A spectroscopic study of proton transfer and photochromism in N-(2-hydroxybenzylidene)aniline

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J. W. LEWIS and C. SANDORFY. Can. J. Chem. 60, 1738 (1982).

The infrared spectral characteristics of N-(2-hydroxybenzylidene)aniline, its deuterium substituted analogue, N-(2-hydroxybenzylidene)-m-toluidine, and their photoproducts have been investigated. The infrared spectrum of a low temperature polycrystalline film of N-(2-hydroxybenzylidene)aniline exhibits new absorption bands at 3380, 1646, 1537, 1502, 1319, and 1310 cm⁻¹ upon irradiation at 365 nm. Likewise, the spectrum of the m-toluidine derivative exhibits new absorption bands at 3320, 1650, 1535, 1503, 1321, 1310, and 995 cm⁻¹ upon irradiation at 365 nm. These new data, in conjunction with the newly acquired data on the hydrochloride and deuterochloride of the title compound, indicate that the photoproduct is a zwitterion, not an *ortho*-quinone. It is also inferrred that the photoproduct exists in a conformation which is *cis* about the central carbon-nitrogen double bond.

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Les spectres infrarouges de l'*N*-(2-hydroxybenzylidène)aniline (HBA), de son analogue deutérié, de l'*N*-(2-hydroxybenzylidène)-*m*-toluidine et ceux de leurs produits obtenus par irradiation ont été examinés. Dans le spectre infrarouge de l'HBA de nouvelles bandes apparaissent à 3380, 1646, 1537, 1502, 1319 et 1310 cm⁻¹ après irradiation à 365 nm. D'une manière analogue le spectre du dérivé *m*-toluidinique présente des bandes nouvelles à 3320, 1650, 1535, 1503, 1321, 1310 et 995 cm⁻¹ après irradiation à 365 nm. Ces données nouvelles à obtenues pour l'hydrochlorure et le deutérochlorure du HBA indiquent que le produit de l'irradiation est un zwitterion et non pas une *ortho*-quinone. En outre, on peut conclure que le produit d'irradiation a une configuration *cis* par rapport à la liaison centrale C=N.

Introduction

In recent years, there has been much interest in the thermochromic and photochromic activities of salicylaldehyde anils. Many publications on various aspects of these phenomena have appeared. For example, Cohen et al. (1-10) have reported that some crystalline anils are photochromic while others are thermochromic, but none of the anils was found to exhibit both properties. Insofar as different crystalline modifications of an anil are concerned, however, one modification might be thermochromic while another is photochromic. These studies also provided proof that the 2-hydroxy group of the salicylaldehyde portion of the anil is a necessary, but insufficient, condition for the observation of the photochromic or the thermochromic phenomenon in the solid state. The sufficient condition was established to be related to the molecular packing in the crystal. A "loose" packing which permits movement of parts of the molecule upon absorption of ultraviolet light was found to be necessary for the observation of photochromism. In a similar manner, a "tight" packing in the crystal was related to the thermochromic behavior of some solid anils. These investigators also demonstrated that in rigid glassy matrices all anils derived from salicylaldehyde and substituted salicylaldehydes are photochromic, independently of whether or not they are so in crystalline form.

In 1962, Cohen and Schmidt (3) proposed mechanisms for the two phenomena. These mechanisms involve the existence of the three tautomers shown in Scheme 1.

In these formulae the labels *cis* and *trans* refer only to the relative positions of the oxygen atom and the hydrogen atom that is covalently bound to the nitrogen atom, and not to any specific conformation of the molecule. The thermochromic process thus involves a simple proton transfer that is made possible by means of certain unspecified intermolecular interactions. The photochromic process involves a proton transfer and a geometric rearrangement (an isomerization about the ring carbon – azomethine carbon bond).

A number of publications on the subject of photochromic anils have appeared since 1962 (4–10, 11-26). With few exceptions, these papers



0008-4042/82/131738-09\$01.00/0

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¹Revision received March 1, 1982.

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would appear to confirm the basic proposals of Cohen and Schmidt. That is, the *cis*-quinoid should be identified with the species produced in the thermochromic process as well as the second species found in solutions of anils in hydrogenbonding solvents, and the *trans*-quinoid should be identified with the species produced photochemically. The exceptions include those of Cohen and Flavian (7, 8), Richey and Becker (14), Rosenfeld *et al.* (18), Wettermark and Dogliotti (15), and Anderson and Wettermark (16).

