then is the emission from the transition state of the anil. After photo-conversion, excitation into the new absorption band produces the emission spectrum of the photo-colored species. This consists of an onset near 495 m $\mu$  with maxima at 570 and 610 m $\mu$ .

### F. Benzylidene-2-hydroxyaniline

In order to compare the photochemistry of the o-hydroxybenzaldehyde anils with that of the anil containing the hydroxy group ortho to the amino group, benzylidene-2-hydroxyaniline was synthesized. At room temperature in a 3-methylpentane solution the absorption spectrum of this compound shows a long wavelength onset near 410 mµ with two strong bands

SALICYLIDENE-4-NITROANILINE: ABSORPTION SPECTRA 10<sup>-4</sup> M IN 2Me-THF

- (a) 77°K before irradiation
- (b) 77°K after 25 min. irradiation



having maxima near 359  $m_{\mu}$  and 273  $m_{\mu}$ . At 77°K the absorption spectrum of this solution shows a blue shift in the long wavelength band ( $\lambda$  max = 344  $m_{\mu}$ ) and a blue shift and relative increase in intensity for the second band ( $\lambda$  max = 263  $m_{\mu}$ )(see Figure 21).

The room temperature absorption spectrum of this anil was obtained for a 2,2,2-trifluoroethanol solution. For the anils of salicylaldehyde it has been determined (8,9) that in this solvent the anils of salicylaldehyde exist primarily as the cis-keto tautomer. This cis-keto species for the salicylideneanilines results from proton transfer from oxygen to nitrogen and an electron redistribution to produce a quinoid type molecule. Since there is little possibility for the formation of the keto species in the case of benzylidene-2-hydroxyaniline, the strongly hydrogen bonding solvent probably results in the formation of a species in which the proton is partially transferred to the nitrogen. The absorption spectrum in trifluoroethanol is very similar to that of the low temperature, 3methylpentane solution. The partial transfer of the proton is apparently the cause of spectral change with decreasing temperature.

Irradiation of the 3-methylpentane solution at low temperature (77°K) results in an appreciable diminution of the intensity of the long wavelength band and a blue shift with a slight increase in intensity of the second band. Warming the solution to room temperature after irradiation causes the absorption spectrum to revert to that observed originally at this temperature.

Anderson and Wettermark (10) found that flash irradiation of room . temperature solutions of anils resulted in decreased absorption between

## BENZYLIDENE-2-HYDROXYANILINE: ABSORPTION SPECTRA

- (a)  $2.5 \times 10^{-4}$  M 3MP, room temp.
- (b) 2.5 x 10<sup>-4</sup> M 3MP, 77°K
- (c) 2.5 x 10<sup>-4</sup> M 3MP, 77°K, 30 min. irradiation
- (d)  $2.5 \times 10^{-4}$  M in 2,2,2-trifluoroethanol, room temp.



350 and 400 mµ. Their evidence indicated that this spectral change corresponded to the isomerization about the imine double bond to produce the transient cis form. The findings in the present investigation for the hydroxy aniline anil are parallel in several respects.

Irradiation causes no formation of a long wavelength absorbing species as is the case for the salicylaldehyde anils. Since the keto species is energetically very unfavorable, the possibility of the type of isomerism found for the salicylaldehyde anils is remote. The differences in the absorption spectrum after irradiation are therefore attributed to cis-trans isomerization about the C=N- double bond.

### 6. 2-Hydroxynaphthylideneaniline

As an extension of the study of photochromism and thermochromism of the anils of salicylaldehyde, 2-hydroxynaphthylideneaniline was prepared and investigated in the same manner. Dudek and Dudek (8) have found from observing  $N^{15}$ -H spin coupling in NMR that for 2-hydroxynaphthylidineaniline the cis-keto tautomer accounts for 15% of the total anil molecules even in such a non-polar solvent as carbon tetrachloride. By comparing the variation of the observed  $N^{15}$ -H spin coupling and the ultraviolet absorption intensities with solvent, the absorption in the region 410-450 mµ has been assigned to the cis-keto tautomer.

### 1. Absorption Studies:

The 3-methylpentane solution at room temperature has two strong bands in the near ultraviolet with intensity maxima at 375 m $\mu$  and 318 m $\mu$ 

with a shoulder at 330 m $\mu$  on the latter band. These bands are assigned to the enol tautomer. The presence of some cis keto tautomer is revealed by two weak bands with maxima at 435 and 455 m $\mu$  (see Figure 22).

