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The Crystal Spectra of Molecular Compounds of 1,6-Diaminopyrene

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Polarized absorption spectra were observed on the single crystals of molecular compounds which involve 1,6-diaminopyrene as electron donor and *p*-chloranil, *p*-bromanil, *p*-iodanil, and tetracyano-*p*-quinodimethane as electron acceptor. It is shown that, in spite of the low ionization potential of diaminopyrene 6.56 eV, its solid molecular compounds with chloranil, bromanil, and iodanil are of non-ionic type, and their crystal spectra exhibit the general features characteristic of a typical charge-transfer molecular compound composed of neutral molecules. The diaminopyrene-TCNQ compound was found to be of ionic type. Although the bromanil and iodanil compounds of diaminopyrene exhibit two charge-transfer bands, in the region below 10 kK and at about 20 kK respectively, the chloranil compound does not show the near-infrared charge-transfer band corresponding to the charge transfer from the highest occupied orbital of the donor to the lowest vacant orbital of the acceptor. A discussion is given for this phenomenon from the overlap between the donor and acceptor orbitals.

The solid molecular compounds of 1,6-diaminopyrene with chloranil and bromanil have been reported to be organic semiconductors of relatively good electrical conductivity.[2–6] The visible absorption spectra of the crystalline powders of these molecular compounds were first examined by Kronick *et al.* and Scott *et al.* by using the KBr-pellet method.[7,8] They concluded from the observed spectra that a considerable fraction of the constituent molecules are in ionic states at room temperature, and estimated the ionic fraction as 90

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[2] M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.*, **33**, 868 (1960).

[3] P. L. Kronick and M. M. Labes, *ibid.*, **35**, 2016 (1961).

[4] M. Schwartz, D. W. Davies, and B. J. Dobriansky, *ibid.*, **40**, 3257 (1964).

[5] W. H. Bentry and H. G. Drickamer, *ibid.*, **42**, 1573 (1965).

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

[7] P. L. Kronick, H. Scott, and M. M. Labes, *J. Chem. Phys.*, **40**, 890 (1964).

percent in the chloranil compound and 30 percent in the bromanil compound.

The spectra of these molecular compounds were reexamined later by Matsunaga.[9] He applied the method of diffuse reflectance spectroscopy on the crystalline powder of these molecular compounds, and obtained results considerably different from those reported by the previous workers. He suggested that both molecular compounds are of an essentially nonionic type.

In view of the considerable discrepancies found between the spectra reported by the two groups, it seems worthwhile to examine the single crystal spectra of these molecular compounds. In the present paper, we will report on the polarized absorption spectra of the single crystals of the 1,6-diaminopyrene compounds which involve *p*-chloranil, *p*-bromanil, *p*-iodanil, and tetracyano-*p*-quinodimethane (TCNQ) as electron acceptor.

Experimental

TCNQ and 1,6-diaminopyrene were synthesized by the methods described in literatures.[10,11] Chloranil was obtained commercially, and purified by recrystallization and sublimation *in vacuo*. Bromanil and iodanil were kindly supplied by Prof. T. Handa of Science University of Tokyo. The crystals of all molecular compounds except that of diaminopyrene-TCNQ were prepared from benzene or toluene solutions containing appropriate amounts of the donor and acceptor. The crystal of the diaminopyrene-TCNQ was prepared from an acetonitrile solution.

The composition of each molecular compound was determined by elemental analysis of crystals. Polarized absorption spectra of the 10—35 kK region were measured on single crystals of microscopic size with a microspectrophotometer.[12] The edges of a prominent face of the crystal were tentatively chosen as the directions of the polarization of light in the measurement of the polarized absorption spectra.

Results

Diaminopyrene-Chloranil. This compound crystallizes from a benzene solution as brown needles or parallelepiped crystals.[13] The mole ratio of the donor to the acceptor was found to be 1:1. The crystal exhibits a marked dichroism when observed under a polarizing microscope.

