The Polymorphism and Physical Properties of the 1,6-Diaminopyrene-*p*-chloranil and Related Molecular Complexes[1]

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The 1,6-diaminopyrene-*p*-chloranil complex is dark blue when crystallized from chloroform and brown when crystallized from benzene. These two substances are distinctly different in X-ray diffraction, electronic spectrum, vibrational spectrum, and also electrical resistivity. The brown form, the resistivity of which is about 10^5 ohm cm, can be transformed into a third form, exhibiting only a few ohm cm, by compression in the presence of benzene or some other aromatic solvents. Dimorphic forms are also found with the complexes of trichloromonobromo- and dichlorodibromo-*p*-benzoquinones. One of these forms is of a similar nature to the dark blue-colored *p*-chloranil complex. The other form is brown. Only the brown form is obtainable for the complexes of monochlorotribromo-*p*-benzoquinone and *p*-bromanil. All the brown complexes except that of *p*-chloranil are similar and exhibit resistivities of the order of 10^3 ohm cm. In addition, black products exhibiting resistivities of several ohm cm can be prepared by using acetone as the solvent with 1,6-diaminopyrene and tetrahalo-*p*-benzoquinones. Contrary to the afore-mentioned complexes, no definite composition can be assigned to these low-resistivity products.

A large number of molecular complexes formed by interaction between organic electron-donors and acceptors have been examined for semiconductivity and related electronic properties in the past two decades. Among them, the 1,6-diaminopyrene-*p*-chloranil complex seemed to be particularly interesting because of the following reasons: 1) It has been well established that crystal complexes are rather sharply divided into two groups, namely, non-ionic and ionic complexes.[2-4] Furthermore, the complexes with electrical resistivities of 10^6 ohm cm or less have been shown to be ionic.[5] The 1,6-diaminopyrene-*p*-chloranil and related molecular complexes were the only exceptions to this rule known before our recent work on benzidine complexes.[6]

2) The resistivity values recorded for the *p*-chloranil complex are scattered over a wide range, 10^3—10^4 ohm cm for the pressed polycrystalline samples and 10^5—10^9 ohm cm in the three directions of the single crystal.[7-9] In a preliminary report, one of the present authors suggested that these scattered values can be correlated with the polymorphic forms.[10]

3) The brown form of the *p*-chloranil complex can be transformed into a new form with a resistivity of only a few ohm cm if compressed with a small amount of benzene.[10]

Previously we presented a way of demonstrating the effects of the size and shape of the component molecules on the electronic structure of crystal complexes.[11] The diagram proposed there revealed that the 1,6-diaminopyrene-*p*-chloranil is located near the border line between non-ionic and ionic complexes of this donor. Moreover, the tetramethylbenzidine-*p*-chloranil complex, which exhibits a resistivity of 10^6 ohm cm, is near the above-mentioned location in the diagram. Thus, non-ionic complexes seem to exhibit relatively low electrical resistivities only when their charge-transfer absorptions are in an exceptionally low energy region. Guided by this working hypothesis, we have prepared several non-ionic complexes of benzidine and its derivatives with resistivities of 10^3—10^5 ohm cm.[6] An examination of the electronic properties of the 1,6-diaminopyrene-*p*-chloranil and related complexes in more detail was highly desirable in order to verify the above-mentioned hypothesis. As the existence of some polymorphic forms has been noted, such a study would provide an excellent chance of demonstrating the importance of the stacking of the component molecules as one of the factors determining the electronic properties of molecular complexes. Furthermore, we were very much interested in the possibility of obtaining low-resistivity complexes without the process of compression.

Experimental

Materials. The *p*-chloranil, 2,5-dichloro-, and 2,6-dichloro-*p*-benzoquinones, and the *o*-chloranil were commercially obtained. The other component compounds were prepared following the procedures described in the references cited: 1,6-diaminopyrene,[12] trichloromonobromo-*p*-benzoquinone,[13] 2,5-dichloro-3,6-dibromo-*p*-benzoquinone,[14] 2,6-dichloro-3,5-dibromo-*p*-benzoquinone.[14] monochlorotribromo-*p*-benzoquinone,[15] *p*-bromanil,[16] 2,3-dichloro-

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[1] A part of the present work was performed by Y. M. while employed at the Central Research Division of American Cyanamid Company, and was presented at the Symposium on Molecular Structures, Nagoya, 1965.

