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The Size and Shape of the Component Molecules as the Factors Determining the Electronic Structure of Crystal Complexes

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The molecular complexes of six aromatic diamines with various acceptors were classified into those complexes having essentially non-bonding ground states and those having dative ground states on the basis of their vibrational spectra. A method to arrange the complexes by the difference between the ionization potential of the donor molecule and the electron affinity of the acceptor molecule was proposed to demonstrate how important the size and shape of the component molecules are as the factors determining the electronic structures of crystal complexes. The electrostatic energies per molecule in 1 : 1 crystal complexes were found to range from 2.3 to 2.6 eV.

On the basis of the electronic and vibrational spectra, it has been shown that most donor-acceptor crystal complexes can be rather sharply divided into two groups, namely, those having essentially non-bonding ground states and those having essentially dative ground states.[1,2] The complexes in the former group are often called as weak or non-ionic complexes and those in the latter group as strong or ionic complexes. In general, when the ionization potential of the donor molecule is low and the electron affinity of the acceptor molecule is high, the resulting complex tends to have a dative ground state. However, the formation of such a crystal complex must be governed not only by the energy needed to charge the molecules, but also by the electrostatic energy of the charged lattice. The latter quantity depends on the packing of the component ions, which in turn depends on the molecular size and on the shapes of the donor and the acceptor. The present work was started with the hope of demonstrating how important the molecular size and shape can be as factors determining the electronic structures of donor-acceptor crystal complexes.

The crystal complexes were characterized in the following way. If the vibrational spectrum of a complex is well approximated by a superposition of the spectra of the component compounds, the complex has a non-bonding ground state. There are slight shifts in frequency and some alternation of intensity, reflecting the molecular association; however, it is generally easy to point out the pattern due to each component.[3,4] When the vibrational spectrum consists of the spectra of the ionized components, namely, D^+ and A^- free-radical ions, the ground state of the complex is considered to be essentially dative. The difference in the vibrational spectrum between the D molecule and the D^+ ion or that between the A molecule and the A^- ion is generally so remarkable that the characterization of crystal complexes by their spectra is not difficult.[2]

The method of selecting the component compounds must be now mentioned. It is highly desirable to have component compounds of similar nature but with different molecular sizes and shapes. The following six aromatic diamines were thought to best fulfill these requirements: *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) (I), 1,6-diaminopyrene (II), *N,N,N′,N′*-tetramethylbenzidine (III), diaminodurene (IV), 1,5-diaminonaphthalene (V), and *p*-phenylenediamine (VI). The donor I has the lowest ionization potential, and VI, the highest, among these compounds. Fortunately, even the latter is known to be able to form some authentic cation-radical salts with vibrational spectra comparable with those of the complexes. The donors II, III, and V represent diamines with pyrene, biphenyl, and naphthalene nuclei respectively. The donor IV, the ionization potential of which is presumably not far from that of I, was also included because of the higher stability of its crystal complexes. The acceptors must cover a range so wide that the diamine complexes with some acceptors have essentially non-bonding ground states, while those with some others have dative ground states. The following compounds were chosen: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (a), tetracyano-*p*-benzoquinodimethane (TCNQ) (b), tetracyanoethylene (TCNE) (c), 2,3-dicyano-α-naphthoquinone (d), 9-dicyanomethylene-2,4,7-trinitrofluorene (e), *p*-chloranil (f), *p*-fluoranil (g), 2,5-dichloro-*p*-benzoquinone (h), 2,4,7-

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[1] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963).

[2] Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).

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trinitrofluorenone (i), and dichloro-*p*-xyloquinone (j).

Experimental

All the crystal complexes were prepared by crystallization or by precipitation from solutions. The solvents used were mostly benzene and chloroform. The vibrational spectra in the NaCl region were recorded as Nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer. The visible absorption spectra of systems containing combinations of appropriate amounts of the donors and acceptors dissolved in chloroform were measured with a Beckman DK2A spectrophotometer.

