BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (1), 299—300 (1977)

Excited-State Dipole Moments of Picrates of Pyridine, 2-Methylpyridine, 3-Methylpyridine, and 4-Methylpyridine

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(Received May 13, 1976)

Synopsis. Measurements of the excited-state dipole moments for picrates of pyridine and methylpyridines have been carried out by spectrophotometry. The contribution of the dative structure $\Psi(D^+A^-)$ in the excited state of these picrates is larger than the contribution of $\Psi(D^+A^-)$ in the ground state.

The excited-state dipole moments of electron donor–acceptor (EDA) complexes provide valuable information on the nature of binding in the excited state of the complexes. Recently, Rao and Dwivedi[1] have investigated the excited-state dipole moments of several EDA complexes by using the expression of McRae[2] to describe solvent shifts of electronic spectra. In the case of weak EDA complexes, they have observed red shifts of the CT bands and have concluded that the excited-state dipole moments μ_e are larger than the ground-state dipole moments μ_g. In the case of strong EDA complexes, they have observed solvent blue shifts and $\mu_e < \mu_g$. A lower μ_e compared to μ_g in strong EDA complexes was indeed a new observation.

Under these circumstances, it seems important to obtain experimental knowledge concerning the excited-state dipole moments of strong EDA complexes. We used picrates of pyridine, 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine as strong EDA complexes. The purpose of our research was to determine the μ_e of these picrates from solvent shifts of electronic spectra and to investigate the contribution of the dative structures $\Psi(D^+A^-)$ and $\Psi(D^-A^+)$ in the excited-states of such strong EDA complexes.

Experimental

Materials and Their Purification. According to the procedure described by Raman and Soundararajan,[3] picrates of pyridine, 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine were synthesized. All four picrates were recrystallized from ethyl alcohol three times. The 1:1 complexes precipitated from the solution.[4] The solvents used were carefully purified according to the descriptions in Ref. 5.

Measurements. The dielectric contants were determined with a home-made resonance-method apparatus. The refractive indices were measured by means of a Pulfrich refractometer. The dielectric constant (ε) and the refractive index (n_D) at the sodium D line of the solvents agreed with the values cited in Ref. 5. The densities of the solutions were measured by the use of a pycnometer for volatile liquids. The absorption spectra were taken with a Shimadzu UV-200 recording spectrophotometer equipped with a thermostated cell holder. Matched pairs of stopped silica cells of 1 cm path lengths were used. All measurements were made on deaerated samples at 20 °C.

Determination of Excited-state Dipole Moments. When two polar solvents I and II of similar n_D are used, the solvent shifts ($\Delta\nu$) of electronic spectra can be simplified from the expression of McRae[2] in the following manner:

$$\begin{aligned}\Delta\nu &= \nu_{\max}(\mathrm{I}) - \nu_{\max}(\mathrm{II}) \\ &= C\{[(\varepsilon-1)/(\varepsilon+2)]_{\mathrm{I}} - [(\varepsilon-1)/(\varepsilon+2)]_{\mathrm{II}}\} \qquad (1)\end{aligned}$$

The constant C is given by Eq. 2:

$$C = (2/hc)[\mu_g(\mu_g-\mu_e)/a^3] \qquad (2)$$

where a is the cabity radius in Onsager's theory[6] of the reaction field and is estimated from the molal volume on the assumption of the spherical radius of the complexes.

Rao and Dwivedi[1] have shown that the acetonitrile-diethyl ether solvent system can be used to obtain μ_e of EDA complexes from Eq. 1. When we used this solvent system, all four picrates dissociated completely into their donor and acceptor components in acetonitrile.[7] Instead of the acetonitrile-diethyl ether solvent system, we employed the acetone-diethyl ether solvent system. The validity of this solvent system was confirmed from the fact that the μ_e value, 9.8 D, for the hexamethylbenzene–chloranil complex was almost identical to the value, 10.0 D[1], obtained in the acetonitrile-diethyl ether solvent system.

Results and Discussion

The absorption spectra of pyridine picrate are shown in Fig. 1. The absorption band around 410 nm was assigned as the CT band of the picrate. The method of continuous variation was employed at 410 nm to establish the stoichiometry of the complex in the solvent. When the sum of the pyridine and picric acid concentrations was kept constant at 6.70×10^{-3} M, the Job curves showed a distinct maximum for equal concentrations of donor and acceptor, characteristic of a 1:1 complex (see Fig. 2). The results thus obtained for the picrates of three methylpyridines were the same as the above results for pyridine picrate. Since the IR spectra of the four picrates are the same as the IR spectra of the complexes between 2,4,6-trinitroanisole and pyridine and the three methylpyridines, and the complexes show the CT bands at almost the same

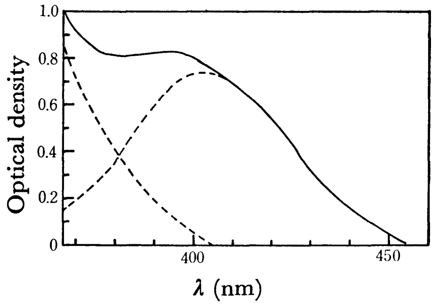

Fig. 1. The absorption spectra of pyridine picrate in diethyl ether at 30 °C. The dashed line shows the best fit of Gauss-curve for the CT band.