Upon lowering the temperature of the 3-methylpentane solution to 77°K, changes occur in the absorption spectrum similar to those noted for the anils of the nitrosalicylaldehydes. The long wavelength cis keto absorption is red shifted slightly and undergoes a 40% increase in intensity relative to the first strong band at 373 mµ. This strong band acquires shoulders at 393 and 359 m $\mu$ , and the second band splits into two peaks at 319 and  $333 \text{ m}_{\mu}$ . When this low temperature rigid solution is irradiated for 20 minutes using wavelengths below about 390 m $_{\mu}$ , an increase of about 70% in the intensity of the long wavelength cis keto bands is observed; however, no new absorption is seen at longer wavelengths. When this solution is further irradiated using only wavelengths which correspond to the long wavelength cis keto absorption, the intensity of the absorption produced photolytically is reduced to the original level. Thus, in the case of 2-hydroxynaphylideneaniline in contrast to the salicylideneanilines, cis keto alone is produced by irradiation with light, and, further, it may be erased by selecting the proper wavelength of irradiation. Also, rewarming the previously irradiated solution causes the absorption spectrum to revert to that observed at room temperature originally.

On the basis of these observations it may be stated that 2-hydroxynaphylideneaniline shows both photochromism and negative thermochromism. The photochromism observed for this compound is significantly different

from that observed for the salicylideneanilines for in this case, the action of light causes the cis keto tautomer to be formed whereas in the others the photo-colored species has been shown to be something other than the cis keto.

A point of interest is that the low temperature spectrum of this anil does not look like that obtained by Cohen, et al. (7), for a hydrocarbon solution of nearly the same concentration. Instead it resembles that of a solution diluted ten times (7). The major difference is in the intensities of the long wavelength cis keto bands relative to those at shorter wavelengths. Cohen, et al. (7) explained this difference on the basis of concentration differences. However, we found that the spectrum at low temperature of Cohen, et al. (7), may be reproduced exactly if a minute amount of a water-ethanol mixture is added to the 3-methylpentane solution. The close resemblance of this spectrum to that obtained in 2,2,2-trifluoroethanol solution at room temperature indicates that this anil exists almost entirely in the cis keto tautomer at low temperature in 3-methylpentane solution to which a slight amount of water-ethanol mixture has been added. Instead of the energy difference between enol and cis keto depending on concentration (7), it is solvent dependent. A strongly hydrogen bonding solvent stabilizes the cis keto ` to the point that it lies lower in energy than the enol. This explains the shift in the equilibrium strongly in favor of the cis keto as the temperature is lowered for the case of a solution containing strongly hydrogen bonding species. It will also be noted that irradiation into the

cis keto band produced at low temperature in the 3-methylpentane-waterethanol mixture results in neither the production of any more cis keto nor the eradication of any already present.

In order to check the statement of Cohen, et al. (7), that the photoactivity of the hydroxynaphthaldehyde anils is greater near -75°C than at -196°, 2-hydroxynaphthylideneaniline was dissolved in ethylphthalylethylglycolate, a non-hydrogen bonding solvent, which forms a rigid glass near -60°C. The absorption spectrum in this solvent at room temperature consists of a strong peak at 380  $m_{\mu}$  and two weaker maxima at 437 m<sub>µ</sub> and 457 m<sub>µ</sub>. [see Figure 23]. It will be noticed that the long wavelength absorption is much more intense as compared to the same absorption in 3-methylpentane at 77°K, thus indicating that more cis-keto tautomer is present. Also, absorption below 330  $m_{\mu}$  is essentially that resulting from the solvent. After the temperature is lowered to -75°C and a rigid solution forms, the absorption spectrum consists of a strong peak at 381 m $\mu$  with the appearance of a shoulder on this band at 362 mu. The long wavelength cis keto absorption intensity increases relative to that of the enol absorption band [see Figure 23]. The intensity maxima of the long wavelength band occurs at 437  $m_{\!\!\! 1}$  with a shoulder at 460 mu.

After 20 minutes irradiation with a kilowatt Hg-Xe lamp the spectral shape remains unchanged; however, the intensity of the long wavelength band now exceeds that of the absorption band near 380 m<sub>µ</sub>. Thus, the conclusions are the same as those arrived at for the 3-methylpentane solution. That is, lowering the temperature results in the formation of more cis keto anil as compared to that present at room temperature,

and irradiation produces addition cis keto. However, no significant increase in photoactivity at -75° is observed.

### 2. Emission Studies

Two emissions are observed for 2-hydroxynaphthylideneaniline in 3-methylpentane solution at 77°K. Excitation at 450 m $\mu$  produces an emission with onset near 465 m $\mu$  and intensity maxima at 480 and 510 m $\mu$ [see Figure 24]. Excitation at 385 m $\mu$  produces an emission with onset near 455 m $\mu$  and intensity maxima at 484 and 502 m $\mu$ . The former emission is that of the cis keto whereas the latter is that of the transition state.

The assignment of these emissions is confirmed by the excitation spectra [see Figure 24]. If the emission intensity at 470 m $\mu$  is monitored, two small peaks near 438 and 465 m $\mu$  and a strong peak with maximum at 393 m $\mu$  are observed. If the emission intensity at 540 m $\mu$  is monitored, the long wavelength peaks with maxima at 438 and 469 m $\mu$  are stronger than that peak at 393 m $\mu$ .

