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# Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. V.[1] Tryptophan Picrate

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In connection with our work on molecular complexes in which charge-transfer and proton-transfer interactions operate simultaneously between the component molecules, and also in connection with a recent report on the crystal and molecular structures of red-colored serotonin picrate monohydrate by Thewalt and Bugg,[1-3] a spectroscopic examination of the tryptophan picrate has been undertaken. The preparation of this picrate was reported by Mayeda as early as 1907.[4] He noted also that the color is similar to that of the indole picrate.

The tryptophan picrate was crystallized from water following the procedure described by Mayeda, and

1) Part IV: G. Saito and Y. Matsunaga, This Bulletin, **46**, 714 (1973).

2) Y. Matsunaga and G. Saito, *ibid.*, **45**, 963 (1972).

3) U. Thewalt and C. E. Bugg, *Acta Crystallogr., B*, **28**, 82 (1972).

4) M. Mayeda, *Z. Physiol. Chem.*, **51**, 263 (1907).

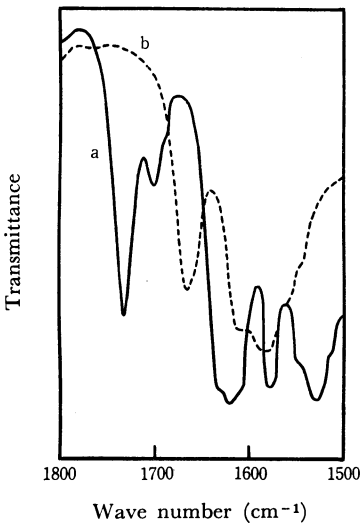
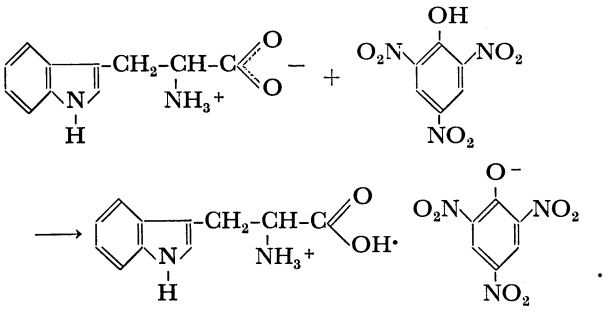



Fig. 1. Vibrational spectra of a) the tryptophan picrate and b) tryptophan.

the indole picrate, from chloroform. As was pointed out by Briegleb and Delle,[5] the infrared spectrum of the latter complex, well approximated by the superposition of the spectra of the component compounds, clearly indicates the absence of proton transfer.

Tryptophan is in the form of the zwitter ion; therefore, the vibrational spectrum in the region from 2000 to 4000 $cm^{-1}$ is dominated by the pattern due to the $NH_3^+$ group. Although this pattern remains through the picrate formation, a big change is observed in the region from 1500 to 1800 $cm^{-1}$ (see Fig. 1). A strong band located at 1740 $cm^{-1}$ in the picrate should be assigned to the carbonyl stretching vibration. These pieces of evidence indicate that the proton-transfer from picric acid to tryptophan occurs in the following way:




Both of the complexes are reddish orange. Their visible spectra, measured by the diffuse reflectance method, are plotted using the Kubelka-Munk function in Fig. 2. Indole and its derivatives have been shown to be electron donors.[6] The charge-transfer absorption in the indole-*s*-trinitrobenzene complex in carbon tetrachloride is expected to appear around 26 kK by the extrapolation of the plot of the energies corresponding to the band maxima of indole with each of a series of acceptors against the energy maxima

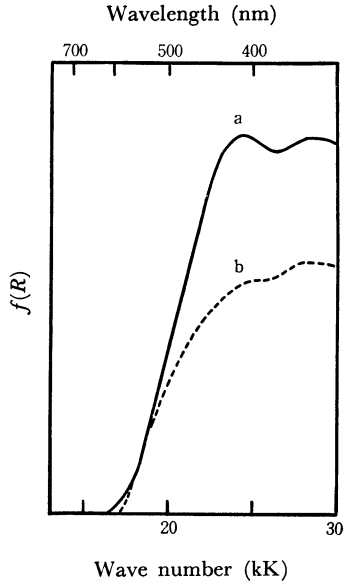



Fig. 2. Diffuse reflection spectra of a) the tryptophan picrate and b) the indole picrate.

of the spectra of the corresponding hexamethylbenzene-electron-acceptor complexes. As the electron-acceptor strength of picric acid is comparable with that of *s*-trinitrobenzene, the absorption maximum observed at about 25 kK in the solid indole picrate may be attributed to the charge-transfer interaction. The intense maximum located at 24.4 kK in the tryptophan picrate is possibly due to the picrate ion; however, the contribution from this yellow-colored anion must end by 21 kK.[7] No absorption beyond this limit is present in either component species alone. As the indole nucleus and the functional groups in protonated tryptophan are separated by the $-CH_2-CH-$ group, the electron-donating ability is expected to be essentially determined by that of the indole nucleus. Moreover, we have shown that the picrate anion is as strong as picric acid itself as an electron-acceptor.[1,2,7] Because of the intense absorption due to the picrate ion, the maximum of the charge-transfer absorption band in the tryptophan picrate cannot be located. Nevertheless, the similarity in the spectrum below 20 kK between the indole and tryptophan complexes strongly supports the assumption that the color of the tryptophan complex arises from the charge-transfer interaction between the indole nucleus and the picrate anion.

Thewalt and Bugg have found that protonated serotonin cation, which is very closely related to the protonated tryptophan cation, and the picrate anion are arranged in alternatingly stacked arrays to form continuous columns in the red-colored crystal. On the basis of its color and those crystallographic observations, they have concluded that the picrate is a complex of the electron donor-acceptor type.[3] The results of the present spectroscopic study of the tryptophan picrate seem to be in conformity with their conclusion.

5) G. Briegleb and H. Delle, *Z. Elektrochem.*, **64**, 347 (1960).
6) R. Foster and P. Hanson, *Trans. Faraday Soc.*, **60**, 2189 (1964).
7) G. Saito and Y. Matsunaga, This Bulletin, **45**, 2214 (1972).