The polarized absorption spectra observed on a thin parallelepiped crystal are shown in Fig. 1. We will denote the two edges of the crystal by X- and Y-directions. The spectra were observed for light polarization parallel and perpendicular to the X-direction, which we will call the $/\!/X$ and $\perp X$ spectra, respectively. The results are shown in Fig. 1(a). A broad absorption band with a maximum of 18—19 kK and a sharper peak at 24.5 kK appear in the $/\!/X$ spectrum. The intensity is larger in the former and smaller in the latter in the $/\!/X$ spectrum as compared with the $\perp X$ spectrum. The difference of polarization direction in the above two absorption bands can be seen much more clearly in the $/\!/Y$ and $\perp Y$ spectra, shown in Fig. 1(b). The first band appears only in the $/\!/Y$ spectrum with a maximum at 18.5 kK, while the 24.5 kK peak appears only in the $/\!/Y$ spectrum.

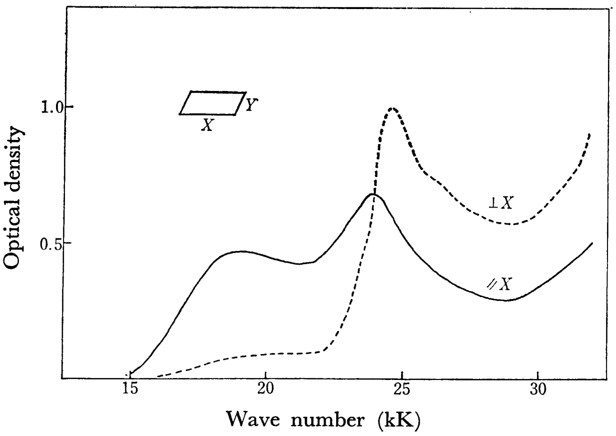

Fig. 1(a). Polarized absorption spectra of diaminopyrene-chloranil crystal: $/\!/X$ and $\perp X$ spectra

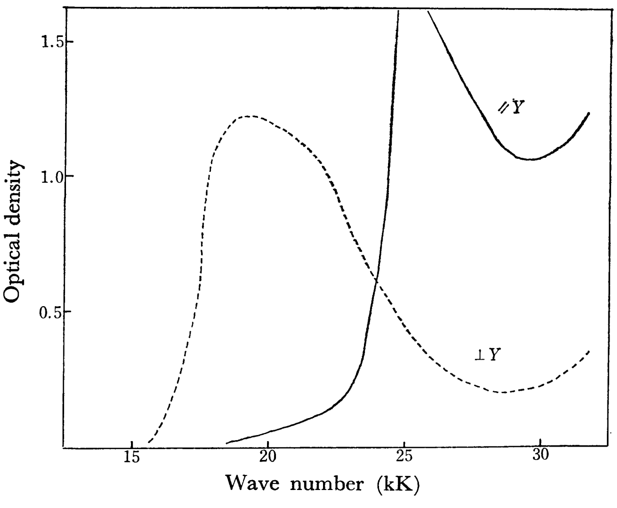

Fig. 1(b). Polarized absorption spectra of diaminopyrene-chloranil crystal: $/\!/Y$ and $\perp Y$ spectra

In order to confirm the polarization direction of these absorption bands, we observed the variations of the optical densities at 18.5, 23.5, and 25 kK as a function of the direction of light polarization. The results are shown in Fig. 2, which shows clearly, first, that the principal axis of absorption at 18.5 kK is perpendicular to that at 25 kK, and, second, that the former makes an angle of about 30° with respect to X-direction.

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[8] H. Scott, P. L. Knonick, P. Charige, and M. M. Labes, *J. Phys. Chem.*, **69**, 1740 (1965).

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

[10] H. Vollman, H. Becker, M. Correll, and H. Streek, *Ann.*, **531**, 1 (1937).

[11] D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84** 3370 (1962).

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

[13] It has been reported by Matsunaga[9] that there are two crystalline forms, brown and green. From the benzene solution, we could obtain only the brown crystal which seems to correspond to Matsunaga's brown form. However, when chloroform or diethyl ether was used as solvent, we noticed that a small amount of green crystals were formed besides the brown crystals. The former exhibited an absorption spectrum quite different from the latter. The nature of the green crystal is not clear, but seemingly it is associated with some oxidation products of diaminopyrene.

