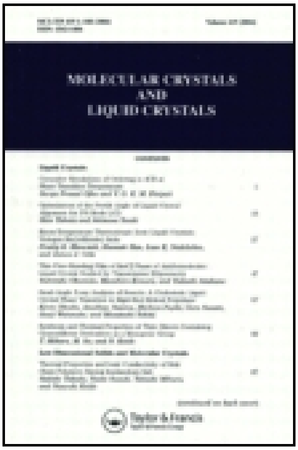

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Acceptors for Some Early Organic Semiconductors

Y. Matsunaga [a]

[a] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060, Japan

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Acceptors for Some Early Organic Semiconductors

Y. MATSUNAGA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 Japan

This review will deal mainly with the acceptors frequently employed for charge-transfer complexes in the first decade of the organic semiconductor research. Particularly, the properties and characterization of the following combinations with organic donor compounds will be described in detail: perylene-bromine, perylene-iodine, phenothiazine-iodine, and aromatic diamine-*p*-chloranil and -*p*-bromanil. Many of these complexes have been known long before their recognition as organic semiconductors. The author attempted to present how their close examinations have provided useful features to further studies.

Since the discovery of the unusual electrical properties of "perylene-bromine complex," there has been a tremendous amount of work aimed at gaining new conducting "charge-transfer complexes." The term "charge-transfer complex" means a substance formed by the interaction of two or more component molecules or ions the presence of which may be recognized by its color. The acceptors successfully employed for early semiconducting complexes; namely, bromine, iodine, *p*-chloranil, and *p*-bromanil, were relatively strong and suitable to produce the complexes exhibiting low electrical resistivities as it appeared later that such complexes are largely ionic or dative in Mulliken's terminology. Therefore, most of them may be regarded as ion-radical salts and they are often called charge-transfer salts. Among them, the complex ion-radical salts, the composition of which is different from 1:1, in other words, in which both neutral and charged molecules of the donor or acceptor compound coexist, tend to exhibit resistivities much lower than the corresponding 1:1 salts. Consequently, complex ion-radical salts may be considered as mixed-valence compounds. Thus, various terms may be used for the compounds to be described in this review. The complexes examined in the first decade of the research were not necessarily designed for this purpose but have been known for twenty years or more by organic chemists.

BROMINE AND IODINE

Bromine and iodine have been widely employed as oxidizing agents in the formation of charge transfer salts with organic molecules. The tendency of these halogens to form polyhalide ions or mixtures thereof, is advantageous in constructing linear chain stable mixed-valence lattices, but often makes the chemistry very complicated. Several polybromides and polyiodides were described long before their recognition as organic semiconductors. They have been very frequently called molecular complexes or addition compounds because of the difficulty of clarifying their character as described below.

Perylene polyhalides

Brass and Clar published five papers under the title of "unpaired halides" or "anomalous halides" between 1932 and 1939. The formation of deep brownish black needles by the addition of bromine to a benzene solution of perylene was described in their first paper.[1] The product was found to have the composition of perylene tribromide, $C_{20}H_{12}Br_3$. These authors assumed that an electron in the perylene molecule in the biradical state is donated to the Br_3 moiety. Perylene triiodide was similarly prepared by them.

The formation of a black mass in the process of reaction of bromine vapor with pulverized perylene was noted as early as 1925 by Zinke and his coworkers, who published a long series of papers entitled "studies on perylene and its derivatives."[2] Zinke and Pongratz repeated the preparation of the "tribromide" described by Brass and Clar and failed to obtain a stable product with a definite composition. They found that pulverized perylene quickly absorbs bromine up to four atoms per molecule and that the greenish black product immediately begins to liberate hydrogen bromide.[3] The unstable intermediate was concluded to be an addition compound with no unpaired electron and the formula $C_{20}H_{12}Br_4$ was assigned to it.

