

Pressure dependence of the polarized reflectance spectrum of the solid charge-transfer complex, perylene–TCNQ: Estimation of microscopic parameters

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The polarized reflectance spectrum of the perylene–TCNQ complex has been measured at high pressure up to 27 kbar using a diamond anvil cell incorporated into a microspectrophotometer. The degree of charge transfer (ρ), the transfer integral (t), and the site-energy difference (Δ) are estimated at each pressure from analysis of the charge-transfer band. The pressure dependences of t and Δ are found to be $\partial \ln t / \partial P = +2.3\% \text{ kbar}^{-1}$ and $\partial \Delta / \partial P = -6.4 \text{ MeV kbar}^{-1}$, respectively. It is shown that the observed pressure dependence of the stabilization energy of the charge-transfer excited state is mainly attributable to the change in the electrostatic energy accompanying the lattice contraction.

I. INTRODUCTION

The electronic structure of a solid charge-transfer (CT) complex composed of a mixed donor and acceptor stack is expected to show a significant pressure dependence since the charge-transfer interaction between donor and acceptor molecules is strongly dependent on the intermolecular separation. There are two very important microscopic parameters which determine the degree of charge transfer ρ and the energy and intensity of the CT band. One is the site-energy difference, $\Delta = I_D - A_A - E_S$, where I_D is the ionization potential of the donor, A_A the electron affinity of the acceptor, and E_S the stabilization energy of the CT excited state due to the electrostatic and polarization energies¹; the other is the transfer integral t (or Mulliken's resonance integral² β). Both of these parameters depend upon the overlapping mode and the distance between the donor and acceptor molecules, and so will be significantly affected by the volume contraction caused by the application of high static pressure. Recently, Jurgensen *et al.* reported a high pressure study of the electronic and vibrational spectra of a powdered sample of the hexamethyl-benzene–tetracyanoethylene (HMB–TCNE) complex, in which the spectral measurements were made using the transmission method.³ They estimated the pressure dependence of the degree of charge transfer from the shift of the CT band and the vibrational peaks. However, as they commented, the shift of a vibrational peak is affected not only by the degree of charge transfer but also by the intracrystal environment.

More direct information about the microscopic parameters and their pressure dependence can be obtained from analysis of the optical spectrum of a single crystal observed over a wide range of applied pressure. However, few experimental studies of the optical properties of single crystals of CT complexes under high pressure have been reported, because of the experimental difficulty. We have developed an

experimental system to measure the polarized reflectance spectrum of a very small single crystal under high pressure by use of a diamond anvil cell incorporated into a microspectrophotometer covering the visible and near-infrared regions. In this paper we present the results of a high pressure spectroscopic study on a single crystal of perylene–TCNQ, a typical CT complex having a mixed-stack structure with a nominally neutral ground state.

II. EXPERIMENTAL

Perylene was first purified by repeated sublimation and then by column chromatography. TCNQ was recrystallized from acetonitrile solution and subsequently sublimed *in vacuo*. Single crystals of the perylene–TCNQ complex were prepared by slowly evaporating the chloroform solution of the complex. A crystal measuring $0.1 \times 0.2 \times 0.05 \text{ mm}^3$ was selected for the high pressure experiment. The perylene–TCNQ complex is known to have two modifications having different donor/acceptor ratio; 1:1 and 3:1. These two modifications can be easily distinguished from their reflectance spectra.⁴ The crystal used in the present experiment was identified as the 1:1 modification.

High pressure was generated using a diamond anvil cell of Bassett-type,⁵ with a thin plate gasket made of Inconel X750. The thickness of the gasket was 0.5 mm and the aperture was 0.5 mm in diameter. Pressure was determined by a conventional ruby fluorescence method.⁶ As a pressure medium, we used the colorless lubrication oil, Idemitsu LAGD, which could be handled more easily than a volatile liquid such as pentane–isopentane mixture. The homogeneity of pressure in the pressure cell was confirmed from the observation of the peak width of ruby fluorescence. The optical geometry employed in the present study to measure the reflectance spectrum was analogous to that reported by Syassen *et al.*⁷ As the reference for the determination of absolute reflectivity, a thin silver film was deposited *in vacuo* onto half of one face of the sample crystal.

