BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (4), 1211—1212 (1979)

The Dimorphism and Spectral Properties of 4-Anilino-1,2-naphthoquinones

Yoshio MATSUNAGA* and Nobuhiko MIYAJIMA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

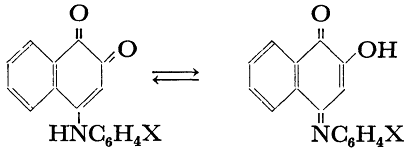
(Received September 18, 1978)

Synopsis. On the basis of vibrational spectra, especially in the region from 3050 to 3350 cm^{-1}, solid 4-anilino-1,2-naphthoquinones carrying substituents on the phenyl ring are classified into two groups. The *p*-methyl and *p*-ethyl derivatives are dimorphic and can be members of both the groups.

We have previously examined the vibrational spectra of a number of the derivatives of 2-anilino-1,4-naphthoquinones which carry substituents on the phenyl ring.1) On the basis of the location and the sharpness of the single band appearing in the region from 3150 to 3350 cm^{-1}, most of the derivatives could be classified into two groups. Furthermore, over ten derivatives were shown to be dimorphic. One of the dimorphic forms exhibits a relatively sharp band near 3300 cm^{-1}; the other, a relatively broad one at a lower wave number. Thus these derivatives can belong to either group. Here, the results of our work extended to the isomeric compounds, the derivatives of 4-anilino-1,2-naphthoquinones, will be presented.

The condensation reaction between 1,2-naphthoquinone and anilines was carried out in warm or boiling ethanol as reported by Zincke or Elsbach.2,3) The vibrational spectra in the rock-salt region and the electronic spectra in the visible region were measured by the procedures described in the previous paper.1) The search for dimorphic forms was made by comparing the vibrational spectrum of the crystals deposited from a reaction mixture with that of the sample sublimed in a vacuum. When they were clearly different, recrystallization of the former sample was attempted.

The crystals of the *p*-methyl derivative as deposited from a reaction mixture and also those recrystallized from ethanol are reddish orange. As is shown in Fig. 1a, the vibrational spectrum shows a single band at 3315 cm^{-1}, which may be assigned to the N–H stretching. By sublimation in a vacuum, the color turns deep red and the single vibrational band is replaced by a complicated pattern consisting of at least four bands, appearing at 3070, 3120, 3185, and 3220 cm^{-1}, probably arising from nonequivalent N–H bonds (see Fig. 1b). As the single band and/or the pattern noted here are also observed with the other derivatives, the form giving the former spectrum will be named, for the sake of convenience, form I, and that giving the latter, form II. The spectra of these two in the region below 1700 cm^{-1} are not very different from each other. Therefore, the difference in vibrational spectrum seems to be attributed to a change in the molecular configuration centered round the N–H group, as has been concluded for the case of 2-anilino-1,4-naphthoquinones, rather than the tautomerism involving *o*-quinonoid and *p*-quinonoid forms:



This conclusion seems to be in accordance with the finding by Harmon *et al.* that 4-anilino-1,2-naphthoquinones in aqueous solutions exist predominantly in the aminoquinone form except in strongly acidic solutions, where the hydroxyquinone imine form becomes more stable.4) Figure 2 presents the Kubelka-Munk plots of the electronic spectra of the dimorphic forms and also the absorption spectrum of the same compound dissolved in chloroform. Form I gives two maxima located at about 515 and 545 nm and form II gives a maximum at 500 nm, with a shoulder around 540 nm.