In 1951, Ubbelohde and his coworkers published their work on the pseudometallic properties of graphite-bromine.[4] They found that the marked diamagnetism associated with the pi-electrons in graphite is destroyed and the electrical conductance is increased on forming the lamellar compound. When we came across the papers on the "perylene tribromide" or "perylene-bromine complex," it seemed to us highly likely that this fancy compound has something in common with graphite-bromine. The specimens examined by us for the electrical resistivity and magnetic susceptibility were prepared by the method of Zinke and Pongratz. The pressed pellets of the product exhibited resistivities of about 8 ohm cm.[5,6] The observed diamagnetic susceptibility, -62×10^{-6}, was much smaller than that estimated by the additivity rule, -286×10^{-6}, which is applicable to ordinary molecular complexes.[7] Therefore, the emergence of unpaired electrons upon the complex formation seemed to be quite probable, in conformity with the concept of "unpaired halides." It was found that about eighty percent of the hydrocarbon in their specimens were converted to dibromoperylene during the process of preparation. Nevertheless, the apparent composition can be four bromine atoms per molecule because dibromoperylene produces also a black compound combining two bromine atoms per molecule.[8]

In an attempt to obtain information on the structure, Labes *et al.* have examined the vibrational spectrum of the bromine complex, perylene-$(Br_2)_{3.5}$, at $-140°C$.[9] This temperature was low enough to stop the bromination of the hydrocarbon. The spectrum was quite different from that of either the parent compound or the reaction product indicating a significant decrease in symmetry accompanying the complex formation. They suggested that the decrease in symmetry is either due to close association of bromine to particular carbon atoms in the perylene rings or to a pi-complex in which the symmetry of some benzene rings is sufficiently distorted.

The 54th paper in the series "perylene and its derivatives" reported the physicochemical studies on the composition and the character of the perylene-halogen complexes in the solid and dissolved states performed by Pestemer and Treiber.[10] They observed that the electronic absorption spectrum of mixtures of perylene and iodine or dibromoperylene and bromine is closely similar to a superposition of the band of the components; therefore, the molecular complexes were concluded to be either not salt-like or radical compounds but addition compounds. They proposed that a solid compound, perylene $(I_2)_2$ is formed in this system and gives mixed crystals with an excess of iodine. The electrical resistivities of perylene-iodine complexes were independently reported by three groups; namely, 2–3 ohm cm for perylene $(I_2)_3$ by Labes *et al.*,[11] 8 ohm cm for $(\text{perylene})_2$ $(I_2)_3$ by Kommandeur and Hall,[12] and 9 ohm cm for $(\text{perylene})_2$ $(I_2)_3$ and 10 ohm cm for perylene-$(I_2)_3$ by Uchida and Akamatu.[13] More recently, Labes and his coworkers have succeeded in growing single crystals of perylene $(I_2)_4$ and observed a metallic temperature dependence of their highly anisotropic conductivity from 235 to 340 K.[14]

The iodine content of the benzene solution which is in equilibrium with the precipitated complex was examined by Uchida and Akamatu as a function of the composition of the solid complex.[13] Their result agrees qualitatively with that reported by Pestemer and Treiber but not quantitatively; that is, a solid solution is formed between $(\text{perylene})_2$ $(I_2)_3$ and perylene $(I_2)_3$. It should be noted that the former composition is consistent with the triiodide of Brass and Clar. The diamagnetic susceptibility deviates from the value estimated by the additivity rule but its magnitude is markedly smaller than that in the bromine complex, about 80×10^{-6} for $(\text{perylene})_2$ $(I_2)_3$.[7] The complex exhibits an ESR absorption the intensity of which corresponds approximately to the above-mentioned deviation of the susceptibility.[13,15,16] The conventional structural model of a molecular complex "$(\text{perylene})_2$ $(I_2)_3$" cannot interpret these electrical and magnetic properties. Because the iodine complex is completely opaque to infrared radiation, no spectroscopic work has been reported until 1979. On the basis of the resonance Raman and iodine-129 Mössbauer spectral data, Marks *et al.* could formulate the approximate charge distribution as $(\text{perylene})^{+0.4}$ $(I_3^-, 2I_2)_{0.4}$ and concluded that the complex is a partially oxidized mixed-valence compound.[17]

1.2 Phenothiazine polyhalides

In 1913, Pummerer and Gassner isolated a blackish brown product on adding iodine to a chloroform solution of phenothiazine and reported its composition to be $C_{12}H_9NSI_2$.[18] This work was followed by its characterization as the semiquinoid diiodide by Kehrmann and Diserens.[19] The latter group also reported the preparation of the semiquinoid bromide by the oxidation of phenothiazine dissolved in ether with bromine at 0°C. The semiquinoid salt defined by them is equivalent to the cation-radical salt in our nomenclature.