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p-benzoquinone,¹⁷⁾ and *o*-bromanil.¹⁸⁾

The complexes were crystallized when hot solutions of the components were mixed. For example, a solution of 1,6-diaminopyrene (0.70 g) in 350 m*l* of hot chloroform was added to a solution of *p*-chloranil (0.73 g) in 150 m*l* of hot chloroform. Dark blue crystals were filtered out and washed with the solvent. The yield was 0.85 g. Calcd for $C_{16}H_{12}N_2 \cdot C_6Cl_4O_2$: C, 55.3; H, 2.5; N, 5.9; Cl, 29.7%. Found: C, 55.2; H, 2.4; N, 6.1; Cl, 29.4%. When a solution of the quinone (1.48 g) in 150 m*l* of hot benzene was added to a solution of 1,6-diaminopyrene (1.40 g) in 700 m*l* of the same solvent, brown needles appeared on cooling. The yield was 1.70 g. Found: C, 55.9; H, 2.9; Cl, 28.7%. The *p*-bromanil complex was brown when similarly prepared from both chloroform and benzene. Calcd for $C_{16}H_{12}N_2 \cdot C_6Br_4O_2$: C, 40.3; H, 1.8; N, 4.3; Br, 48.8%. Found: C, 40.6; H, 2.0; N, 4.7; Br, 49.5% for a preparation from chloroform. C, 40.3; H, 1.9; N, 4.4; Br, 48.1% for a preparation from benzene.

When acetone was used as the solvent, the product showed various compositions depending upon the conditions of preparation, *e.g.*, the ratio of the donor to the acceptor employed and their concentrations. The following examples show two extremes in the combination of 1,6-diaminopyrene and *p*-chloranil. The diamine (0.46 g) dissolved in 20 m*l* of acetone was added to 1.48 g of *p*-chloranil in 80 m*l* of hot acetone. The mixture was kept overnight in a stoppered flask, and then the black crystalline deposits were filtered. The yield was 0.43 g. Found: Cl, 16.2% (No. 1 in Table 3). An acetone solution containing 1,6-diaminopyrene and *p*-chloranil in a mole ratio of 1 : 3 was evaporated to dryness at room temperature. The free *p*-chloranil in the deposits was removed by extraction with benzene using a Soxhlet apparatus. The remaining sample was analysed. Found: C, 46.8; H, 2.1; N, 4.6; Cl, 36.3; O, 8.6% (No. 2 in Table 3). One preparation of the 1,6-diaminopyrene-*p*-bromanil crystallized from acetone had the following composition: C, 36.8; H, 1.8; N, 2.9; Br, 53.4% (No. 9 in Table 3).

Measurements. The X-ray measurements were made with a Toshiba recording X-ray diffractometer, Model ADG-301, using filtered copper radiation. The electronic spectra of the crystal complexes were recorded on a Beckman DK-2A spectrophotometer, and the vibrational spectra, on a Jasco IR-G infrared spectrophotometer, both as Nujol mineral oil mulls. The resistivities were measured with a Yokogawa Wheatstone bridge, Type 2768, employing a cell similar to that designed by LaFlamme.¹⁹⁾ During the measurements, the samples were compressed by applying a pressure of about 0.8 kilobars. The temperature was adjusted in the range from room temperature to 100°C using a heating tape wrapped around the cell and with the aid of a Chino temperature-indicating controller.

Results and Discussion

The 1 : 1 Complexes. *p*-Chloranil and trichloromonobromo- and dichlorodibromo-*p*-benzoquinones form dark blue-colored complexes with 1,6-diaminopyrene in chloroform. As they are green when pulverized, hereafter "green form" will be used to designate them. All the quinones give brown-colored complexes if mixed with 1,6-diaminopyrene in benzene. The same brown-colored *p*-chloranil complex can be crystallized from the following solvents; toluene, xylene, mono- and *o*-di-chlorobenzenes. The green form is transformed into the brown form when recrystallized from benzene. With monochlorotribromo-*p*-benzoquinone and *p*-bromanil, the brown forms are crystallized even from chloroform. The X-ray diffraction patterns are schematically presented in Fig. 1. The patterns given by all the green forms are similar to each other. However, the brown form of the *p*-chloranil complex is apparently different from the others; hereafter, the latter will be called "the brown form of the second type." Thus, the existence of polymorphic forms in the present complexes is evident. As will be described in the following paragraphs, the difference between the green and brown forms and also that within the brown forms are markedly reflected in their physical and chemical properties. Although only the complexes with *p*-chloranil and *p*-bromanil were analysed, the other complexes mentioned above are doubtlessly of a 1 : 1 composition, also.