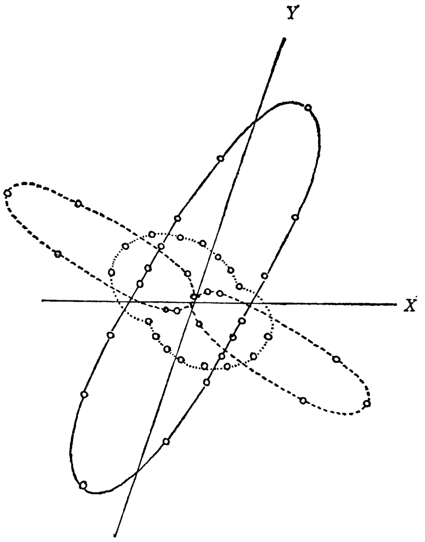

Fig. 2. Dependence of optical density on the direction of light polarization observed on a prominent face of diaminopyrene-chloranil crystal.
------: 18.5 kK ······: 23.5 kK ——: 25.0 kK

It was not possible to obtain an accurate absorption spectrum of a needle crystal, but the main features of the spectra obtained for the light polarizations parallel and perpendicular to the elongated axis, were found to be similar to the $_\perp Y$ and $_{//}Y$ spectra of a parallelepiped crystal, shown in Fig. 1.

Our results for the brown crystal agree with the results reported by the previous workers as regards the locations of the above two bands, but we find no peak corresponding to the sharp peak at 17.5 kK reported by Kronick *et al.*,[7] who attributed it to the monopositive ion of diaminopyrene, neither we find any band corresponding to the 8 and 15 kK ones reported by Matsunaga.[9,14]

The infrared spectrum of the crystalline powder of this compound can be explained by assuming that the crystal is essentially composed of neutral molecules of the donor and acceptor as suggested by Matsunaga.[9,15] The powder was found to be diamagnetic around room temperature. Although a very weak paramagnetic resonance absorption was detectable, it was most likely to be associated with the presence of a trace of impurities or some oxidation products. All these data suggest that the brown form of diaminopyrene-chloranil crystal has an essentially non-ionic ground state.

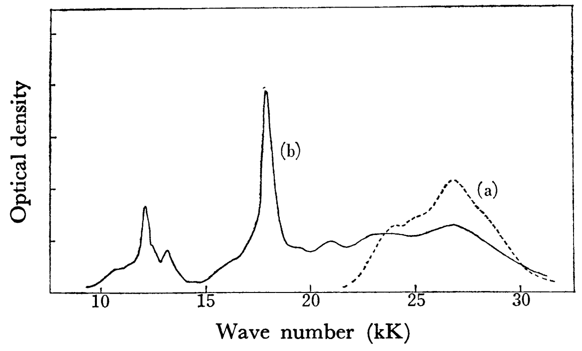

Fig. 3. Absorption spectra of diaminopyrene (a) and its monopositive ion (b) in ethanol. The ion was prepared from the interaction of chloranil in the ethanol solution.

The absorption spectra of the diaminopyrene and that of the diaminopyrene cation are reproduced in Fig. 3. If we assume a non-ionic structure for the diaminopyrene-chloranil compound, we can assign the strong absorption band in the 23—30 kK region of the crystal spectrum to the one associated with the lowest π–π^* transition of diaminopyrene. In the 10—22 kK region, we can not expect any local excitation band associated with an intramolecular transition of the donor or acceptor. Thus the 18.5 kK band should be considered as a charge-transfer band. Apparently the above interpretations are consistent with observed polarizations of the absorption bands in the crystal spectrum.

It should be noted, however, that the 1:1 complex formed between diaminopyrene and chloranil in a chloroform solution exhibits two charge-transfer bands in the visible region, the maxima of which are located respectively at 9.9 and 19.0 kK. It is hard to expect that the first charge-transfer band appearing at 9.9 kK in the solution is shifted to a higher energy as much as 10 kK in the crystal. In fact, the corresponding charge-transfer band does appear at about 7 kK in the crystal spectra of the bromanil or iodanil compounds of diaminopyrene. Therefore, we should assign the 18.5 kK band of the diaminopyrene-chloranil to one corresponding to second or third charge-transfer excitation, and not

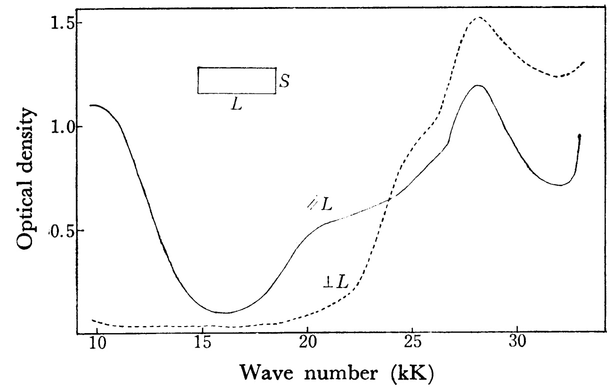

Fig. 4. Polarized absorption spectra of diaminopyrene-bromanil crystal.

