The Dimorphism and Electronic and Vibrational Spectra of 2-Anilino-1,4-naphthoquinones

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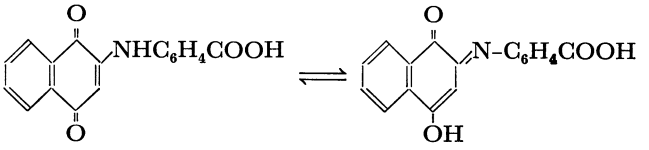
Dimorphic forms were isolated for over ten derivatives of 2-anilino-1,4-naphthoquinone, 2-anilino-3-chloro-1,4-naphthoquinone, and 2-anilino-3-bromo-1,4-naphthoquinone carrying substituents on the phenyl ring. One of the two forms exhibits a relatively sharp vibrational band near 3300 cm^{-1}, the other, a relatively broad band at a lower wave number. The spectra in the region from 700 to 1700 cm^{-1} are often markedly different from each other. In several instances, the two forms are differently colored. This difference is attributed to the appearance of, or a change in the intensity of, an intermolecular charge-transfer absorption band. Not only the dimorphic forms, but also most of the derivatives examined, could be classified into two groups on the basis of the location and the sharpness of the vibrational band appearing in the region from 3150 to 3350 cm^{-1}.

A large number of the condensation products of 1,4-naphthoquinone and its 2,3-dihalo derivatives with various anilines have been synthesized and examined for possible use as vat dyestuffs and as bactericides.[1-9] Among them, 2-(*p*-carboxyanilino)-1,4-naphthoquinone was isolated as yellow and red crystals by Hauschka.[7] The tautomerism involving *p*-quinonoid and *o*-quinonoid forms:



was pointed out as a possible cause of the marked difference in color. However, he added that the spectroscopic study failed to provide concrete evidence in support of this assumption. Because of the recent work on a related compound by Bloom and Dudek, a further study of the suggested tautomerism seemed to be desirable. These authors found that the electronic absorption spectrum of 4,8-dianilino-1,5-naphthoquinone is solvent-dependent.[10] In polar, associating solvents, the lowest-energy absorption appearing at 661 nm is of maximum intensity and decreases with a decrease in the solvent-associating ability. Further evidence for the existence of a tautomeric equilibrium in solution has been provided by their work on the proton magnetic resonance of the ^{15}N-substituted compound.

As we have reported for the dimorphic forms of *o*- and *p*-anisyl-*p*-benzoquinones,[11] there is another possible explanation for the difference in color. The molecule consists of an electron-donating and an accepting moieties; therefore, the color of the crystal may depend upon the intermolecular charge-transfer absorption, the location and the intensity of which can be modified, to some extent, by the mode of molecular stacking. No matter which is the cause, the dimorphism is certainly influenced by the kind and the position of substituent, and one may isolate more dimorphic forms by examining closely related compounds. Spectroscopic studies of many pairs of such modifications may be fruitful in deciding the origin of this phenomenon. Accordingly, a careful examination of various 2-anilino-1,4-naphthoquinones and its 3-chloro and 3-bromo derivatives was set up.

Experimental

Materials. The naphthoquinone and its 2,3-dichloro derivative were obtained commercially. The 2,3-dibromo-1,4-naphthoquinone was prepared following the method reported by Miller.[12] The condensation reaction between the naphthoquinones and anilines was carried out in boiling ethanol unless otherwise stated. The isolation of dimorphic forms was attempted by sublimation in a vacuum and by recrystallization from appropriate solvents, and under various conditions. Hereafter, X denotes the substituent on the phenyl group, and Y, the atom attached to the 3 position of the quinone.

Measurements. The vibrational spectra in the rock-salt region were recorded on a Jasco IR-G infrared spectrophotometer as Nujol mineral oil or hexachlorobutadiene mulls.

The diffuse reflectance of solid samples was measured using a Beckman DK-2A spectroreflectometer in the range from 325 to 700 nm. The anilinoquinone crystals were pulverized with sodium chloride in a concentration of the order of one weight percent. The spectra were recorded as the difference between the mixture and pure sodium chloride and were plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. In all the figures in this paper, the electronic spectra are plotted taking the maxima of the lowest-energy absorption arbitrarily as 1.00.