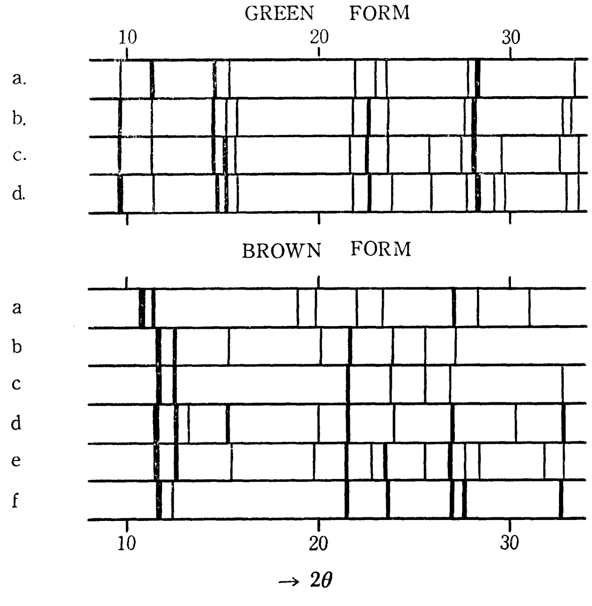

Fig. 1. X-Ray diffraction patterns of the 1,6-diaminopyrene complexes with (a) *p*-chloranil, (b) trichloromonobromo-*p*-benzoquinone, (c) 2,5-dichloro-3,6-dibromo-*p*-benzoquinone, (d) 2,6-dichloro-3,5-dibromo-*p*-benzoquinone, (e) monochlorotribromo-*p*-benzoquinone, and (f) *p*-bromanil.

The measurements of the electronic spectra of the complexes of *p*-chloranil and *p*-bromanil have been attempted by Kronick *et al.*²⁰⁾ In their measurements the specimens were ground with potassium bromide and pressed into disks. The absorption spectra obtained by them in the range from about 14 to 40 kK showed the complexes to be mostly radical-ion salts. For instance, the mole fractions of the ionic component of the *p*-chloranil complex was estimated to be as high as 0.90. As was pointed out in our previous paper, the vibrational spectrum is in contradic-

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tion with their characterization.[5] Therefore, we examined the electronic spectra of the present complexes by measuring the diffuse reflectance in the range from 6 to 30 kK of the specimens diluted with sodium chloride or naphthalene.[10] Contrary to the spectra presented by Kronick *et al.*, ours showed strong absorptions extended into the near-infrared region. As the charge-transfer absorption of the *p*-chloranil complex is located at 9.9 kK in chloroform and at 8.8 kK in toluene, our observation seemed to be consistent with the view that the complexes are non-ionic. Nevertheless, all the spectra, especially those of the brown forms, contained an extra band appearing at 14 kK. This location can well be compared with a band in the spectrum of 1,6-diaminopyrene monobromide reported in our previous work.[21] The intensity was increased by prolonged grinding, and also by storage; therefore, the cation-radical may be supposed to be formed in these processes. Apparently the discrepancy between the spectra presented by Kronick *et al.* and ours arises from the instability of the complexes ground with potassium bromide. In the present work, we attempted various methods to prevent the appearance of the band at 14 kK. The measurements as Nujol mineral oil mulls was found to be the best from this standpoint. However, with this technique it is not possible to estimate how large the light scattering is or how it depends on the wavenumber, because then the specimens absorb light over the entire measurable range. The apparent spectra newly-obtained for the *p*-bromanil complex and the green and brown forms of the *p*-chloranil complex are shown in Fig. 2. The green form withstands grinding better than the brown form. Consequently, we see that the spectrum of the green form of the *p*-chloranil complex is in essential agreement with that previously measured by the diffuse-reflection method. The spectrum of the brown form is very much improved by the present technique. The absorption maximum of the low-energy band is located around 7 kK. This value is lower by about 2 kK than the energy of the charge-transfer band of this complex dissolved in toluene, from which this form can be crystallized. On the other hand, the low-energy band in the green form appears at exactly the same place as the charge-transfer band of the complex dissolved in chloroform. The overall patterns of these two are similar, and both are certainly of charge-transfer complexes. However, a shoulder on the low-energy side of the absorption band in the visible region is observed only in the spectrum of the brown form, not in that of the green form. Very recently Amano *et al.* presented the crystal spectra of diaminopyrene complexes.[22] In their spectrum of the brown-colored *p*-chloranil complex, there is no charge-transfer band in the near-infrared region. This serious disagreement has yet to be explained. The *p*-bromanil complex, the representative of the brown forms of the second type, shows a spectrum similar to that of the brown-colored *p*-chloranil complex.