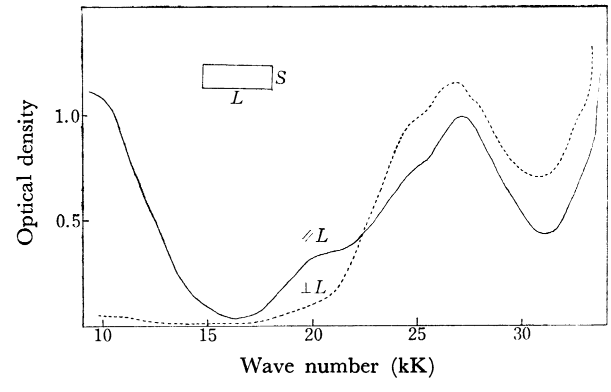

Fig. 5. Polarized absorption spectra of diaminopyrene-iodanil crystal.

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[14] We found absorption maxima at 8 and 15 kK in the spectra of the green crystal.

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

to one associated with the lowest charge-transfer excitation.

Diaminopyrene-Bromanil and Diaminopyrene-Iodanil. Both these compounds crystallized as dark-brown needle crystals, and the mole ratio of donor to acceptor was found to be 1:1.

We observed the polarized absorption spectra of the crystals for light polarizations parallel and perpendicular to the elongated axis of a needle crystal, which we will call the L-axis of the crystal.

The observed spectra are shown in Fig. 4 and Fig. 5. As can be seen, the crystal spectra of the two molecular compounds are quite similar to each other. Both show a strong near-infrared absorption band[16] polarized exclusively in the L-axis direction, and another strong band of different polarization in the 24—32 kK region, which exhibits an appreciably higher intensity in the $\perp L$ spectrum than in the $/\!/L$ spectrum. Besides these two absorption bands, there is one weak band of $/\!/L$ polarization around 20 kK, which appears as a shoulder at the tail of the strong ultraviolet band.

Table 1. Charge-transfer bands of 1,6-diaminopyrene-haloanil molecular compounds
(kK units)

Acceptor	1st CT band		2nd CT band	
	$CHCl_3$ soln.	cryst.	$CHCl_3$ soln.	cryst.
Chloranil	9.9_0	—	*ca* 19	19.2
Bromanil	9.2_6	<10	*ca* 19	~20
Iodanil	9.5_2	<10	*ca* 19	~20

The 1:1 molecular complex formed in a chloroform solution between diaminopyrene and bromanil exhibits two charge-transfer bands, the first located at 9.26 kK and the second at 19 kK. In the case of the diaminopyrene-iodanil complex in a chloroform solution, the first charge-transfer band is at 9.52 kK and the second at 19 kK. Since there is no absorption band of diaminopyrene in the region below 22 kK, it is most likely that the first two absorption bands of $/\!/L$ polarization found in the crystal spectra of the bromanil and iodanil compounds of diaminopyrene are associated with the charge transfer from a donor molecule to a neighboring acceptor molecule, and the ultraviolet band is a local-excitation band associated with the intramolecular transitions of diaminopyrene. The general features of the crystal spectra mentioned above are in accord with the behaviors usually found for the crystal spectrum of a typical charge-transfer molecular compound composed of neutral molecules. On the other hand, it is impossible to understand the observed crystal spectra of the bromanil and iodanil compounds of diaminopyrene if we assume an ionic structure for their ground state. Their infrared spectra are also quite similar to each other, which can be understood by assuming that they are composed of neutral molecules of the components.