In their investigation of the luminescence properties of the anils, Cohen and Flavian proposed that ionic species are involved in the long wavelength absorption and emission. Richey and Becker suggested that the final photocolored product is a nonequilibrium form of the true *cis*-quinoid tautomer. Rosenfeld and co-workers, on the basis of theoretical calculations and experimental results, suggested that more than one photocolored species is produced in the forward photochemical reaction. Wettermark and Dogliotti, as well as Anderson and Wettermark, proposed that there are two equilibria in the photochemical reaction. One equilibrium involves proton transfer and tautomerization and the other involves a *trans* \rightarrow *cis* isomerization about the central carbon-nitrogen double bond. Other authors (5, 6, 22) have also suggested that more than three molecular species may be involved in these processes.

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Hadjoudis *et al.* (26) have studied the thermochromic and photochromic properties of a series of Schiff bases derived from 2-hydroxybenzaldehydes and 2-aminopyridines. It was found that none of these compounds, in the form of crystalline films, was photochromic. The crystalline films did show thermochromic effects and, in solution, the compounds were photochromic. These authors concluded that in the crystalline state the compounds are essentially planar and thermochromic, whereas in solution the molecules are able to assume various geometries and are photochromic.

Despite this apparent wealth of spectroscopic data, very little direct structural information concerning the forward (photochemical) and the reverse (photochemical or thermochemical) reaction products of the anils is to be found in the literature. The lack of infrared spectral changes, upon the irradiation of these compounds with ultraviolet light, has been attributed to the unfavorably small quantity of the photoproduct that is attainable by means of ordinary laboratory techniques.

Due to the structural and electronic similarity of these compounds to *N*-benzylideneaniline, it is convincing to argue that the photochemistry should also be somewhat similar. The spectral properties are, however, further complicated by internal hydrogen bonding and by proton transfer in the excited state. In this paper, the nature of the stable photoproduct of N-(2-hydroxybenzylidene)aniline will be discussed. On the basis of this investigation it is concluded that it is not necessary to invoke the presence of *ortho*-quinone tautomers to explain the spectral changes that are observed to occur.

Experimental

N-(2-Hydroxybenzylidene)aniline (HBA) and *N*-(2-hydroxybenzylidene)-*m*-toluidine were prepared and purified by the methods described in the preceding papers. The deuterium substituted anil was prepared by refluxing the parent anil in a one-to-three mixture of D_2O and methanol- d_1 . The process was repeated twice and the final product contained > 90%—OD. The thin polycrystalline films of the anils were produced from a melt between either quartz or sodium chloride plates. Ultra thin films were produced by means of the technique described by Cohen *et al.* (9).

The light source used for the irradiation of the compounds was an Oriel Model 7340 equipped with a 200 W medium pressure mercury arc. The excitation wavelengths were isolated by means of an Oriel Model 7240 monochromator. The bandwidths of the excitation lines were approximately 20 nm, according to the manufacturer's specifications.

The low temperature infrared cell was constructed after the pattern described by Wagner and Hornig (27). The ultraviolet-visible absorption spectra were recorded by means of a Cary 17 spectrometer and the infrared spectra were recorded by means of a Perkin-Elmer 621 spectrometer. The reported infrared frequencies were calibrated to the known bands of polystyrene.

Results and discussion

A. Ultraviolet-visible measurements

Several absorption spectra of thin polycrystalline films of N-(2-hydroxybenzylidene)aniline (HBA) are reproduced in Fig. 1. The visible absorption spectra of the irradiated films exhibit a broad new absorption band with maximum absorbance near 480 nm. In contrast to the featureless absorption band near 440 nm that is observed in the spectra of anils in hydrogen-bonding solvents, the photochemically produced band of this anil has some structure. The spectrum shows shoulders at about 550, 510, and 460 nm in addition to the maximum at 478 nm. The absorption band observed in these spectra has been assigned to a $\pi^* \leftarrow \pi$ transition of the *trans*-quinoid tautomer (3).