Irradiation for 30 minutes produces no new emission nor does it change the spectral shape of the excitation spectrum. Thus, the emission and excitation spectra serve to verify the conclusions obtained on the basis of the absorption data. That is, at low temperatures in hydrocarbon solvents an appreciable amount of the 2-hydroxynaphthylideneaniline molecules exist as the cis keto tautomer, and irradiaiton results in the production of some more cis keto, but no other molecular species.

### 2-HYDROXYNAPHTHYLIDENEANILINE, ABSORPTION SPECTRA

- (a)  $4 \times 10^{-4}$  M in 3MP, 77°K
- (b) 4 x  $10^{-4}$  M in 3MP, 77°K, 20 min. irradiation into spectral region below 400 mµ
- (c)  $4 \times 10^{-4}$  M in 3MP + 1 drop ETOH-H<sub>2</sub>O per 5 ml, 77°K
- (d) 4 x 10<sup>-4</sup> M in 3MP, 77°K, irr. as for (b) plus 30 min. irr. into long wavelength band


## FIGURE 23

### - 2-HYDROXYNAPHTHYLIDENEANILINE:

## ETHYLPHTHALYLETHYLGLYCOLATE SOLUTION

- (a) Absorption spectrum, room temp.
- (b) Absorption spectrum, -75°C
- (c) Absorption spectrum, -75°C + 20 min. irradiation

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### FIGURE 24

## 2-HYDROXYNAPHTHYLIDENEANILINE:

EMISSION AND EXCITATION SPECTRA, 3MP SOLUTION, 77°K

- (a) Emission spectrum,  $\lambda_{ex} = 385 \text{ m}\mu$
- (b) Emission spectrum,  $\lambda_{ex} = 460 \text{ m}_{\mu}$
- (c) Excitation spectrum,  $\lambda_{mon.}$  = 555 m $\mu$
- (d) Excitation spectrum,  $\lambda_{mon.} = 470 \text{ m}\mu$



#### H. Erasure Studies and Viscosity Effects

Cohen, et al. (6), observed that the photo-colored species of the salicylideneanilines in paraffin oil solutions at  $-75^{\circ}$ C could be eradicated by irradiation into the absorption band of this species. They found light of 5460 Å to be most effective for erasure purposes. Also, they indicated that absorption at the maximum (4800Å) may be "appreciable" after the absorption at longer wavelengths drops to zero.

Originally, attempts were made to the photo-colored species of salicylideneaniline in a ethylphthalylethylglycolate solution of at -70°C. Surprisingly, irradiation into the photo-colored band produced no more diminution of intensity than that attributible to the dark, thermal back reaction at that temperature.

A paraffin oil (Nujol) solution of salicylideneaniline was prepared and the irradiation-erasure experiment performed as before. In this case, complete erasure occurs after 5 minutes irradiation into the absorption band of the photo-colored species using a 1 KW xenon lamp and narrow band pass filters in order to selectively irradiate in various regions of the absorption band. No sign of any absorption remains near 480  $m_{\mu}$  and the solution is colorless. Therefore erasure involves the reaction

# photo-colored species $\xrightarrow{hv}$ enol

with no cis keto intermediate. From the results of Cohen, et al (6), some cis keto could be responsible for the remaining absorption near

480 mµ when that at longer wavelengths disappeared. However, our studies show that erasure causes the absorption in the entire region of photo-colored species absorption 400 mµ to 470 mµ, to drop to the base line present before irradiation. Also, we find that when using a tungsten source, erasure using light in the 540 mµ region is no more effective than that in the 470 mµ region. Cohen's statement (6) concerning effectiveness of the 5460 Å line is correct only for a Hg lamp. This occurs because the intensity of this line far exceeds that of any other line or the background continuum in this region.

The temperature of the Nujol solution was lowered to -100°C and erasure studied at this temperature. Two differences are noted: (1) the same irradiation time as was used at -70°C produces about 20% less photocolored species at -100°C; and (2) only about 30% of the erasure observed at -70°C occurs at -100°C under identical conditions. These observations indicate that there is a viscosity effect involved in both the forward and back photo-reactions.

Greenspan and Fischer (19) have studied the viscosity of several solvents and solvent mixtures at low temperatures. The approximate viscosity for the isooctane-isononane mixture at  $-180^{\circ}$ C is 3 x  $10^{12}$  cp whereas that of 2-methylpentane at the same temperature is 7 x  $10^{6}$  cp. Although both solvents form a rigid glass at  $-196^{\circ}$ C (77°K) the data mentioned above indicates that the isooctane-isononane solution should be significantly more rigid than the 2-methylpentane solution.

