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# Electronic Properties of the Neutral Radicals from Phenothiazines

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In the course of numerous studies of phenothiazine radicals, it has been found by the ESR method that a neutral phenothiazinyl radical is produced from phenothiazine by photochemical and chemical oxidations.[1-4] However, little attention has been paid to the substituted radicals or to the electronic spectrum of the non-substituted radical itself. In this note we shall discuss the assignment of the electronic spectra of the phenothiazinyl radicals, with reference to the ESR spectra and the effect of air-contact upon the radical decay, and with the aid of a theoretical calculation of the electronic spectra.

## Experimental and Calculation

1-Methylphenothiazine and 1-methoxyphenothiazine were prepared by the thionation of the corresponding diarylamines.[5] The compounds used were purified by repeated sublimations under a high vacuum. Two different methods, that is, the chemical method of Tsujino[4] and the photochemical method of Shine and Mach,[1] were used for the radical formation because such by-products as the phenothiazine nitroxide radical and phenothiazine dimers, which would be less destroyed by air-contact than the phenothiazinyl radical, are likely to be produced by these methods. The solvent used in the chemical oxidation was prepared by mixing equimolar amounts of spectro-grade dimethyl sulfoxide and acetic anhydride. The radical solutions were prepared by dissolving materials in degassed solvents. The solutions were filtered by means of a glass filter and directly led to a UV cell or an ESR tube. All of these procedures were performed in a vacuum line. The electronic absorption spectra were recorded with a Hitachi EPS-2 spectrophotometer using a 10 mm cell. The ESR spectra were obtained with a Nippon-Denshi JES-3BS-X spectrometer with 100 KHz modulation.

The calculations of the electronic spectra of phenothiazinyl radicals were performed by means of the open-shell SCF method[6] with limited CI. The two-center Coulomb integrals were evaluated by means of the Nishimoto-Mataga formula, and the core-resonance integrals by means of the variable $\beta$-core method. The CI calculations were done including 24 singly-excited configurations composed of $(i\rightarrow k)_\alpha$, $(i\rightarrow k)_\beta$, $(i\rightarrow m)$, and $(m\rightarrow k)$, where $\varphi_m$=half-occupied orbital; $i=m$-3, $m$-2, $m$-1, and $k=m+1$, $m+2$, $m+3$; the notations of $(i\rightarrow k)_\alpha$ and $(i\rightarrow k)_\beta$ were taken from Ref. 7.

## Results and Discussion

As is shown in Fig. 1, new absorption maxima appear at 462 and 615 nm upon the chemical oxidation of phenothiazine. The longer-wavelength band has a shoulder near 645 nm. The $\lambda^{\max}_{\mathrm{nm}}$ values for 1-methylphenothiazine were 464 and 610 nm. The absorption curve changes in the wavelength region shorter than 400 nm had to be excluded on account of the largely overshadowing absorption of the parent molecules. These solutions exhibited the strong ESR spectra due to the corresponding neutral radicals. The ESR spectrum of the 1-methylsubstituted radical shown in Fig. 2 is reported for the first time here. Though not completely resolved, the spectrum could be analyzed with $a^{\mathrm{N}}=7.0$—$7.2$, $a^{\mathrm{H}}_{3,7}=3.5$, $a^{\mathrm{H}}_{9}=2.2$—$2.5$, and $a^{\mathrm{H}}_{2,8}=0.7$—$0.9$ gauss. These values are not very different from the values for the non-substituted radicals.[2,4] On the other hand, only a weak absorption with $\lambda^{\max}_{\mathrm{nm}}$ ~470 nm appeared upon the chemical oxidation of 1-methoxyphenothiazine, and a weak ESR signal was observed only after the temperature had been lowered to −30°C.

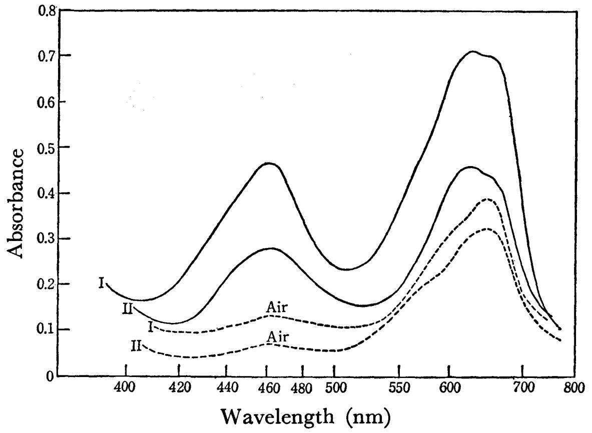

Fig. 1. The electronic spectra observed at the formation of phenothiazinyl radicals in a degassed DMSO+$Ac_2O$ solution. (I) non-substituted and (II) 1-methyl-substituted phenothiazines.

After the exposure of the solutions to air, the absorbance of the longer-wavelength peak showed considerable values even when no ESR spectrum of the radicals could be detected clearly. At this stage, the location of the $\lambda^{\max}_{\mathrm{nm}}$ of the longer-wavelength band shifted to 640—645 nm, just in the region where a shoulder had been observed in the initial spectrum. The solutions which were exposed to air until the ESR spectrum could not be detected were submitted to thin-layer chromatography using petroleum ether–ether (2 : 1) as the developing solvent. The 1,10′- and 3,10′-dimers of phenothiazine were detected by

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[1] H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1965).

[2] B. C. Gilbert, P. Hanson, R. O. C. Norman and B. T. Sutcliffe, *Chem. Commun.*, **1966**, 161.

[3] C. Jackson and N. K. D. Patel, *Tetrahedron Lett.*, **1967**, 2255.

[4] Y. Tsujino, *ibid.*, **1968**, 4111.