As has been reported previously, the vibrational spectrum of the brown form of the *p*-chloranil complex is well approximated by the superposed spectra of the compounds.[5] The green forms and the brown forms of the second type give similar spectra, indicating that they are also non-ionic. However, the patterns in

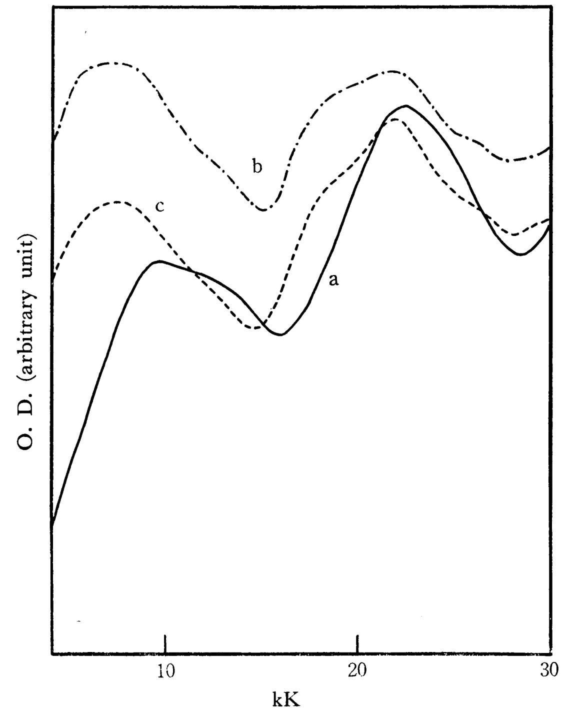

Fig. 2. Electronic spectra of (a) the green form and (b) the brown form of the *p*-chloranil complex and (c) the *p*-bromanil complex.

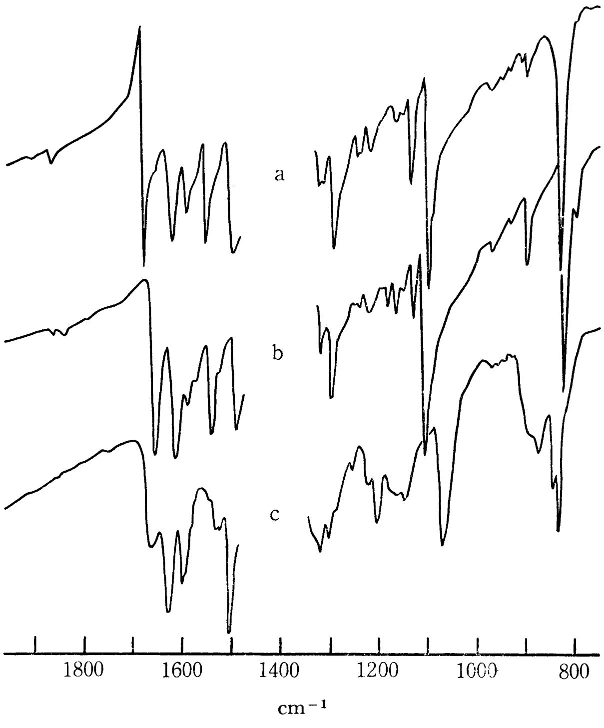

Fig. 3. Vibrational spectra of (a) the brown form and (b) the green form of the *p*-chloranil complex and (c) the *p*-bromanil complex.

