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Electronic States of the Picric Acid Complexes with 1-Methylnicotinamide, Tryptamine, DL-Tryptophan, and Serotonin

Masashi TANAKA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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The polarized reflection spectra of the crystals of the picric acid complexes with 1-methylnicotinamide, tryptamine, DL-tryptophan and serotonin have been measured from 15000 to 40000 cm^{-1} and the molar extinction coefficient of these crystals has been obtained by the Kramers-Kronig transformation. Furthermore, the theoretical calculation of the electronic states of these complexes has been made and compared with the experimental results. This analysis shows that the appearance of the new band in the region of 20000 cm^{-1} is the origin of the reddish color of the crystals of tryptamine picrate, DL-tryptophan picrate, and serotonin picrate; the new band can be assigned to the charge-transfer band from the picrate anion to the indole nucleus.

Indole derivatives are widely distributed through biological systems and form donor-acceptor complexes with a variety of aromatic acceptors. Szent-Gyorgyi and Isenberg[1)] reported the formation of colors on mixing electron donors such as indole with certain electron acceptors and further showed that the new band, not present in either component alone, can be assigned to the charge-transfer band.

The charge-transfer interactions were shown to play an important part in such biological processes as the binding of nicotinamide[2—3)] and flavin coenzymes[4)] to tryptophan residues of enzymes, the interactions of indoles with nucleotides and with nucleic acid,[5)] and the binding of serotonin and hallucinogenic tryptamines to synaptic receptor sites.[6)]

The simplest of the substituted nicotinamides, 1-methylnicotinamide, forms donor-acceptor complexes with iodide ions.[7)] Freeman and Bugg[8)] determined the crystal structure of the iodide of 1-methylnicotinamide and compared the interactions and structural features in this iodide salt with the crystal structures of the chloride and picrate salts of 1-methylnicotinamide, where charge-transfer forces are expected to be of little or no importance.

Tryptamine picrate is obtained as a reddish orange salt; DL-tryptophan picrate is prepared as a reddish brown crystal; and serotonin crystallized as a dark red picric salt. Since these amino acids are colorless and the picrate ion is pale yellow, the red color of the picrate salts is unexpected and suggests the formation of a donor-acceptor complex. Thewalt and Buug[9)] determined the crystal structure of serotonin picrate monohydrate in order to examine the solid state interactions between serotonin and the picrate ion. Gartland, Freeman, and Bugg[10)] described the crystal structures of the picrate complexes of tryptamine and DL-tryptophan in order to obtain information about the structural factors involved in the indole interactions with aromatic acceptors.

The complexes of picric acid with amines revealed that a proton is transferred from picric acid to amine and the interaction between the picrate ion and the amine molecule is capable of producing a charge-transfer absorption band. Matsunaga[11)] reported that the picrate anion is as strong as picric acid as an electron acceptor and the indole derivatives are the electron donors and the color of the tryptophan picrate complex aries from the charge-transfer interaction between the nucleus and the picrate anion.

The author undertook the spectroscopic examination of the crystals of the picrate complexes with 1-methylnicotinamide, tryptamine, DL-tryptophan, and serotonin molecules by measuring the microscopic polarized reflection spectra. Furthermore, we studied theoretically the electronic states of these complexes and showed that the new band in the region of 20000 cm^{-1} is the charge-transfer band from the picrate anion to the indole nucleus.

Experimental and Theoretical

Single crystals of the picrate complex with 1-methylnicotinamide, tryptamine, DL-tryptophan, and serotonin were crystallized by the slow evaporation of the solution of the salt.

Reflection spectra at the normal incidence have been measured over a range of 15000—40000 cm^{-1} with a reflection spectrophotometer made in our laboratory and the absorption spectra have been obtained by the Kramers-Kronig transformation.

The electronic states of the molecules are calculated by the Pariser-Parr-Pople[12)] SCF method in order to obtain the molecular orbitals and the orbital energies.