Further evidence of this viscosity effect is provided by comparing the amount of formation of photo-colored species for 2-methylpentane

solution of salicylideneaniline and an isooctane-isononane (1:1) solution of salicylideneaniline. Both solutions had the same concentration, and irradiation times, and the same combination of absorption cell and dewar was used. Both solutions were irradiated for 10 minutes; however, the intensity of absorption of the photo-colored species in the case of the isooctane-isononane solution was reduced by 42% compared with that obtained in the 2-methylpentane solution. Thus, both the process of production of the photo-colored species and the photoerasure of the absorption band resulting from this species involve crossing a potential energy barrier which contains a viscosity component in addition to the thermal component. Moreover the existence of this viscosity effect provides further evidence that the photo-colored species is formed as the result of some geometrical rearrangement of the molecule. The existence of the viscosity effect also explains why in the thermal back reaction mentioned previously, the color changes from orange to yellow as the rigid glass begins to soften even though the temperature increase is only 10-15°C above that of liquid nitrogen.

## I. <u>Generalizations Concerning the Molecular Species and Mechanism</u> Encountered in this Study

It has been well established that the salicylideneanilines exist almost exclusively as the enol tautomer in non-polar solution (8).

78<sup>-</sup>

In the ground state the enol tautomer is essentially planar except that the aniline ring is rotated out of plane to overcome some steric hindrance with the imine hydrogen (15). The nitrogen is an  $\text{SP}^2$  hybrid with the  $p_Z$  orbital involved in the C=N  $\pi$  bond. Upon excitation, a charge redistribution occurs to produce an electronic arrangement appropriate to the keto tautomer (16). However since the absorbtion is of Franck-Condon allowed shape, no displacement of the nuclei occurs upon excitation, and thus, the geometry of the excited state enol is still appropriate to the ground state enol.

On the other hand in strongly hydrogen bonding solvents Dudek (8) and Ledbetter (9) have shown that a portion of the anil exists as the cis keto tautomer.



We have obtained absorption spectra of the anils in strongly hydrogen bonding solvents such as trifluoroethanol and have found as did the previous investigators (8,9) that the characteristic band of the cis keto tautomer is a long wavelength band with maximum intensity in the region  $400-450 \text{ m}\mu$ .

In a study of substituent effects on the intensity of the cis keto band it was found (6) that electron releasing groups on the aniline ring caused an increase in intensity. We find that even more increase is observed for electron withdrawing groups substituted on the salicylal-

dehyde ring. Both these substitutions favor proton transfer from the oxygen to the nitrogen to produce the keto form. The electron releasing group on the aniline ring causes the nitrogen to be somewhat more basic, whereas the electron withdrawing group on the salicylaldehyde ring makes the oxygen less basic.

A very small amount of an organic acid such as propionic acid added to the hydrocarbon solution of the anils produces the characteristic cis keto band at low temperatures. Since the strongly hydrogen bonding solvents such as trifluoroethanol do not form rigid glasses at low temperatures, the low temperature absorption and emission spectra of the cis keto species can not be obtained in such a solvent. However the use of the acid-hydrocarbon solvent mixture such as propionic acid-3-methylpentane (1 drop: 25 ml) provides an excellent means to obtain the spectra of the cis keto tautomer. In addition, the emission allows: an excitation spectrum of the cis keto which provides a picture of its absorption with no interference from the enol.

The enol emission is offset from its absorption by as much as  $4590 \text{ cm}^{-1}$ . Because of this split, it could be assumed that this is a phosphorescence. However previous investigations (4,13) have indicated that this emission is a fluorescence. We have checked it and found that it will not pass through the phosphoroscope. Therefore the emission must be originating from a molecular species different from the enol.

The close similarity of this emission to that of the cis keto both in band shape and spectral position indicates that this molecular species from which the emission originates is very much like the cis keto. How-

ever, the two are not identical because there are some differences in energy and shape. In order to produce a species similar to the cis keto tautomer, proton transfer from the oxygen to the nitrogen must occur from the excited state of the enol. As has been mentioned previously, no emission is ever observed from the enol excited state, and the quantum efficiency values for the corrected excitation spectrum of salicylideneaniline indicate that there is complete conversion of the enol excited state to the excited transition state. Thus, the rate constant for the production of the transition state must be on the order of  $10^{10}$  to  $10^{11}$ sec<sup>-1</sup> to cause the emission from the enol\* to be undetectable by our instrumentation. The proximity in space of the proton to the nitrogen, the formal negative charge on the nitrogen, and the partial bond formation present in the form of the hydrogen bond all serve to favor a rate constant for proton transfer like that required above.

This cis keto-like transition state will be designated as cis<sup>‡</sup>. Since the proton transfer will require the molecule to remain in the planar configuration of the enol, the cis<sup>‡</sup>\* will be formed in this configuration. However, this will be a high energy species due to the strain imposed on the molecule because of the forced rehybridization of the nitrogen to  $SP^3$ . Thus, emission of a photon to produce the ground state is followed by an immediate conversion back to the enol.