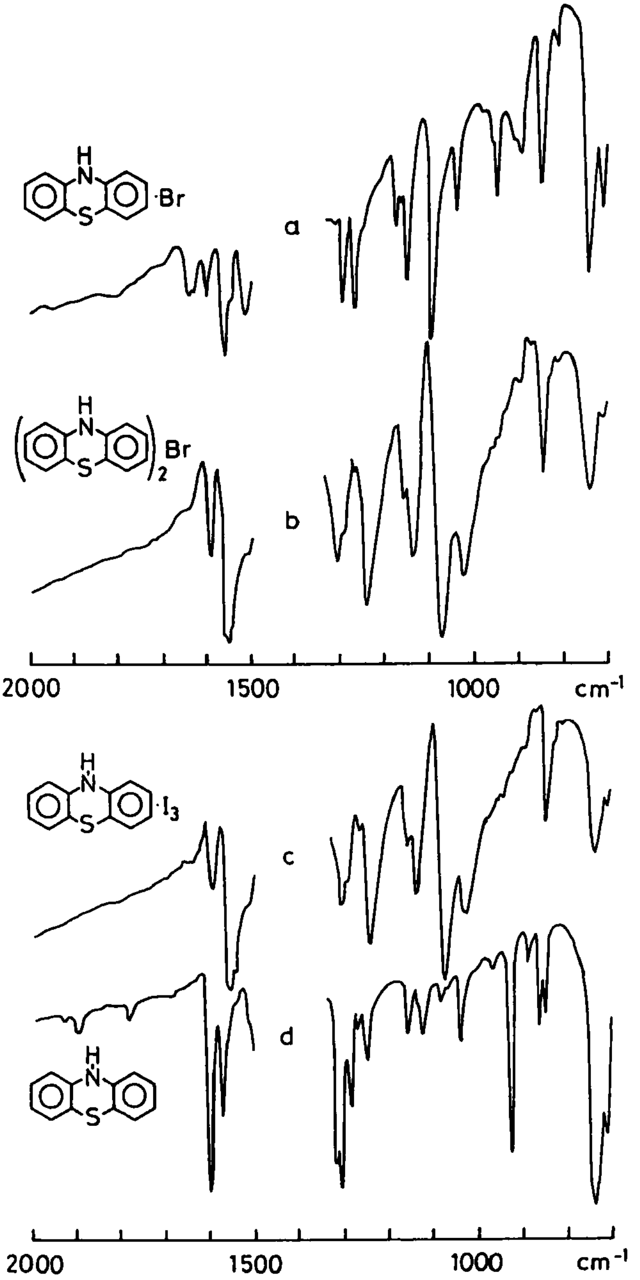

FIGURE 1 Vibrational spectra of simple phenothiazine cation-radical bromide (a), the complex cation-radical bromide (b), the iodine complex (c), and phenothiazine itself (d).

Fortunately, these compounds are transparent to infrared radiation and the vibrational spectra have been a powerful tool to characterize the electronic structure of the organic component molecule. The spectra shown by the bromide samples freshly prepared following the procedure given by Kehrmann and Diserens are often superpositions of two patterns, *a* and *b* in Figure 1, in various ratios. We could ascribe one of them to the simple cation-radical bromide, the other, to the complex cation-radical bromide of the 2:1 type.[20] Thus, the simple cation-radical bromide, the complex cation-radical bromide and polybromide seem to be all formed under similar condition. The simple salt once isolated is gradually transformed into the complex salt(s) during the storage and the rearrangement may be accelerated by the addition of phenothiazine or iodine. The resistivity-composition isotherm of the phenothiazine bromide-iodine system exhibits a minimum of 4 to 5 ohm cm around the mole ratios of 0.25, suggesting the formation of a complex cation-radical salt, $(\text{phenothiazine})_2^{+}\text{Br}_2\text{I}^{-}$.[21]