The two-center coulomb integrals γ_{pq} are estimated by Nishimoto-Mataga's method.[13)] The one-center core coulomb integrals α_p and the two-center core resonance integrals β_{pq} are approximated in the following equations:

$$\alpha_p = -I_p - (n_p-1)\gamma_{pp} - \sum_{r\neq p} n_r\gamma_{pr},$$

$$\beta_{pq} = -K(I_p+I_q)S_{pq},$$

where the constant K is taken to be 0.39. The overlap integrals S_{pq} are calculated between the nearest neighbor atoms by using the Slater type AO's and neglected in other cases. Then, the overlap integrals S_{CN} between the 2pπ AO's of the carbon atom on the benzene ring and the nitrogen atom on the nitro group are estimated by the equation

$$S_{CN} = S^{\circ}_{CN}\cos\theta,$$

where θ is the dihedral angle between the two 2pπ AO's χ_C and χ_N. The overlap integrals S°_{CN} are determined by using the 2pπ AO's χ°_C and χ°_N on the same plane. The values of the first ionization potentials I_p are taken from Pilcher and Skinner's[14)] table and the one-center coulomb integrals γ_{pp} are given by the relation $\gamma_{pp}=I_p-A$. These parameters (I_p, γ_{pp}, and n_p) are given in Table 1.

The intermolecular overlap integrals are written as follows:

Table 1. The values of the ionization potentials (I_p in eV), the one-center intergrals (γ_{pp} in eV), and the core charge (n_p) used in the SCF calculation

Atom		I_p	r_{pp}	n_p	Bonding type
Carbon	$t_1t_2t_3z$	−11.22	10.60	1	–CH=CH–
Nitrogen	$t_1{}^2t_2t_3z$	−14.51	13.31	1	–N=CH–
	$t_1t_2t_3z^2$	−12.26	13.31	2	–NH–, –NO_2
Oxygen	sx^2y^2z	−17.76	13.89	1	–NO_2
	$t_1{}^2t_2t_3z^2$	−14.97	14.89	2	–OH
	$t_1{}^2t_2{}^2t_3z^2$	−14.97	14.89	1	–O^-

$$\begin{aligned} S_{ai,bj} &= \int \phi_a^i(1)^*\phi_b^j(1)d\tau \\ &= \sum_{p,q} C_{ai,p}C_{bj,q}(\chi_p^a|\chi_q^b) \end{aligned}$$

where ϕ_a^i is the i-th molecular orbital on the molecule a and ϕ_b^j the j-th molecular orbital on the molecule b. χ_p^a is the 2pπ AO of the p-th atom on the molecule a and χ_q^b the 2pπ AO of the q-th atom on the molecule b. Then, the intermolecular overlap integrals involve the integrals between two 2pπ AO's χ_p^a and χ_q^b at orientations determined by the crystal structure. The line joining the atoms p and q defines the z axis and the y axis may be chosen to be perpendicular to one orbital, defining

$$\begin{aligned} &A = \boldsymbol{n}\cdot x_p, \quad &B = \boldsymbol{n}\cdot y_p = 0, \quad &C = \boldsymbol{n}\cdot z_p, \\ &D = \boldsymbol{m}\cdot x_q, \quad &E = \boldsymbol{m}\cdot y_q, \quad &F = \boldsymbol{m}\cdot z_q, \end{aligned}$$

when $\boldsymbol{n}$ and $\boldsymbol{m}$ are unit vectors in the direction of the 2pπ orbitals located on the centers p and q, respectively. Then, the atomic overlap integrals may be expressed as

$$(\chi_p^a|\chi_q^b) = AD(2p\pi_p^a|2p\pi_q^b) + CF(2p\sigma_p^a|2p\sigma_q^b).$$

The calculation of the excitation energy of the charge-transfer complex is carried out by the composite molecule method. That is, the matrix elements between the ground configuration Φ_o, the locally excited configuration $\Phi_{ai\to aj}$, and the charge-transfer configuration $\Phi_{ai\to bj}$ are given in the zero-differential overlap approximation as follows.

