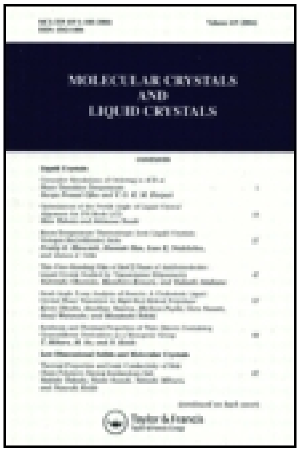

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Electronic Spectra of a Zwitterionic Molecular Crystal: Picolyltricyanoquinodimethane

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Electronic Spectra of a Zwitterionic Molecular Crystal: Picolyltricyanoquinodimethane

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Polarized reflection spectra and the Kramers-Kronig transformed absorption spectra of the crystalline picolyltricyanoquinodimethane (P3CNQ) are presented. Observance of an intermolecular CT transition at 12400 cm^{-1}, besides an intramolecular CT excitation at 18600 cm^{-1}, has been reported for this homo-molecular crystal. On different crystalline faces occurrence of the same IRCT band at an energy separation of the order of thousands of wave number has been explained in the light of the exciton energy shift. For both the IRCT and INCT transitions, band energies, oscillator strengths etc. are calculated in view of the composite-molecule model. An important emphasis is paid to the CT transition that takes place intermolecularly.

Keywords: Electronic spectra, charge transfer band, (Zwitterionic) molecular crystal.

INTRODUCTION

In spite of their usual insulating behavior, a study of the homomolecular complexes becomes illuminating when a few of them, mod-

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ified by substituents, occasionally show characteristics close to those of the hetero-molecular complexes.[1,2] Z-β-(N-methyl-2-pyridinium)-α-cyano-4-styryl dicyanomethide, trivially, picolyltricyanoquinodimethane (P3CNQ), is a zwitterionic molecule prepared by the reaction of 1,2-dimethylpyridinium iodide with LiTCNQ in acetonitrile.[3] It is composed of a positively charged pyridinium moiety and a negatively charged dicyanomethide group. The crystalline structure of P3CNQ was determined by Metzger *et al.*,[3] and it was found that the molecules are stacked in such a way that the positively charged group of one molecule is overlapped with the negatively charged part of the neighboring molecule.

In most zwitterionic molecules, an intermolecular charge transfer (INCT) absorption is found in the visible or in the near ultraviolet region. In the crystals composed of the zwitterionic molecules, an INCT absorption is expected to appear in the energy region lower than that of the intramolecular charge transfer (IRCT) band, because the overlap of the donor and the acceptor parts of the molecules is significant in the crystalline state. In one of the crystalline forms of the squarylium dye, Tristani-Kendra and Eckhardt[4] have found an INCT band in the stacks of dimethylaminohydroxybenzene as the donor and squarylium moiety as the acceptor part. Similarly, in 1,1'-cyanine dye crystals,[5] the J-type band has been found to appear as an INCT transition between the neutral and the positively charged isoquinoline rings; it may be regarded as another example of the CT excitation between two homo-molecular species.

In the present study we report that the INCT band and the polarization of the IRCT band of crystalline P3CNQ show a universal character of the CT interaction in the amphoteric molecular crystals.

EXPERIMENTAL

The small, green, elongated crystals of P3CNQ (space group, $P2_1/c$) were used without further recrystallization. By comparing the oscillation as well as the Weissenberg X-ray photographs with the unit cell parameters, crystal faces suitable for reflection measurement were determined. Reflection spectra of the crystal on the (100) and (001) planes were measured for the vertical incidence of the polarized light. Two measurements, one parallel and the other perpendicular to the crystallographic *b*-axis (needle axis), were performed in the range of $4000-35000\ \mathrm{cm}^{-1}$. The micro-spectrophotometer used consists of a Carl-Zeiss double monochromator, tungsten/ Xenon lamps as sources, a reflecting-lens microscope, and PbS/photomultiplier as detectors.