For the purpose of the present experiment, the single-beam manually operated microspectrophotometer system

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which was developed in our laboratory,⁸ was further modified so that it could be controlled by a microcomputer. In this automated system, the intensity of the light reflected from the sample and that from the silver film covering half of the sample surface were alternately measured at each wavelength. The focal spot on the sample was typically 40 μm in diameter. In order to eliminate the effect of light reflected from the diamond window, we utilized only light at a relatively high incident angle ($12^\circ < \theta < 24^\circ$). For this purpose, we used an objective lens with a numerical aperture of 0.40, and place a mask at its center covering about a quarter of its area. The principle of this method is illustrated in Fig. 1. The light reflected from both surfaces of the diamond window should be eliminated when the focus of the objective lens is at the sample surface. In fact, as we varied the distance of the diamond anvil cell from the objective lens so that the focus moved from the top surface of the diamond window to the surface of the sample crystal, the intensity of the light detected by the spectrometer showed three peaks, as shown in Fig. 1. These correspond to reflections from the top surface of the diamond window, from its inner surface, and from the sample surface, respectively. Note that the light from the inner surface of the diamond window and that from the sample surface cannot be separated if the distance between these two surfaces is too small. Thus the maximum pressure attainable is restricted by this allowable minimum separation.

Since the refractive index of the lubrication oil used as the pressure medium is not known at high pressure, we estimated it from observation of the reflectivity at the diamond/oil interface. In this process, we neglected the absorption of

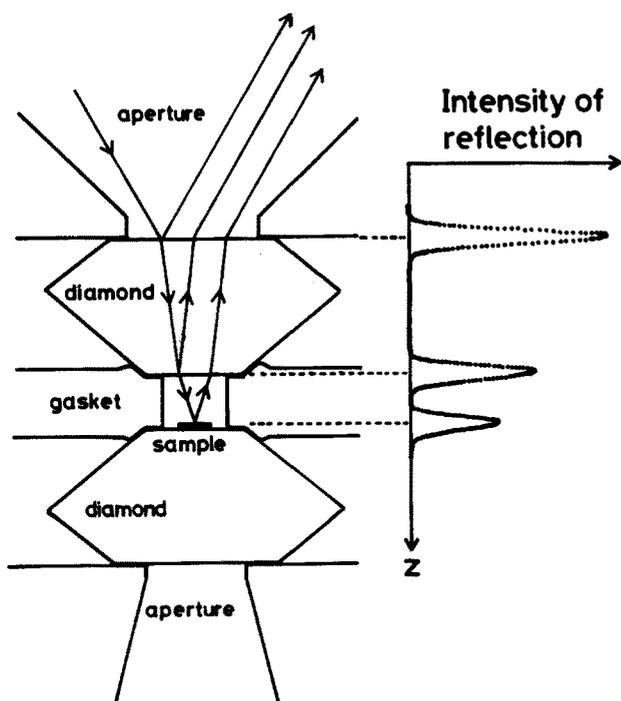


FIG. 1. Geometry of the optical system for measurements using the diamond anvil cell. The diagram on the right shows the variation of the light intensity detected by the spectrometer when the diamond anvil cell is moved along the Z direction.

diamond, the pressure dependence of its refractive index and the dispersion of the refractive index of the medium in the spectral region from 5000 to 25 000 cm^{-1} . The pressure dependence of the refractive index (at 18 000 cm^{-1}) thus determined is shown in Fig. 2.

III. RESULTS AND DISCUSSIONS

A. Analysis of reflectance spectrum

Since the crystal in the diamond anvil is immersed in the pressure medium, its reflectance spectrum at ambient pressure is quite different from that measured by placing the same sample in the ordinary atmosphere (see Fig. 3). Although the Kramers-Kronig analysis is the standard procedure for analyzing reflectance data, it is difficult to be applied in the present case since there are several unknown parameters which depend upon the refractive indices of the medium surrounding the sample.⁹ Therefore, we analyzed reflectance data by the dispersion analysis method. We performed a least-squares calculation to reproduce the observed reflectance spectrum by use of the following functions:

$$\epsilon(\omega) = \epsilon_c - \sum_j \frac{\Omega_{pj}^2}{\omega^2 - \omega_j^2 + i\Gamma_j\omega\omega_j}, \quad (1)$$

$$R(\omega) = \left| \frac{[\epsilon(\omega)]^{1/2} - n_0}{[\epsilon(\omega)]^{1/2} + n_0} \right|^2, \quad (2)$$

where $R(\omega)$ is the reflectance at the sample-medium interface, $\epsilon(\omega)$ the complex dielectric function of the sample, n_0 is the refractive index of the pressure medium, ω is the frequency of the incident light, and ϵ_c , Ω_{pj} , ω_j and Γ_j are the parameters of the Lorentz oscillator functions. We used three Lorentz oscillators to simulate the observed spectrum, treating ϵ_c , Ω_{pj} , ω_j , and Γ_j as adjustable parameters; one oscillator for the main peak at 10 000 cm^{-1} , one for the shoulder at 12 000 cm^{-1} , and a third for the dispersion around 22 000–23 000 cm^{-1} .

Figure 3(a) shows the reflectance data observed for

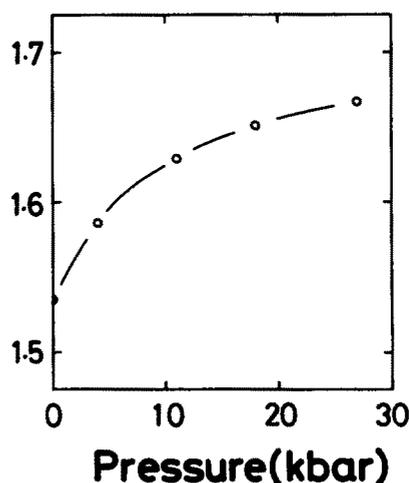


FIG. 2. Pressure dependence of the refractive index n_0 of the lubrication oil, Idemitsu LAGD.

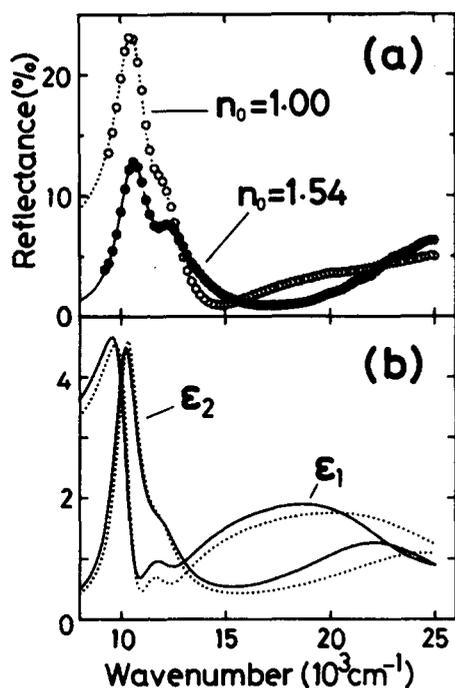


FIG. 3. (a) Reflectance spectra polarized along the a axis which were measured in the pressure medium ($n_0 = 1.54$, solid circles) and in the atmosphere ($n_0 = 1$, open circles). The solid and dotted lines are the calculated spectra based on the Lorentz oscillators. (b) The dielectric functions calculated by the dispersion analysis. Solid and dotted lines were obtained from the spectra drawn by the solid and open circle data, respectively.

light polarized parallel to the a axis. The open circles are the reflectance data measured with the crystal in the ordinary atmosphere ($n_0 = 1$), and the solid circles with the crystal immersed in the pressure medium ($n_0 = 1.54$) in the diamond anvil. The results of simulation are shown by dotted and solid lines, respectively. In both cases, the observed reflectance spectrum is well reproduced by the simulation employing three Lorentz oscillators. Although the observed reflectance spectra are different for the two cases, the dielectric function of the sample crystal derived from the analysis should be the same if the reflectance data are reliable and the data analysis has been carried out correctly. The real and imaginary parts of the dielectric function ϵ_1 and ϵ_2 obtained by this analysis, are compared in Fig. 3(b) for the two cases. They are in good agreement with each other. This fact shows the reliability of the reflectance data and the analysis, as well as the n_0 value estimated for the pressure medium. A slight difference in the high wave number region between the two sets of data probably arises from the decrease of the reflectivity of the silver film from 100% in this region and/or from the limitation of the measured wave number region. However, this small difference will not significantly affect the analysis of the CT band given below, since the CT band is located in a much lower wave number region.