Results and Discussion

Earlier the present author discussed the ionic character and charge transfer in molecular complexes in terms of the electronegativity of the highest occupied orbital of the donor molecule and that of the lowest vacant orbital of the acceptor molecule.[5] The condition;

$$\varepsilon_i < (I_D - A_A)/2 \qquad (1)$$

was obtained in the case where the charge on each molecule, ρ, in a 1:1 crystal complex is less than one half and:

$$\varepsilon_i > (I_D - A_A)/2 \qquad (2)$$

in the case where $\rho > 1/2$. Here, ε_i is the electrostatic energy per molecule when there is a unit positive or negative charge on each molecule, I_D is the ionization potential of the donor molecule, and A_A is the electron affinity of the acceptor molecule. It is apparent that the condition (1) is fulfilled in complexes having essentially non-bonding ground states and the condition (2), in those complexes with essentially dative ground states.

If one could arrange complexes placing the ionization potentials of donors on the abscissa and the electron affinities of acceptors on the ordinate, lines with a slope of -1 would become the scale for $I_D - A_A$. Such an arrangement of complexes seems to be convenient for demonstrating how the electrostatic energy, ε_i, can vary with the kind of component molecules. Unfortunately, the ionization potentials and the electron affinities are not available in the desired accuracy.

The energy of the charge-transfer absorption, $\boldsymbol{h}\nu_{CT}$, in a 1:1 single complex with an essentially non-bonding ground state may be given by:

$$\boldsymbol{h}\nu_{CT} = I_D - A_A - C + W + R + R', \qquad (3)$$

where C is the electrostatic energy in the dative bond structure, W is the energy due to van der Waals interaction in the no-bond structure, and R and R' are the energy changes due to the resonance interaction between these two structures in the ground and excited states respectively.[6] In a series of complexes of a given acceptor with various donors, when A_A is constant, it has been well established that a plot of $\boldsymbol{h}\nu_{CT}$ against I_D yields a straight line. Therefore, $C - W - R - R'$ is a relatively insensitive function of the donor, and one may write as a good approximation;[7]

$$\boldsymbol{h}\nu_{CT} \fallingdotseq I_D - A_A - C'. \qquad (4)$$

Here the electrostatic energy, C, in Eq. (3) is supposed to make the major contribution to the term C'. The energy of charge-transfer absorptions in complexes of a given donor with various acceptors may also be approximated by Eq. (4). Consequently, the energy of the charge-transfer absorption in the *s*-trinitrobenzene complex, X, measured in a chloroform solution was taken in this experiment as a measure of the ionization potential, and that in the pyrene complex, Y, as a measure of the electron affinity. The complexes on line of $Y = -X +$ constant in Fig. 1 must all exhibit charge-transfer absorptions at nearly the same energy. For example, the upper line corresponds to an energy of 15kK, and

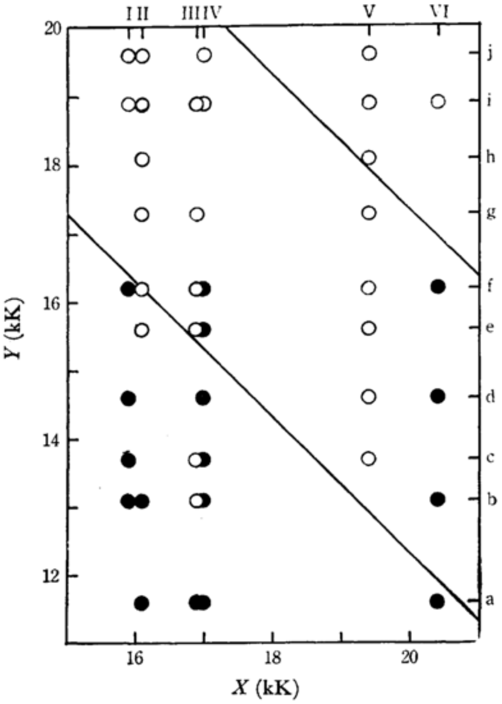

Fig. 1. Electronic structures of molecular complexes as revealed by the vibrational spectra. The complexes having non-bonding ground states are indicated by open circles and those having dative ground states by shaded circles. As to notations I—VI, a—f, and X and Y, see text.

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[6] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).

[7] H. M. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

the lower one, to 10 kK. To check the validity of this diagram, the energies of charge-transfer absorptions observed in a solution for possible combinations of the donors I—VI and the acceptors a—j were plotted against the energies read on the diagram. As Fig. 2 shows, the agreement is generally excellent.