The solution spectrum of P3CNQ in acetonitrile ($c = 7.8789 \times 10^{-5}$ M) was observed in the range of 4000 – 50000 cm^{-1} by using a Hitachi Model 330 spectrophotometer. All the computations were done by FACOM M-382 in the computation center of Nagoya University.

RESULTS AND DISCUSSION

In the solution spectra of P3CNQ in CH_3CN as represented by Figure 1, absorption bands of varying intensities are found to appear near the visible and the UV regions. The intense absorption of 16800 cm^{-1} is symmetrical in shape and has an oscillator strength of 0.49. The polarized reflection spectra of P3CNQ on the (100) plane are shown by Figure 2 where *//b* and ⊥ *b*, respectively, represent the spectra parallel and perpendicular to the crystallographic *b*-axis. Figure 3 shows the corresponding absorptions calculated by the Kramers-Kronig transformation method.[6] The *//b* spectra is characterized by a single absorption in the region of 12400 cm^{-1} whereas in the ⊥ *b* component the first absorption is near 11800 cm^{-1}, and a sharp, symmetric band appearing at 21800 cm^{-1}. In both the parallel and the perpendicular spectra there is gradual increase in absorptivity as the energy increases indicating some other strong absorption, but unfortunately, it could not be observed fully due to the small size of the crystals studied. Henceforth, our discussion is confined only to the absorptions observed in the visible region.

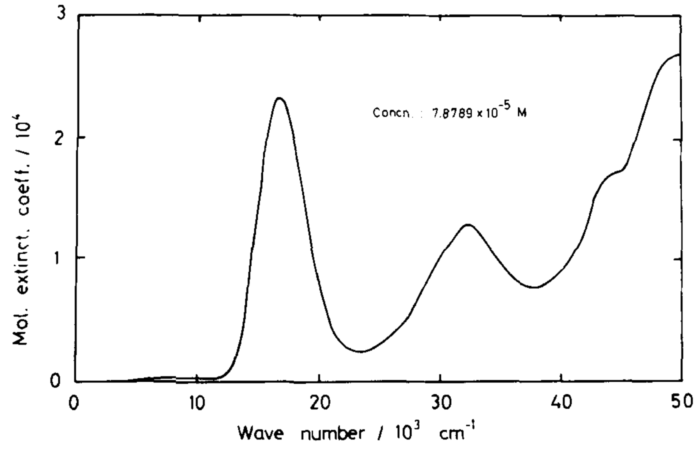

FIGURE 1. Room temperature solution spectrum of P3CNQ in acetonitrile.

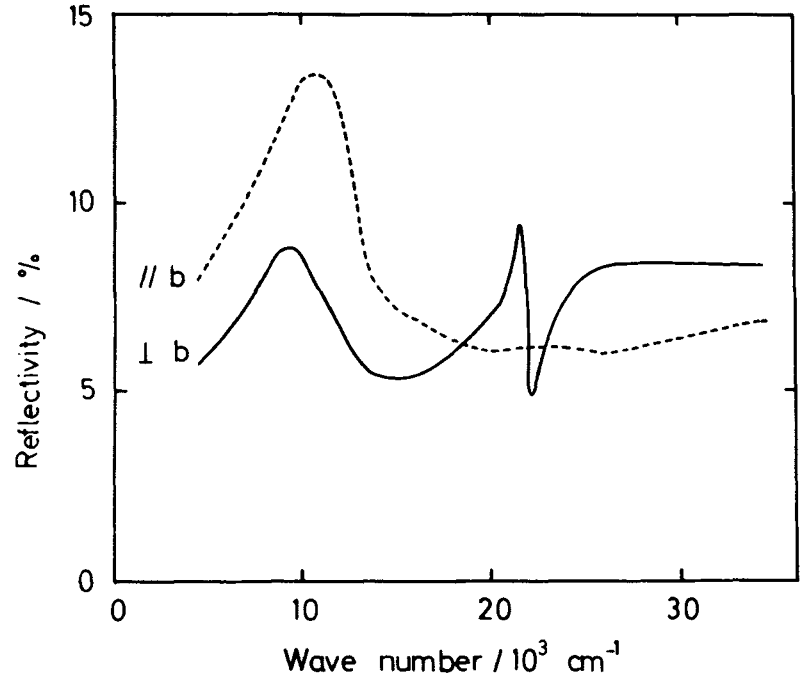

FIGURE 2. Polarized reflection spectra of P3CNQ on the (100) face.