Results

2-(Carboxyanilino)-1,4-naphthoquinones (X=COOH, Y=H). The vibrational spectra of the yellow form and the red form of the *p*-derivative obtained by vacuum sublimation are presented in Fig. 1. There is a marked difference in the region from 3150 to 3350 cm^{-1}. The yellow form exhibits a sharp absorption band at 3310 cm^{-1}, and the red form, a rather broad one at 3220 cm^{-1}. They may be assigned to the N–H or O–H stretching vibration. As their locations are known to be strongly affected by hydrogen bonding, it is difficult to decide whether or not the shift is an indication of the tautomerism. For example, 2-hydroxy-1,4-naphthoquinone, which is isomeric with 4-hydroxy-1,2-naphthoquinone, shows a very broad O–H stretching band at 3150 cm^{-1}, suggesting the presence of strong hydrogen bonding. On the other hand, 2-amino-3-hydroxy-1,4-naphthoquinone gives a sharp band at 3450 cm^{-1} and a broad one at 3300 cm^{-1}. As is shown in Fig. 1, the dimorphic forms significantly differ from

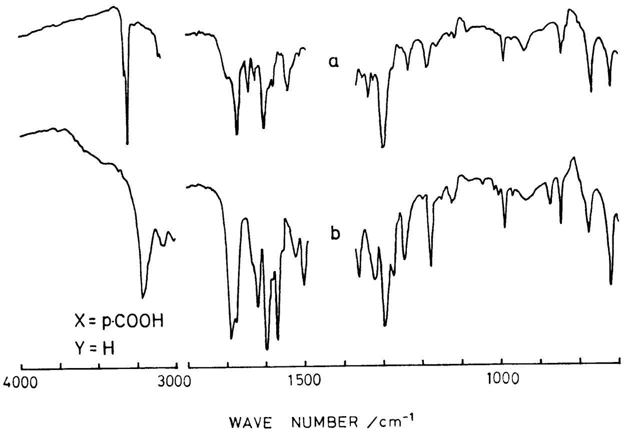


Fig. 1. Vibrational spectra of 2-(*p*-carboxyanilino)-1,4-naphthoquinone: (a) the yellow form and (b) the red form.

each other also in the pattern of the region from 1000 to 1700 cm^{-1}.

The electronic spectra of the yellow and red forms are given in Fig. 2. The absorption maximum is located at 435 nm in the yellow form and at 510 nm in the red form. As the location of the shoulder appearing in the former spectrum coincides exactly with the maximum in the latter, our yellow sample may be contaminated with a small amount of the red form. The maximum in the yellow form is close to the one observed in an acetone solution, 450 nm. No appreciable change was detected either in the location or in the intensity when methanol, ethyl acetate, chloroform, and pyridine were employed as the solvents. The temperature-dependence measured in the last mentioned solvent revealed that the absorption maximum decreases and shifts a little bit to the short wavelength side when the temperature is elevated, *e.g.*, 464 nm at 18 °C and 457 nm at 66 °C. The isosbestic points appearing at 360 and 422 nm probably arise from this shift. The present molecule is flexible, and the electronic transition considered is of the charge-transfer type; therefore, the temperature-dependence may be interpreted in terms of the thermal excitation of the distortion modes, as has been suggested by Kordes *et al.*[13]

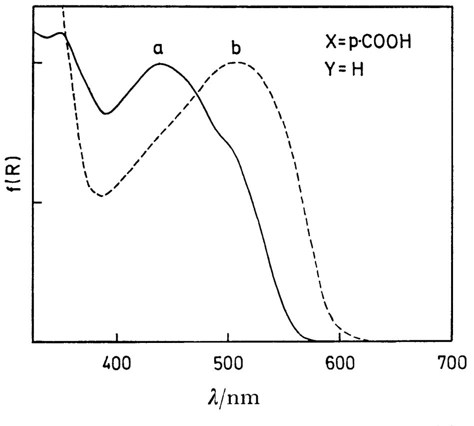


Fig. 2. Electronic spectra of 2-(*p*-carboxyanilino)-1,4-naphthoquinone: (a) the yellow form and (b) the red form.