Irradiation of the enol at low temperatures in rigid solution causes the previously colorless solution to acquire an orange hue. The absorption, emission, and excitation spectra of the molecular species produced by irradiation do not correspond to either those of the enol or cis keto tautomers mentioned previously. In their work with the crystalline anils Cohen and Schmidt (4) proposed that the photo-colored species is a trans keto anil.



As mentioned in the discussion of some of the various anils studied \_ in this investigation, the thermal back reaction,

photo-colored species 
$$\xrightarrow{\Delta}$$
 cis keto

occurs upon warming the previously irradiated solution to the softening point of the rigid solution although for the case of 3-methylpentane this temperature is only 10-15° above that of liquid nitrogen. This low energy requirement for the conversion of the photo-colored species to the cis keto is totally inconsistent with the normal energy requirements for cis-trans isomerization about a C=C bond.

It is observed that the formation of the photo-colored species is always accompanied by emission from the  $cis^{\ddagger*}$ . Thus, the reaction

 $cis \xrightarrow{\ddagger} photo-colored species$ 

is in competition with the fluorescence from  $\operatorname{cis}^{+*}$ , and must have a rate constant of  $10^8 - 10^9 \operatorname{sec}^{-1}$ . As was previously noted this  $\operatorname{cis}^{+*}$  state will be planar and the molecule will be subjected to a great deal of strain because of this planarity. A change in the molecular geometry will

remove the strain on the nitrogen. This might be accomplished by a slight twist about the C=C bond with an accompanying breaking of the internal hydrogen bond. This would produce a species very much like a sterically hindered ethylene (20). It is such a species that the evidence acquired in this investigation requires. Thus, from this point the photo-colored species will be designated as "cis".

None of the absorption, emission, or excitation spectra obtained after irradiation of the enol shows any sign of production of the cis keto except in the special case of 2-hydroxynaphthylideneaniline. In fact in the case of the acid-3-methylpentane solution for which some cis keto is already present at -196° before photoconversion, irradiation into the long wavelength cisketo absorption band produces no "cis" and no new cis keto. Thus, the forward photo reaction is

enol <u>hy</u> "cis"

and the following reactions do not occur:

cis keto <sup>h</sup>y "cis"

and

enol 
$$\stackrel{hv}{\longleftarrow}$$
 cis keto.

If the previously irradiated solution is allowed to warm from -196° about 10-15° to just the softening point of the 3-methylpentane rigid glass, the color changes from orange to yellow. This yellow color may be maintained indefinitely if the temperature of the solution is lowered

back to -196°. Comparison of the absorption, emission, and excitation spectra of this yellow solution with those of cis keto form, shows an excellent correspondence exists between them. Continued warming to room temperature results in a colorless solution since all of the anil molecules revert to the enol form. Thus, the thermal back reaction is

"cis"  $\xrightarrow{\Delta}$  cis keto  $\xrightarrow{\Delta}$  enol

Irradiation of the cis keto produced upon warming the previously photo-colored solution, gives the same result as that obtained for the cis keto anil produced in the acid-3-methylpentane solution at -196°. That is, no "cis" is formed and no additional cis keto specie is formed.

The fact that the thermal back reaction involves passing through the cis keto tautomer as an intermediate is strong evidence that the photoproduced orange species is the "cis" species. One of the requirements for stability of the photo-colored "cis" species is a high-viscosity of the solution. So long as the solution is quite viscous, the only way the molecule can avoid the strain on the nitrogen imposed in the transition state is to twist about the C=C bond and break the internal hydrogen bond. However, as soon as the viscosity decreases to a certain point the bonds to the nitrogen may assume their pyramidal configuration with a restoration of the internal hydrogen bond, or, in other words, produce the cis keto tautomer.

On the basis of the experimental evidence obtained in this study and the identification of the various molecular species involved in the photo

and thermal reactions, the following potential energy diagram may be constructed where the dotted portions refer to the viscosity contributions to the barriers between states. The energy differences are appropriate for salicylideneaniline.



Increasing the viscosity hinders the twisting about the C=C bond and thus decreases the amount of "cis" produced. In terms of the potential energy diagram,the increasing viscosity increases the energy barrier between cis<sup>‡\*</sup> and "cis". Therefore, under high viscosity conditions the rate of crossing to the "cis" is less competitive than the rate of fluorescence from the cis<sup>‡\*</sup>, and thus the yield of "cis" is lowered. This is exactly what is observed in the case of salicylideneaniline in isooctane-isononane solution when compared to the same anil in 2-methylpentane solution. The 2-methylpentane solution is much less viscous at 77°K than is the isooctane-isononane mixture and the yield of "cis" is appreciably greater in the less viscous solution.

Under certain conditions coloration may be obtained when fluid solutions are irradiated. At temperatures below -150° the yellow color characteristic of the cis keto tautomer is produced upon irradiation. Lowering the temperature to -196° to produce rigid conditions maintains this color. Absorption and emission spectra show that it is the result of cis keto tautomer. Thus, under fluid conditions the absence of the viscosity barrier between "cis" and cis keto allows all the "cis" produced photolytically to convert immediately to the cis keto. At these low temperatures, few of the cis keto molecules cross the barrier to enol with the result of a net production of cis keto upon irradiation. At higher temperatures, irradiation produces no colored forms since the rates of the thermal back reactions are sufficiently fast to reduce the concentrations below detectable limits.