Reflectivities as observed on the (001) plane are shown in Figure 4 and the corresponding absorptions in Figure 5. Here, the //*b* spectra show only a weak absorption in the region of 12400 cm^{-1}. The ⊥*b* component, on the other hand, comprises of a very intense (ϵ = 5.72 × 10^4) as well as a broad absorption (band-width ~ 10000 cm^{-1}) at 18600 cm^{-1}, and a shoulder-like absorption at about 32000 cm^{-1}. The projection figure of P3CNQ onto the (001) plane, as represented by Figure 6, demonstrates that the molecular long-axis of this species is in a direction perpendicular to the crystallographic *b*-axis. The same onto the (100) plane (Figure 7) reveals that the molecules form stacks although its direction is slightly shifted off the crystalline *b*-axis. The strongest absorption along the molecular long-axis is that of 18600 cm^{-1}. In the crystalline spectra on the (100) plane a similar but less intense band appears at 21800 cm^{-1}. These two bands closely resemble the absorption of 16800 cm^{-1} of the P3CNQ solution spectra. Therefore, it leads to suggest that all three bands may have originated from the same transition. Furthermore, the direction of polarization, position, and width of the band suggest that it may be due to an

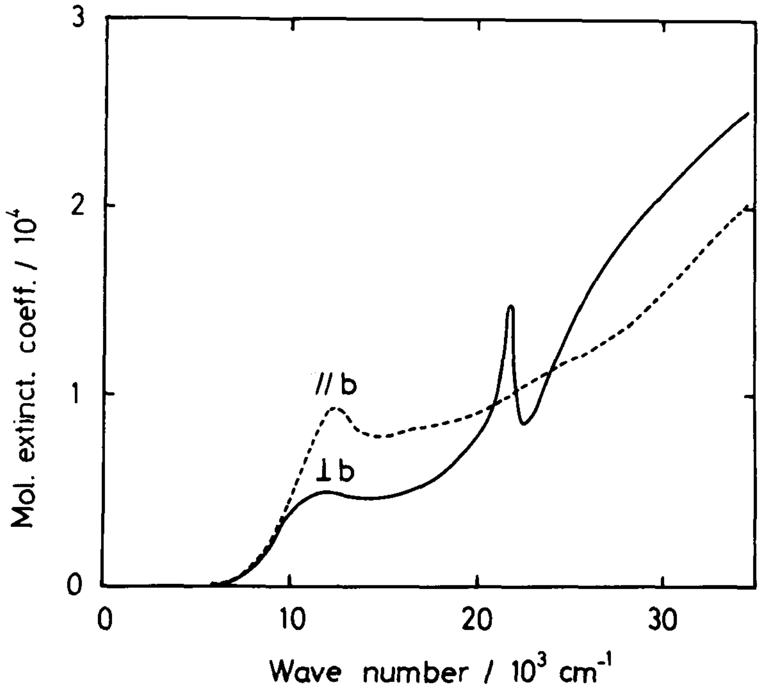

FIGURE 3. The Kramers-Kronig transformed absorption spectra of P3CNQ on the (100) plane.

