A Cation-dependent Conformational Change of the 2,2′:6′,2″-Terpyridine Anion Radical

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Although the structure of the ion pair between the aromatic anion radical and the alkali metal cation in solution has been extensively studied by means of ESR and optical spectra, the case in which the conformation of the anion radical varied with the species of the counter cation has not yet been reported. In the present work, the visible spectra of the 2,2′ : 6′,2″-terpyridine anion radical revealed the presence of two species of ion pairs. The solvent and cationic dependence of the equilibrium between the two species indicated that the species can be distinguished by means of the conformation of the anion.

The visible spectrum of the anion radical produced with lithium in tetrahydrofuran (THF) exhibited an absorption maximum in the 610-mμ range, together with a slight shoulder in the 560-mμ range. With the change in the alkali metal in the order of increasing cationic radius, the shoulder was developed at the expense of the peak in the 610-mμ range. In the spectrum of the cesium-produced radical, the intensity in the 560-mμ range exceeded that in the 610-mμ range. The relative intensity of two peaks also depended on the solvent. The use of 2-methyl tetrahydrofuran (MTHF) enhanced the intensity of the peak in the 610-mμ range, while the use of dimethoxyethane (DME) weaken the intensity of the same peak. The maximum in the 610-mμ range almost disappeared in the spectrum of the cesium-produced radical in DME. The spectrum of the radical in dimethylformamide showed a single maximum, at 573-mμ, which was independent of the metal used. This absoprtion certainly arises from the free terpyridine anion. ESR studies of the nitrogen-hetrocyclic anion radicals have proved that those anions existed as ion pairs in an ethereal solvent.[1–5] Each of the two separated bands in the ranges of 560 mμ and 610 mμ should be assigned to one of the structurally-different ion pair. Examples of the spectra are presented in Fig. 1.

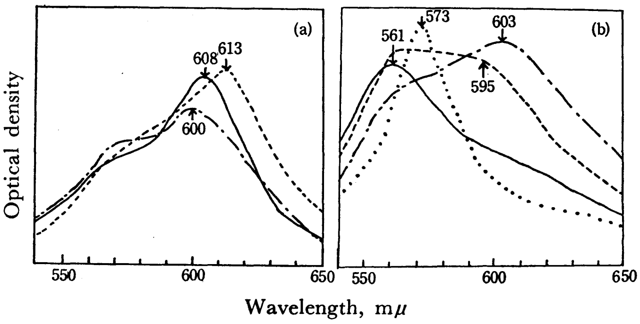

Fig. 1. Visible spectra of the terpyridine anion.
(a): Cationic dependence of the spectra in THF.
----, Li; ——, Na; —·—·—, Rb.
(b): Solvent dependence of the spectra of the cesium-produced radical.
——, DME; ----, THF; —·—·—, MTHF; ······, DMF.
Concentration of the radical, $(1-5)\times10^{-3}$ mol/*l*.

The repulsions among the nonbonding and antibonding electrons on the three nitrogen atoms of the terpyridine anion keep those atoms far from each other. This situation holds with regard to the conformation of the free terpyridine anion. Three nitrogen atoms are able to coordinate to a cation only when the interaction of the cation with nitrogen atoms is strong enough to compensate for the above repulsions. The interaction of a cation with an anion, especially with the nonbonding electrons on the anion, is intensified by a decrease in the cationic size, while an increase in the solvation of the cation in the order of MTHF<THF<DME[6] weakens such interactions. Both the solvent dependence and the cationic dependence of the relative intensities of the two peaks, therefore, strongly suggested that, in the species exhibiting the peak of the 610-mμ range, the cation is enclosed by three nitrogen atoms and several solvent molecules. When an additional solvent molecule participates this first layer surrounding the cation, one of the nitrogen atoms will become free from coordination to the cation, as is schematically shown in Fig. 2. In such a case, an appreciable change in the spectrum can be expected. The shift of the absorption maximum from the 610-mμ range to the 560-mμ range is due to this conformational change.

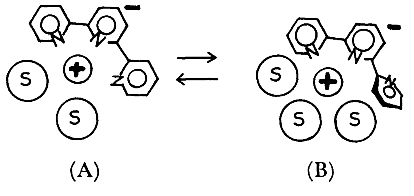

Fig. 2. Possible structures of the ion pair.
The species with absorption maximum in 610 mμ range (A) and in 560 mμ range (B).

Contrary to the case observed thus far, the increase in the cationic field, which resulted from the decrease in the cationic size or in the solvation of the cation, caused a red shift of the absorption maximum in the 610-mμ range.

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