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The Polarized Absorption Spectra of Solid Molecular Compounds of Chloranil and Aromatic Amines

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The polarized absorption spectra of the single crystal were observed for six molecular compounds which involve chloranil as the electron acceptor and aromatic amines as the electron donor. The molecular compounds of *N*, *N*-dimethylaniline, 1-naphthylamine, and *N*, *N*-dimethyl-2-naphthylamine have a non-ionic ground state. In these cases, the locations of the charge-transfer bands in the crystal spectra are similar to those of the corresponding bands of the 1 : 1 molecular complexes formed in the solution. The solid molecular compounds of *p*-phenylenediamine, *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylenediamine, and diaminodurene can be regarded as ionic crystals composed of the positive ion of the donor and the negative ion of the acceptor. In these cases, the absorption bands associated with the component ions are observed in the crystal spectra, but they are broadened and appreciably shifted to a higher energy as compared with the case of the solution spectra of the ions. The absorption band associated with the charge transfer between ions is observed in the near-infrared region of the crystal spectra of these molecular compounds.

In most solid molecular compounds, the charge transfer from the electron donor to the electron acceptor is quite small in their ground states. It has been suggested, however, that a molecular compound composed of a strong electron donor and a strong electron acceptor may have an ionic ground state. Such an example can actually be found among the solid molecular compounds which involve aromatic amines as the electron donor, and *p*-chloranil or another quinone derivative as the electron acceptor.[1-5] These molecular compounds are also interesting from the view point of organic semiconductors, since they often exhibit a relatively good electronic conduction.[6-8]

The optical absorption spectra of the solid molecular compounds formed between aromatic amines and chloranil have been studied by several workers in an attempt to elucidate the electronic structures of these molecular compounds.[3-7,9,10] In most cases, however, the spectra were measured on powder samples by means of the KBr-pellet method or by the diffuse reflection method. Consequently, the absorption bands were usually not well resolved in the observed spectra, and their assignments were often quite ambiguous. As is well known, it is of great significance to study the polarized absorption spectra of the single crystal in order to examine the nature of the transition associated with an absorption band. No single crystal spectrum has been reported on the aromatic amine-chloranil compounds except the specular reflection spectra of the compound composed of tetramethyl-*p*-phenylenediamine and chloranil, which spectra have been recently reported by Anex and Hill.[11] Therefore, we have studied the polarized absorption spectra of the single crystals of various aromatic amine-chloranil compounds, including the ones with non-ionic ground states as well as those with ionic ground states.

In the present paper, we shall report on the crystal spectra obtained for the six molecular compounds which involve *N*, *N*-dimethylaniline, 1-naphthylamine, *N*, *N*-dimethyl-2-naphthylamine, *N*, *N*, *N'*, *N'* - tetramethyl - *p* - phenylenediamine (TMPD), *p*-phenylenediamine, and diaminodurene as the electron donors.

Experimental

The polarized absorption spectra of the single crystals were measured with a microspectrophotometer. The

1) H. Kainer, D. Bijl and A. C. Rose-Innes, *Naturwissenschaften* **41**, 303 (1954).
2) D. Bijl, H. Kainer and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 675 (1959).
3) H. Kainer and A. Überle, *Chem. Ber.*, **88**, 1147 (1955).
4) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59** 296 (1963).
5) D. L. Kronick, H. Scott and M. M. Labes, *J. Chem. Phys.*, **40**, 890 (1964).
6) Y. Matsunaga, *Nature*, **211**, 183 (1966).
7) Y. Matsunaga, *ibid.*, **205**, 72 (1965).
8) D. D. Eley, H. Inokuchi and M. R. Willis, *Discussions Faraday Soc.*, **28**, 54 (1959).
9) M. M. Labes, R. Sehr and M. Bose, *J. Chem. Phys.*, **32**, 1570 (1960); *ibid.*, **33**, 868 (1960).
10) Y. Matsunaga, *ibid.*, **40**, 3453 (1964); *ibid.*, **42** 1982 (1965).
11) B. G. Anex and E. B. Hill, Jr., *J. Am. Chem. Soc.*, **88**, 3648 (1966).

