BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3584—3585 (1973)

The Dimorphism and Electronic Spectra of Anisyl-*p*-benzoquinones

Jun-ichi Aihara, Goichi Kushibiki,* and Yoshio Matsunaga
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received June 25, 1973)

The coexistence of orange-yellow crystals (mp 58—59 °C) and red crystals (64—65 °C) has been noted by Brassard and L'Ecuyer in an *o*-anisyl-*p*-benzoquinone sample recrystallized from a mixture of acetone, methanol, and water (1: 1: 1 by volume).[1] We have examined the electronic spectra of these dimorphic forms and also those of some closely-related compounds in the first of our attempts to study self-complexing by a charge-transfer interaction in solids.

Phenyl-*p*-benzoquinone and its *o*- and *p*-MeO derivatives were prepared by the method of the abovementioned authors. The preparation of the *m*-MeO and *o*- and *p*-EtO derivatives was similarly attempted. The purification of these three substances was found not to be easy. The crude products were repeatedly recrystallized, then sublimed in a vacuum, and finally recrysallized again. Their melting points were 121,81, and 115 °C respectively. The diffuse reflectance (R) of solid samples diluted with sodium chloride was measured at a concentration of 1.00% by means of a Beckman DK-2A spectroreflectometer. The spectra were plotted using the Kubelka-Munk function $f(R) = (1-R)^2/2R$.

The orange-yellow form of *o*-anisyl-*p*-benzoquinone could be isolated, by chance, during the processes of recrystallization, sublimation in a vacuum, and also solidification of the melt. Except for a shift of the absorption maximum to the wavelength side longer by about 25 nm, the spectrum is very similar to that displayed by the compound dissolved in ethanol (see Fig. 1). On the other hand, the red form shows an additional absorption with its maximum located around 500 nm.

p-Anisyl-*p*-benzoquinone recrystallized from an aqueous ethanol solution is orange-red, as has been reported by Brassard and L'Ecuyer. When the melt is quickly cooled, the yellow form is obtained. Although this form can be kept for months without noticeable change, it is not so stable as the orange-yellow form of the *o*-anisylquinone. The color immediately turns orange-red when it is exposed to acetone vapor. Furthermore, the conversion to the stable form is markedly accelerated by grinding. As is shown in Fig. 2, the solid-state spectrum of the yellow form resembles the solution spectrum. The absorption maximum is located at about 420 nm in both of the states. The feeble structure observed around 500 nm in the solid-state spectrum can be assigned to the *n*-*π* transition. The appearance of a shoulder around 470 nm was noted in the spectrum of the orange-red form. The stable form melts at 126—127 °C, and the unstable form, at 118—119 °C. Curiously, the value reported by Brassard and L'Ecuyer, who observed only the orange-red form, agrees with the latter.

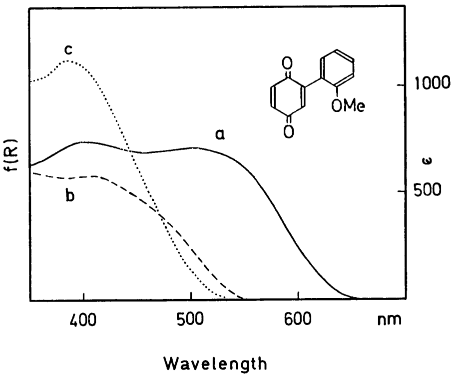

Fig. 1. Diffuse reflection spectra of (a) the red form and (b) the orange-yellow form of *o*-anisyl-*p*-benzoquinone and (c) the absorption spectrum in ethanol.

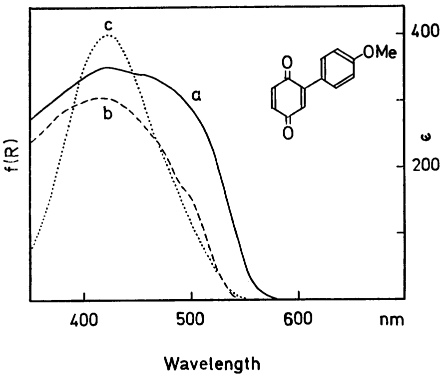

Fig. 2. Diffuse reflection spectra of (a) the orange-red form and (b) the yellow form of *p*-anisyl-*p*-benzoquinone and (c) the absorption spectrum in ethanol.

As the anisyl groups are excellent electron-donors, and as the quinone nucleus is a fairly good electron-acceptor, the absorptions appearing around 400 nm may be regarded as intramolecular charge-transfer transitions involving the transfer of an electron from a level which is akin to the highest occupied orbital of the anisyl group to the lowest vacant orbital, which is essentially of the quinone nucleus. The locations are shifted to the longer-wavelength side compared with that of the intermolecular charge-transfer absorption band in the anisole-*p*-benzoquinone complex, which has been located by Kuboyama at about 355 nm in carbon tetrachloride.[2] This assignment is supported by the observations that the absorption maximum in solid phenyl-*p*-benzoquinone is at 375 nm, while that in the *p*-NO_2 derivative is below 325 nm. In these two cases, the *n*-*π* transitions are well separated from

---

* Present address: Oki Electric Industry Co., Hachioji, Tokyo.

[1] P. Brassard and P. L'Ecuyer, *Can. J. Chem.*, **36**, 700 (1958).

[2] A. Kuboyama, *Nippon Kagaku Zasshi*, **81**, 558 (1960).

the intramolecular charge-transfer bands. There is little doubt that the *o*-anisyl-*p*-benzoquinone molecule is farther from co-planarity than the *p*-anisylquinone molecule because of the increased steric hindrance. This accounts for the fact that the extinction coefficient of the charge-transfer absorption band in the former compound is approximately one-fourth of that in the latter. The additional absorptions observed in the deeply-colored forms disappear upon melting. Thus, they may be attributed to the intermolecular charge-transfer interaction between the anisyl group in one molecule and the quinone nucleus in the neighboring molecule. Such a head-to-tail overlap in solids seems to be specific to these two compounds. The *m*-MeO and *o*- and *p*-EtO derivatives are all yellow-colored and exhibit no additional absorption on the longer-wavelength side of the intramolecular charge-transfer absorption band.