Diaminopyrene-TCNQ. This compound crystallizes as a dark-brown parallelepiped crystal. The mole ratio in the crystal is again 1:1. The polarized absorption spectra are shown in Fig. 6. The general features of the crystal spectra are quite different from those of the preceeding three molecular compounds. Although this compound also exhibits an intense near-infrared absorption band polarized parallel to the longer edge of the crystal (the X-direction), its maximum is located at considerably low energy as compared with the corresponding bands of other molecular compounds. The absorption in the visible and ultraviolet region is strongly polarized in the $\perp X$ direction, where we find three absorption maxima located at about 13, 19, and 23 kK, respectively.

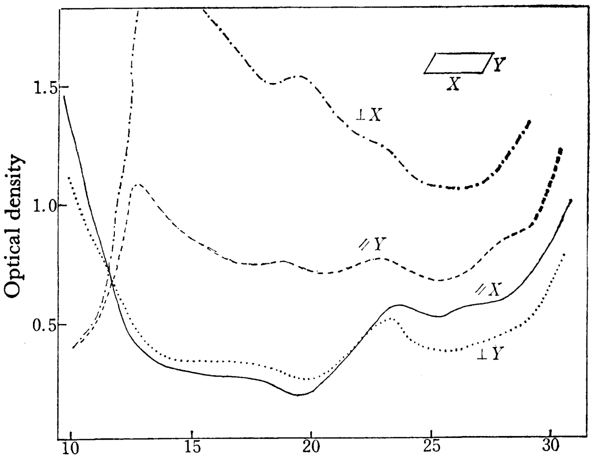

Fig. 6. Polarized absorption spectra of diaminopyrene-TCNQ crystal.

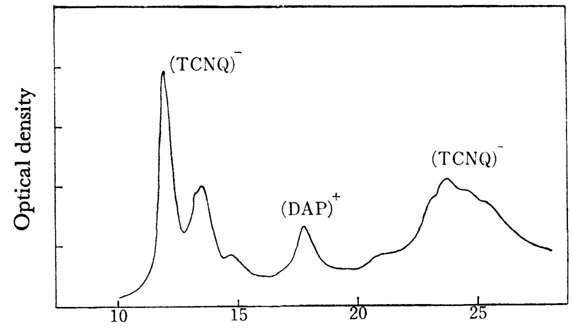

Fig. 7. Absorption spectrum of the acetonitrile solution of diaminopyrene-TCNQ.

The absorption spectrum of an acetonitril solution of the diaminopyrene-TCNQ is shown in Fig. 7, which corresponds to the superposition of the spectrum of the monopositive ion of diaminopyrene and that of the mononegative ion of TCNQ. Although both ions have their first absorption bands in the 10—15 kK region, the peaks in this region of the solution spectrum are almost entirely due to the TCNQ ion. The 17.8 kK sharp peak is due to the second band of the diaminopyrene ion, and the broad band in the 22—27 kK region

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[16] We were unable to determine the wavenumber of the absorption maximum from the observation of the single crystal spectrum, due to the inapplicability of our microspectrophotometer to this region. From observation of the powder spectra of these molecular compounds, the maximum was found to be at about 7kK in both cases.

is due to the TCNQ ion.

If we compare the crystal spectrum of the diaminopyrene-TCNQ with its solution spectrum, we note that all absorption bands in the crystal spectrum except the near-infrared one which is polarized in the $/\!/X$ direction, can be understood as the local-excitation bands associated with the transitions of the diaminopyrene ion or those of the TCNQ ion. Presumably, the 12.5 kK strong band is mainly associated with the lowest π–π^* transition of the TCNQ ion, and the 19.5 kK weak band is due to the 17.8 kK transition of the diaminopyrene ion. They are considerably broadened and shifted as compared with the corresponding bands in the solution spectrum. The absorption band of the TCNQ ion in the 22—27 kK region is known to be composed of two transitions,[17)] one strong transition with the transition moment parallel to the long axis of the TCNQ ion, and one weak one with the transition moment parallel to the short axis. We could attribute the weak band found at 24.6 kK in the $/\!/X$ spectrum of the crystal to the one associated with the short-axis polarized transition of the TCNQ ion. Seemingly, the absorption band associated with the long-axis polarized transition of the TCNQ ion is markedly shifted to higher energy in the crystal. We could attribute the steep rise of absorption above 28 kK to the tail of this absorption band.

