BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(8), 2063—2064 (1974)

Molten-State Spectra of Anisyl-*p*-Benzoquinones[1)]

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(Received February 7, 1974)

Synopsis. The absorption spectra of three anisyl-*p*-benzoquinones were observed in the molten state. Interestingly, only the *p*-anisyl isomer was found to form a self-complex in the molten state as in the solid state. Possible explanation was presented for this effect.

In the previous paper, we reported on dimorphism of anisyl-*p*-benzoquinones.[2)] These compounds are typical intramolecular charge-transfer compounds, in which the electron-donating anisyl moiety is directly bonded to *p*-benzoquinone with an electron affinity of 1.34 eV.[3)] Among them, *o*- and *p*-anisyl-*p*-benzoquinones were found to crystallize in two forms. Of these two isomers, one form is spectroscopically monomeric and another form exhibits an additional electronic transition on the low-energy side, which is missing in the solution spectrum. Such a transition was considered as due to intermolecular charge-transfer interactions. That is, there is supposedly a finite overlap between the donor orbital of one molecule and the acceptor orbital of the adjacent molecule in the crystal. Only one crystalline form of the *m*-anisyl isomer was monomeric.

In order to extend our understanding of the organic self-complex, we attempted to observe the absorption spectra of these compounds in the molten state. To the best of our knowledge, there have been no investigations of this kind except some visual observation of molten charge-transfer complexes.[4)]

Experimental

The experimental technique concerning spectrophotometry was described earlier.[5)] Instead of the powdered sample, a melt was sandwiched between two quartz plates. The apparent reflectance obtained by this method was quite similar to the transmittance of the sample. The reflectance from the interface between the sample and the quartz plate is negligible. Accordingly, the absorbance of the melt can be derived by applying Beer's law to the apparent reflectance. The relative absorbance was checked by comparing the ordinary solution spectra taken by this method and the transmission spectroscopy. The spectrum thus obtained is excellently reproducible unless the absorbance varies by two or more orders of magnitude within the energy range concerned.

The measurements were made at temperatures about 15 °C above the melting points. Fortunately, the present compounds have relatively low melting points; 64—65, 121 and 126—127 °C for *o*-, *m*- and *p*-anisyl-*p*-benzoquinones, respectively, in the stable form.[2)]

Results and Discussion

Figures 1—3 show the absorption spectra of *o*-, *m*- and *p*-anisyl-*p*-benzoquinones, respectively, in two fluid phases. Every solution spectrum displays an intramolecular charge-transfer band in the visible region. The absorption peaks are located at 25800, 27500 and 23800 cm^{-1} for *o*-, *m*- and *p*-anisyl isomers, respectively, in ethanol. On the other hand, the melts are yellowish, yellowish and red, respectively. The red melt of *p*-anisyl-*p*-benzoquinone is suggestive of the presence of the dimeric species. Actually, such visual observation is supported by the molten-state spectra of these compounds.

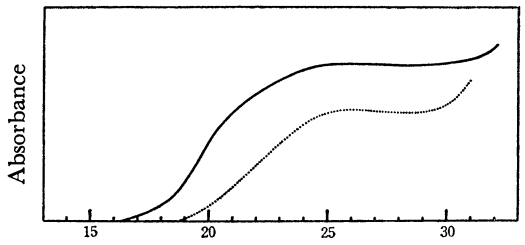

Fig. 1. Absorption spectra of *o*-anisyl-*p*-benzoquinone in ethanol (·····) and in the molten state (——).

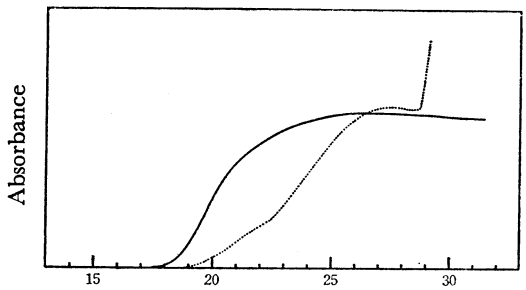

Fig. 2. Absorption spectra of *m*-anisyl-*p*-benzoquinone in ethanol (·····) and in the molten state (——).