The constitution of the polyiodide appeared to be more complicated. The "triiodide" easily isolated from benzene solutions exhibits a resistivity of about 20 ohm cm at room temperature.[22] When it is dissolved in a large amount of benzene, molecular iodine is liberated and the composition can be determined by titration against sodium thiosulfate. This observation cannot be an indication that the "triiodide" is actually a molecular complex since its vibrational spectrum is different from that of the parent compound but identical to that of the complex cation-radical bromide mentioned above (compare patterns *b*, *c*, and *d* in Figure 1). However, six atoms of iodine per two molecules of phenothiazine do not fit to the composition of any known polyiodide. As is shown in Figure 2, a shoulder in the resistivity-composition isotherm, a decrease in the activation energy for semiconduction by a factor of two, and a change in the sign of the Seebeck coefficient from negative to positive can be seen at the composition of two molecules of phenothiazine to five atoms of iodine ($\text{PT-I}_{2.5}$).[23] The charge carriers generated by the incorporation of extra a half mole of iodine to the complex cation-radical pentaiodide, $(\text{PT})_2^{+}\text{I}_5^{-}$, appeared to be responsible to the resistivity decrease from about 800 ohm cm to a minimum of 20 ohm cm. The formation of the complex cation-radical pentaiodide is clearly manifested by the stepwise increase of the electromotive force (emf) of a solid-state galvanic cell, Ag/AgI/PT-I_n, at $n = 2.5$.[24] On the other hand, the emf increases rather continuously in the range from $n = 2.8$ to 3 indicating the appearance of a nonstoichiometric phase (see Figure 3). The minimum in the resistivity-composition isotherm corresponds with the upper limit of this existence range. The Gibbs energies in terms of the complex formation reactions are as follows:

$$-17.5 \text{ kJ mol}^{-1} \quad \text{for PT} + 2.5/2\text{I}_2 \rightarrow \text{PT-I}_{2.5}$$

$$-19.5 \text{ kJ mol}^{-1} \quad \text{for PT} + 2.8/2\text{I}_2 \rightarrow \text{PT-I}_{2.8}$$

$$-20.5 \text{ kJ mol}^{-1} \quad \text{for PT} + 3/2\text{I}_2 \rightarrow \text{PT-I}_3$$

Finally, it may be worthy to note that single crystals of the "triiodide" of the

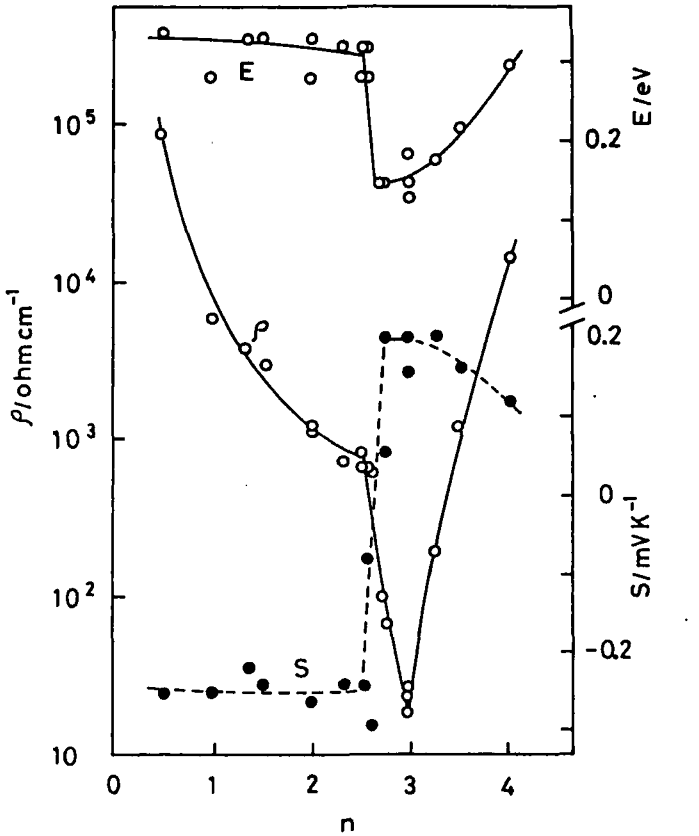

FIGURE 2 Electrical resistivity (ρ), activation energy for semiconduction (*E*), and Seebeck coefficient (*S*) of phenothiazine-I_n at 20°C plotted against *n*.

dimensions of 1.5 × 1.2 × 0.5 mm^3 have been prepared by Oza.[25] The room temperature resistivities were reported to be 0.08–0.17 ohm cm along the needle direction.

p-CHORANIL AND *p*-BROMANIL

As early as 1909, Schlenk and Knorr reported the preparation of some deeply colored "quinhydrone-like" addition compounds employing quinones and aromatic diamines.[26] The compounds studied by them included *p*-phenylenediamine- and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD)-*p*-chloranil. More than thirty years later, Weiss considered the possibility of ionization in solid complexes between quinones or polynitro compounds and aromatic hydrocarbons.[27] Although the complexes considered by Weiss were not really ionic, Kainer, Bijl, and Rose-Innes supposed that such complexes can be found among those described by Schlenk and proved that several of such complexes exhibit ESR absorptions.[28,29] While the