The new absorption band reproduced in Fig. 1 is observable only after the irradiation of the anil. (In this work the irradiation was normally carried out at 365 nm since this is the most intense line in the ultraviolet portion of the medium pressure mercury arc spectrum.) The new absorption band is erased or bleached by irradiation at any wavelength which

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FIG. 1. Absorption spectra of N-(2-hydroxybenzylidene)aniline; upper curves: ultra-thin polycrystalline film, ----- before irradiation, --- after irradiation at 365 nm; lower curves: thin polycrystalline film; lower right: absorbance at 478 nm as a function of time of irradiation.

lies within this band. It is then obvious that once a sufficient, and small, quantity of the photoproduct has accumulated, the photoproduct begins to absorb the 365 nm radiation and the bleaching commences. In this manner, a limiting concentration of the photoproduct is quickly attained. The development of absorbance at 478 nm as a function of time of irradiation is shown in the bottom right of Fig. 1. In addition to the screening effect or inner filter effect, thermal bleaching is also a contributor to the observed nonlinearity. In these room temperature experiments there is considerable deviation from linearity even after only two minutes of irradiation, although there continues to be an increase in 478 nm absorbance throughout at least fifteen minutes of irradiation.

The thermal bleaching is effectively eliminated by lowering the sample temperature to 77 K, where the photocolor is stable for long periods of time. The inner filter effect is not eliminated, however, by lowering the temperature. Both the forward and the reverse photochemical transformations of crystalline HBA occur at 77 K, but the quantum yields of both are greatly reduced as compared with the room temperature yields. Therefore, some advantage in the form of slightly higher concentration of photoproduct and the elimination of thermal bleaching is gained by lowering the sample temperature to 77 K, but only at the expense of greatly lengthened irradiation times.

It should also be mentioned that the recorded absorption spectra are not corrected for thermal bleaching nor for the photochemical bleaching caused by the measurement process. It is estimated that these errors amount to less than about 8%. (This estimate was made by scanning the entire spectrum, then rapidly returning to various wavelengths within the absorption band and measuring the decrease in absorbance.) The overall shape of the absorption spectra should not, therefore, be greatly affected.

In an attempt to reduce the inner filter effect, irradiation of low temperature thin films of polycrystalline HBA was carried out at 340, 330, 313, and 303 nm. In each case there was no significant change in the amount of photoproduct attained. This could mean that the photoproduct also absorbs at these wavelengths or simply that, due to the diminished intensity of the source at these wavelengths, a much longer period of irradiation is necessary.

At this point, it is perhaps of interest to make

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some comments relative to the apparent molar absorption coefficient of the photoproduct. The spectra of an irradiated and a nonirradiated ultra thin film are also shown in Fig. 1. Clearly the increase in absorbance at 478 nm is at least ten times greater than the decrease in absorbance at 340 nm. If it is assumed that absorbance at 340 nm is linear with concentration of the enol, then it must be concluded that the coefficient of the photoproduct is ten times that at the solid enol. It is, of course, a distinct possibility that enol absorbance at 340 nm is not linear with concentration despite the fact that the total absorbance is less than 1.0. Cohen et al. (5, 6) report the spectra of irradiated and nonirradiated low temperature solutions of several N-salicylideneanilines and in all cases it appears that the increase in absorbance at the visible wavelength is greater than the decrease in absorbance at the near ultraviolet wavelength. In no case, however, is the ratio so large as in the case of the ultrathin polycrystalline film reported here. Some of the photoproduct spectra reported by Cohen and coworkers may also indicate an additional new absorption band in the region of the lowest energy band of the enol. The spectra reported in this present work do not give such an indication. While no conclusions may be made, it appears that the absorption coefficient of the photoproduct exceeds that of the enol. In any case, it is a matter which requires further investigation.

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On the basis of similar electronic structure, it might be assumed that the photochemistry of HBA and N-benzylideneaniline (BA) are also closely related. The scheme shown (Scheme 2) might be proposed for overall photoproduct formation. Like BA, the initial enol of HBA exists in a conformation which is *trans* about the C=N bond and the aniline ring is somewhat twisted out of the molecular plane. (Note that *trans* and *cis*, as used here, describe the conformation about the C=N bond and not the relative positions of the hydrogen and oxygen atoms as was the case in Scheme 1.) The absorption of a photon causes an ultrafast proton transfer (24) which might be followed by a slower inversion at the nitrogen. The inversion results in a conformation which is *cis* about the C=N bond. This model differs considerably from that proposed by other investigators. It has been argued that the trans-quinoid (see Scheme 1) is produced by means of a rotation about the ring carbon – imine carbon bond (13), but there is no valid reason to suspect that the photochemistry of HBA and BA should be so different.