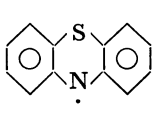
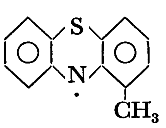
[5] S. P. Massie and P. K. Kadaba, *J. Org. Chem.*, **21**, 347 (1956).

[6] H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. Ser. A*, **68**, 591 (1955).

[7] A. Ishitani and S. Nagakura, *Theoret. Chim. Acta*, **4**, 236 (1966).

[8] Y. Tsujino, *Nippon Kagaku Zasshi*, **90**, 304 (1969).

Table 1. Observed and calculated results of electronic spectra

| | $\Delta E_{\text{obsd}}$ (eV) | Without CI $\Delta E_{\text{calcd}}$ (eV) | Without CI $f_{\text{calcd}}$ | With CI $\Delta E_{\text{calcd}}$ (eV) | With CI $f_{\text{calcd}}$ |
|---|---|---|---|---|---|
| a) Phenothiazinyl Radical  | ~2.02 | 2.31 | 0.09 | 1.59 | 0.11 |
| | 2.69—2.70 | 2.72 | 0.52 | 1.90 | 0.01 |
| | | 2.88 | 0.07 | 2.21 | 0.05 |
| | | | | 2.28 | 0.04 |
| | | | | 2.49 | 0.08 |
| | | | | 2.87 | 0.27 |
| b) 1-Methyl-phenothiazinyl Radical  | ~2.03 | 2.28 | 0.12 | 1.32 | 0.06 |
| | 2.68—2.69 | 2.72 | 0.45 | 1.34 | 0.05 |
| | | 3.89 | 0.09 | 1.89 | 0.01 |
| | | | | 2.43 | 0.10 |
| | | | | 2.63 | 0.15 |
| | | | | 2.78 | 0.41 |

*) Parametrizations are as follows:

The valence-state $I_p$ and $E_A$ in eV:

| | C | N | S | $H_3$ |
|---|---|---|---|---|
| $I_p$ | 11.16 | 14.12 | 23.59 | 10.256 |
| $E_A$ | 0.03 | 1.78 | 10.54 | 0.93 |

The core-resonance integrals ($\beta_{rs}$) in eV:

$\beta_{C-C}=-0.51\,P_{C-C}-1.84$, $\beta_{C-N}=-0.53\,P_{C-N}-2.02$, $\beta_{C-S}=-0.33\,P_{C-S}-1.80$, $\beta_{C-H_3}=-4.111$.

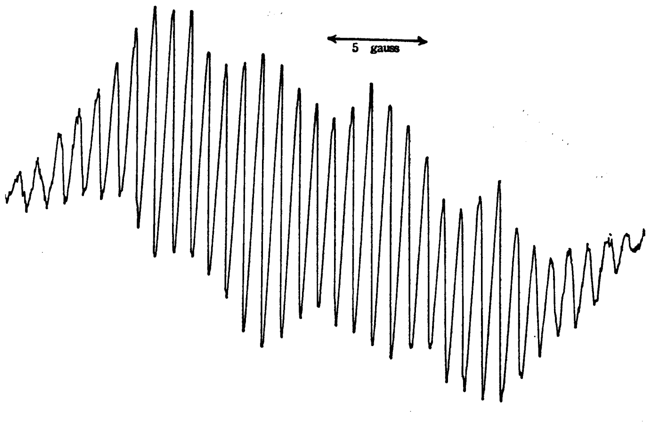


Fig. 2. The ESR spectrum of 1-methylphenothiazinyl radical produced in DMSO+$AC_2O$ at room temperature.

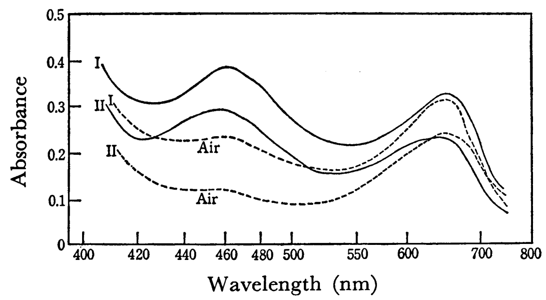


Fig. 3. The electronic spectra observed at the formation of phenothiazinyl radicals in a photoirradiated ethanol solution. (I) non-substituted and (II) 1-methyl-substituted phenothiazines.

means of the spots with $R_f$=0.8—0.9 and 0.4—0.5 respectively, in accordance with the findings of Tsujino.[8] The 3,10′-dimer of 1-methylphenothiazine was also detected with the spot, $R_f$=0.3—0.4. The spots, $R_f$=0.0—0.2, which are probably related to the polymerized by-products, were also found in the two systems. These results serve to correlate the 640—645 nm absorption with the radical-decay products.

In the photochemical oxidations, the $\lambda_{\text{nm}}^{\text{max}}$ values of the new absorption maxima are 459 and 650 nm for the phenothiazine solution, and 462 and 653 nm for the 1-methylphenothiazine solution. When these solutions were exposed to air until the ESR signal could not be detected, the longer-wavelength bands alone retained considerable values of absorbance. According to the results of the adopted method of irradiation using an Ushio XS–501A xenon lamp, the changes in the absorption spectrum of the 1-methoxyphenothiazine solution took place very slowly, to the extent that a weak absorption maximum around 650 nm was found after 15 hr's irradiation.

The calculated data of the electronic spectra indicate the existence of weak transitions below 2 eV which might be masked by the strong absorptions of the radical-decay products. This trend appears to be promoted remarkably by the CI calculation. The calculated data both with and without CI suggest that moderately intense transitions of the neutral radicals exist in the region of the shorter-wavelength bands which are observed upon the radical formations.

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