In accordance with the observation by Hauschka, the *o*-derivative is obtainable as orange-red crystals, and the *m*-derivative, as red crystals. In the region near 3300 cm^{-1}, no vibrational band is found for the former compound, but a sharp band at 3280 cm^{-1} is found for the latter. The electronic spectrum of the *o*-derivative has a maximum at 475 nm, and the *m*-derivative, one at 520 nm.

Other 2-Anilino-1,4-naphthoquinones (Y=H). Among the sixteen compounds examined, only the *p*-methoxy and *m*-ethoxy derivatives were found to be dimorphic. When the condensation reaction between the quinone and *p*-anisidine was carried out in boiling ethanol, reddish violet crystals were deposited. The same form could be obtained by recrystallization under various conditions and also by sublimation in a vacuum. This stable form gives a broad vibrational band at 3215 cm^{-1}. Because of the reasoning to be presented later, the preparation was repeated in cold media with the hope of isolating the unstable form. A bluish violet product of the condensation in ethanol at room temperature showed a sharp band at 3325 cm^{-1} in addition to the above-mentioned broad one. The whole vibrational pattern, which is more complicated than that of the reddish violet form, suggested the coexistence of two forms. Since the transformation was suspected to be accelerated by the solvent, the reaction in cold water, in which the product is hardly soluble, was also attempted. This time, the product gave no broad band near 3200 cm^{-1}; however, the purity did not seem to be high, as the spectrum consists of rather broad bands. Thus, the unstable form could not be isolated. The *m*-ethoxy derivative prepared in boiling ethanol was reddish brown and showed a band at 3320 cm^{-1}. Upon sublimation in a vacuum the color turned dark red, and the vibrational spectrum was considerably modified. The above-mentioned sharp band was replaced by a broad one at 3255 cm^{-1}. The difference in the electronic spectrum is not large for this compound; the maximum is at 500 nm in both forms. These two compounds were initially prepared by Grossmann, but he did not note the dimorphism.[8]

For all the other derivatives, we saw no indication of dimorphism. On the basis of the vibrational band in the region from 3150 to 3350 cm^{-1}, they can be classified into two groups. The first group consists of the following derivatives, exhibiting a sharp band near 3300 cm^{-1}: X=H (3310 cm^{-1}), *m*-Me (3305), *p*-Me (3325), *o*-MeO (3300), *m*-MeO (3320), *o*-EtO (3330), *p*-EtO (3320), and 3,4-Me$_2$ (3315). On the other hand, a broad band was observed near 3200 cm^{-1} only with the halo derivatives—namely, *m*-Cl (3180 cm^{-1}), *p*-Cl (3185), *m*-Br (3180), *p*-Br (3200), and *p*-I (3200). The *p*-ethyl and *m*-carboxy derivatives are exceptional. A band with an intermediate breadth was found at 3280 cm^{-1}. Grossmann noted that the color of the *m*-methoxy derivative appreciably varies with the kind of solvent; that is, the pyridine solution is light yellow, the benzene solution is orange red, and the ethanolic solution is bluish red.[8] Nevertheless, we found that the absorption spectrum in pyridine is identical with that in ethanol. The maximum at room temperature is at 470 nm in both solvents.

2-Anilino-3-chloro-1,4-naphthoquinones (Y=Cl). Dimorphic forms could be isolated with the *m*-methyl, *p*-ethyl, 2,4-dimethyl, *m*-ethoxy, and *m*-carboxy derivatives. In the case of the *m*-methyl derivative, the form deposited from the reaction mixture gives a sharp vibrational band at 3300 cm^{-1}, while the other form, obtained by recrystallization from ethanol, gives a broad band at 3245 cm^{-1}. A mixture of the two forms was obtained by sublimation in a vacuum. The difference in the other region is less significant compared with the case shown in Fig. 1 (X=*p*-COOH, Y=H). The former form is dark reddish violet and gives an absorption maximum at 485 nm and a shoulder at 515 nm. The latter is bright reddish violet, and its maximum is located at 510 nm.

The crystals of the *p*-ethyl derivative, separated from the reaction mixture and also purified by vacuum sublimation, are reddish violet and give a sharp vibrational band at 3270 cm^{-1}, while the crystals deposited from acetone are similarly colored, but give a broader band at 3235 cm^{-1}. In both the dimorphs, the absorption maxima are located at 515 nm.