details of the apparatus and the procedures of measurement have been described in a previous paper.[12] Minute crystals of the molecular compounds were prepared by crystallization from solutions containing an appropriate amount of each component. The crystals thus obtained were usually in the form of a needle or a lath elongated along one of the crystal axes. The absorption spectra were measured from the direction normal to the developed face of the crystal with the polarizations, both parallel and perpendicular, to the elongated axis. In the present paper, we shall denote the elongated axis as the "l-axis." In most cases, this is the direction along which donor and acceptor molecules are alternately stacked on each other. All the measurements were carried out at room temperature. The infrared absorption spectra of the solid molecular compounds were also examined in order to ascertain the ionic character of the ground state.

Results and Discussion

***N, N*-Dimethylaniline-Chloranil (1 : 1) Compound.** Deep blue needle crystals of this compound can be obtained from a dimethylaniline solution of chloranil. This compound has a non-ionic ground state. The crystal spectrum observed with the light polarized parallel to the l-axis, "the $//l$ spectrum", and that observed with the light polarized perpendicular to the l-axis, "the $\perp l$ spectrum", are shown in Fig. 1. There is a relatively strong absorption band with a maximum located at 15.3 kK in the $//l$ spectrum, but no corresponding band can be found in the $\perp l$ spectrum. Seemingly the 15.3kK band is exclusively polarized along the l-axis. The second absorption band, located at about 32.8 kK, is different from the first band as regards the direction of the transition moment: its intensity is stronger in the $\perp l$ spectrum that in the $//l$ spectrum.

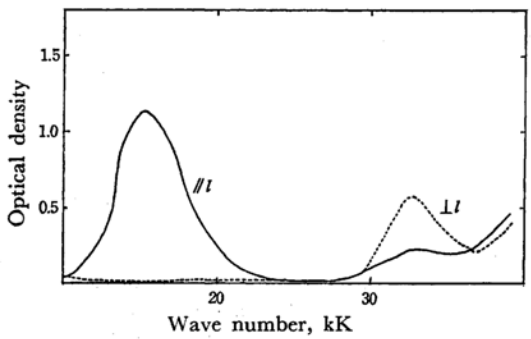

Fig. 1. Absorption spectra of *N, N*-dimethylaniline-chloranil compound.

Neither dimethylaniline nor chloranil exhibits any absorption in the 10—25 kK region. The lowest π–π^* transition of dimethylaniline is located at 33.9 kK ($\log \varepsilon = 3.2$), while that of chloranil is at 27 kK ($\log \varepsilon = 2.5$).[13] Therefore, the 15.3 kK band of the $//l$ spectrum can not be attributed to any intramolecular excitation of the component molecules. It must be a band associated with the intermolecular charge-transfer. In the spectrum of the 1 : 1 complex formed between dimethylaniline and chloranil in a carbon tetrachloride solution, the chrage-transfer band appears at 15.4 kK, a value which is associated with the charge transfer from the highest occupied molecular orbital of dimethylaniline to the lowest vacant molecular orbital of chloranil. Apparently the 15.3 kK band of the crystal spectrum corresponds to this charge-transfer band of the 1 : 1 complex. Therefore, we assign it to the charge transfer from the highest occupied orbital of a dimethylaniline molecule to the lowest vacant orbital of the nearest chloranil molecules in the crystal lattice. On the other hand, the polarization of the 32.8 kK band is that expected for a band associated with intramolecular transitions of the component molecules; also, the location of the band nearly corresponds to the lowest π–π^* transition of dimethylaniline or the 34.3 kK π–π^* transition of chloranil. We thus consider that this band of the molecular compound is a local excitation band associated with these transitions of the component molecules.