On the basis of these observations, one may conclude that for any temperature there is an optimum viscosity for photocoloration. The requirements are that it be low enough to allow a high percentage of the molecules in the cis<sup>‡\*</sup> state to cross to "cis", and, yet, be high enough to stabilize the "cis" by hindering the passage over the barrier from "cis" to cis keto.

This potential energy diagram shows the ground state "cis" crossing the cis $^{+*}$  at lower energy than the excited state "cis", thus indicating that the course of the photocoloration is

enol  $\xrightarrow{h_{\nu}}$  enol\*  $\longrightarrow$  cis<sup>‡\*</sup>  $\longrightarrow$  "cis"

The basis for this conclusion is the fact that although emission from the "cis" species may be obtained by excitation into its absorption band after it has been formed, no "cis" emission is ever observed upon irradiation of the enol. If the photolytic formation of the photocolored "cis" species involved crossing from the cis<sup>‡\*</sup> to the excited state of the "cis", then "cis" emission should be observed in this process.

The photochemistry apparently occurs through the singlet states. The rate constant for intersystem crossing is in the range of  $10^8$ - $10^9$ sec<sup>-1</sup>. From the estimated rate of the reaction for the production of  $cis^{+*}$  (10<sup>10</sup>-10<sup>11</sup> sec<sup>-1</sup>), it would appear that crossing to the triplet of the enol could not be competitive. Therefore cis<sup>‡\*</sup> must be formed in the excited singlet state. As mentioned before the rate of reaction for the production of "cis" from cis<sup>+\*</sup> must be on the order of 10<sup>8</sup>- $10^9$  sec<sup>-1</sup>. The production of "cis" could involve crossing to the triplet cis<sup>‡</sup> then to the triplet "cis". However, if this were the case one might expect to see an enhancement in the rate of "cis" formation for a molecule such as 5-bromosalicylidene-o-toluidene because of increased spin-orbit coupling resulting from the presence of the heavy bromine atom. This phenomenon is not observed. Thus, while there is no direct evidence concerning the multiplicity of states involved in the production of the photo-colored "cis" species, the conclusion that singlets are involved exclusively is consistent with the experimental data obtained in this investigation.

The photo-erasure experiments show that no cis keto is produced upon erasure so that the process is as follows

"cis"  $\xrightarrow{hv}$  "cis"\*  $\longrightarrow$  cis<sup>‡</sup>  $\xrightarrow{t}$  cis<sup>‡</sup>  $\longrightarrow$  enol

Theoretically one should be able to observe emission from the cis<sup>‡\*</sup>, however, none is observed during the erasure probably for several reasons. First, the concentration of "cis" is fairly small and thus the potential total number of emitting molecules is also fairly small. Second, the emission lies precisely in the region of "cis" absorption, thus reabsorption could decrease the intensity of the cis<sup>‡\*</sup> emission below detectable limits.

The fact that photo-erasure does not proceed at  $-196^{\circ}$  in rigid solution is explained as follows: At  $-196^{\circ}$ C there is not enough thermal energy to cross the barrier between "cis"\* and cis<sup>‡\*</sup> because the barrier heighth has been increased by the addition of a viscosity component. However in mineral oil solution at  $-75^{\circ}$  there is enough thermal energy available to cross this barrier. Lowering the temperature of the mineral oil solution to  $-100^{\circ}$  results in an appreciably less efficient erasure because of the additional viscosity component to the potential energy barrier resulting from the increased viscosity and decreased thermal energy.available at  $-100^{\circ}$  compared to  $-75^{\circ}$ C.

On the other hand for ethylphthylethylglycolate solution at -75° no erasure is observed although a great deal of "cis" is produced upon irradiation. As has been noted previously for salicylideneaniline in two rigid solutions of greatly differing viscosities, the less viscous

solution produces more "cis" with the same irradiation time. Thus, the lower the viscosity barrier between cis<sup>‡\*</sup> and "cis" the more photocolored form is produced.

The fact that no erasure is observed for the glycolate solution is explained as follows. The thermal Jarrier between "cis"\* and cis<sup>‡\*</sup> must be relatively low because of the observed erasure in mineral oil solution at -75°C. Also, the viscosity barrier for the glycolate solution must be low because of the amount of "cis" produced upon irradiation. Thus, a large percentage of the excited "cis" molecules cross to the cis<sup>‡\*</sup>; however, because of the low viscosity barrier between cis<sup>‡\*</sup> which already has been noted, most of these molecules in the excited state cis<sup>‡</sup> undergo transition back to the ground state of the "cis". As a result of this cycle, little or no net erasure is observed. Some erasure probably occurs; however, it is difficult to distinguish from that caused by thermal fading.