The 2,4-dimethyl derivative, as prepared in boiling ethanol, was found to be a mixture of two forms. The reddish brown form isolated by recrystallization from ethanol shows a sharp vibrational band at 3305 cm^{-1}. The color turns reddish violet upon vacuum sublimation, and the sharp band is replaced by a broad one appearing at 3250 cm^{-1}. The splitting of the carbonyl stretching vibrational band is observed only in the former form. The electronic absorption maximum is at 495 nm in the form obtained by recrystallization and at 505 nm in the form obtained by sublimation.

The *m*-ethoxy derivative is dimorphic; that is, the vibrational spectrum of the crystals as prepared in ethanol differs from that of the crystals obtained by vacuum sublimation or by recrystallization from ethanol. The former form gives a sharp band at 3325 cm^{-1}, and the latter, a broad one at 3240 cm^{-1}. The electronic spectra are essentially the same, both having a maximum at 500 nm.

Two forms distinctly differnt in color were isolated for the *m*-carboxy derivative. The crystals deposited from the reaction mixture are yellow or yellowish orange. Upon vacuum sublimation the color turned scarlet. Although Buu-Hoi carried out his preparation in the same solvent, the color he described seems to be in agreement with the latter.[9] The former form shows a sharp vibrational band at 3340 cm^{-1}, and the latter, a broad one at 3275 cm^{-1}. The electronic spectra of these dimorphs are presented in Fig. 3. The maxima are located at 450 and 490 nm respectively. In addition, the scarlet form gives a shoulder at 525 nm. Both a sharp vibrational band at 3325 cm^{-1} and a broad one at 3225 cm^{-1} were observed with the *p*-propyl derivative, suggesting the existence of two forms. Unfortunately, we could not separate them.

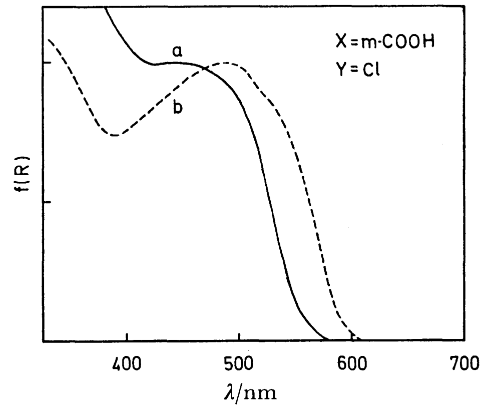


Fig. 3. Electronic spectra of 2-(*m*-carboxyanilino)-3-chloro-1,4-naphthoquinone: (a) the yellow form and (b) the scarlet form.

Only one form each was obtained for the seventeen other derivatives examined. Among them, the following six derivatives give sharp vibrational bands near 3300 cm^{-1}: X=2,3-Me_2 (3295 cm^{-1}), 2,4,5-Me_3 (3290), *o*-MeO (3340), *o*-EtO (3320), *o*-COOH (3300), and *p*-COOH (3300). Broad bands are observable with the following eleven, including the unsubstituted compound: X=H (3245 cm^{-1}), *o*-Me (3240), *p*-Me (3220), 2,4-Me_2 (3225), 3,4-Me_2 (3250), *m*-MeO (3220), *p*-MeO (3245), *p*-EtO (3235), *m*-Cl (3225), *p*-Cl (3230), and *p*-I (3260). In this series, not only the halo derivatives, but also some alkyl and alkoxy derivatives, are classified into the second group. Therefore, it is apparent that the form with a broad vibrational band near 3200 cm^{-1} favors the substitution with the chlorine atom at the 3 position of the naphthoquinone. When the X derivative with Y=H belongs to the first group and the corresponding derivative with Y=Cl belongs to the second group, it is likely that the effect of the X substituent is nearly matched by the effect of the Y substituent. Assuming that the chance of finding dimorphs is high with these two derivatives, they were particularly carefully examined.