1 - Naphthylamine - Chloranil (1 : 1) Compound. This molecular compound is obtainable as green needles from a carbon tetrachloride solution. The ground state seems to be non-ionic. The $//l$ spectrum and the $\perp l$ spectrum are shown in Fig. 2. There are two absorption bands which appear more strongly in the $//l$ spectrum than in the $\perp l$ spectrum. Their maxima are located at 15 kK and at 24 kK. Evidently the 15 kK band can not be assigned to a local excitation, since neither component molecule has any transition in the corresponding region. The 1 : 1 complex of 1-naphthylamine and chloranil

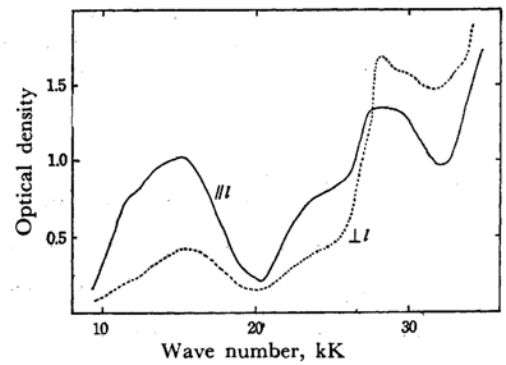

Fig. 2. Absorption spectra of 1-naphthylamine-chloranil compound.

12) H. Kuroda, T. Kunii, S. Hiroma and H. Akamatu, *J. Mol. Spectry.*, **22**, 60 (1967).

13) "Organic Electronic Spectral Data", Vols. I, II, III, IV, Interscience Publishers, New York.

formed in the carbon tetrachloride solution shows a charge-transfer band with a maximum at 15.9 kK. Therefore, we shall assign the 15 kK band of the crystal spectra to the lowest charge-transfer excitation.

The orbital energies of the highest and second-highest occupied molecular orbitals of 1-naphthylamine are, respectively, −8.37 and −9.88 eV according to the SCF MO calculations.*1 Therefore, we can expect that the band associated with the charge-transfer from the second-highest occupied orbital of a naphthylamine molecule to the lowest vacant orbital of the nearest chloranil molecules will be located, if it appears at all, at a wave number separated by about 12 kK from the first charge-transfer band. This means that the location of its absorption maximum will be at about 27 kK. Seemingly the 24 kK band observed with $//l$ polarization corresponds to this absorption band. The charge-transfer band corresponding to this band of the crystal spectra may also be expected to appear in the spectrum of the 1 : 1 complex formed in solution, but it should be hardly observed since it overlaps with the tail of the absorption band of naphthylamine. The π-π^* transitions of 1-naphthylamine are located at 29.9 kK ($\log \varepsilon = 3.8$), 31.3 kK ($\log \varepsilon = 3.9$), and 32.8 kK ($\log \varepsilon = 3.9$) according to the spectrum observed for the cyclohexane solution.[13] The absorption in the 28—35 kK region of the crystal spectra is probably associated with these transitions of naphthylamine or with the π-π^* transitions of chloranil.

N, N-Dimethyl-2-naphthylamine - Chloranil (1 : 1) Compound. The crystals of this compound were obtained from a carbon tetrachloride solution as blue-green needles. The $//l$ and $\perp l$ spectra are shown in Fig. 3. The 11.9 kK band is exclusively polarized along the l-axis. We assign it to the lowest charge-transfer excitation. In the spectrum of the 1 : 1 complex in the carbon tetrachloride solution, two charge-transfer bands are observed; their absorption maxima are located at 13 and at 21.8 kK. Apparently the 11.9 kK band in the $//l$ spectrum of the crystal corresponds to the first charge-transfer band of the 1 : 1 complex. The band corresponding to the second charge-transfer band of the 1 : 1 complex, however, is hardly observed in the crystal spectra. Probably the overlap between the second-highest occupied orbital of the donor and the lowest vacant orbital of the acceptor is quite small for the relative orientation of the donor and acceptor in the crystal of this compound.