It is well known that protonation of the imine nitrogen actually stabilizes the *cis*-conformation of



BA (28). For example, the irradiation of room temperature solutions of BA produces no stable photoisomers, although the *cis*-conformer may be observed by means of flash techniques (29). The irradiation of room temperature solutions of BA in 96% sulfuric acid, on the other hand, results in the formation of the thermally stable *cis*-*N*-benzyl-ideneanilinium cation (28). In this solvent system BA is protonated in the ground state, hence the protonated imine nitrogen inhibits the return to the *trans*-conformation. It would be of interest to know whether a similar phenomenon occurs in solvent systems wherein BA is not protonated in the electronic ground state but in which protonation could occur in the excited state.

The ultraviolet-visible absorption spectrum of irradiated solutions of thin polycrystalline films of HBA may then contain contributions from three species. These are the original intramolecularly hydrogen bonded enol, an enol that is not internally hydrogen bonded, and the *cis* "ion-pair". The spectrum is dominated by the absorption of the original hydrogen bonded enol because inner filter effects (reverse, $cis \rightarrow trans$ photoisomerization) limit the concentration of the *cis* "ion-pair".

B. Infrared measurements

According to the arguments presented in the previous sections, the infrared spectrum of an irradiated thin polycrystalline film of HBA should reflect changes similar to those of an irradiated film of BA. In addition to the spectral changes that result from the *trans* \rightarrow *cis* isomerization, changes indicating the transferred proton and changes involving the phenolate anion are to be expected. It should be added that perhaps very little change in the Ar—N stretching frequency is expected since there can be little favorable nitrogen lone pair – aniline ring interactions (see Scheme 2).

The 3500-2500 and 1700-1500 cm⁻¹ regions of the spectra of irradiated and nonirradiated thin films of HBA are shown in Fig. 2. As was expected, the new photoproduct bands are weak but assignments are entirely possible. The three new bands at

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FIG. 2. Infrared absorption spectra of N-(2-hydroxybenzylidene)aniline; upper curve: thin polycrystalline film before irradiation, 77 K; lower curve: thin polycrystalline film after irradiation at 365 nm, 77 K.

3380, 1646, and 1537 cm⁻¹ are directly associated with the development of the 478 nm optical absorption band. These bands may be bleached by re-irradiating the sample at 547 nm, for example, or by allowing the sample to warm. The irradiation and re-irradiation of the sample may be repeated at will without any sign of fatigue or photodecomposition. The new bands in the spectrum of the irradiated sample shown in Fig. 2 result from six hours of continuous irradiation at 365 nm of a film maintained at 77 K. A similar intensity of the 1646 cm⁻¹ band may be developed by only 30 min of irradiation at 365 nm of a room temperature sample; however, in the infrared beam of the spectrometer, the photocolor fades very rapidly as attempts to record a spectrum are made. For example, during the time required for the normal recording of the spectrum from 1700 to 1500 cm^{-1} , the 1537 cm⁻¹ band will have decreased in intensity by more than one-half. It is thus not surprising that ordinary infrared spectra of the photoproduct have not previously been published.

Nakagaki *et al.* (23) have obtained a difference spectrum, by means of Fourier transform infrared techniques (FTIR), of N-(2-hydroxybenzylidene)-m-toluidine. These authors' results are summarized in Table 1. In view of our observations, it seems to be necessary to modify some of these assignments.

(a) It is rather unusual that the C=N stretching frequency of a deuterium substituted Schiff base should be higher than that of the hydrogen derivative. It is true that intramolecular hydrogen bonding does not produce the magnitude of spectral

TABLE 1. Infrared bands of N-(2-hydroxybenzylidene)-m-toluidine after Nakagaki et al. (23)^a

Assignment	Frequency (cm ⁻¹)(—OH)	Frequency (cm ⁻¹)(OD)
	1616	1620
Ring skeletal stretching	1597	1597
	1570	1570
C=0	1651	1644
A mide vinylog and ring	1539	1529
skeletal stretching	1510	1505
skeletal stretelling	1487	1487
C—N	1319	1319

"The recorded data were obtained from an FTIR difference spectrum of a KBr disc at room temperature.

shifts that might be expected on reasonable theoretical grounds and intermolecular hydrogen bonding has essentially no effect at all, but the shifts, when observed, are generally in the proper direction.