2-Anilino-3-bromo-1,4-naphthoquinones (Y=Br). With the *p*-ethyl, 2,3-dimethyl, 3,4-dimethyl, and *o*-ethoxy derivatives, dimorphic forms could be isolated. A broad vibrational band appearing at 3240 cm^{-1} was observed with the crystals of the *p*-ethyl derivative as prepared in boiling ethanol and also with those recrys-

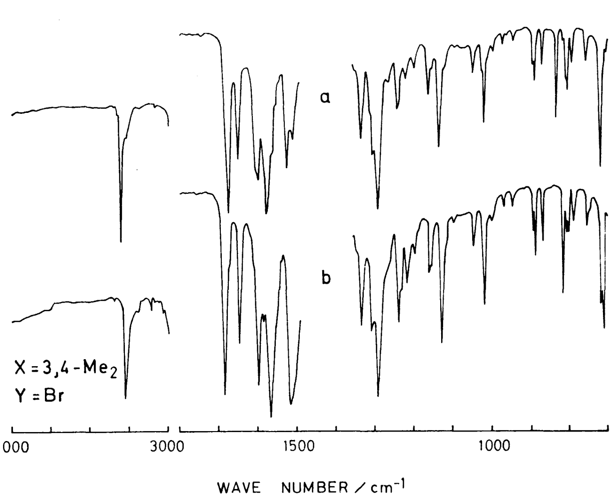


Fig. 4. Vibrational spectra of 2-(3,4-dimethylanilino)-3-bromo-1,4-naphthoquinone: (a) the form deposited from the reaction mixture and (b) the form isolated by recrystallization from aqueous ethanol.

tallized from the same solvent. By adding water to the cold solution and then letting stand the mixture overnight, crystals showing a sharper band at 3275 cm^{-1} were deposited. In the electronic spectra, the maximum is at 510 nm in the former form and shifts to 495 nm in the latter.

The difference in the vibrational spectrum is small in the dimorphic forms of the dimethyl derivatives, as is exemplified by the 3,4-derivative shown in Fig. 4. The reaction products show a band at 3280 cm^{-1} in both cases. A sharp band appears at 3305 cm^{-1} upon the vacuum sublimation of the 2,3-derivative. The crystals deposited from the reaction mixture show an electronic absorption maximum at 505 nm, while the crystals obtained by sublimation show a maximum at 485 nm. On the other hand, the form showing a sharp band at 3310 cm^{-1} was isolated by recrystallization from aqueous ethanol in the case of the 3,4-derivative. The maximum in the electronic spectrum is at 505 nm for both of the dimorphs.

The two forms for the *o*-ethoxy derivative do not differ much from each other in the vibrational spectrum; that is, the crystals deposited from the reaction mixture exhibit a sharp band at 3340 cm^{-1}, while the crystals obtained by sublimation in a vacuum or by recrystallization from benzene show a sharp band at 3325 cm^{-1}. The absorption maximum in the electronic spectrum is at 515 nm in the former form and at 530 nm in the latter. Nevertheless, the two spectra can be almost superposed on each other.

The presence of dimorphic forms was noted for the *m*- and *p*-methyl derivatives, but they could not be separated. A sharp band was observed at 3325 cm^{-1} with the crystals of the former compound deposited from the reaction mixture, and also with those recrystallized from ethanol. Upon vacuum sublimation, an additional band appeared at 3225 cm^{-1}. On the other hand, the synthesis, recrystallization, and vacuum sublimation yielded the form showing a broad band at 3225 cm^{-1} for the latter. However, the appearance of an additional sharp band at 3335 cm^{-1} was noted when the crystals were deposited from a cold aqueous ethanolic solution.

The following six derivatives of the anilinobromonaphthoquinone are classified into the first group: X= *p*-Pr (3280 cm^{-1}), *o*-MeO (3355), *m*-EtO (3330), *m*-COOH (3280), *p*-COOH (3320), and 2,4,5-Me_3 (3295). The second group consists of X=H (3245 cm^{-1}), *o*-Me (3255), *m*-MeO (3225), *p*-MeO (3255), *p*-EtO (3250) 2,4-Me_2 (3265), and 2,5-Me_2 (3225). The halo derivatives expected to be members of this group were not included in this study, as the observation of dimorphism with them seemed to be very unlikely. It may be added that the locations are generally at higher wave numbers compared with those of the corresponding derivatives in the chloronaphthoquinone series.