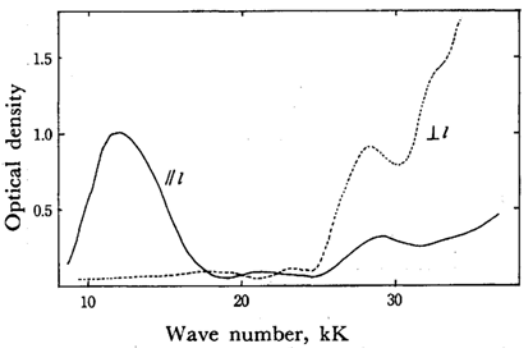

Fig. 3. Absorption spectra of *N, N*-dimethyl-2-naphthylamine-chloranil compound.

The absorption in the 25—35 kK region is stronger in the $\perp l$ spectrum than in the $//l$ spectrum. This indicates that the local excitations are responsible for the absorption in this region. In the ethanol-solution spectrum of the dimethyl-2-naphthylamine, the absorption maxima are found at 29 kK ($\log \varepsilon = 3.35$) and 35.5 kK ($\log \varepsilon = 3.86$).[13] It seems that the 28.3 kK band of the crystal spectra is associated with the 29 kK π-π^* transition of dimethyl-2-naphthylamine. The shoulder at about 32.4 kK could be a band associated with the 35.5 kK π-π^* transition of the amine or with the 34.3 kK π-π^* transition of chloranil.

N, N, N', N'-Tetramethyl-p-phenylenediamine-Chloranil (1 : 1) Compound. A reddish-brown crystalline powder of this molecular compound was prepared from a benzene solution. The crystal is either a needle or a thin plate elongated in one direction. This molecular compound

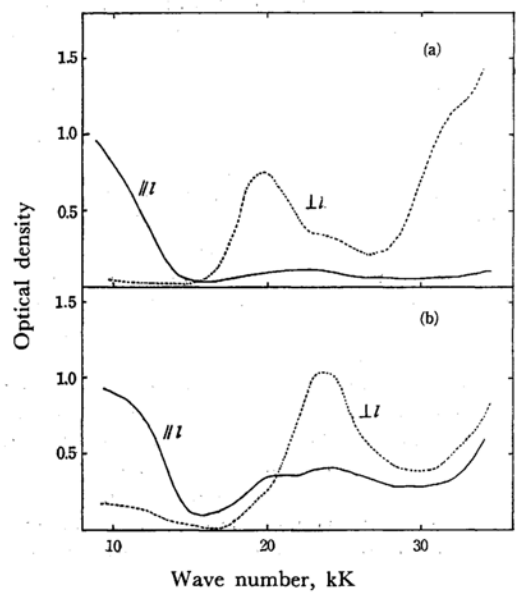

Fig. 4. Absorption spectra of *N, N, N', N'*-tetramethyl-*p*-phenylenediamine-chloranil compound.
(a) needle crystal
(b) plate crystal

*1 The calculations were made by T. Kunii of our laboratory (Thesis, The University of Tokyo, 1967).

is known to have an ionic ground state.[7,14,15] The spectra observed for a needle crystal and those observed for a plate crystal are shown in Fig. 4a and Fig. 4b respectively. An appreciable difference is found between these two cases. This is probably due to the fact that the developed face of a needle crystal is crystallographically different from that of a plate crystal.

Both Fig. 4a and Fig. 4b indicate the presence of a strong absorption band in the near-infrared region. It is polarized along the *l*-axis, which is the direction of the alternate stacking of donors and acceptors. The band maximum seems to be located at a wave number appreciably lower than 10 kK, but we were not able to determine its location exactly since the spectral region measurable with our microspectrophotometer is limited to the area above 9 kK. This band seemingly corresponds to the 8 kK band found by Kainer and Überle[3] in the powder spectrum observed by means of the KBr-pellet method.

