ELECTRONIC STRUCTURE AND ABSORPTION SPECTRA OF PRODUCTS FROM SINGLE-ELECTRON REDUCTION OF DERIVATIVES OF 4,4'-DIPYRIDYL

I. P. Krainov, O. M. Tsyguleva,
and S. F. Kramarenko

The Hartree-Fock absolute method has been used in the \( \pi \)-electron approximation to investigate the absorption spectra of a number of cation-radical salts of derivatives from 4,4'-dipyridyl with the objective of explaining the interrelation between their electronic structure and the nature of the set of these salts with the spectroscopic characteristics. The characteristic absorption spectrum of cation-radicals of 4,4'-dipyridyl and its derivatives is formed due to the merging of three absorption bands of different natures, localized on the dipyridyl fragment. In the absorption spectra of products from single-electron reduction of dications of 4,4'-dipyridyl a band is observed from charge transfer between the cation-radical and the dication, and also an absorption band of the \( \pi \)-dimers being formed as a result of spin-spin interaction of the cation-radicals.

The quaternary salts of 4,4'-dipyridyl, having the capacity for reversible single-electron reduction, the products of which are intensely colored stable cation-radicals find wider application in electrochemical-chromic equipment for presenting information and in variable density light filters [1-3]. The optical characteristics of these salts depend substantially on the electronic structure of the dications [4], the cation-radicals and their solvatochromism. In contrast to the anion-radical salts the solvatochromism of the cation-radicals have been inadequately investigated, although an understanding of the natures of the solvation shells and the structure of the new particles having formed in solution is a necessary condition for explaining the reactivities and optical properties of the cation-radical salts.

The authors have investigated the electronic absorption spectra of a number of cation-radical derivatives of 4,4'-dipyridyl with the objective of explaining the interrelation of their electronic structure and the nature of the set of cation-radical salts with the spectroscopic characteristics. The objects of the investigations were selected cation-radical derivatives of 4,4'-dipyridyl.

\[
\begin{align*}
&I - R = H, \quad A = \text{ClO}_4; \quad II - R = \text{Ph}, \quad A = \text{ClO}_4; \quad III - R = 4\text{-Cl-Ph}, \quad A = \text{ClO}_4; \\
&IV - R = 4\text{-CN-Ph}, \quad A = \text{ClO}_4; \quad V - R = 4\text{-CH}_3\text{O-Ph}, \quad A = \text{ClO}_4.
\end{align*}
\]

The cation-radical salts I-V were obtained by chemical and electrochemical reduction of the appropriate tertiary salts of derivatives from 4,4'-dipyridyl in media of polar organic solvents (acetonitrile, propylene-glycol carbonate, dimethylformamide) in an anaerobic atmosphere. The solvents were prepared in accordance with the methods given in [5]. In order to remove traces of air the frozen solutions were evacuated and purged by argon. The original salts of derivatives from 4,4'-dipyridyl were obtained by the methods given in [6] with subsequent recrystallization from methanol and acetone. The materials obtained were identified by UV absorption spectra [7] and by polarographic data [8]. The chemical reduction of solutions of the appropriate salts of derivatives from 4,4'-dipyridyl was carried out by

means of zinc amalgam. The salt concentrations were varied over the range $10^{-4}$ to $5 \cdot 10^{-3}$ M. The electrochemical reduction was conducted at the potential for single-electron reduction determined from polarographic data in an electrochemical cell on current-conducting electrodes made from indium oxide [9], transparent in the range 350-1500 nm. In this case the concentrations of the initial salts was not less than $5 \cdot 10^{-2}$ M. The anodic depolarizer used was ferrocene ($10^{-1}$ mole/liter), for which the spectrum of the cation-radical is known from [10]. The chemical and electrochemical production of the cation-radicals was carried out directly in the cell for the specimens of the model Hitachi-330 spectrophotometer. The absorption spectra were identical for cation-radicals obtained by both methods.

The excited states of the investigated compounds have been investigated within the frame-work of the absolute Hartree-Fock method in the $\pi$-electron approximation [11, 12] with the parameters given in [13]. Analysis of the excited states of the cation-radicals has been carried out on the basis of the device for the transition matrix of densities in the frame-work of the schemes described in [14]. As a result for the assigned excited states values were obtained which provided a means of determining the degrees of association of the electronic states ($\kappa$) and the localization number of these excitations on the fragments of the cation-radicals ($L_{fr}$).

The absorption spectra of products from the single-electron reduction of dications from derivatives of 4,4'-dipyridyl in the visible and near-IR regions are characterized by five maxima of the absorption spectra (Fig. 1). The intensity of the longest wave band depends to a significant degree on the nature of the substituent in the para-positions of the phenyl rings of the cation-radicals. The introduction of electron acceptor substituents in the para-positions of the phenyl rings leads to a small bathochromic shift of the absorption band and to an increase of its intensity. The dielectric permeability of the medium has almost no influence on the location and intensity of this band, which is evidence of the weak solvation ability of the products from single-electron reduction of dication derivatives of the 4,4'-dipyridyl. This position is almost independent of the nature of the anion bonded to the cation-radical body. In solutions with cation-radical concentrations less than $10^{-4}$ M this absorption band is not observed. Investigations of the concentration dependence for the intensity of the long-wave absorption band (Fig. 2) have shown that its intensity depends not only on the cation-radical concentration but also on the concentration of the original dication. Application of the isomolar series method [15] provides a basis to consider that this band is due to charge transfer between the cation between the cation-radicals and the dication derivatives of 4,4'-dipyridyl. As a result of calculations by the Benosi-Hildebrand method [16] it has been found that the stability constant of the complex with

![Figure 1](image-url)

**Fig. 1.** Electronic absorption spectra from products of the single-electron reduction of dications from derivatives of 4,4'-dipyridyl.