Figure 4 shows the reflectance spectra at three pressures. The solid circles and lines denote the observed data and the simulated spectra, respectively.

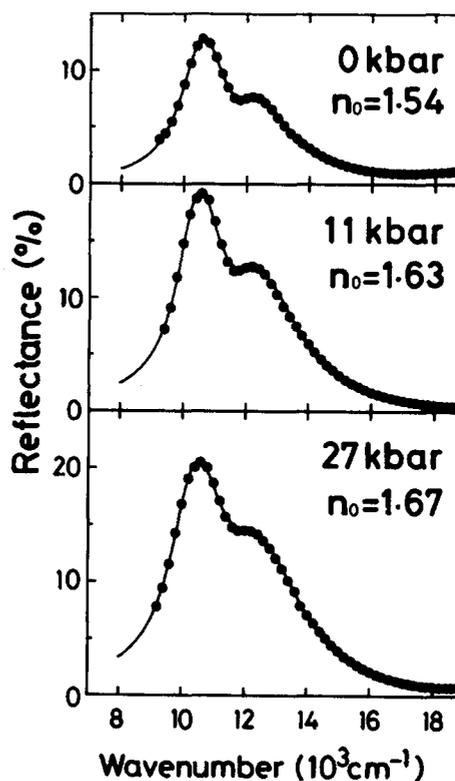


FIG. 4. Reflectance spectra polarized along the a axis at three pressures.

B. Estimation of microscopic parameters

The oscillator strength of the CT band per donor-acceptor ($D-A$) pair, F_{CT} , was calculated by Eq. (3),

$$F_{CT} = \sum_j F_j = \frac{m}{4\pi N e^2} \sum_j \Omega_{pj}^2, \quad (3)$$

where Ω_{pj} is a parameter defined in Eq. (1), m and e the electron mass and charge, and N the number of $D-A$ pairs per unit volume. The average excitation energy ($\hbar\omega_{CT}$) of the CT band can be defined by the following equation¹⁰:

$$\hbar\omega_{CT} = \frac{F_{CT}}{\sum_j F_j / \hbar\omega_j}. \quad (4)$$

The values of F_{CT} and $\hbar\omega_{CT}$ at each pressure are given in the second and third columns of Table I. While the excitation energy $\hbar\omega_{CT}$ little varies with pressure, the oscillator strength F_{CT} increases considerably. Naturally, the oscillator strength depends on the density of the crystal, which should increase slightly when a high pressure is applied. However, the observed marked increase of oscillator strength cannot be attributed entirely to density increase, since the latter is only about 1% kbar⁻¹,¹¹⁻¹³ in a typical organic crystal.

The CT excitation energy $\hbar\omega_{CT}$ of an isolated neutral $D-A$ pair can be described in terms of the transfer integral t and the site energy difference Δ , i.e., $\hbar\omega_{CT} = (\Delta^2 + 8t^2)^{1/2}$. The transfer integral increases on decreasing the intermolecular separation, but at the same time the site energy differ-

TABLE I. Pressure dependence of the average excitation energy, oscillator strengths, degrees of charge transfer, transfer integrals, and site energy differences.

P (kbar)	$\hbar\omega_{CT}$ (eV)	F_{CT}	ρ	t (eV)	Δ (eV)
0 ^a	1.34	0.49	0.10	0.25	1.22
0 ^b	1.33	0.52	0.11	0.25	1.19
4	1.32	0.57	0.11	0.27	1.21
8	1.33	0.62	0.12	0.28	1.17
10	1.30	0.76	0.15	0.31	1.08
11	1.33	0.82	0.16	0.34	1.12
18	1.33	0.90	0.17	0.36	1.10
24	1.32	0.99	0.19	0.38	1.04
27	1.31	1.00	0.19	0.39	1.04

^a Reflectance data at the sample-air interface.