$$\begin{aligned}
(\Phi_{ai\to aj}|H|\Phi_{ai\to aj}) &= E_0 + \varepsilon_{aj} - \varepsilon_{ai} - (\phi_a^i\phi_a^i|\phi_a^j\phi_a^j) \\
&\quad + 2(\phi_a^i\phi_a^j|\phi_a^i\phi_a^j) \\
(\Phi_{ai\to bj}|H|\Phi_{ai\to bj}) &= E_0 + \varepsilon_{bj} - \varepsilon_{ai} - (\phi_a^i\phi_a^i|\phi_b^j\phi_b^j) + P \\
(\Phi_{ai\to aj}|H|\Phi_{ak\to al}) &= 2(\phi_a^i\phi_a^j|\phi_a^k\phi_a^l) - (\phi_a^i\phi_a^k|\phi_a^j\phi_a^l) \\
(\Phi_{ai\to aj}|H|\Phi_{bk\to bl}) &= 2(\phi_a^i\phi_a^j|\phi_b^k\phi_b^l) \\
(\Phi_{ai\to bj}|H|\Phi_{ak\to bl}) &= -(\phi_a^i\phi_a^k|\phi_b^j\phi_b^l) \\
(\Phi_{ai\to bj}|H|\Phi_0) &= \sqrt{2}K'S_{ai,bj} \\
(\Phi_{ai\to bj}|H|\Phi_{ai\to bl}) &= K'S_{bj,ql} \\
(\Phi_{ai\to bj}|H|\Phi_{bk\to bj}) &= -K'S_{ai,bk} \\
(\Phi_0|H|\Phi_{ai\to aj}) &= (\Phi_{ai\to aj}|H|\Phi_{ak\to bl}) = (\Phi_{ai\to bj}|H|\Phi_{bk\to al}) \\
&= 0
\end{aligned}$$

Here P is the term which takes into account the polarization effect and K' is a constant. ε_{ai} is the orbital energy of the i-th MO on the molecule a and ε_{bj} the orbital energy of the j-th MO on the molecule b.

In the calculation of the picrate complexes, P is taken to be 0.8 eV and K' given as −15.0 eV. All of the above-mentioned computations were carried out on a FACOM 230-75 computer at the Nagoya University computation center.

Results and Discussion

1-Methylnicotinamide Picrate. The picrate salt of 1-methylnicotinamide was crystallized as yellow prisms by slowly cooling a hot, saturated aqueous solution containing approximately equimolar quantities of 1-methylnicotinamide chloride and of picric acid.[8] The projection onto the ab plane of the picrate salt is shown in Fig. 1. The amino group of 1-methylnicotinamide is hydrogen bonded to the oxygen atom of the C–O^- bond in the picrate anion. The picrate and 1-methylnicotinamide moieties do not overlap and there are no unusually short intermolecular contacts except for the hydrogen-bonded interactions. Therefore, the charge-transfer interactions are probably of little importance in the crystals of 1-methylnicotinamide picrate.

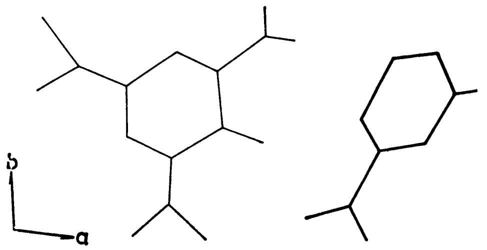

Fig. 1. Projection onto the ab plane of the crystal of 1-methylnicotinamide picrate.

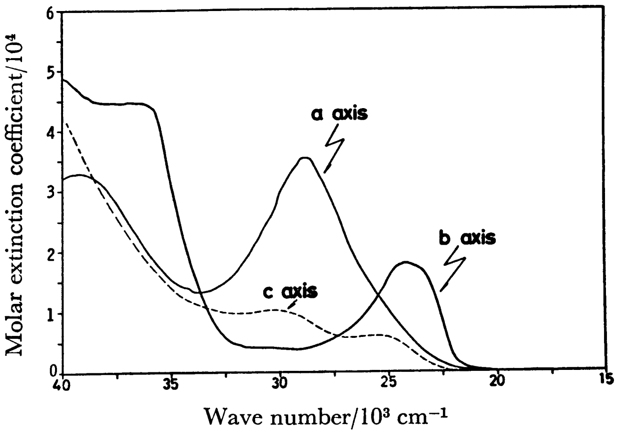

Fig. 2. The polarized absorption spectra of the crystal of 1-methylnicotinamide picrate obtained by the K-K transformation of the reflection spectra.

The absorption spectra transformed from the reflection spectra of the crystal of this salt are depicted in Fig. 2. The 23400 (LE_1) and 28800 (LE_2) cm^{-1} bands can be assigned to the local excitation band of the picrate anion. The LE_1 band is observed in the b axis spectrum and the LE_2 band in the a axis. Therefore, the LE_1 band is allowed for the light polarized perpendicular to the C–O^- bond of the picrate anion and the LE_2 band is active for the light polarized parallel to the C–O^- bond.