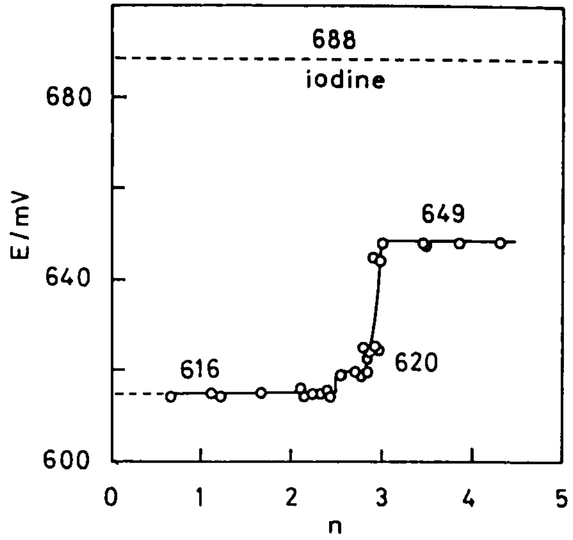

FIGURE 3 Electromotive force of the solid-state cell, Ag/AgI/phenothiazine-I_n versus n at 25°C.

spin concentration in the TMPD-*p*-chloranil complex was merely 0.002 per molecule and was detectable only by ESR, the concentration as high as 0.8 was achieved for the TMPD-*o*-bromanil complex according to the susceptibility measurements.[30] Kainer and Überle showed that the electronic absorption spectrum of the TMPD-*p*-chloranil complex dissolved in acetonitrile can be reproduced by a superposition of the spectra of Würster blue perchlorate and sodium salt of tetrachloro-*p*-benzosemiquinone.[30] The visible absorption spectra of the TMPD-quinone complexes formed in various solvents and also those in the solid state were thoroughly studied by Foster and Thomson.[31,32] These solid complexes could be classified into ionic and non-ionic ones on the basis of the electronic spectra.

Kainer and Otting measured the vibrational spectra of twenty molecular complexes and established that the spectra of weakly polar complexes such as benzidine-*s*-trinitrobenzene and *N*,*N*-dimethylaniline-*p*-chloranil can be well approximated by superpositions of the spectra of the component compounds.[33] On the other hand, their partially paramagnetic TMPD-*p*-chloranil and related complexes showed the spectra different from such superposed ones. Comparing the spectra of the TMPD complexes with different quinones, they pointed out that the spectrum of the anion-forming component is more affected than that of the cation-forming component by complex formation. During the course of their ESR experiments, Bijl, Kainer, and Rose-Innes noticed the considerable reduction of the *Q* of the cavity by specimens of *p*-phenylenediamine-*p*-chloranil and carried out measurements over the temperature range 293–263 K on the variation of dc resistance of pressed pellets.[29] The resistivity at 273 K was about 5 × 10^5 ohm cm with the energy gap of about 0.5 eV. Eley, Inokuchi, and Willis examined the dc and ac electrical resistivities of the *N*,*N*-dimethylaniline and TMPD complexes.[34] The dc resistivity of the complexes in the former group was found in the range from 10^8 to 10^9 ohm cm and those in the latter in the range from 10^4 to 10^6 ohm cm.

Labes and his coworkers extended the work to various diamine-quinone complexes.[35,36] The lowest resistivity of 10^3 ohm cm was recorded for the 1,6-diaminopyrene-*p*-chloranil. They have reported that the electronic spectra of this complex and its *p*-bromanil analog in the visible region are characteristic of a large radical-ion component.[37] Comparing the observed spectra with the computed spectra for mixtures of free components and radical ions, they estimated the mole fraction of ionic component for the complexes as 0.65 with *p*-bromanil and 0.90 with *p*-chloranil. It was concluded that the presence of large amounts of the oxidized and reduced forms of diamine-quinone complexes appears to correlate with low resistivity.