To supplement the above results, we carried out spectral measurements of the condensation product between two moles of 2,3-dichloro-1,4-naphthoquinone and one mole of 3,3′-dimethoxybenzidine. The color of this particular compound has been reported to be red in hot xylene and to turn reddish violet upon cooling.[14] However, we could record no unusual temperature dependence with this system.

Discussion

In order to examine the relative stabilities of the possible tautomeric forms within the framework of the HMO method, we compared the bonding energies of the two forms of the unsubstituted anilinonaphthoquinone. This approach has been employed by Kuder as a criterion of the tautomeric stability of hydroxyarylazo compounds.[15] The bonding energy is given by the difference between the total π-electron energy and the energy of the π-electrons localized on atomic *p*-orbitals. The latter is defined by $\sum_{i=1}^{n} s_i\alpha_i$, where n is the number of atomic centers, s_i is the number of electrons contributed by the i atom to the π-electron system, and α_i is the Coulomb integral for the i atom. The tautomeric form with the larger bonding energy or bonding energy per electron may be considered to be more stable. The heteroatom parameters, h_x and k_{xy}, in the Coulomb and resonance integrals, $\alpha_x=\alpha+h_x\beta$ and $\beta_{xy}=k_{xy}\beta$, were the same as those used by Kuder, namely, $h_{NH}=1.50$, $h_O=1.00$, k_{C-N}(the bond to naphthoquinone)$=0.90$, k_{C-N}(the bond to phenyl group)$=0.70$, and $k_{C=O}=1.00$ for the *p*-quinonoid form and $h_N=0.50$, $h_O=1.00$, $h_{OH}=2.00$, $k_{C=N}=1.10$, $k_{C-N}=0.90$, $k_{C=O}=1.00$, and $k_{C-O}=0.80$ for the *o*-quinonoid form. The effect of an intramolecular hydrogen bond, O···H–N, was also considered by taking the following parameters: $\alpha'_{NH}=\alpha_{NH}-0.20\beta$, $\alpha'_{O-H}=\alpha_O+0.20\beta$, $\beta_{O-H-N}=0.20\beta$. The bonding energies computed in terms of the carbon-carbon resonance integral, β, are shown below:

	p-Quinonoid	*o*-Quinonoid
No hydrogen bond	24.851	24.823
With a hydrogen bond	24.967	—

Consequently, the *p*-quinonoid form appears to be more stable than the *o*-quinonoid form, regardless of the hydrogen bond. It has been argued by Kuder that a difference in bonding energy per electron in excess of 0.002 β leads to the presence of only one tautomer. This criterion suggests that only the *p*-quinonoid form of the anilinonaphthoquinone will be seen if the hydrogen bond is formed.

The above-mentioned situation may be affected, to some extent, by the introduction of a substituent on the phenyl group. However, our observations cannot be correlated with the nature of the substituents. Not only the derivative with an electron-withdrawing group, but also the one with an electron-donating group on the same position were found to be dimorphic: *e.g.*, X= *p*-COOH and *p*-MeO with Y=H and X=*m*-COOH, *m*-EtO, and *m*-Me with Y=Cl. Furthermore, the electronic spectrum not being sensitive to the nature of solvents and its small temperature-dependence seem to be inconsistent with the presence of a tautomeric equilibrium in solutions. The molar absorption coefficient of the band in the visible region is in the range from 2600 to 5400, depending mainly upon the kind and position of the X substituent. This absorption may be attributed to an intramolecular charge-transfer transition. The difference in vibrational spectrum must, then, be due to a change in the molecular configuration. The change appears to be large in the case shown in Fig. 1 (X=p-COOH, Y=H) and small in the case shown in Fig. 4 (X=3,4-Me_2, Y=Br). In other cases, the difference varies between these extremes. The band appearing in the region from 3150 to 3350 cm^{-1} can now be definitely assigned to the N–H stretching vibration. The shift implies that the strength of the hydrogen bond varies with the configuration. As the mode of stacking is governed by the molecular configuration, the difference in color between dimorphic forms may be attributed largely to changes in the location and the intensity of the intermolecular charge-transfer absorption between the electron-donating moiety of a molecule and the accepting moiety of the neighboring molecule.

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