Tryptamine Picrate. Tryptamine picrate was obtained as a reddish orange crystal upon mixing aqueous solutions of tryptamine and picric acid. The

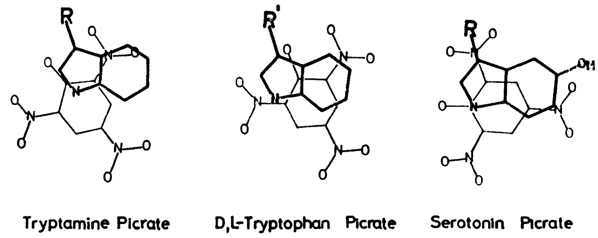

Fig. 3. Stacking patterns in the crystals of tryptamine picrate, DL-tryptophan picrate-methanol and serotonin picrate monohydrorate.

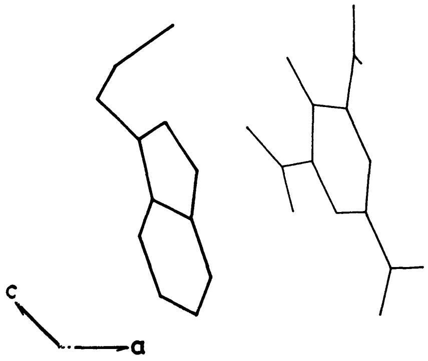

Fig. 4. Projection onto the ac plane of the crystal of tryptamine picrate.

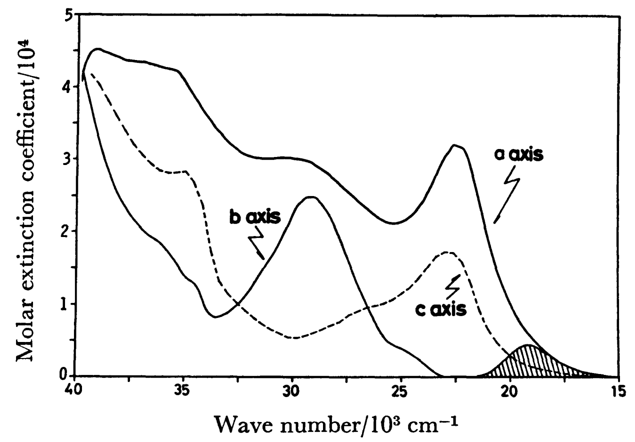

Fig. 5. The polarized absorption spectra of the crystal of tryptamine picrate obtained by the K-K transformation of the reflection spectra.

crystal packing scheme for the tryptamine picrate is described in Fig. 3 and the projection onto the ac plane in Fig. 4.[10)]

The absorption spectra transformed from the reflection spectra of the crystal of this complex are shown in Fig. 5. The LE$_1$ band is observed at 22500 cm^{-1} in the both the a and c axes spectra and the LE$_2$ band at 28200 cm^{-1} mainly in the b axis spectra, as predicted from the directions of the transition moments of the LE$_1$ and LE$_2$ bands. Furthermore, the new, quite diffuse band appears as a long extension on the side of the longer wave length of the LE$_1$ band in the a axis spectrum. Because of this overlap, the position of the maximum of the new band cannot be known, and so the shaded region may be thought to be a new absorption band which has its peak at 19200 cm^{-1}.

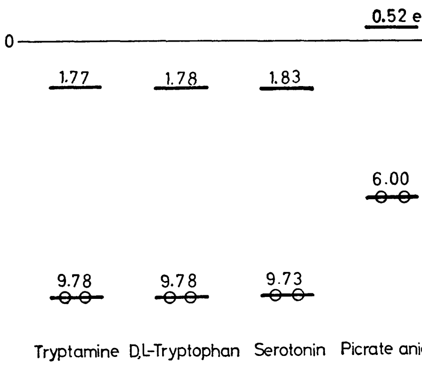

Fig. 6. The orbital energy diagram of the donor and acceptor molecules in the picrate salt system.