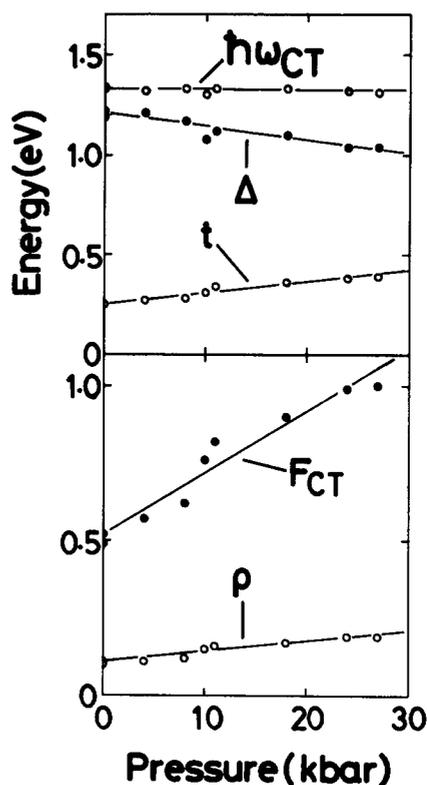
^b Reflectance data at the sample-pressure medium interface.

ence should decrease because of the increase of the electrostatic stabilization energy of the CT state. Therefore, the shift of the CT band will be determined by the balance between these two changes. This could offer a qualitative explanation for the small peak shift with pressure. However, such an isolated dimer model² (or a trimer model¹⁴) is not sufficient for a quantitative discussion, unless the transfer integral is very small compared with the site energy difference ($t/\Delta \ll 1$). This condition is not necessarily satisfied in the case of the perylene-TCNQ complex, in particular when it is under high pressure. Recently Painelli and Girlando solved numerically the modified-extended Hubbard Hamiltonian of the one-dimensional tight-binding model for a mixed-stack CT crystal, neglecting doubly ionized states, using diagrammatic valence-bond theory.^{10,15} They calculated the degree of charge transfer, the transfer integral and the site energy difference from the excitation energy and the transition dipole moment of a CT transition. The square of the transition dipole moment is given by

$$\mu_{CT}^2 = \frac{\hbar^2 F_{CT}}{2md^2 \hbar\omega_{CT}}, \quad (5)$$

where d is the distance between the centers of the neighboring donor and acceptor molecules in a mixed molecular column. Using the transition dipole moment thus estimated and the excitation energy determined from Eq. (4), we calculated the degrees of charge transfer and the transfer integral by interpolation based on the numerical table given by Painelli and Girlando.¹⁰ The site-energy difference was estimated by interpolating the numerical table given by Girlando and Painelli,¹⁵ using a cubic function. In this analysis, we used the oscillator strength values listed in Table I, which have not been corrected for the increase of the number density of $D-A$ pairs caused by the volume contraction, since this correction has a negligibly small effect on the estimation of transition dipole moment.

The results of the above analysis are listed in the last three columns of Table I. As shown in Fig. 5, each parameter changes linearly with applied pressure, within experimental error. The pressure dependence found here is consistent with


 FIG. 5. Pressure dependence of the average excitation energy $\hbar\omega_{CT}$ and oscillator strength F_{CT} , and the microscopic parameters t , Δ , and ρ .

that found in a high pressure study on the Raman spectra of the perylene-TCNQ complex.¹⁶ The rate of change of t with pressure is given by $\partial \ln t / \partial P = +2.3\% \text{ kbar}^{-1}$. There is no corresponding data for other mixed-stack CT complexes. The value of $\partial \ln t / \partial P$ has been reported for TTF-TCNQ ($+2\% \text{ kbar}^{-1}$) and $(\text{BEDT-TTF})_2\text{I}_3$ ($+2.0\% \text{ kbar}^{-1}$ for α -phase crystal and $+3.2\% \text{ kbar}^{-1}$ for β -phase crystal). These charge-transfer complexes contain segregated rather than mixed stacks. The value for the TTF-TCNQ salt was determined from the observation of the spectral change in the plasma-edge region caused by the application of high pressure,¹⁷ it being also theoretically estimated by combining the compressibility data with the quantum chemical calculation of overlap integral.¹¹ The values for $(\text{BEDT-TTF})_2\text{I}_3$ salts were derived from the analysis of the pressure dependence of the static magnetic susceptibility.¹⁸ It is to be noted that the values of $\partial \ln t / \partial P$ are around $+2\% \text{ kbar}^{-1}$, both in the perylene-TCNQ complex studied in the present study and in the charge-transfer salts mentioned above, despite the great difference in the crystal type and the large difference in the absolute value of t .