The absorption in the 20—35 kK region is different as regards the polarization from the near-infrared band described above. This can be most clearly seen in Fig. 4a. The absorption is stronger in the $\perp l$ spectrum than in the $//l$ spectrum. There seem to be three absorption bands, located at 19.4, 23.5, and 32 kK. In the $\perp l$ spectrum of Fig. 4a, a strong absorption maximum is found at 19.4 kK, accompanied by a weak shoulder located at about 24 kK. On the other hand, the 23.5 kK band is much stronger than the 19.4 kK band in the $\perp l$ spectrum of Fig. 4b. These facts clearly indicate that the direction of the transition moment is different in the 19.4 kK band and in the 23.5 kK band. From a comparison between Fig. 4a and Fig. 4b, we may also conclude that the polarization of the 32 kK band is the same as that of the 19.4 kK band. These conclusions are in good agreement with the observations reported by Anex and Hill.[11]

The absorption spectrum of the TMPD monopositive ion has been studied by Albrecht and Simpson,[16] who have shown that the π-π^* transitions located at 17.7 kK and at 30.8 kK are polarized along the long axis of TMPD, whereas the weak π-π^* transition at 25.3 kK is of the short-axis polarization. We consider that the 19.4 kK band and the 32 kK band of the molecular compound are associated, respectively, with the 17.7 kK band and the 30.8 kK band of the TMPD ion. There is a possibility that the 23.5 kK band of the molecular compound is due to the 25.3 kK band of the TMPD ion. However, the 23.5 kK band seems to be too strong for this assignment to be acceptable. An alternate assignement is to attribute it to the lowest π-π^* transition of the chloranil ion, located at about 22.2 kK, a transition which has been identified as a transition polarized perpendicular to the molecular axis that passes through the two oxygen atoms of chloranil.[17] It has been reported by Wallwork[18] that, in the crystal of the TMPD-chloranil compound, the component molecules are alternately stacked, face-to-face, on each other along a crystal axis, and that the molecular axis of chloranil mentioned above is parallel to the long axis of TMPD. Therefore, we can predict that the polarization of the local excitation band associated with the 22.2 kK band of the chloranil ion will be perpendicular to those of the bands assocaited with the long-axis polarized transitions of the TMPD ion. This is in agreement with the observed polarization of the 23.5 kK band of the molecular compound.

In conclusion, let us assign the near-infrared absorption band of the molecular compound to the charge transfer from the chloranil ion to the TMPD ion; the 19.4 and 32 kK bands, to the local excitation associated with the TMPD ion, and the 23.5 kK band, to the lowest π-π^* transition of the chloranil ion. It should be noticed, however, that the local excitation bands are considerably broadened and are shifted to a higher energy as compared with the corresponding bands observed in the solution spectrum of each component. These facts, as well as the high intensity of the charge-transfer band, suggest the presence of a relatively strong electronic interaction between the TMPD and chloranil ions.

***p*-Phenylenediamine - Chloranil (1 : 1) Compound.** A greenish-black crystalline powder of this compound was obtained from a benzene solution. This is also known as an ionic compound.[7,15] The observed crystal spectra, shown in Fig. 5, are very similar to the spectra observed

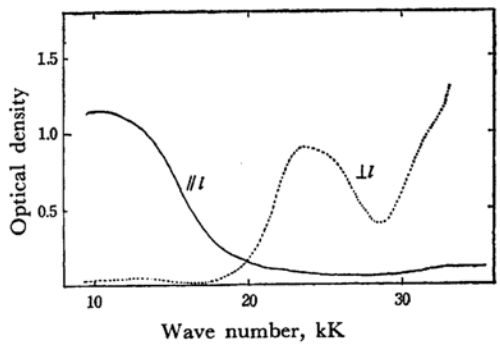

Fig. 5. Absorption spectra of *p*-phenylenediamine-chloranil compound.