The infrared spectrum of the crystalline powder of the diaminopyrene-TCNQ suggests also that TCNQ is, in fact, in the ionic state in this molecular compound. Interestingly, however, the intensity of the paramagnetic resonance absorption is so small that the spin concentration estimated from the observed intensity corresponds to only 6.6 percent of the value expected when each ion provides one independent spin center. This suggests the presence of a strong interaction between neighboring radical ions. The appearance of a very strong charge-transfer band in the crystal spectrum is in accord with this interpretation.

Discussion

From the energy of the first charge-transfer band of the diaminopyrene-chloranil complex in solution, the ionization potential of diaminopyrene can be estimated as 6.54 eV.[18)] The value estimated from the energy of the corresponding band of the diaminopyrene-bromanil complex is 6.57 eV.[19)] Thus the average value is 6.56 eV.

We carried out the calculation of π-orbitals of diaminopyrene by the *variable-β* modification of the Pariser-Parr-Pople method.[20)] The occupied molecular orbitals thus obtained are given in the appendix.

From the result of such a calculation, we can predict the ionization potential of diaminopyrene as 6.51 eV, which is in good agreement with the experimentally estimated values mentioned above.

Thus we believe that the ionization potential of diaminopyrene is 6.5—6.6 eV, which is smaller than the ionization potential of tetramethyl-*p*-phenylenediamine (TMPD). It should be noted that, in spite of this low ionization potential of diaminopyrene, the solid molecular compounds of diaminopyrene with chloranil, bromanil and iodanil, are of the non-ionic type, whereas TMPD forms an ionic compound with chloranil.[22)]

The electron affinity has been estimated by Briegleb as 1.37, 1.40, 1.36, and 1.7 eV respectively for chloranil, bromanil, iodanil, and TCNQ.[23)] Thus, the difference between the ionization potential of the donor, I_D, and the electron affinity of the acceptor, A_A, is about 5 eV for the chloranil, bromanil, and iodanil compounds of diaminopyrene, and below 5 eV for the diaminopyrene-TCNQ. This means that the lower limit of $I_D - A_A$ that gives a non-ionic crystal is located below 5 eV when the electron donor is diaminopyrene. This seems to be markedly low as compared with the molecular compounds of various other amines. A similar situation can be found, however, in the molecular compounds of tetramethylbenzidine. Presumably this is associated with the effect of molecular size of the donor on the Coulomb energy term which is to have significant contribution to the stability of the ionic structure.

Another problem to be considered is the absence of the first charge-transfer band in the crystal spectrum of the diaminopyrene-chloranil. As shown in the appendix, the diaminopyrene molecule has two closely spaced occupied levels of the symmetries, b_g and a_u at about 1.6 eV below the highest occupied orbital of the symmetry of b_g. In the bromanil and iodanil compounds of diaminopyrene, the first charge-transfer band must be associated with the charge transfer from the highest occupied orbital of a diaminopyrene molecule to the lowest vacant orbital of the neighboring acceptor molecule, and the second charge-transfer band at 19 kK must be associated with the charge transfer from either one of the second or third occupied orbitals, or with those from both of them. The energy difference between the first and second charge-transfer bands is nearly equal to the difference of the orbital energies.

In the case of diaminopyrene-chloranil, we were unable to find any absorption band corresponding to the first charge transfer bands of the bromanil and iodanil compounds. We must attribute the charge-transfer band found at 18.5 kK in the crystal spectrum of the diaminopyrene-chloranil to the one corresponding to the 19 kK charge-transfer band found for the diamino-

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17) S. Hiroma, H. Kuroda, and H. Akamatu, This Bulletin, **44**, 9 (1971).

18) We have newly established the empirical relation

$$h\nu_{CT} = 0.87 I_D - 4.46 \text{ (eV)}$$

between the frequency of the charge-transfer band of a chloranil complex and the ionization potential of the donor. The equation was used to the estimate the ionization potential of diaminopyrene.

19) Here we assumed the relation

$$h\nu_{CT} = 0.928 I_D - 4.95 \text{ (eV)}$$

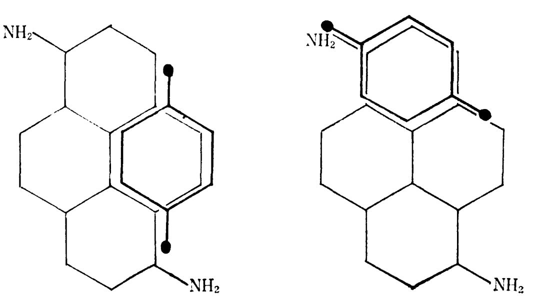
cf. M. Kinoshita, This Bulletin, **35**, 1609 (1962).