In the theoretical calculation, the overlap integral between the HOMO of the indole ring in the tryptamine cation and the LUMO of the picrate anion is 0.0084; the orbital energy diagram of the donor and acceptor molecules is shown in Fig. 6. The calculated excitation energy (E_{CT}) and the wavefunction (Ψ_{CT}) of the lowest excited state are shown as follows.

$$E_{\mathrm{CT}} = 20250\ \mathrm{cm}^{-1},$$

$$\begin{aligned}\Psi_{\mathrm{CT}} = {} & 0.9769\Phi(\phi_2^{10}\rightarrow\phi_1^{6}) - 0.1231\Phi(\phi_2^{9}\rightarrow\phi_1^{6}) \\ & + 0.1019\Phi(\phi_2^{10}\rightarrow\phi_2^{11}) + 0.0929\Phi(\phi_1^{5}\rightarrow\phi_1^{6}) \\ & + 0.0755\Phi_0.\end{aligned}$$

The stabilization energy (ΔE) and the wave function (Ψ_0) of the ground state are written in the following equations:

$$\Delta E = 0.019\ \mathrm{eV},$$

$$\Psi_0 = 0.9966\Phi_0 - 0.0721\Phi(\phi_2^{10}\rightarrow\phi_1^{6}),$$

where ϕ_1^i is the i-th molecular orbital of the tryptamine molecule and ϕ_2^j the j-th molecular orbital of the picrate anion.

Therefore, the new band at 19200 cm^{-1} can be assigned to the chrage-transfer band from the picrate anion to the indole nucleus.

DL-*Tryptophan Picrate-Methanol.* Reddish brown crystals of the DL-tryptophan picrate-methanol complex were obtained by slowly evaporating a methanol solution that contained an equimolar mixture of DL-tryptophan and picric acid. The crystal packing scheme for the DL-tryptophan picrtate-methanol is depicted in Fig. 3 and the projection onto the bc plane in Fig. 7.[10)]

The absorption spectra transformed from the reflection spectra of the crystal of this complex are shown in Fig. 8. The LE$_1$ band is observed at 23400 cm^{-1} in the

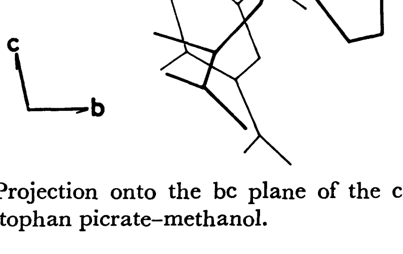

Fig. 7. Projection onto the bc plane of the crystal of DL-tryptophan picrate-methanol.

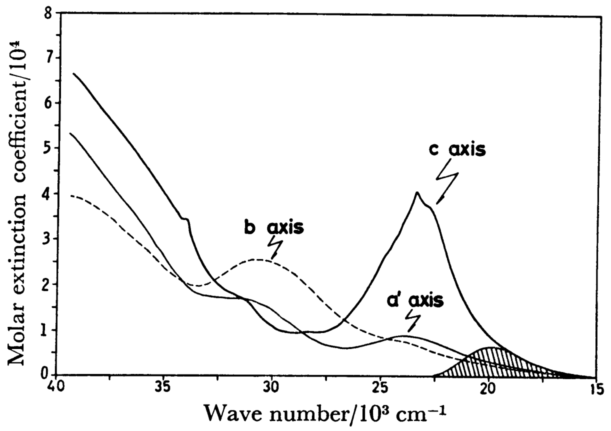

Fig. 8. The polarized absorption spectra of the crystal of DL-tryptophan picrate obtained by the K-K transformation of the reflection spectra.

c axis spectrum and the LE_2 band at 30600 cm^{-1} in the b axis spectrum, as predicted from the directions of the transition moments of the LE_1 and LE_2 bands. Furthermore, the new diffuse band appears as a long extension on the side of the longer wavelength of the LE_1 band in the c, b, and a' axes spectra. The maximum of the new band cannot be located but the shaded region may be thought to be a new band which has its peak at 19600 cm^{-1}.

In the theoretical calculation, the overlap integral between the HOMO of the indole ring in the tryptophan cation and the LUMO of the picrate anion is 0.0077 and the relation of the orbital energies of the donor and acceptor molecules is shown in Fig. 6. The calculated excitation energy (E_{CT}) and the wavefunction (Ψ_{CT}) of the lowest excited state are expressed as follows:

$$E_{CT} = 19020\ \mathrm{cm}^{-1},$$

$$\Psi_{CT} = 0.9918\Phi(\phi_2^{10}\rightarrow\phi_1^6) + 0.0502\Phi(\phi_1^4\rightarrow\phi_1^6) + 0.0443\Phi(\phi_1^5\rightarrow\phi_1^6) + 0.0679\Phi_0.$$

The stabilization energy (ΔE) and the wavefunction (Ψ_0) of the ground state are written in the next equations:

$$\Delta E = 0.024\ \mathrm{eV},$$

$$\Psi_0 = 0.9959\Phi_0 - 0.0692\Phi(\phi_2^{10}\rightarrow\phi_1^6) + 0.0444\Phi(\phi_2^9\rightarrow\phi_1^6),$$

where ϕ_1^i is the i-th molecular orbital of the tryptophan molecule and ϕ_2^j the j-th molecular orbital of the picrate anion.