The nitrosalicylideneanilines are negatively thermochromic in that lowering the temperature below room temperature results in the appearance of some cis keto tautomer, but are not photochromic. Both these phenomena are manifestations of the increased strength of the internal hydrogen bond with the nitro-substitution on the salicylaldehyde ring. This substitution decreases the basicity of the oxygen and thus facilitates proton transfer to produce the cis keto tautomer. For this reason the energy of the cis keto tautomer becomes comparable or lower than that of the enol, and at low temperatures the equilibrium shifts toward the cis keto tautomer. In addition the strength of the hydrogen bond greatly increases the potential energy barrier between cis<sup>‡\*</sup> and "cis". The cis<sup>‡\*</sup> is

known to be produced upon excitation of the enol tautomer of the nitrosalicylideneanilines as for the other salicylideneanilines on the basis of the emission data. As previously noted the formation of "cis" from  $cis^{\ddagger*}$  involves twisting about the C=C bond with an accompanying breaking of the internal hydrogen bond. Therefore in the case of the nitrosalicylideneanilines the strength of the internal hydrogen bond causes the potential energy barrier between  $cis^{\ddagger*}$  and "cis" to be so high that the rate of crossing between these states cannot compete with fluorescence, and no photo-coloration is observed.

The action of light of 2-hydroxynaphthylideneaniline represents a departure from the generalizations which can be made concerning the salicylideneanilines. Irradiation of a 3-methylpentane solution at -196° results in the production of more cis keto tautomer in addition to that present at low temperatures. No evidence of the photo production of "cis" is ever noted. Also the photo-produced cis keto may be erased by light at -196°. Thus, this molecule is similar to the nitrosalicylideneanilines in that the strength of the internal hydrogen provides such a high energy barrier between cis<sup>‡\*</sup> and "cis" that none of the photo-colored "cis" is observed. However, because of the increased stability of the keto species for the naphtho-cases as compared to the benzo- cases, the potential energy surface of the cis keto crosses that of the cis<sup>‡\*</sup> at lower energy in the case of 2-hydroxynaphthylideneaniline and thus results in some photo-production of the cis keto tautomer.

In light of the results of this investigation many points in previous studies may now be explained. The observation of De Goauck and

Le Fevre (3) that photochromism of anils does not occur in fluid solutions is correct for "high" temperatures because any "cis" species formed immediately undergoes the fast thermal back reactions

"cis" 
$$\xrightarrow{\Delta}$$
 cis  $\xrightarrow{\Delta}$  enol

The fact that no color is produced upon irradiation does not mean that the photoreaction

enol 
$$\xrightarrow{hv}$$
 "cis"

does not occur but that the thermal back reactions are so fast that no net formation of "cis" results.

The photo-coloration of the crystalline anils (5) is observable only between lower and upper temperature limits. The upper temperature will be due to the process described above for the fluid solutions. The lower temperature limit results because in the crystal the viscosity barrier is already quite high, an' at some point the temperature becomes too low to provide enough energy to cross the barrier separating cis<sup>‡\*</sup> and "cis". In this case only fluorescence is observed. The statement (5) that the photochromic anil crystals were not fluorescent above the lower temperature limit indicates that there is complete conversion from cis<sup>‡\*</sup> to "cis", and that this reaction has such a high rate that the fluorescence process is not competitive. Our observations of the photocoloration of rigid solutions show that fluorescence from the cis<sup>‡</sup> always accompanies the production of the photo-colored "cis" species. It is difficult to understand why in the crystal the rate of production of "cis" should be so much greater than that in rigid solution, and further why there is not a gradual appearance of fluorescence as the crystal is cooled to the lower temperature limit.

As we have shown, the trans keto tautomer proposed (4) as the photo-colored species is not a realistic assumption in view of the small energy requirement necessary to convert the photo-colored species to the cis keto tautomer. Thus, the species which more consistently conforms to the experimental data is a cis keto tautomer in which the internal hydrogen is broken and some twisting occurs about the C=C bond. The close resemblance of this species to a sterically hindered ethylene causes it to have a relationship between the potential energy curves of the ground and excited states similar to that noted by Jaffé and Orchin (20). This explains the Franck-Condon forbidden shape of the absorption and emission spectra.

The explanation of Cohen and Schmidt (4) that photochromism is not observed in those crystals which have plane-to-plane packing because the cis-trans isomerization is sterically prohibited applies equally well if the photo-colored species is identified as the "cis" species. One important difference between the experimental observations for the crystals and rigid solutions is that the crystals show a positive thermochromism, lowering the temperature shifts the enol-cis keto equilibrium toward the enol, whereas for rigid solutions thermochromism is always negative, that is, the equilibrium is shifted toward the cis keto as the temperature

is lowered. In rigid solution thermochromism is a function of solvent and/or substituents; however, in the crystals, thermochromism is a function of crystalline structure only. Thus, the difference must lie in the fact that plane-to-plane packing in the crystal will stabilize the cis keto of any anil, but the energy of the cis keto is still above that of the enol, and lowering the temperature shifts the equilibrium toward the enol. For those anils in solution which show negative thermochromism such as the nitrosalicylideneanilines and 2-hydroxynaphthylideneaniline, the cis keto form is stabilized to such an extent that the cis keto ground state energy is below that of the enol, and lowering the temperature shifts the equilibrium toward the cis keto.