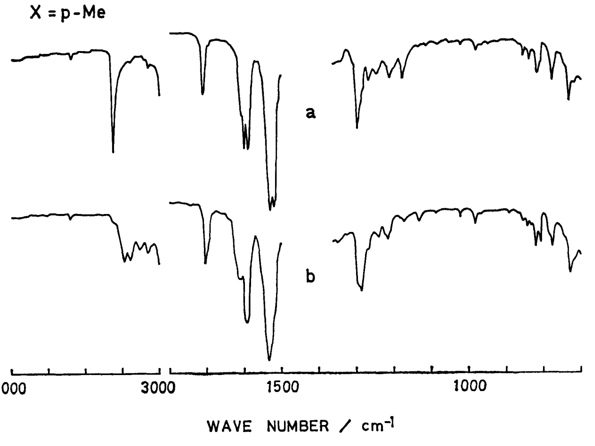


Fig. 1. Vibrational spectra of 4-(*p*-methylanilino)-1,2-naphthoquinone: (a) the form I (recrystallized from ethanol) and (b) the form II (sublimed in a vacuum).

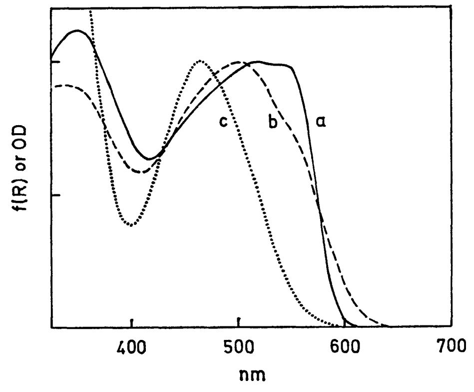


Fig. 2. Electronic spectra of 4-(*p*-methylanilino)-1,2-naphthoquinone: (a) the form I (recrystallized from ethanol), (b) the form II (sublimed in a vacuum), and (c) the compound dissolved in chloroform. The maximum in the visible region was arbitrarily taken as 1.00 in each spectrum.

On the other hand, the maximum of the absorption band is observed at about 463 nm with a chloroform solution. Thus, the band seems to shift to about 500 nm upon the solidification. Since the molecule consists of an electron-donating moiety and an accepting one, this electronic transition is probably of the intramolecular charge-transfer type. The additional bands appearing in the solid-state spectra may be assigned to the intermolecular charge-transfer transition. The location and the intensity of such an absorption are supposed to depend on the mode of molecular stacking in the crystals, as we have reported for a number of cases.[1,5,6]

Form I was found for only three more derivatives: the unsubstituted compound (3320 cm^{-1}), the *p*-ethyl (3310), and the 2,3-dimethyl (3300) derivatives. Among them, the *p*-ethyl derivative was found to be dimorphic, but the other two are not. The *p*-ethyl derivative crystallizes in form I from ethanol and is transformed into form II by vacuum sublimation. The former crystals are reddish brown and the latter are brown. The maxima of the electronic absorption are at about 510 and 500 nm, respectively. In this case too, the intensity in the spectrum of form I changes more steeply in the long-wavelength side than that of form II.

The second group of compounds, obtained only in the form II, consists of a number of derivatives: *o*-methyl, *m*-methyl, *p*-propyl, *m*-chloro, *p*-chloro, *p*-iodo, *m*-methoxy, *p*-methoxy, *m*-ethoxy, *p*-ethoxy, *m*-carboxy, *p*-carboxy, 2,4-dimethyl, 2,5-dimethyl, 3,4-dimethyl, and 2,4,5-trimethyl derivatives. Thus the classification does not seem to be correlated with the electronic nature of the substituents. Their absorption bands are rather broad and the maxima are located around 500 nm. The compounds available in form II are generally darker than those in form I because the absorption bands extend to the longer wavelengths.

References

1) Y. Matsunaga, N. Miyajima, and A. Togashi, *Bull. Chem. Soc. Jpn.*, **50**, 2234 (1977).

2) Th. Zincke, *Ber.*, **14**, 1493 (1881).

3) L. Elsbach, *Ber.*, **15**, 685 (1882).

4) R. E. Harmon, L. M. Phipps, J. A. Howell, and S. K. Gupta, *Tetrahedron*, **25**, 5807 (1969).

5) J. Aihara, G. Kushibiki, and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **46**, 3584 (1973).

6) Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **49**, 1411 (1976).