BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2852—2854 (1968)

Diffuse Reflection Spectra of Some Dinitrobiphenyl Complexes

Kunihiro ABE, Yoshio MATSUNAGA and Gunzi SAITO
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received May 6, 1968)

The 4,4′-dinitrobiphenyl complexes with benzidine and tetramethylbenzidine, in which the long axes of the component molecules are known to be perpendicular to each other, were examined for the diffuse reflection spectra. The deep coloration in these complexes was found to be due to the appearance of broad, weak charge-transfer absorptions.

A common feature in the crystal structures of electron donor-acceptor complexes is a plane-to-plane stacking of the molecules.(1) As the structure of a particular complex is a compromise between those molecular orientations most favorable to donor-acceptor interaction and those which give the most efficient molecular packing, the maximum overlap between π-orbitals of the component molecules is not always attained. 4,4′-Dinitrobiphenyl has been known to form complexes with biphenyl and its 4- and 4,4′-derivatives with a structure in which dinitrobiphenyl molecules form a stack with the planar molecules overlying each other, while the other component molecules are in the tubular cavities resulting from the parallel packing of the stacks.(2) The composition is determined by the number of dinitrobiphenyl

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1) S. C. Wallwork, *J. Chem. Soc.*, **1961**, 491.

2) W. S. Rapson, D. H. Saunder and E. T. Stewart, *ibid.*, **1946**, 1110.

molecules in a stack that can be accommodated at right angles to each donor molecule. Thus, the structure of these molecular complexes is exclusively determined by geometrical considerations. Nevertheless, the complexes with benzidine and its tetramethyl derivative are much more deeply colored than the component compounds. This is known to be a general feature in electron donor-acceptor complexes. Therefore, it seemed very interesting to find out whether or not the deep coloration in these dinitrobiphenyl complexes, which are supposed to be in crystal structures unfavorable to $\pi-\pi$ interaction, is due to the appearance of new low-energy electronic absorptions, charge-transfer absorptions.

Experimental

The complexes with biphenyl, 4,4′-dihydroxybiphenyl, 4,4′-dimethoxybiphenyl, benzidine, and *N,N,N′,N′*-tetramethylbenzidine were prepared as has been described by Rapson *et al.*[2] The pulverized sample was diluted with sodium chloride, mostly in a ratio of 1 : 100 by weight, by grinding it in order to obtain a reasonable reflectance. The spectra were recorded as the difference in reflectance between the mixture and pure sodium chloride by a Beckman DK-2A spectroreflectometer and then plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. The complexes of dimethoxybiphenyl, benzidine, tetramethylbenzidine, and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine with various acceptors were examined in a chloroform solution for the charge-transfer absorptions using a Beckman DK-2A spectrophotometer.

Results and Discussion

The compositions of the red benzidine and dark red tetramethylbenzidine complexes are known to be 1 : 4. Tetramethylbenzidine also forms a steel-gray colored complex with a composition of 1 : 1. Their diffuse reflection spectra are presented in Fig. 1, along with the spectrum of dinitrobiphenyl. The absorptions of the other component compounds appear at wave numbers larger than that of dinitrobiphenyl. All these complexes are found to show new low-energy absorptions. Although the appearance of the tetramethylbenzidine 1 : 1 complex is quite different from that of the 1 : 4 complex, their spectra are very much alike. The difference in color arises from a small shift in the low-energy absorption. As these absorptions are weak and broad, and overlap with the strong dinitrobiphenyl absorption, there is some uncertainty in the location of their maxima. The following values may, however, be obtained as rather rough estimates: about 18.5 kK for the tetramethylbenzidine 1 : 1 complex, about 21 kK for the 1 : 4 complex, and about 22.5 kK for the benzidine complex. The complexes with biphenyl, 4,4′-dihydroxybiphenyl, and 4,4′-dimethoxybiphenyl have compositions of 1 : 3, 1 : 3 and 2 : 7 respectively. They have approximately the same colors with dinitrobiphenyl. The only difference observed in the spectra is little tails extending from the small-wave number side of the dinitrobiphenyl absorption.

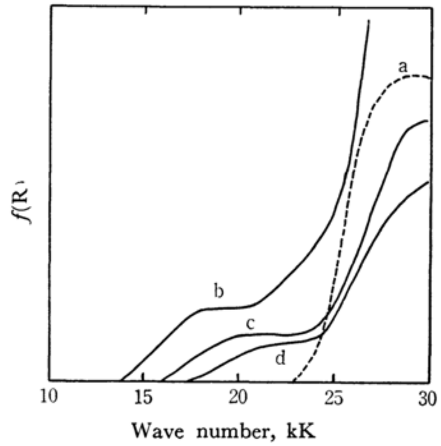

Fig. 1. Diffuse reflection spectra of dinitrobiphenyl (a), the tetramethylbenzidine 1 : 1 (b) and 1 : 4 (c) complexes and the benzidine 1 : 4 complex (d).