(b) The band assigned by Nakagaki and coworkers as due to a C=O stretching and two of the three bands assigned to modes of a "quinoid ring and the amide vinylog, HN-C=C-C=O", of the photoproduct exhibit deuterium isotope shifts of 7, 10, and 5 cm^{-1} , respectively. On the other hand, the C-N (single bond) stretching mode, which is subject to a greater isotope effect since this bond is nearer to the site of deuterium exchange, shows no isotope effect at all. The proposed structure of the photoproduct, a trans-quinoid (see Scheme 1), is not capable of exhibiting hydrogen (deuterium) bonding, hence the reported isotope shifts must be due to a mass effect. The mass effect must be transmitted along the DN-C=C-C=O chain and, as a result, the lack of an effect on the adjacent C-N bond is hard to understand.

(c) One of the 1579, 1510, and 1487 cm⁻¹ bands must be the so-called amide II band. Amide II bands are normally ascribed to an interaction between the N—H bending and the C—N stretching modes (30–32). The resultant two bands, amide II and amide III, are sensitive to isotope effects. Deuterium shifts are smaller than expected but still amount to about 6% (32) or approximately 100 cm⁻¹ in the case of the amide II band. The small deuterium frequency shifts observed by Nakagaki and co-workers are then not easily reconcilable with an amide II band assignment.

In the present work, experiments have also been carried out with HBA- d_1 , and the spectra are reproduced in Fig. 3. Before further discussion of the photoproduct spectral bands, it is of interest and indeed necessary to examine the spectrum of a polycrystalline film of nonirradiated HBA- d_1 . It is observed that this spectrum exhibits bands at 1614,

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FIG. 3. Infrared absorption spectra of N-(2-hydroxybenzylidene)aniline- d_1 ; upper curve: thin polycrystalline film before irradiation; lower curve: thin polycrystalline film after irradiation at 365 nm.

1589, 1578 (shoulder), and 1558 cm⁻¹. The corresponding spectrum of HBA shows bands at 1615, 1590, 1578 (shoulder), and 1571 cm⁻¹. It is quite obvious that the shift of the 1571 cm⁻¹ band to 1558 cm⁻¹, upon deuterium exchange, cannot be explained if its assignment as a pure ring skeletal vibration is retained. In the preceding article it was shown that the band at 1571 cm⁻¹ in the spectrum of polycrystalline HBA is influenced by Fermi resonance with the 1615 cm^{-1} C=N stretching mode. For HBA- d_1 the same arguments are applicable if the changed conditions for Fermi resonance are taken into account. The expected downward deuterium shift of the C=N stretching band is not accurately represented by the negligible 1 cm^{-1} shift of the 1615 cm⁻¹ component. Deuterium substitution leads to increased repulsion between the two states and leads to the apparent lack of a shift of the 1615 cm⁻¹ band and the observed shift of the 1571 cm^{-1} band to 1558 cm^{-1} . The extent of the deuterium shift on the C=N stretching frequency is, therefore, not known since the true position of the C=N stretching frequency is in question.

Percy and Thornton (33), in a study of 28 N-(2-hydroxybenzylidene)anilines, assign a pair of bands in each infrared spectrum as due to the C=N stretching mode. In these examples the high frequency band occurs in the range from 1629 to 1613 cm⁻¹ and the low frequency band occurs in

the range from 1582 to 1568 cm^{-1} . Further, these authors discuss the infrared spectra of 38 Co(II), Ni(II), Cu(II), and Zn(II) chelates derived from these Schiff bases. A pair of bands attributable to the C=N stretching mode were found in 37 of the 38 infrared spectra. In these examples the high frequency bands were found in the 1618 to 1602 cm⁻¹ range and the low frequency bands were found in the 1597 to 1574 cm^{-1} range. They also invoked Fermi resonance in order to interpret their spectra.