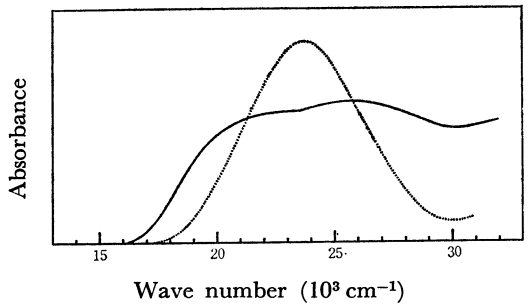

Fig. 3. Absorption spectra of *p*-anisyl-*p*-benzoquinone in ethanol (·····) and in the molten state (——).

The molten-state spectrum of the *o*-anisyl isomer closely resembles that of the *m*-anisyl isomer. The intermolecular interactions in the solid *o*-anisyl-*p*-benzo-

quinone are found to be effectively blocked by the fluidity of the melt. The molten-state spectrum of the *m*-anisyl isomer is a reproduction of the solid-state spectrum. Though these spectra are undoubtedly monomeric, they are somewhat different from the solution spectra in that the low-energy portions are considerably intensified.

In each spectrum, there is a round hump around 21000 cm^{-1}, which is energetically assignable to the n-π^* transition characteristic of the *p*-benzoquinones.[2,6] In the solution spectra of the *o*- and *p*-anisyl isomers, such an n-π^* transition overlaps totally with a more intense intramolecular charge-transfer band. However, the n-π^* transition is partially disclosed in an appropriate region of the solution spectrum of *m*-anisyl-*p*-benzoquinone, since the intramolecular band is much shifted to the higher-energy side for this isomer. The assignment of the hump to the n-π^* transition seems to be thus rationalized.

On the other hand, the absorption spectrum of the molten *p*-anisyl-*p*-benzoquinone is in marked contrast to the solution spectrum. From the viewpoint of the spectral shape, the presence of two different absorption bands is fairly obvious besides the missing n-π^* transition. The absorption peak around 25700 cm^{-1} corresponds well to the intramolecular transition in the solution spectrum. Since each band appears very smooth in the molten state, the break, *i.e.*, the inflection point, near 23500 cm^{-1} difinitely suggests that another absorption band is present on the low-energy side. In analogy with the solid-state spectrum, this band is assigned to the intermolecular charge-transfer transition.[2]

For *p*-anisyl-*p*-benzoquinone, the relative intensities of the intra- and inter-molecular charge-transfer bands are comparable to each other in the molten state as in the dimeric solid. Considering that, if the crystal is dimeric at all, the self-complex formation is attained to 100 percent in it, we might safely say that such a situation is almost preserved in the molten *p*-anisyl-*p*-benzoquinone. The association constant of this self-complex is extimated to be very large in the melt.

As was suggested in the previous paper,[2] the steric effect of the methoxy group might determine the optical behavior of the three anisyl-*p*-benzoquinones in condensed phases. This effect makes the dimer of the *p*-anisyl isomer the most stable of all. However, it is not sufficient to elucidate the monomeric aggregation of the *m*-anisyl isomer which is free from the steric hindrance. As was described above, the absorption peak of the intramolecular charge-transfer transition of the *m*-anisyl isomer is located at the highest energy in solution. This fact may reflect the weak donor ability of the *m*-anisyl isomer.

In summary, the intermolecular interactions of this kind are considered to be very weak, and are not always primary factors in determining the structure of the condensed phase.

References

1) Part II of "Organic Charge-Transfer Self-Complexes": Ref. 2 is hereafter referred to as Part I. This work was financially supported by Fuji Photo Film Co., Ltd.

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