As the alkali salts of semiquinones derived from *p*-chloranil and *p*-bromanil were known by the work of Torrey and Hunter,[38] the vibrational spectra of the ionic diamine-quinone complexes could be compared with those of the semiquinone salts. However, this task was not done by Kainer and Otting. The present author subsequently accumulated the spectra of a number of quinone complexes and could confirm the presence of complexes exhibiting the vibrational pattern of the semiquinone ion instead of that of the quinone.[39] For example, the vibrational spectra of *p*-chloranil, the lithium salt of the semiquinone, and the *p*-phenylenediamine complex are presented in Figure 4. It was pointed out by the same author that most of the known quinone complexes having relatively low electrical resistivity exhibit the pattern of the semiquinone ion.[39,40] The above-mentioned 1,6-diaminopyrene complexes were found to be exceptional. Contrary to the high fractions of ionic component estimated by Kronick *et al.*,[37] these 1:1 complexes were characterized to be essentially non-ionic on the basis of the vibrational spectra.[41,42] The electronic spectra measured by the present author do support his conclusion. The discrepancy between the spectra presented by Kronick *et al.* and those by Koizumi and Matsunaga apparently arises from the instability of the complexes ground with potassium bromide.

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 be ionic. 1,6-Diaminopyrene is supposed to have an ionization potential lower than that of *p*-phenylenediamine; nevertheless, the results mentioned above are not in accordance with such a tendency. The formation of an ionic solid complex must be governed not only by the energy needed to charge the molecules, but also by the electrostatic energy of the charged lattice.[43] The latter quantity depends on the packing of the component ions, which in turn depends on the size and shape of the donor and the acceptor molecules. If one could arrange complexes placing the ionization potential of donors (I_D) on the abscissa and the electron affinities of acceptors (E_A) on the ordinate, lines with a slope of -1 would become the scale for $I_D - E_A$. Such an arrangement of complexes would demonstrate how the electrostatic energy can vary with the kind of component molecules. In Figure 5, the energy of the charge-transfer absorption maximum in the *s*-trinitrobenzene complex in a chloroform solution, X, is taken as a measure of I_D and that in the pyrene complex, Y, as a measure of E_A. The

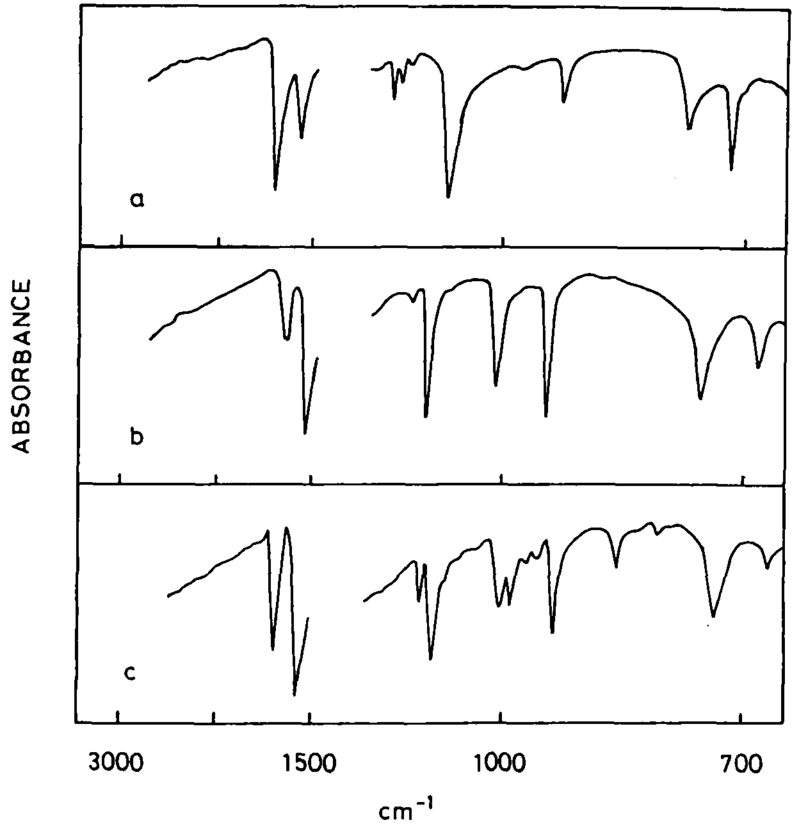

FIGURE 4 Vibrational spectra of *p*-chloranil (a), the lithium salt of the semiquinone (b), and the *p*-phenylenediamine complex (c).