A comparison of Figs. 2 and 3 reveals that the photoproduct bands of HBA at 1646 and 1537 cm⁻¹ are apparently shifted to 1642 and 1529 cm⁻¹, respectively, in the spectrum of the deuterium substituted photoproduct, HBA- d_1 . It will also be noted that the ordinary infrared spectra of the HBA and HBA- d_1 photoproducts exhibit only one band in the 1550-1510 cm⁻¹ range, whereas Nakagaki and co-workers report two bands in this region of the FTIR difference spectra of the N-(2-hydroxybenzylidene)-m-toluidine photoproduct and its deuterium substituted photoproduct. Obviously, the comments made earlier with respect to the assignments of Nakagaki and co-workers are also applicable here in the case of HBA and HBA- d_1 . The small apparent isotope effects that are observed are not consistent with the assignment of these bands to the C=O stretching and the C=C or H—N (D—N) + C—N (amide II) stretching modes. On the one hand, a large (100 cm^{-1}) deuterium shift is expected for an amide II band and the observed shift is only 8 cm^{-1} , and, on the other hand, only a negligible deuterium shift is expected for a C=O stretching vibration and a 4 cm⁻¹ shift is observed. It is quite possible, however, that the 1537 cm⁻¹ band observed in the spectrum of the HBA photoproduct is of different origin than the 1529 cm^{-1} band of the HBA- d_1 photoproduct.

The band at 3380 cm^{-1} in the spectrum of the HBA photoproduct is attributed to the N⁺—H stretching vibration. This spectrum provides the first recorded experimental evidence related to the disposition of the phototransferred proton. Clearly the sharpness of this band and its relatively high frequency (34, 35) eliminate the possibility of hydrogen bonding to the phenolate oxygen or to neighboring molecules. Unfortunately, an N⁺—D stretching band was not located in the spectrum of the HBA- d_1 photoproduct. It is likely, however, that the N⁺—D stretching band is much weaker than the already weak N⁺—H stretching band.

It is proposed, therefore, that the 1646 and 1537 cm^{-1} bands in the spectrum of the HBA photoproduct are attributable to the C=NH⁺

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stretching and the N-H deformation modes. These modes are not completely independent. It was shown previously that these modes of the HBA hydrochloride are strongly coupled, so there is every reason to suspect that they would also be coupled in this case. The differences between the frequencies of the photoproduct bands and those of the hydrochloride may be rationalized in terms of changes in the degree of coupling. For example, the photoproduct is necessarily a zwitterion, which is probably in a *cis*-conformation about the C=N bond, while the hydrochloride is a true salt. In addition, the spectrum of the hydrochloride was obtained from a solution while that of the photoproduct was obtained from a polycrystalline film. These environmental perturbations could exaggerate the frequency differences.

The stretching frequency of a C=NH⁺ group is expected to decrease some $25-35 \text{ cm}^{-1}$ (36) when the hydrogen is replaced by a deuterium atom. The observed frequency shift in the spectrum of the HBD- d_1 photoproduct is only 4 cm^{-1} . Meanwhile the HBA photoproduct band at 1537 cm⁻¹ apparently shifts to $1529 \,\mathrm{cm}^{-1}$ in the spectrum of the HBA- d_1 photoproduct. These small isotope shifts would appear to invalidate the above assignments for the photoproduct of HBA, but it must be recalled that the lower frequency infrared bands in the spectra of the hydrochloride and deuterochloride of HBA were interpretable only (paper II) when different degrees of Fermi resonance, by which the bands are affected, are considered. There are small differences between the corresponding band positions of the photoproduct and the deuterochloride, but these may be satisfactorily accounted for by differences in the structure of the two species and by changes in the amount of resonance.

The infrared spectra of a polycrystalline film of N-(2-hydroxybenzylidene)-m-toluidine, recorded before and after irradiation at 365 nm, are presented in Fig. 4. These spectra are severely distorted in the range from 1650 to 1550 cm^{-1} , as may be ascertained by a comparison with the accompanying spectrum which was obtained from a chloroform solution of the compound. Numerous attempts to obtain a better quality film were not successful and KBr discs, even after repeated grindings, failed to yield a quality spectrum in the $1650-1550 \,\mathrm{cm}^{-1}$ region. In order not to complicate the spectra only those regions wherein major spectral changes occur are reproduced in Fig. 4. Despite the quality of the spectra, new photoproduct bands are observable at near 3320, (1650), 1535, 1503, 1321, 1310, and 995 cm⁻¹. Note that the band



FIG. 4. Infrared absorption spectra of N-(2-hydroxybenzylidene)-*m*-toluidine; upper curves: ----- thin polycrystalline film before irradiation, — thin polycrystalline film after irradiation at 365 nm, 77 K; lower curve: chloroform solution.

located near 1650 cm^{-1} appears only as a slight broadening.