14) H. Kainer and W. Otting, *Chem. Ber.*, **88**, 1921 (1955).
15) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).
16) A. C. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 4454 (1955).
17) G. Giacometti, D. L. Nordio and G. Rogatti, *Nuovo Cimento*, **23**, 433 (1962).
18) S. C. Wallwork, *J. Chem. Soc.*, **1961**, 494.

for the TMPD-chloranil compound. There is a strong absorption band in the near-infrared region; this band is exclusively polarized along the *l*-axis. We assign this band to the charge transfer between the *p*-phenylenediamine mono-positive ion and the chloranil mono-negative ion. The absorption maximum of this band is located at about 10 kK.

The broad absorption band located at 23.5 kK and polarized perpendicular to the *l*-axis can be regarded as a local excitation band. The p-phenylenediamine ion has the lowest π-π^* transition at 21.6 kK, while the chloranil ion has its at 22.2 kK. The 23.5 kK band of the molecular compound seems to be due to either of these transitions of the ions. In the present study, we were not able to determine which of these two transitions is actually responsible for the 23.5 kK band. In any case, however, we should consider that the local excitation band in the crystal spectra is shifted to a considerably higher energy as compared with the corresponding absorption band of the free ions.

Diaminodurene-Chloranil (1 : 1) Compound. A black crystalline powder of this compound was prepared from a benzene solution. This compound has an ionic ground state.[7,15] The crystal spectra are shown in Fig. 6. The general features of the crystal spectra are again quite similar to those of the TMPD-chloranil compound. The strong absorption band in the near-infrared region is polarized along the *l*-axis. This band can be assigned to the charge transfer from the chloranil mono-negative ion to the diaminodurene mono-positive ion. The absorption maximum of this charge-transfer band is located at about 10 kK.

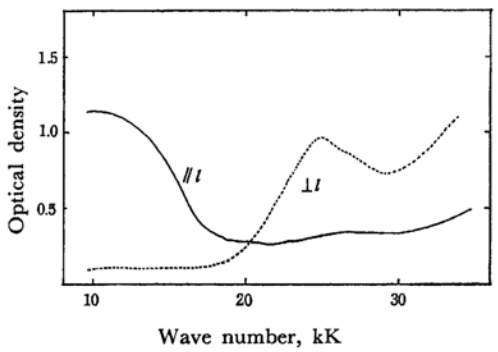

Fig. 6. Absorption spectra of diaminodurene-chloranil compound.

The 25 kK band in the $\perp l$ spectrum must be a local excitation band. The diaminodurene ion has its lowest π-π^* transition at 20.8 kK. We can not tell whether the 25 kK band is associated with this transition of the diaminodurene ion or with the 22.2 kK transition of the chloranil ion. At any rate, though, we can conclude that the local excitation band is shifted to a higher energy than the corresponding bands of the component ions.

Conclusion

We have studied the polarized absorption spectra of solid molecular compounds composed of aromatic amines and chloranil. The observed spectra can be classified into two types: the spectra of the non-ionic molecular compounds, and the spectra of the ionic molecular compounds. In the spectra of a non-ionic compound, the charge-transfer band appears at a wave number similar to that of the corresponding charge-transfer band of the (1 : 1) complex formed in the solution, and the locations of the local excitation bands also are not very different, or are shifted to an energy only a little lower, from those of the absorption bands in the solution spectrum of each component. In most cases the charge-transfer band is definitely polarized in the direction of the alternate stack of donors and acceptors. These general features of the crystal spectra are quite similar to those of the spectra of the molecular compounds formed between polycyclic aromatic hydrocarbons and tetracyanoethylene, which have been reported on in a previous paper.[12]

In the case of the ionic compounds, an absorption band associated with the charge transfer between ions is observed in the near-infrared region with a relatively high intensity. The band associated with the intra-molecular transitions of the component ions are appreciably broadened and are shifted to considerably higher energies compared with the corresponding bands in the solution spectra of the free ions. These phenomena suggest the presence of a relatively strong charge-transfer interaction between the radical ions in the solid molecular compounds.