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the region between 1500 and 1700 cm^{-1} are very characteristic of each form. For example, Fig. 3 presents the spectra of the complexes of *p*-chloranil and *p*-bromanil. In the spectrum of the brown-colored *p*-chloranil complex, the bands at 1500, 1595, and 1625 cm^{-1} may be assigned to the donor, and those at 1560 and 1680 cm^{-1}, to the acceptor. The carbonyl stretching band is shifted to 1655 cm^{-1} in the spectrum of the green form. The *p*-bromanil complex gives the highest energy band in this region at 1655 cm^{-1}, but its intensity is markedly weaker than that of the band at 1625 cm^{-1}. Thus, the deviation from the superposed spectrum in the above-mentioned region is appreciable in both the green forms and brown forms of the second type. This observation indicates that the mode of intermolecular interaction is somewhat different in these forms.

The electrical resistivities of compressed polycrystalline samples of the complexes obey the usual exponential law;

$$\rho = \rho_0 \exp (E_a/kT),$$

where ρ is the resistivity, ρ_0 is a constant, and E_a is the activation energy for semiconduction. As has been found in many semiconductors, the value in the high-temperature range is often larger than that in the low-temperature range. For example, the results of the measurements of the complexes of *p*-chloranil, trichloromonobromo-*p*-benzoquinone, and *p*-bromanil are plotted in Fig. 4. The data on all the complexes are listed in Table 1. Kronick and Labes grew their single crystal of the *p*-chloranil complex from chloroform and obtained the following resistivities at 25°C in three directions: 10^5, 10^6, and 10^9 ohm cm.[9] Considering the solvent employed by them, these values may be compared with our value for the green form. The present result agrees reasonably well with the geometric mean of the values observed by Kronick and Labes. In addition, the activation energy in one of the three directions reported by them, 0.19 eV, is in good agreement with our value for the high-temperature range. As may be noted in Table 1, the values of the resistivity and the activation energy in the green forms of the other three complexes are similar to those of the *p*-chloranil complex.

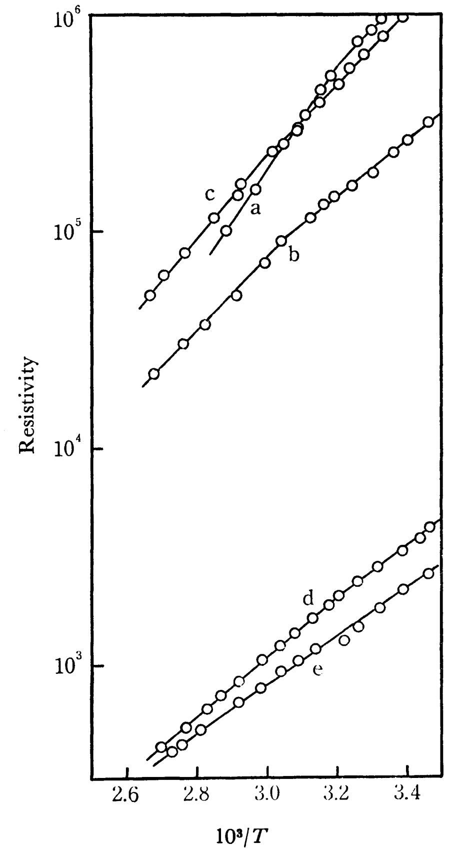

Fig. 4. Electrical resistivities of (a) the green form and (b) the brown form of the *p*-chloranil complex, (c) the green form and (d) the brown form of the trichloromonobromo-*p*-benzoquinone complex, and (e) the *p*-bromanil complex.

After careful drying, the brown-colored *p*-chloranil complex exhibits a resistivity of the order of 10^5 ohm cm, as is listed in Table 1. This value can be quickly decreased by compression in the presence of benzene. Even a trace of the solvent remaining in the sample can result in a lowering of the resistivity to 10^3—10^4 ohm cm, the values reported by earlier workers.[7,8] If the amount of the solvent is enough, *e.g.*, a few drops per gram, a resistivity as low as a few ohm cm can be achieved. Not only benzene but also the following aromatic liquids were found to be more or less effective in effecting the transformation; toluene, xylene, chlorobenzene, *o*-dichlorobenzene, dimethylaniline, nitro-