The appearance of the absorption band with intensity maximum near 440 m $\mu$  in polar solvents is due to the formation of some cis keto tautomer. The enhancement of intensity of this band by electron donating groups on the aniline ring (6) is the result of increasing the basicity of the imine nitrogen and thus facilitating proton transfer.

The attempts of Minkin, et al. (11,12), to show that the cis keto tautomer is not a factor in the chemistry and spectroscopy of salicylideneanilines and hydroxynaphthylideneanilines seems to be untenable in light of this and other (8,9) investigations. It is interesting to note that in their investigation of the dipole moments of salicylidenanilines (11). discrepancies were noted for 5-nitrosalicylideneaniline, a compound which we have found to readily form some cis keto tautomer upon lowering the temperature of the solution. The proposals of Nurmukhametov, et al. (13), that the photo-colored species is simply the cis keto tautomer must be modified on the basis of the present investigation. Also their idea that the photo-produced cis keto was formed in the excited state by passing over the potential energy barrier between enol and cis keto via an excited vibronic state of the enol is quite unlikely. This is supported by our discovery that formation of the transition state,  $cis^{**}$ , can occur from the zero vibrational level of the first excited state of the enol from which the photo-colored "cis" species is produced.

Nurmukhametov, et.al. (13), attributed the differences in the fluorescence spectra in going from a hydrocarbon solvent to a proton donating solvent on the basis of a distortion of the quasi-aromatic ring formed by the internal hydrogen bond. On the basis of this investigation and those of Dudek (8) and Ledbetter (9) the difference in the fluorescence spectra must be attributed to the formation of some cis keto tautomer in the presence of hydrogen bonding solvents.

Minkin (12) and Nurmukhametov (15) have assigned the long wavelength absorption band with  $\lambda$  max near 440 m $\mu$  to be an  $n \rightarrow \pi^*$  transition of the enol. Dudek (8) conclusively associated this band with the cis keto tautomer, and the results of the present investigation are in agreement with this interpretation.

IV.

# CONCLUSIONS

#### CONCLUSIONS

1. The forward photoreaction is

enol  $\xrightarrow{h\nu}$  enol\*  $\longrightarrow$  cis<sup>‡\*</sup>  $\longrightarrow$  "cis"

a) Excitation of the enol results in no emission from enol\* and complete conversion to  $cis^{\ddagger*}$  indicating that the rate constant for photochemistry in this case is on the order of  $10^{10}sec^{-1}$ .

b) Because the last step must compete with fluorescence from  $cis^{+*}$ , its rate constant must be  $10^8 - 10^9 sec^{-1}$ .

2. The back photoreaction is

"cis" 
$$\xrightarrow{h\nu}$$
 "cis"\*  $\rightarrow$  cis<sup>‡</sup>  $\xrightarrow{}$  cis<sup>‡</sup>  $\rightarrow$  enol

3. The thermal back reaction is

"cis"  $\xrightarrow{\Delta}$  cis  $\xrightarrow{\Delta}$  enol

4. The cis<sup>‡</sup> species is a high energy transition state closely resembling the cis keto tautomer:



in which the bonds to the SP<sup>3</sup> nitrogen remain in the planar configuration of the enol.



5. The "cis" species is the photo-colored species and is a cis keto anil which has twisted about the C=C bond and broken the internal hydrogen bond in order to remove the strain on the nitrogen in the  $cis^{\ddagger}$  species.

6. In the case of the salicylideneanilines the following reactions do not occur:

cis  $\xrightarrow{hv}$  "cis" enol  $\stackrel{hv}{\longleftrightarrow}$  cis

This latter reaction does occur for 2-hydroxynaphthylideneaniline, although in this case the reaction enol  $\frac{h_{\nu}}{2}$  cis" does not occur.

7. In rigid solution, the high viscosity produces an additional potential energy barrier between cis<sup>‡</sup> and "cis", and between "cis" and cis.

8. The nitrosalicylideneanilines are not photochromic because of a strong internal hydrogen bond in these molecules preventing the formation of the "cis"; however, the cis<sup>‡\*</sup> is formed as indicated by the location of the fluorescence spectrum.

9. The energy difference between enol and cis keto is small and varies under different conditions and for different anils as reflected by the presence of and type of thermochromism.



↑ E

eno]-

cis keto

cis keto enol thermochromic crystalline anils (positive thermochromism)

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