IRCT-type interaction, where an electron has been transferred from the negatively charged dicyanomethide portion to the positively charged pryidinium moiety within a single P3CNQ molecule. However, considerable weakness of this absorption on the (100) plane is reasonable because the IRCT transition moment is mostly *a*-axis polarized, and hence its effective component along the measured *c*-axis should be smaller. It is also noted that in support of the above assignment, MO calculation by the Pariser-Parr-Pople method[7] shows the first intramolecular electron transfer in the molecule of P3CNQ at an energy of 16870 cm^{-1} with an oscillator strength of 3.52. Compared to the solution value of 16800 cm^{-1} with oscillator strength, 0.49, the energy of transition is almost coinciding but there remains a remarkable discrepancy between the observed and the calculated oscillator strengths. From this point of view, the P-P-P method is quite successful in affording the band energies even of the zwitterionic molecules but poorly accounts for their actual oscillator strengths.

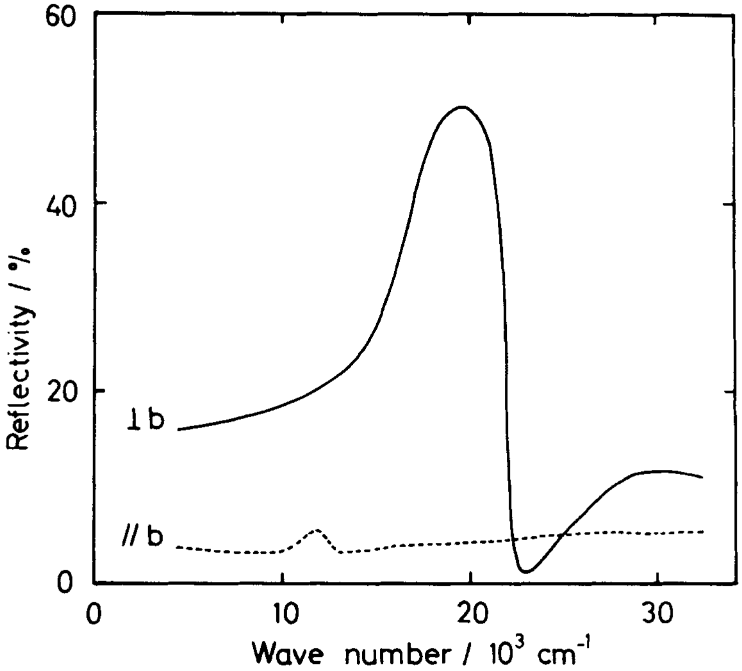

FIGURE 4. Polarized reflection spectra of the crystalline P3CNQ on the (001) plane.

In order to discuss the shift in the position of the IRCT band on the two crystalline faces (with respect to the solution value), calculations of the exciton energy shifts have been made by the dipole-dipole approximation.[5] Satisfactory convergence has been attained by extending the dipole sum over all the molecules in a disc of radius, 800 Å, and thickness, 30 Å. For the present system of $P2_1/c$, existing wavefunctions are those of *Au* and *Bu* symmetries:

$$Au\colon \psi_{(b)} = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} (\psi_{1i} - \psi_{2i} - \psi_{3i} + \psi_{4i})\, e^{ik\cdot R_i} \qquad (1)$$

$$Bu\colon \psi_{(ac)} = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} (\psi_{1i} - \psi_{2i} + \psi_{3i} - \psi_{4i})\, e^{ik\cdot R_i} \qquad (2)$$

Here, ψ_{1i}, ψ_{2i}, ψ_{3i}, and ψ_{4i} designate the wavefunctions in the *i*th unit cell where excitation occurs at the 4 sites with the space group operators, E, i, σ, and C_2, respectively; each wavefunction further meaning that in a unit cell while the concerned site is excited all the others