Table 1. Electrical properties of the 1,6-diaminopyrene complexes

Acceptor	Form	Resistivity at 20°C (ohm cm)	E_a (eV)[a)]
p-Chloranil	Green	1.3×10^6	0.14, 0.20
	Brown	2.7×10^5	0.11, 0.14
Trichloromonobromo-*p*-benzoquinone	Green	9.7×10^5	0.14, 0.17
	Brown (II)	3.3×10^3	0.10, 0.12
2,5-Dichloro-3,6-dibromo-*p*-benzoquinone	Green	3.3×10^6	0.15, 0.19
	Brown (II)	4.0×10^3	0.12, 0.13
2,6-Dichloro-3,5-dibromo-*p*-benzoquinone	Green	2.3×10^6	0.14, 0.16
	Brown (II)	1.3×10^4	0.11
Monochlorotribromo-*p*-benzoquinone	Brown (II)	2.4×10^3	0.10
p-Bromanil	Brown (II)	2.3×10^3	0.10

a) The first value is for the low-temperature range, and the second for the high-temperature range.

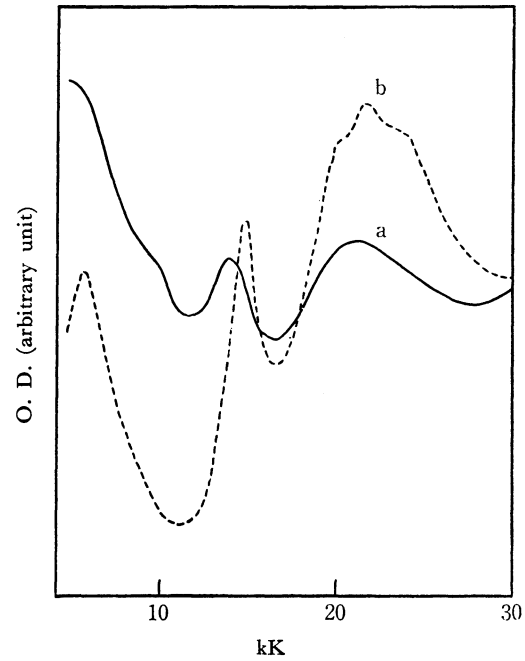

Fig. 5. Electronic spectra of (a) the low-resistivity form of the *p*-chloranil complex and (b) 1,6-diaminopyrene monobromide.

benzene, and pyridine. Contrary to the green and brown forms, which are stable up to about 160°C, the low-resistivity form is not very stable, even at room temperature. After storage for several years, a resistivity of about 100 ohm cm was recorded. The electronic spectrum is shown in Fig. 5, along with that of 1,6-diaminopyrene monobromide measured by the same technique. The absorption in the near-infrared region is appreciably stronger than that in the visible region, and it is shifted to the low-energy side compared with those in the green and brown forms. This behavior seems to be consistent with its low-electrical resistivity, as was noted at the beginning of this paper.

The presence of some diaminopyrene cation-radicals indicated by the peak at 14.0 kK must be mentioned. In the process of the transformation, the complex is compressed; therefore, the pellet produced must be crushed for further examination. As was mentioned earlier, this final step is possibly accompanied by the formation of the cation-radical. The presence of a fair amount of the cation-radical may correlate with the low resistivity, as has been suggested by Kronick *et al*;[20)] however, it must be pointed out that the low resistivity can be observed before the crushing. As may be expected from the electronic spectrum shown in Fig. 5, this form shows a strong absorption in the rock-salt region. The vibrational pattern in the above-mentioned characteristic region consists of bands at 1500, 1530, 1580, and 1635 cm^{-1}. If the last one arises from the carbonyl-stretching vibration, it is shifted to the low-energy side as much as 50 cm^{-1}. This unusually large shift may indicate that the crystal structure allows an appreciable contribution of the dative structure to the ground state. It may be suggested that the low-resistivity form has an electronic structure which is intermediate between non-ionic and ionic.

All the brown-colored complexes of the second type exhibit resistivities of the order of 10^3 ohm cm. This value is in accordance with that reported for the *p*-bromanil complex by Labes *et al.*[7)] They are stable under compression in the presence of benzene as well as the green forms of the complexes of *p*-chloranil and

TABLE 2. CLASSIFICATION OF THE 1 : 1 COMPLEXES

	Halogen atoms on quinonone molecule				
Solvent	Cl_4	Cl_3Br	Cl_2Br_2[a)]	$ClBr_3$	Br_4
Chloroform	Green form Resistivity 10^6 ohm cm			Brown from (II) 10^3 ohm cm	
Benzene	Brown form 10^5 ohm cm		Brown form of (II) Resistivity 10^3 ohm cm		

a) 2,5-dichloro-3,6-dibromo- and 2,6-dichloro-3,5-bromo-*p*-benzoquinones.