complexes on line of $Y = -X +$ constant in this figure must all exhibit charge-transfer absorptions at nearly the same energy. For example, the upper line corresponds to an energy of 15×10^3 cm^{-1}, and the lower one, to 10×10^3 cm^{-1}. The following six diamines are presented in this diagram: *N*,*N*,*N*′,*N*′-teramethyl-*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 acceptors employed here are 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (a), tetracyano-*p*-benzoquinodimethane (TCNQ) (b), tetracyanoethylene (TCNE) (c), 2,3-dicyano-1,4-naphthoquinone (d), 9-dicyanomethylene-2,4,7-trinitrofluorene (e), *p*-chloranil (f), *p*-fluoranil (g), 2,5-dichloro-*p*-benzoquinone (h), 2,4,7-trinitrofluorenone (i), and dichloro-*p*-xyloquinone (j). The complexes which were found to be essentially non-ionic by the vibrational spectra are indicated by open circles and those found to be largely ionic by shaded circles.[44] As expected, most of the complexes in the region where both X and Y are high are represented by open circles, and those in the region where both X and Y are low, by shaded circles. However, there

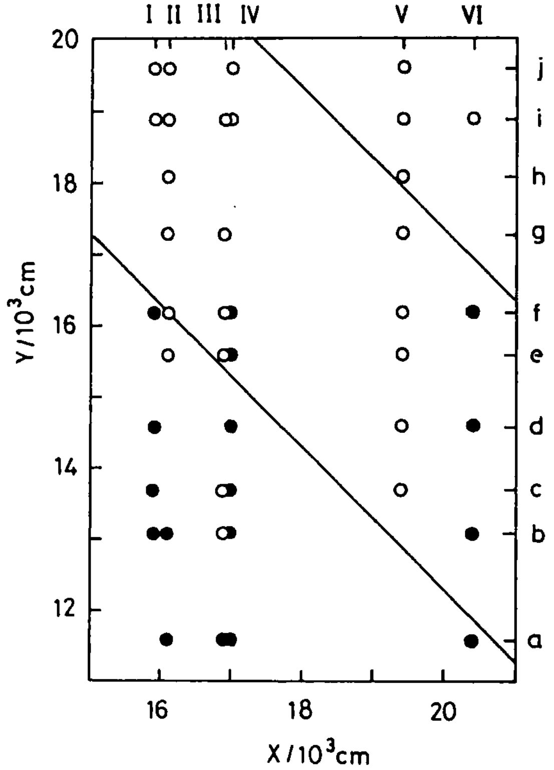

FIGURE 5 Electronic structures of molecular complexes as revealed by the vibrational spectra. The essentially non-ionic complexes are indicated by open circles and the largely ionic complexes by shaded circles. As to notations I-VI, a-j, and X and Y, see text.

are many exceptions which reflect the effects of the size and shape of component molecules on the electronic structure of the solid complexes. Among these, *p*-phenylenediamine (VI), which is supposed to have the highest I_D, shows a strong tendency to form ionic complexes, whereas the *N*,*N*,*N*′,*N*′-tetramethylbenzidine complexes tend to be non-ionic in spite of the low I_D. The difference in I_D-E_A between these two extremes is, at least, 0.8 eV. Apparently, the 1,6-diaminopyrene-*p*-chloranil (IIf) is located near the borderline between the non-ionic d ionic complexes of this donor. The non-ionic *N*,*N*,*N*′,*N*′-tetramethylbenzidine-*p*-chloranil (IIIf), which exhibits a resistivity of 10^6 ohm cm, is found near the 1,6-diaminopyrene-*p*-chloranil. Thus, complexes near the borderline seemed to exhibit relatively low electrical resistivities. Later, it has been demonstrated that complexes or ion radical salts located in this borderline region display metallic conductivity due to incomplete charge transfer. For instance, Saito and Ferraris arranged sixty-one structurally-related TTF-TCNQ-based complexes in a diagram similar to that given in Figure 5, employing the electrochemical half-wave potential of the donor, $E_{\frac{1}{2}}$ (D), and that of the acceptor, $E_{\frac{1}{2}}$ (A), in solutions as measures of the I_D and the E_A.[45] The combinations in the narrow redox potential range of $-0.02 < E_1(D) - E_1(A) < 0.34$ V were shown to have a high possibility of being "organic metals."

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