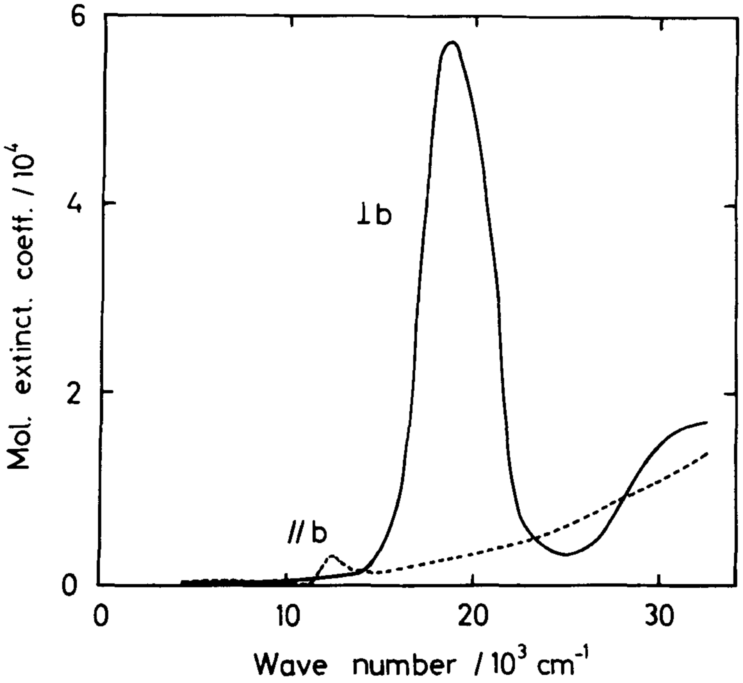

FIGURE 5. Calculated absorption spectra of P3CNQ on the (001) plane.

remain in their ground states. Actually, on both of the planes only the wavefunction with *Bu* symmetry is found to be significant. Table 1 shows the calculated exciton energies and oscillator strengths. From this table it may be found that on the (100) plane a blue shift occurs in agreement with the observation, and the oscillator strength is very close to the observed value. The slight difference in the observed and calculated energies may possibly be due to the interference effect of the neighboring high energy band on this IRCT absorption. On the other hand, for the (001) face though the oscillator strengths are comparable, calculation shows a red shift of about 1660 cm^{-1}. The observed blue shift of 1800 cm^{-1} may possibly be due to any difference in the geometrical configurations of the molecule in the solution and in the crystal.

The zwitterionic nature of P3CNQ molecule itself and a typical array of the molecules in the crystalline state may lead to suspect an intermolecular charge transfer in this system. This time polarization of the reflection measurement affords the expected results. From the crystal packing it is observed that a molecular stacking is developed

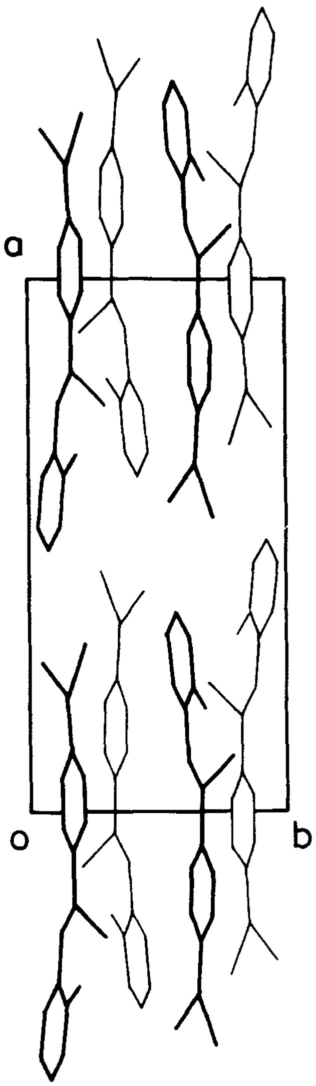

FIGURE 6. Projection figure of P3CNQ onto the (001) plane.

along a direction which is close to the crystalline *b*-axis. Its structural analysis indicates that although a pyridinium plane is twisted 30.13° from that of the quinodimethane ring intramolecularly, intermolecular arrangement allows a D^+A^- type stacking along the crystallographic *b*-axis. Projection figures onto the (100) and (001) planes