C. Calculation of electrostatic energy

From the data given in Table I, the relative change of Δ against pressure was calculated to be $\partial \Delta / \partial P = -6.4 \text{ meV kbar}^{-1}$. The stabilization energy of the CT excited state E_S was calculated at each pressure from the Δ value using the equation $E_S = I_D - A_A - \Delta$ and assuming

TABLE II. Pressure dependence of the stabilization energy of the CT state, the nearest neighbor Coulomb energy, the Madelung energy, the electrostatic stabilization energy.

P (kbar)	EXP E_s^a (eV)	CNDO/2			MNDO		
		V (eV)	E_M (eV)	$E_s'^b$ (eV)	V (eV)	E_M (eV)	$E_s'^b$ (eV)
0 ^c	2.98	2.46	3.01	2.57	2.34	2.93	2.46
0 ^d	3.01	2.46	3.01	2.58	2.34	2.93	2.47
4	2.99	2.48	3.05	2.59	2.40	2.97	2.53
8	3.03	2.50	3.09	2.64	2.42	3.01	2.56
10	3.12	2.52	3.11	2.70	2.43	3.04	2.61
11	3.08	2.52	3.12	2.71	2.43	3.05	2.63
18	3.10	2.56	3.18	2.77	2.45	3.13	2.68
24	3.16	2.60	3.25	2.85	2.50	3.21	2.77
27	3.16	2.61	3.28	2.87	2.52	3.25	2.80

$$^a E_s = I_D - A_A - \Delta.$$

$$^b E_s' = (1 - 2\rho)V + 2\rho E_M.$$

^c Reflectance data at the sample-air interface.

^d Reflectance data at the sample-pressure medium interface.

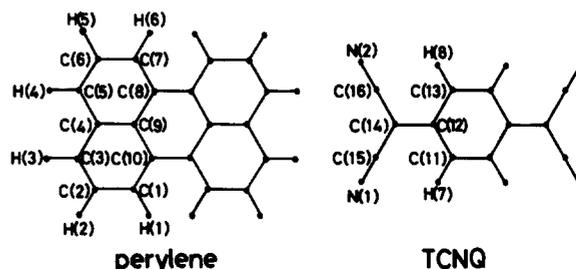
$I_D = 7.00$ eV,¹⁹ $A_A = 2.8$ eV.²⁰ The results are given in the first column of Table II. The contribution of the electrostatic energy to the stabilization energy can be calculated by use of Eq. (6), which was introduced by Girlando *et al.* on the assumption of the mean field theory,¹⁵

$$E_s' = (1 - 2\rho)V + 2\rho E_M. \quad (6)$$

Here ρ is the degree of charge transfer, V the nearest neighbor Coulomb energy between a donor and an acceptor, and E_M the Madelung energy per an ion calculated for the hypothetical ionic lattice where all donor and acceptor molecules in the crystal of the charge-transfer complex are in their ionized states. We calculated the Madelung energy in this hypothetical ionic lattice perylene⁺-TCNQ⁻, putting point charges on each atom in donor and acceptor molecules according to the charge distributions calculated by CNDO/2²¹ and by MNDO.²² The procedure used here is the same as that was used by Metzger in his calculation on TMPD-ClO₄²³ and TTF-chloranil.²⁴ The charge distributions in perylene⁺ and TCNQ⁻ ions, which were computed by CNDO/2 and MNDO, are given in Table III. In these calculations, we assumed the molecular geometries determined by the x-ray crystal structure analysis of the perylene-TCNQ complex at ambient pressure,²⁵ the positions of hydrogen atoms being appropriately determined using a CH-bond length of 1.08 Å and a CCH-bond angle of 120°. Since neither the crystal structure at high pressure nor the compressibility data have been reported for the perylene-TCNQ complex, we assumed that the compressibility is constant up to 27 kbar, with values 0.5% kbar⁻¹ along *a* axis (the molecular stacking direction) and 0.3% kbar⁻¹ along *b* and *c* axes according to the data reported for typical aromatic organic crystals.¹¹⁻¹³ The crystal structure at high pressure was assumed to be that resulting from compression of the atmospheric lattice according to the above compressibility values for the three crystal axes, with no change in molecular geometry. The nearest neighbor Coulomb energy V , the Made-

