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Electronic Spectrum of Dibiphenylene-Ethene Radical Anion

Short Communication

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The electronic absorption spectrum for the dibiphenylene-ethene radical anion (*DBPE*$^{\dot{-}}$), generated electrochemically in dimethylsulfoxide solutions, is reported. Based on calculations by the LCAO-MO method in the *Hückel* approximation and on the analysis of the band positions it is suggested that in the *DBPE*$^{\dot{-}}$ molecule two planar fluorenylidene fragments are twisted (~ 60°) about the central C=C bond.

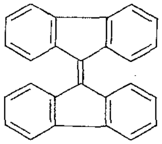
(Keywords: Dibiphenylene-ethene; Radical anion; Electrochemical radical anion generation; LCAO-MO calculations)

Das Elektronenabsorptionsspektrum des Dibiphenylen-Radikalanions
(Kurze Mitteilung)

Das Dibiphenylenethen-Radikalanion (*DBPE*$^{\dot{-}}$) wurde elektrochemisch hergestellt und das Elektronenabsorptionsspektrum aufgenommen. Auf Grund von LCAO-MO Berechnungen in der *Hückel*-Annäherung und der Analyse der Bandenlagen wird nahegelegt, daß im *DBPE*$^{\dot{-}}$-Molekül zwei planare Fluorenyliden-Fragmente ca. 60° um die zentrale C=C-Bindung verdrillt angeordnet sind.

It is known that chemical or electrochemical reductions of organic π-electron compounds in aprotic media yield relatively stable radical anions. The present communication is concerned with preliminary studies on the electronic spectrum of dibiphenylene-ethene radical anion in dimethylsulfoxide solutions.

Polarographically, dibiphenylene-ethene (*DBPE*)



exibits two reversible one electron reduction waves in nonproton donating solvents[1, 2]. It is the first of these

$$DBPE + e \rightleftharpoons DBPE^{\cdot -}$$

which leads to the formation of free radical anions. These radicals are stable in solutions containing $(C_2H_5)_4NClO_4$ as supporting electrolyte; they do not form ion pairs with tetraethylammonium cations[2]. The electrolyte refered to above was used in the present investigations at a concentration of 0.1 *M*.

The compound investigated was electrolyzed on a mercury cathode of a surface area of 15 cm^2 under controlled potential corresponding to the limiting current of the first reduction wave (− 1.20 V vs. SCE). Before electrolysis, solutions in the cell were purged of dissolved oxygen with pure and dry argon. The electrolysis was carried on until the value of the current measured in the circuit was reduced down to below 10% of the initial value and, then, the solution was transferred into a closed system into a Specord recording spectrophotometer. The measurements were taken over the wavelength range from 300 to 800 nm.

As electrolysis proceeded, the solution began to develop a blue-green tinge which was attributed to the $DBPE^{\cdot -}$ radical anion. The electronic spectrum of this species is presented in Fig. 1.

It should be pointed out that the wavelengths of the bands were reproducible in different experiments with an accuracy of ± 5 nm.

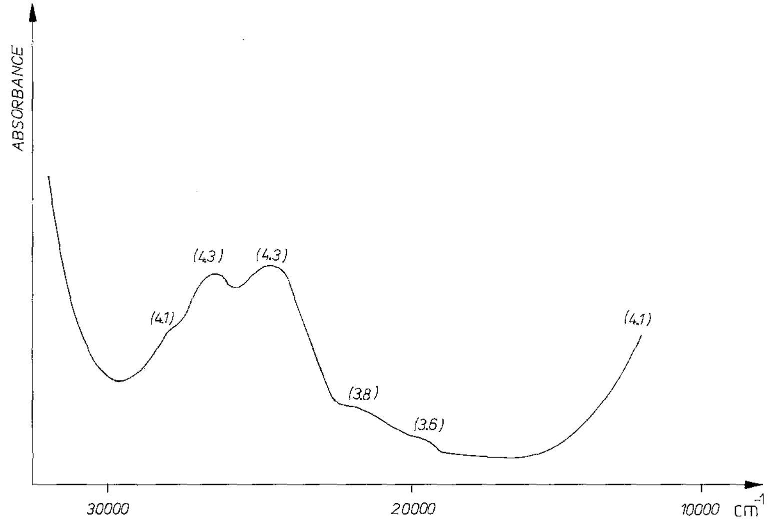


Fig. 1. Electronic spectrum of the dibiphenylene-ethene radical anion in dimethylsulfoxide; estimated values of molar absorptivities (in logarithmic scale) are given in parentheses

It follows from our experiments that:

i) *DBPE*$^{\cdot-}$ radical anion is stable to disproportionation under experimental conditions; as follows from polarographic measurements the value of $K_{\mathrm{disp}} = [DBPE^{2-}][DBPE]/[DBPE^{\cdot-}]^2$ is equal to $4.8 \cdot 10^{-8}$ at 23 °C,

ii) the solutions satisfy (with an accuracy of ± 3%) the *Beer* law, at least up to the concentration of $5 \cdot 10^{-5}$ *M*, and

iii) dibiphenylene-ethene is quantitatively regenerated in the presence of oxygen.

An interesting observation follows from conformational analysis. On the basis of crystallographic results[3] it is evident that the structure of *DBPE* is characterized by two planar fluorenylidene systems which are mutually twisted about the central C=C bond. The angle between the planes of both these fragments is 43°. However, based on calculations by the LCAO-MO method in the *Hückel* approximation and on the comparison of the band positions in the spectra of *DBPE* and *DBPE*$^{\cdot-}$ it can be assumed that the corresponding dihedral angle in the dibiphenylene-ethene radical anion is about 60°.

Further investigations are in progress. This work was supported by a grant of research problem MR I-11.

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