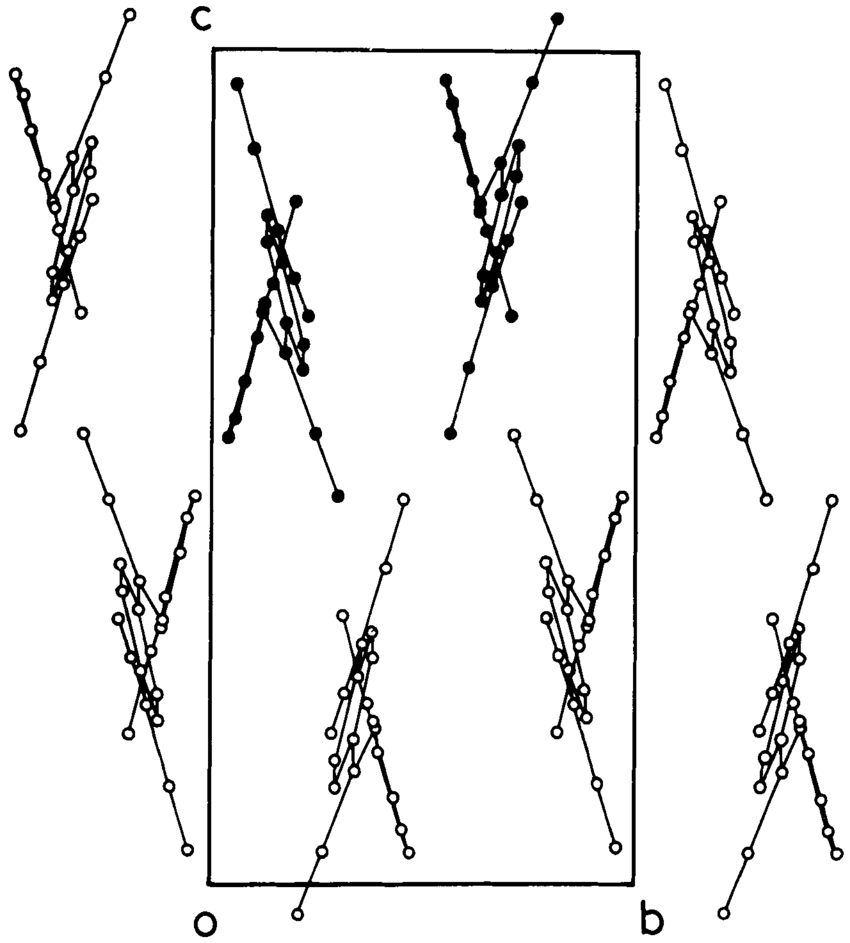

FIGURE 7. Projection figure of P3CNQ onto the (100) plane.

clarify that such a D^+A^- stack has been formed by the parallel array of the negatively charged dicyanomethide moiety of one molecule with the positively charged pyridinium ring in the neighboring molecule. In these figures, in the unit cell molecules acting as an acceptor and donor pair along the stack are distinguished by the similar line drawings. The average interplanar distance between the donor and acceptor in such a pair is 3.54 Å. Therefore, considering the way of packing of the interacting molecules, and also the polarization, position, and breadth of the low-energy bands in the *//b* spectra on the (100) and (001) faces, it may be suggested that an INCT transition

TABLE 1

IRCT Excitation On Different Faces

Plane	direc.	$\Delta E_{(\mathrm{IRCT})}$ in cm^{-1}		f	
		cal.	obs.	cal.	obs.
(100)	⊥b	23770	21800	0.11	0.16
(001)	⊥b	15140	18600	1.33	2.23

may originate when an electron transfer takes place from the negatively charged dicyanomethide group to the positively charged pyridinium moiety in the neighboring molecules acting as the donor and the acceptor, respectively.

In order to assign all the low-energy bands on the two crystalline faces more accurately, the direction of the transition moment for an INCT transition has been calculated trivially from the calculated charge densities and the atomic co-ordinates. On the planes of (100) and (001) the calculated direction of transition moment is tilted to the *b*-axis by about 25° and 8°, respectively. This is in support of the occurrence of an INCT band also in the $\perp$ *b* spectra on the (100) plane, near 11800 cm^{-1}, and also reasons for its comparative weakness with respect to that in the parallel direction. The slight red shift (~ 600 cm^{-1}) of the band in this $\perp$ *b* component may be due to either the INCT exciton shift or the interference effect of the neighboring band of 21800 cm^{-1}. On the (001) face, considerable weakness of the INCT band along the *//b* direction also seems to be justified since the direction of polarization of light on this face is inclined more towards the planes of the donor and acceptor than towards a normal to them.