For the reasons outlined earlier the 3320 cm⁻¹ band is attributable to the N⁺--H stretching mode and the pair of bands at (1650) and 1535 cm^{-1} are attributable to the coupled C==NH⁺ stretching and N⁺—H deformation modes. It is probable that the band located near 1503 cm⁻¹ reflects a slight shift of an aromatic skeletal stretching motion, which is produced by the geometric rearrangement. This assignment is made since a similar band is observed in the spectrum of irradiated N-benzylideneaniline, which is not capable of undergoing any structural change except *trans* \rightarrow *cis* isomerization. The two bands at 1321 and 1310 cm⁻¹ may be related to the phenolate anion; however, it should be mentioned that a pair of bands occurs at these frequencies in the spectrum of the nonirradiated compound. It is likely therefore that these spectral changes represent intensifications of existing bands and do not represent new vibrational modes such as the C-N stretching as proposed by Nakagaki et al. (23). The weak band located near 995 cm⁻¹ is of undetermined origin but may reflect a vibration of the aromatic phenolate nucleus.

The 1500-700 cm⁻¹ region of the infrared spectra of nonirradiated and irradiated films of HBA is not presented since these spectra are very similar to those of N-(2-hydroxybenzylidene)-*m*-toluidine. New but weaker photoproduct bands are observed near 1502, 1319, and 1310 cm^{-1} and these bands

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show no deuterium isotope effects. No new photoproduct band was observed near 1000 cm^{-1} , but an intensification of a band near 863 cm^{-1} is noted.

The infrared study of the photochromic properties of other Schiff bases was also attempted. Films of Schiff bases derived from salicylaldehyde and p-methoxy-, p-bromo-, p-chloro, p-iodo-, and 2,5-dimethylaniline and *p*-aminoacetophenone were formed and tested. Only the film formed from N-(2-hydroxybenzylidene)-p-aminoacetophenone proved to be slightly photochromic, although no useful infrared bands of the photoproduct could be found in the spectrum. This latter compound proved, however, to be most interesting. The solid compound, as obtained by crystallization from ordinary solvents, is highly photochromic, perhaps even more so than any of the compounds studied. Crystals that are derived from a melt, on the other hand, were very weakly photochromic. The 3500-3000 and 1800-1500 cm⁻¹ regions of the infrared spectra of a perchloroethylene solution and a crystalline film (derived from a melt) are shown in Fig. 5. The solid state spectrum is greatly distorted in the $1800-1500 \text{ cm}^{-1}$ region and the carbonyl C=O stretching is split into two bands. Apparently this is due to intermolecular hydrogen bonding between the phenolic O-H and the C=O of the acetyl group. There is also evidence (the sharp band at 3400 cm⁻¹) that at least some of the molecules exhibit free phenolic O-H groups. Thus several different species exist in the melt-derived crystals. The solution spectrum shows no evidence of free



FIG. 5. Infrared absorption spectra of N-(2-hydroxybenzylidene)-p-aminoacetophenone, ----- perchloroethylene solution, ----- thin polycrystalline film.

O—H groups nor of intermolecular hydrogen bonding. It is therefore highly probable that for this particular compound the photochromic character is strictly dependent on the internal chelate ring involving the O—H...N hydrogen bond. Apparently intermolecularly hydrogen bonded and nonhydrogen bonded molecules do not exhibit photochromism.

Conclusion

The infrared spectra of N-(2-hydroxybenzylidene)aniline, its deuterium substituted counterpart, N-(2-hydroxybenzylidene)-m-toluidine, and their photoproducts have been presented. These new data, in conjunction with the information gained in the studies of N-benzylideneaniline and its photoproduct and of the solvent dependent processes of these compounds, permit well founded assignments of the observed bands in the infrared spectra of the photoproducts. The photoproduct is thus determined to be a zwitterion, not an *ortho*-quinone. It is further noted that the *cis*conformation about the C=N bond is required since hydrogen bonding between the C-O⁻ and N⁺--H groups does not exist.

Acknowledgements

Financial assistance from the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Education du Québec, and the Canada Council through the grant of the Killam Memorial scholarship to C. Sandorfy is gratefully acknowledged.

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