Accordingly, the new band at 19600 cm^{-1} can be assigned to the charge-transfer band from the picrate anion to the indole nucleus.

Serotonin Picrate Monohydrate. Serotonin picrate monohydrate was crystallized as dark red prisms by slowly evaporating a saturated aqueous solution containing approximately equimolar quantities of serotonin creatinine sulphate and picric acid. The crystal packing for the serotonin picrate monohydrate is shown in Fig. 3 and the projection onto the bc plane in Fig. 9.[9]

The absorption spectra transformed from the reflection spectra of the crystal of this complex are shown in Fig. 10. The LE_1 band is not observed in the b and c axes spectra but the LE_2 band is observed at 27200 cm^{-1} in the c axis spectrum, as expected from the direction of the transition moments of the LE_1 and LE_2 bands. Furthermore, the new band appears at 21000 cm^{-1} in the b axis spectrum and the observed transition moment is directed along the intermolecular vector between the hydroxyindole and picrate molecules.

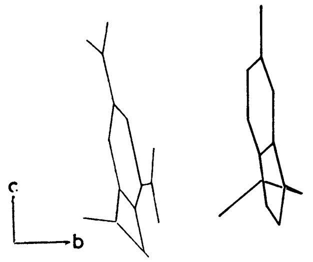

Fig. 9. Projection onto the bc plane of the crystal of serotonin picrate monohydrate.

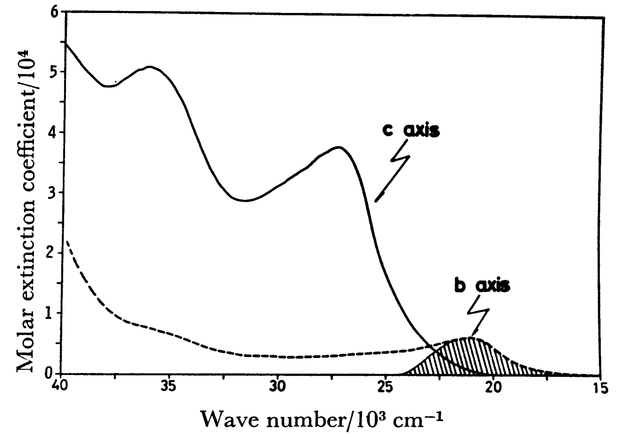

Fig. 10. The polarized absorption spectra of the crystal of serotonin picrate monohydrate.

In the theoretical calculation, the overlap integral between the HOMO of the hydroxyindole ring in the serotonin cation and the LUMO of the picrate anion is 0.0059; the diagram of the orbital energies of the donor and acceptor molecules is shown in Fig. 6. The calculated excitation energy (E_{CT}) and the wavefunction (Ψ_{CT}) of the lowest excited state are written as follows.

$$E_{CT} = 20770\ \mathrm{cm}^{-1},$$

$$\Psi_{CT} = 0.9678\Phi(\phi_2^{10}\rightarrow\phi_1^7) - 0.1735\Phi(\phi_2^9\rightarrow\phi_1^7) + 0.0640\Phi(\phi_2^{10}\rightarrow\phi_1^8) - 0.0623\Phi(\phi_2^{10}\rightarrow\phi_2^{11}) + 0.1289\Phi(\phi_1^5\rightarrow\phi_1^7) + 0.0533\Phi_0.$$

The stabilization energy (ΔE) and the wavefunction (Ψ_0) of the ground state are given in the following equations:

$$\Delta E = 0.013\ \mathrm{eV},$$

$$\Psi_0 = 0.9978\Phi_0 - 0.0491\Phi(\phi_2^{10}\rightarrow\phi_1^7),$$

where ϕ_1^i is the i-th molecular orbital of the serotonin molecule and ϕ_2^j the j-th molecular orbital of the picrate anion.

Therefore, the new band at 21000 cm^{-1} can be assigned to the charge-transfer band from the picrate anion to the hydroxyindole nucleus.

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