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Visible Absorption Spectra of the Phenothiazine Radical Cation and Its 10-Substituted Derivatives

Short Communication

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The visible absorption spectra for the phenothiazine radical cation and its 10-substituted derivatives (the substituents were methyl, phenyl, benzyl and cyclohexyl), generated electrochemically in acetonitrile solutions, are reported. Substituent effects on these spectra are considered in the frame of quantum chemical calculations using the MNDO method.

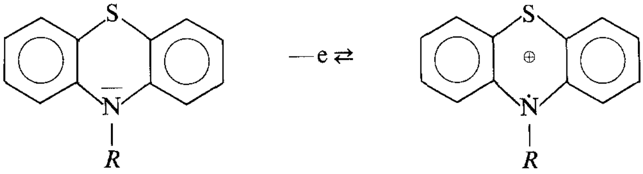
(Keywords: Phenothiazine radical cation; Substituent effect; Electronic spectra)

VIS-Absorptionsspektren des Phenothiazinradikal-Kations und seiner 10-substituierten Derivate (Kurze Mitteilung)

Die Absorptionsspektren des elektrochemisch generierten Phenothiazinradikal-Kations und seiner 10-substituierten Derivate (Methyl, Phenyl, Benzyl und Cyclohexyl als Substituenten) wurden im sichtbaren Bereich vermessen. Die Substituenteneffekte werden im Rahmen der quantenchemischen MNDO-Methode diskutiert.

Phenothiazine derivatives are intensively studied in a number of fields of chemical and pharmaceutical research, primarily because of the biological activity of these substances and, more recently, because of the solar energy transformation [1]. One common property of these compounds is their ease of chemical oxidation; some workers have even suggested that corresponding radical cations may be biologically active (for discussion c.f. [2] and references therein).

Since the pioneer work of *Billon* [3] many facts have been accumulated on the anodic oxidation of phenothiazine (for review see, e.g., [4]). In acetonitrile, the process starts with a reversible one-electron transfer and produces stable radical cations:



The present report is concerned with preliminary studies on the visible absorption spectra of the phenothiazine radical cation (R = H) and its 10-substituted derivatives. The substituents, R were methyl, phenyl, cyclohexyl and benzyl groups, respectively.

The compounds investigated were electrolyzed on a platinum anode of a surface area of 7 cm^2 under controlled potentials corresponding to the first oxidation peaks. The electrolysis (0.1*M* $NaClO_4$ in acetonitrile was used as background electrolyte) was carried on until the value of the current measured in the circuit was reduced down to below 5% of the

Table 1. *Formal potentials of the radical cation/10-substituted phenothiazine redox couples and spectral characteristics of the radicals in acetonitrile*

Substituent in 10-position	$E°$, mV	λ_{max} (log ε)
-H[a]	547	436 (3.64), 462 (3.02), 478 (3.54), 496 (3.67), 512 (3.88), 625 (3.12), 715 (2.85),
$-CH_3$[b]	652	439 (3.55), 463 sh (3.40), 474 (3.63), 492 (3.80), 511 (3.96), 760 (3.08), 830 (3.06),
-phenyl	515	451 (3.53), 481 (3.62), 502 (3.71), 512 (3.86), 710 (3.04), 802 (3.17),
-benzyl	670	452 (3.49), 480 sh (3.25), 503 sh (3.48), 512 (3.72), 807 (3.16),
-cyclohexyl	550	450 (3.70), 485 (3.65), 502 (3.72), 512 (3.83), 810 (3.04)

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[a] The data reported in the literature were as follows: 437 (3.7), 498 (3.8), 517 (3.9) [5] and 435 (3.66), 462, 478, 495, 513 (3.87) [6], both in acetonitrile solutions

[b] The data reported earlier for the radical cation of 10-methylphenothiazine in acetonitrile were: 437 (3.25), 474, 492, 511 (3.66) [6] and 441 (3.56), 512 (3.96), 760 (3.08), 843 (3.08) [7]

initial value and, then, the solution was transferred in a closed system into a Specord recording spectrophotometer. Before electrolysis, solutions were deaerated with pure and dry argon.

The values of the standard potentials of radical cation/parent molecule redox couples are summarized in Table 1. They were determined from cyclic voltammetric curves registered at a platinum microelectrode (scan rate 100 mV s^{-1}).

The parent phenothiazines have no absorption in the 350–850 nm region of the spectrum but their radical cations posess well resolved absorption bands with the characteristics presented in Table 1.

Comparing the data presented in this table one may notice that the spectra should be divided into two groups: the first group contains the spectra of the radical cations of phenothiazine and 10-methylphenothiazine, whereas the second one comprises the spectra of the radicals with such large substituents as phenyl, benzyl and cyclohexyl. What is, however, the possible reason of this division?

The geometry of phenothiazine [8] and its radical cation [9] in the solid state has been established by X-ray diffraction technique. The structure of the parent molecule is presented in Fig. 1, with a dihedral angle of 158.5° [8]. This folding angle increases on radical formation [9]; our calculations performed by the MNDO method [10, 11] leads to the value of 179°. The geometry of the molecule in solutions is not known with certainty,

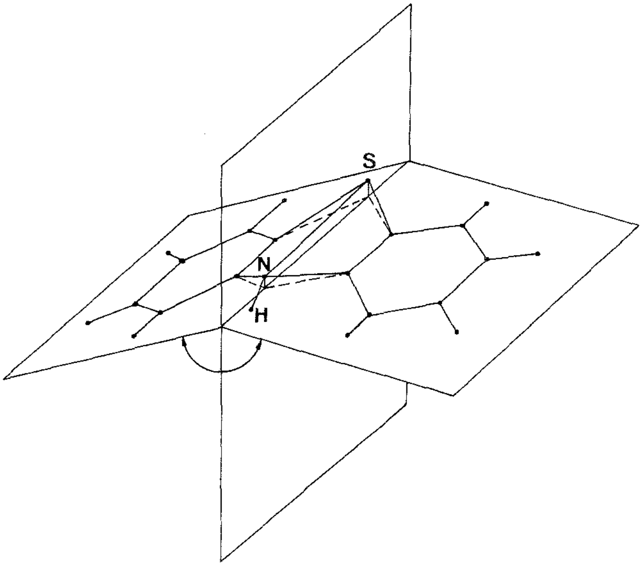

Fig. 1. Structure of the phenothiazinic nucleus from X-ray diffraction data [8]

although studies by *Raman* resonance spectroscopy [6] and esr [12] indicate that the radical cations of phenothiazine and 10-methylphenothiazine are also bent in solutions.

Taking into account these observations we assume that geometrical factors of the radicals are responsible for the different behaviour showing up in Table 1. It seems reasonable to suggest that the dihedral angle in the phenotiazine radical cation changes upon methylation (as it was anyway suggested in [13]), but this variation is considerably greater upon the substituents included in the second group. Our MNDO calculations confirm this idea: we have obtained 178 and 171° for the dihedral angles of the 10-methyl- and the 10-phenylphenothiazinic radical cation, respectively. Generally, the substituent in 10-position appears to hinder the conjugation of the Np_π-orbital with the carbon atoms of the phenothiazinic skeleton and, in this way, changes the spectral properties of the radicals under study.

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