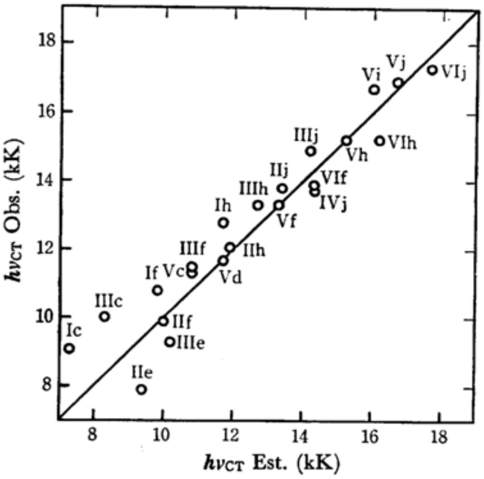

Fig. 2. Comparison between the observed energies of charge-transfer bands measured in solutions and the energies estimated by Fig. 1.

In Fig. 1 the complexes which were found to have essentially non-bonding ground states are indicated by open circles, and those found to have dative ground states, by shaded circles. The data for the DDQ (a) and *p*-chloranil (f) complexes were taken from the author's previous papers.[2,8] The independent characterization of some TCNQ (b) complexes is available in the literature.[9–11] Foster and Thomson have examined the visible absorption spectra of a number of TMPD (I) complexes and suggested that ionization by the complete transfer of an electron from the donor to the acceptor molecule occurs in the ground state of those complexes with several acceptors, including a, b, c, f, and h.[1] The present characterization by vibrational spectra is almost entirely consistent with theirs. Attempts to prepare well-defined complexes were not successful for the combinations missing from this figure. As expected, most of the complexes in the region where both X and Y are high are expressed by open circles, and those in the region where both X and Y are low, by shaded circles.

However, there are many exceptions which reflect the effects of the size and shape of component molecules on the electronic structure of the crystal complexes. Among these, *p*-phenylenediamine (VI), which is supposed to have the highest ionization potential, shows a strong tendency to form complexes with dative ground states, *e. g.*, the complex VIf. On the other hand, the tetramethylbenzidine (III) complexes tend to have non-bonding ground states in spite of the low ionization potential of the donor, *e. g.*, the complex IIIb. The difference in ε_i between these two extremes can be estimated using the following relations;

$$\varepsilon_i(\mathrm{VIf}) > [I_D(\mathrm{VI}) - A_A(\mathrm{f})]/2 \doteqdot [h\nu_{CT}(\mathrm{VIf}) + C']/2$$
$$\varepsilon_i(\mathrm{IIIb}) < [I_D(\mathrm{III}) - A_A(\mathrm{b})]/2 \doteqdot [h\nu_{CT}(\mathrm{IIIb}) + C']/2.$$

Although the crystal complex VIf has a dative ground state, the energy, $h\nu_{CT}$ (VIf), in the complex in solution can be measured using suitable solvents, or the value may be estimated by Fig. 1. Hence;

$$\varepsilon_i(\mathrm{VIf}) - \varepsilon_i(\mathrm{IIIb}) > [h\nu_{CT}(\mathrm{VIf}) - h\nu_{CT}(\mathrm{IIIb})]/2$$
$$= 3.3\,\mathrm{kK} \text{ or } 0.41\,\mathrm{eV}$$

Judging from the results presented in Fig. 1, this difference may be considered to be close to the maximum variation of ε_i.

One might feel that this difference is merely imaginary because, in the process of the estimation of ε_i, a possible change in the term C' in Eq. (4) was not taken into consideration at all. As will be discussed in the following paragraph, the electrostatic term in an ion pair in which the components are different in size and shape is generally smaller than that in which both the components are derivatives of benzene. If the doners to be compared are such as III and VI, the difference in X may be predicted to be smaller than that in I_D. Therefore, the above-mentioned value for ε_i (VIf) $-\varepsilon_i$ (IIIb) is rather underestimated.