Nothing is known of the structure of the tetramethylbenzidine 1 : 1 complex. However, because of its simple composition, the molecules in this complex are presumably in a plane-to-plane stacking. Therefore, the low-energy absorption appearing in this particular complex may be considered to be a charge-transfer absorption arising from electron donor-acceptor interaction between tetramethylbenzidine and dinitrobiphenyl. If so, the weak absorption in the 1 : 4 complex may be of the same nature because of the close similarity in location and shape. As benzidine has a higher ionization potential than its tetramethyl derivative, the charge-transfer absorption in the benzidine complex may be expected to appear at a larger wave number than that of the tetramethylbenzidine complex. This is in accordance with observations. Thus qualitative considerations lead to the tentative conclusion that charge-transfer absorptions are the cause of the deep colors in the dinitrobiphenyl complexes with benzidine and its tetramethyl derivative.

Now we wish to proceed in a more quantitative way. Foster has proposed the empirical relationships that the energies of charge-transfer absorption in a set of complexes of a donor (acceptor) with a series of acceptors (donors) are proportional to those in complexes of the same series of acceptors (donors) with a second donor (acceptor).[3] Such a correlation has been established in a number of

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[3] R. Foster, *Tetrahedron*, **10**, 96 (1960).

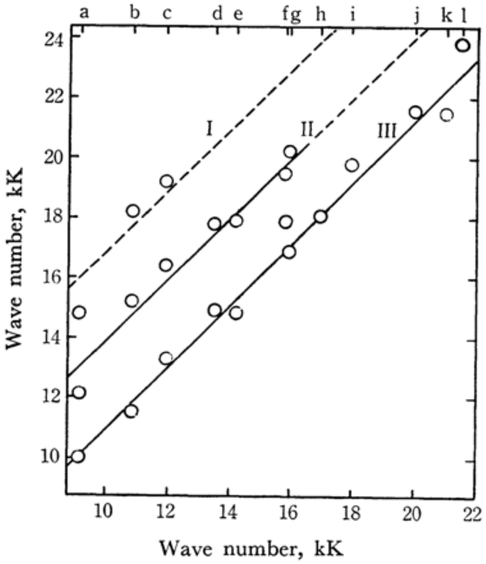

Fig. 2. Plots of wave numbers of maxima of the charge-transfer absorptions in complexes of tetramethyl-*p*-phenylenediamine with the acceptors: tetracyanoethylene (a); *p*-chloranil (b); 2,5-dichloro-*p*-benzoquinone (c); dichloro-*p*-xyloquinone (d); chloro-*p*-benzoquinone (e); *p*-benzoquinone (f); *s*-trinitrobenzene (g); *p*-dinitrobenzene (h); trinitrotoluene (i); *m*-dinitrobenzene (j); dinitrobiphenyl (k); 2,4-dinitrotoluene (l); against wave numbers of the charge-transfer absorptions in the corresponding complexes with the donors: dimethoxybiphenyl (I); benzidine (II); tetramethylbenzidine (III).

the cases by Foster himself and also by Beukers and Szent-Györgyi, and has often been considered as evidence for charge-transfer absorption.[3-5] In Fig. 2 the wave numbers of the absorption maxima in dimethoxybiphenyl, benzidine, and tetramethylbenzidine complexes with each of several acceptors are plotted against those in the corresponding tetramethyl-*p*-phenylenediamine complexes. A large part of the data for the tetramethyl-*p*-phenylenediamine and tetramethylbenzidine complexes was taken from the work by Foster and Thomson.[6] With dinitrobiphenyl as an acceptor (k), the maximum of the low-energy absorption could be located only in the complex of tetramethylbenzidine, the strongest donor among the biphenyl derivatives examined, at about 21.5 kK. This value fits fairly well into the linear relationship shown in Fig. 2, and must be considered to be consistent with the maxima observed in the solid 1 : 1 and 1 : 4 complexes. The appearance of charge-transfer bands in solid complexes at energies a few kK lower than those in a solution is quite common. Furthermore, an examination of Fig. 2 indicates that the charge-transfer interaction between benzidine and dinitrobiphenyl gives an absorption with a maximum around 25 kK. Again, this estimation is in fair agreement with the low-energy absorption in the solid-state spectrum, 22.5 kK. As for the remaining complexes the available data are not enough to enable us to prepare plots like those for benzidine and its tetramethyl derivative. However, if they show charge-transfer absorptions, the maximum in the dimethoxybiphenyl complex may be expected around 28 kK and those in the other two, higher. In accordance with the experimental results, the observation of such absorptions is hardly possible because of the strong absorptions due to the component compounds lying in the same region. Consequently, the thesis that the low-energy absorptions appearing in the solid dinitrobiphenyl complexes arise from charge-transfer interaction, where dinitrobiphenyl acts as an electron acceptor, receives strong support from these considerations.

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4) R. Beukers and A. Szent-Györgyi, *Rec. Trav. Chim.*, **81**, 255 (1962).

5) R. Foster and P. Hanson, *Trans. Faraday Soc.*, **60**, 2189 (1964).

6) R. Foster and T. J. Thomson, *ibid.*, **59**, 1059 (1963).