TABLE III. Point-charge distribution in the molecules of perylene⁺ and TCNQ⁻ calculated by CNDO/2 and MNDO.

Perylene ⁺			TCNQ ⁻		
Atomic label	CNDO/2	MNDO	Atomic label	CNDO/2	MNDO
C(1)	0.039	-0.003	C(11)	-0.036	-0.081
C(2)	0.049	0.036	C(12)	0.062	0.052
C(3)	0.008	-0.063	C(13)	-0.034	-0.081
C(4)	0.069	0.076	C(14)	-0.126	-0.135
C(5)	0.012	-0.099	C(15)	0.102	0.009
C(6)	0.071	0.078	C(16)	0.102	0.011
C(7)	0.004	-0.074	N(1)	-0.267	-0.191
C(8)	0.055	0.051	N(2)	-0.262	-0.188
C(9)	0.039	-0.007	H(7)	-0.019	0.053
C(10)	0.013	-0.013	H(8)	-0.023	0.051
H(1)	0.017	0.077			
H(2)	0.029	0.094			
H(3)	0.025	0.087			
H(4)	0.024	0.085			
H(5)	0.029	0.095			
H(6)	0.024	0.080			



lung energy E_M , and the electrostatic stabilization energy E_s' calculated in this way are given in Table II, together with the stabilization energy E_s obtained from the experimental data. The results calculated from the CNDO/2 and the MNDO charge distributions agree with each other within 0.1 eV. At each pressure, the calculated electrostatic energy E_s' is smaller by about 0.4 eV than the experimentally obtained total stabilization energy E_s . This difference is main-

TABLE IV. Comparison of the microscopic parameters between perylene-TCNQ and TTF-chloranil at ambient pressure.

		Perylene-TCNQ	TTF-chloranil
T	(K)	300	300
$\hbar\omega_{CT}$	(eV)	1.32	0.66 ^a
F_{CT}		0.50	0.49 ^a
ρ		0.10	0.21 ^b
t	(eV)	0.25	0.22 ^b
$I_D - A_A$	(eV)	4.2	4.08 ^c
Δ	(eV)	1.20	0.49
E_s	(eV)	3.00	3.59
E_M	(eV)	3.01	3.53 ^c
E_s'	(eV)	2.57	3.09 ^c

^a Reference 27.

^b Reference 10.

^c Reference 11.

ly attributable to the polarization energy. The results of this analysis indicate that the pressure dependence of the stabilization energy of the CT excited state is determined by the change in the electrostatic energy accompanying the lattice contraction.

Table IV shows the comparison between perylene-TCNQ and TTF-chloranil in relation to the CT transition and the microscopic parameters at 300 K at atmospheric pressure. Perylene-TCNQ retains a neutral ground state at least up to 27 kbar, as shown in the present study, while TTF-chloranil exhibits a neutral-to-ionic phase transition at high pressure,²⁶ although the difference in the $I_D - A_A$ values is only 0.1 eV. The crucial difference between these two complexes is the small site-energy difference Δ in TTF-chloranil. This seems to arise mainly from the difference in Madelung energy. In fact, the calculated value of Madelung energy is larger by 0.5 eV in TTF-chloranil than in perylene-TCNQ, as shown in Table IV. Probably the large Madelung energy in TTF-chloranil originates in the small molecular sizes of TTF and chloranil in comparison with those of perylene and TCNQ.

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