20) Refer to Ref. 21, for the details of calculation and the procedure of estimating the ionization potential.

21) T. L. Kunii and H. Kuroda, *Theoret. Chim. Acta*, **11**, 97 (1968).

22) T. Amano, H. Kuroda, and H. Akamatu, This Bulletin, **41**, 83 (1968).

23) These values seem to be too small to be taken as the absolute values of the electron affinities. In fact, Lyons has recently given the following values: chloranil 2.05 eV, TCNQ 2.46 eV (L. E. Lyons, private communication). The essential point of the discussion given here is unaffected by taking these values, but we have to reduce the value of $I_D - A_A$ by about 0.7 eV for all molecular compounds discussed here.



Model A Model B

Fig. 8. Models for the stacking of molecules of diaminopyrene-quinone.

pyrene-bromanil and the diaminopyrene-iodanil.

At present, we have no information on the relative arrangement of the donor and acceptor in these molecular compounds. We therefore took two models of the molecular arrangement illustrated in Fig. 8, and estimated the overlap between the donor and acceptor orbitals. The results indicate that model A is favorable for the charge transfer from the a_u orbital of diaminopyrene, but not for that from the b_g orbitals, while model B is favorable for the charge transfer from the latter orbitals and not for that from the former orbital. This suggests that the charge-transfer bands associated with charge transfer from the highest and second highest occupied orbitals of the symmetry b_g could appear when the relative arrangement of the donor and acceptor molecules in the crystal is the one illustrated by model B. On the other hand, these bands, would be almost absent and the charge-transfer band observable with a moderate intensity would be the one associated with the charge-transfer from the third highest occupied orbital of the symmetry a_u, if the molecular arrangement is of the type of model A. Presumably, diaminopyrene-chloranil corresponds to the latter case and diaminopyrene-bromanil and diaminopyrene-iodanil to the former.

APPENDIX. OCCUPIED MOLECULAR ORBITALS OF 1,6-DIAMINOPYRENE[a)]

Symmetry	Orbital energy [eV]	Coefficeients in the molecular orbitals[b)]								
		$x_1 \pm x_{10}$	$x_2 \pm x_{11}$	$x_3 \pm x_{12}$	$x_4 \pm x_{13}$	$x_5 \pm x_{14}$	$x_6 \pm x_{15}$	$x_7 \pm x_{16}$	$x_8 \pm x_{17}$	$x_9 \pm x_{18}$
a_u	−13.87173	0.18129	0.29800	0.28595	0.18155	0.16969	0.24316	0.16575	0.32409	0.20778
b_g	−13.24957	0.11337	0.26402	0.41082	0.25140	0.15980	0.10693	−0.01117	0.11012	0.36911
a_u	−12.25836	−0.11929	−0.02926	0.31809	0.13671	−0.04981	−0.24194	−0.18075	−0.25483	0.45433
b_g	−11.99341	−0.29458	−0.12997	−0.05603	0.13446	0.28501	0.37631	0.36963	0.08451	−0.09220
b_g	−10.85024	−0.30456	−0.28218	0.06516	−0.09654	−0.16860	−0.14942	0.14033	−0.17521	0.46142
a_u	−10.59088	0.21598	0.25399	0.00588	−0.35525	−0.43795	−0.20186	0.04791	0.12538	0.10972
a_u	−9.89864	0.38584	−0.06410	−0.00548	0.04713	0.04248	0.00148	0.40655	−0.42114	0.01781
a_u	−9.19109	−0.10654	−0.28805	−0.20186	−0.26803	0.01473	0.27886	0.14872	0.08314	0.43137
b_g	−9.17829	−0.02194	−0.27505	0.05560	0.41566	0.26421	−0.21694	−0.20689	−0.27279	−0.11794
b_g	−7.56899	0.25707	−0.21237	−0.29894	−0.14506	0.26295	0.24020	−0.23842	0.02330	0.30689

a) The SCF·MO's calculated by the procedure described in Ref. 12

b) $x_i + x_j$ for a_u, $x_i - x_j$ for b_g