It is very desirable to know even roughly how large ε_i itself can be. Taking the ionization potential of pyrene as 7.72 eV,[12] the following values were estimated by Eq. (4) using the energies of charge-transfer absorptions in the *s*-trinitrobenzene complexes; 7.0 eV for donor III and 7.5 eV for VI. The electron affinities were assumed to be 2.5 eV for the acceptor b and 2.2 eV for f following the discussion presented in a preceding paper.[5] Then, ε_i (VIf)$>$2.6 eV and ε_i (IIIb)$<$2.3 eV were obtained. Considering the uncertainties mentioned above, one may conclude that ε_i is of the order of magnitude of 2 eV. The electrostatic energy per molecule in a crystal, ε_i, is obtained by multiplying the Madelung constant by the electrostatic energy per molecule in an ion pair, C, in which the relative configuration is supposed to be kept the same.

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[8] Y. Matsunaga, *Nature*, **205**, 72 (1965).

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[12] M. E. Wacks, *J. Chem. Phys.*, **41**, 1661 (1964).

This assumption does not seem to be strictly realized; however, the change in ε_t by the kind of component molecule may be nearly parallel to the corresponding change in C. The values of C were computed for combinations of benzene ion and three other hydrocarbon ions, locating a fractional point charge on each carbon atom. The charge distribution are those given by the Hückel MO theory. The molecular planes were assumed to be parallel to each other and to be separated by 3.40 Å. The results are presented in Fig. 3. The larger the difference in molecular size and shape, the smaller the electrostatic energy, C; therefore, one may expect a greater probability of finding complexes with non-bonding ground states. Although the component compounds used in the present work are not as simple as the hydrocarbons, the prediction is in fairly good agreement with the observed trends shown in Fig. 1. Assuming 1.85 eV for C in the complex VIf and 1.66 eV for C in the complex IIId, the Madelung constants were found in the range from 1.35 to 1.40. It may be worthwhile to note that these values are almost equal to the constant for a one-dimensional ionic lattice.

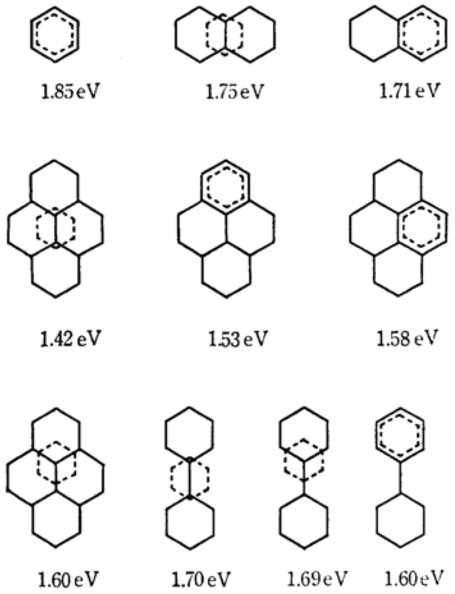

Fig. 3. The electrostatic energies per molecule in ion pairs consisting of aromatic hydrocarbon ions with a separation of 3.40 Å. All the C–C bonds were assumed to be 1.40 Å long.

Most of the quinone complexes with electrical resistivities of 10^6 ohm cm or less were reported to have dative ground states. The only exceptions occurred in the case of 1,6-diaminopyrene-*p*-chloranil (IIf) and related molecular complexes.[8] On the basis of the results presented in Fig. 1, one may conclude that the complex IIf is located near the border line between 1,6-diaminopyrene complexes with non-bonding ground states and those with dative ground states. Furthermore, it has been established that the complex crystallized from benzene can be easily transformed into a new form exhibiting only a few ohm cm. The vibrational spectra indicated that, in this form, the electronic structure of the complex itself is intermediate between no-bond and dative.[13] The tetramethylbenzidine-*p*-chloranil (IIIf), which exhibits a resistivity of 10^6 ohm cm, is located near the 1,6-diaminopyrene complex. Thus, complexes with non-bonding ground states seem to exhibit relatively low resistivities only when the charge-transfer absorptions are in an exceptionally low-energy region. To prepare such complexes, the use of component compounds with a biphenyl or pyrene nucleus may be of great advantage. Attempts in this direction are now in progress.

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[13] Y. Matsunaga, *Nature*, **211**, 183 (1966).