TABLE 3. RESISTIVITIES OFN THE ON-STOICHIOMETRIC COMPLEXES

No.	Quinone	Preparation method	Composition	Resistivity (ohm cm)
1	*p*-Chloranil	Crystallization	See Exptl.	200
2	*p*-Chloranil	Evaporation	See Exptl.	7
3	*p*-Chloranil	Evaporation	1 : 1	870
4	*p*-Chloranil	Evaporation	1 : 1.2	13
5	*p*-Chloranil	Evaporation	1 : 1.4	6
6	*p*-Chloranil	Evaporation	1 : 1.6	4
7	2,5-Dichloro-3,6-dibromo-*p*-benzoquinone	Evaporation	2 : 3	5
8	2,6-Dichloro-3,5-dibromo-*p*-benzoquinone	Evaporation	2 : 3	9
9	*p*-Bromanil	Crystallization	See Exptl.	3
10	*p*-Bromanil	Evaporation	2 : 3	10^7
11	2,3-Dichloro-*p*-benzoquinone	Evaporation	2 : 3	10^6
12	2,5-Dichloro-*p*-benzoquinone	Evaporation	2 : 3	10^4
13	2,6-Dichloro-*p*-benzoquinone	Evaporation	2 : 3	10^5
14	*o*-Chloranil	Evaporation	2 : 3	10^4
15	*o*-Bromanil	Evaporation	2 : 3	10^4

trichloromonobromo- and dichlorodibromo-*p*-benzoquinones. The classification of these 1 : 1 complexes, based on X-ray diffraction and physical properties, is summarized in Table 2. It is interesting to note that the kind of polymorphic form is entirely governed by the number of chlorine (or bromine) atoms on the quinone molecule. The large difference in the optical and electrical properties found in these polymorphic forms shows the importance of the stacking of the component molecules as one of the factors determining the electronic properties of these complexes.

The Non-stoichiometric Complexes.[23] 1,6-Diaminopyrene dissolves well in acetone; therefore, we attempted the preparation of the complexes in acetone in order to avoid the use of a large amount of the solvent. Surprisingly, the complexes prepared in acetone are of an entirely different nature from the 1 : 1 complexes described above. They show no definite composition. The complexes were prepared by crystallization from acetone or by the evaporation of the acetone solution to dryness. The second process was performed by lefting the solution stand in a good hood without heating. As may be seen in Table 3, a low resistivity can be achieved over a fairly wide range of composition (*e.g.*, see Nos. 1 and 2). Although the compositions of Nos. 2 and 9 do not exactly correspond to any simple ratio of the donor to the acceptor, both of them are not far from the calculated values for a mole ratio of 2:3: C, 49.9; H, 2.0; N, 4.7; Cl, 35.5; O, 8.0%, and C, 34.6; H, 1.4; N, 3.2; Br, 55.3%, respectively. Therefore, for the quinones other than *p*-chloranil, the evaporation was carried out only at this mole ratio. It must be added that the complex prepared by the evaporation of an acetone solution to dryness cannot be homogeneous. The composition of No. 1 is markedly different from the ratio of the diaminopyrene to the *p*-chloranil initially dissolved into the solvent. When the solvent is evaporated, the composition of the deposit is expected to vary according to the changes in the mole ratio and also in the concentration. Moreover, we can expect the presence of some decomposition products in the samples made by this method. These two factors may explain the observed difference in resistivity between the samples made by crystallization and those made by evaporation (compare Nos. 9 and 10). In Table 3 we can see that only tetrahalo-*p*-benzoquinones give low-resistivity complexes with 1,6-diaminopyrene in this solvent.

The authors wish to express their thanks to Dr. Toshio Yokokawa for the use of the X-ray diffractometer.

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[23] The resistivities in this section were measured on compressed pellets by a four-probe method using an A. & M. Fell Model B resistivity test rig and a Keithley Model 502 milliohmmeter.