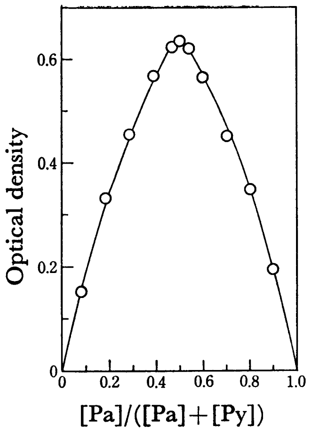

Fig. 2. The continuous variation of pyridine picrate in diethyl ether at 410 nm. The sum of the pyridine (Py) and picric acid (Pa) concentrations was kept constant at 6.70×10^{-3} M.

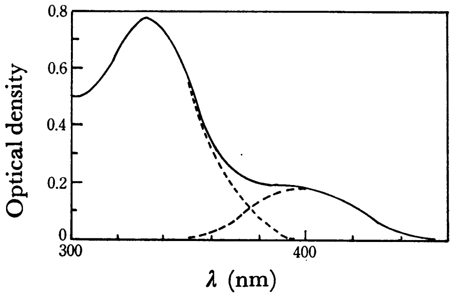

Fig. 3. The absorption spectra of 2,4,6-trinitroanisole-pyridine in diethyl ether at 30 °C. The dashed line shows the best fit of Gauss-curve for the CT band.

wavelength as the CT band of pyridine picrate (*e.g.*, see Figs. 1 and 3), all four picrates are not proton-transfer-typed complexes but EDA complexes. The CT bands of all four picrates were analyzed assuming Gauss-type absorption bands with the method described by Badoz *et al.*[8] (*e.g.*, see Fig. 1). The results are summarized in Table 1.

Table 1. Excited state dipole moments

Complex	ν_{CT}(cm^{-1}) (in ether)	C (cm^{-1})	a (Å)[a]	μ_g (D)[b]	μ_e (D)
Pyridine picrate	24750	−542	4.30	8.70	9.6
2-Methylpyridine picrate	24670	−476	4.25	9.25	10.1
3-Methylpyridine picrate	24650	−610	4.41	9.55	10.4
4-Methylpyridine picrate	24690	−596	4.33	9.60	10.4

a) Estimated from the apparent molal volume in 1,4-dioxane. b) Measured in 1,4-dioxane. See Ref. 3.

As the wave function Ψ_e for the excited state is given by Eq. 3,[1)]

$$\Psi_e = C_1\Psi(DA) + C_2\Psi(D^+A^-) + C_3\Psi(D^-A^+) + C_4\Psi(D^*A) + C_5\Psi(DA^*) \tag{3}$$

the μ_e of the complex is proportional to $|C_2^2-C_3^2|$.

It is concluded from the μ_e thus obtained that the contribution of the dative structure $\Psi(D^+A^-)$ in the excited state of the present picrates is larger than the contribution of $\Psi(D^-A^+)$ is negligible even in the excited state of strong complexes such as the present complexes.

The differences of the ground state dipole moments between pyridine picrate and the picrates of 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine are 0.55, 0.85, and 0.90 D, respectively. The differences of the excited-state dipole moments between pyridine picrate and the three picrates of methylpyridines are 0.5, 0.8, and 0.8 D, respectively. From these facts, it is concluded that the methyl groups of methylpyridines do not play any decisive role in the excited state on CT excitation.

The authors are greatly indebted to Professor Hitoshi Takeshita of Kyushū University for the elemental analysis. One of the present authors (H. Y.) especially wishes to thank Professor F. Yoneda of Kumamoto University for the supply of 2,4,6-trinitroanisole.

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4) Found: C, 42.68; H, 2.68; N, 18.03; O, 36.61%. Calcd for $C_{11}H_8N_4O_7$: C, 42.86; H, 2.62; N, 18.18; O, 36.34%. Found for 2-methylpyridine picrate: C, 44.21; H, 3.13; N, 17.29; O, 35.37%; for 3-methylpyridine picrate: C, 44.57; H, 3.08; N, 17.32; O, 35.03%; and for 4-methylpyridine picrate: C, 44.61; H, 3.09; N, 17.36; O, 34.94%. Calcd for $C_{12}H_{10}N_4O_7$: C, 44.73; H, 3.13; N, 17.39; O, 34.75%.

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