Using the four-term-expanded AOs, and applying the Wolfsberg-Helmholtz approximation,[8] the MOs of P3CNQ have been calculated by the Pariser-Parr-Pople method[7]; valence state ionization potentials and the one-center Coulomb integrals considered here being those of Hinze and Jaffe.[9] By the use of the MOs thus calculated, the overlap integral between two neighboring P3CNQ molecules is obtained at $S = 0.00935$. Therefore, the transfer integral between the intermolecular HOMO and LUMO may be estimated[10] as -0.150 eV from the empirical relation, $t_1 = kS$, at $k = -16$ eV. However, the resonance integral between the two bonded carbons of the donor and acceptor moieties is evaluated as -2.30 eV for $K = 0.39$ in Wolfsberg-Helmholtz's approximation of P-P-P calculation. So the corresponding transfer integral may be estimated simply as the product of this resonance integral and the MO coefficients of the concerned carbons. The calculated t_2 thus obtained is -0.234 eV. These values are quite large and hence may stimulate both the INCT and IRCT excitations in this molecular crystal.

As another point of view, a composite molecule model also seems to be effective in the analysis of the spectral characteristics of the crystalline P3CNQ. From the consideration of its D^+A^- type stacking, P3CNQ crystal may be treated as a simple $A^-D^+A^-$ system. Then, ignoring any possible interaction between the INCT and IRCT configurations, energies for the two transitions may be represented independently by the following expressions[11]:

$$\Delta E_{(\mathrm{INCT})} = (I - E - C_1) + \frac{4t_1^2}{I - E - C_1} \tag{3}$$

and

$$\Delta E_{(\mathrm{IRCT})} = (I - E - C_2) + \frac{2t_2^2}{I - E - C_2} \tag{4}$$

repectively. Here, I and E are the ionization potential and electron affinity of the donor and acceptor, respectively, and they remain unchanged irrespective of the transition type. C_1 and C_2 represent the Coulomb energies, t_1 and t_2 are the previously stated transfer integrals between the HOMO and LUMO for the INCT and the IRCT transitions, respectively. The multiplying constants are different in the above two relations since the former differs from the latter being considered as a two-way CT process. Therefore, it may be possible to have approximate estimations of these CT transition energies if the related terms are known.

The Coulomb integral in each transition is estimated as $Z_1Z_2\, e^2/|r_{12}|$, where Z_1e and Z_2e are the charges on the C.Gs for the HOMO and LUMO, respectively, and r_{12} is the vector distance between them. Now, the only term that remains unknown is $(I - E)$, and if we set the value as 2.65 eV, possible energies for the INCT and the IRCT transitions become 1.52 and 2.18 eV, respectively, compared to the observed values of 1.54 and 2.13 eV. Table 2 represents the calculated as well as the observed values of the transition energies and the oscillator strengths. It is seen that although these calculations are partly based on a guesswork, e.g., value of $(I - E)$, satisfactory agreements are achieved thereby.

Thus, from the above studies it is found that zwitterionicity in the molecules and their suitable packing mode have facilitated a consid-

TABLE 2

CT Transitions In Crystalline P3CNQ

Type	I−E	t	C	$\Delta E_{(CT)}$ in cm^{-1}		f	
	eV	eV	eV	cal.	obs.	cal.	obs.
INCT	2.65	0.150	1.19	12260	12400	0.19	0.23
IRCT	2.65	0.234	0.52	17586	18600	0.94	2.23

erable INCT interaction in the crystalline state. As a result, it seems that effect of this INCT interaction may not be a negligible factor in the overall stabilization of the crystalline ground state of P3CNQ.

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