

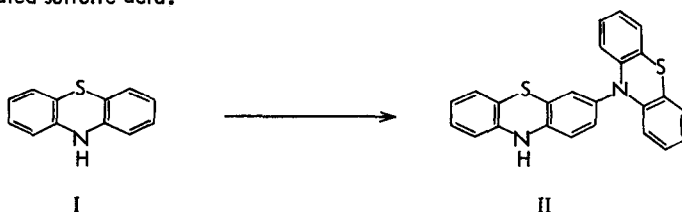
BIRADICAL CATION FROM DIPHENOTHAIAZINYL

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(Received in Japan 9 February 1968; accepted for publication 23 February 1968)

During the studies on the oxidation of phenothiazine (I), it was found that the initial oxidation product was mainly 3,10'-diphenothiazinyl (II) under anhydrous reaction conditions. Thus, II was obtained by the oxidation of I with iodine in dimethylsulfoxide solution, with dimethylsulfoxideacetic anhydride, or with concentrated sulfuric acid.



The e.s.r. spectrum of the solution of II in concentrated sulfuric acid revealed the presence of a triplet species at room temperature: there are two pairs of broad lines due to $\Delta m = 1$ transitions of

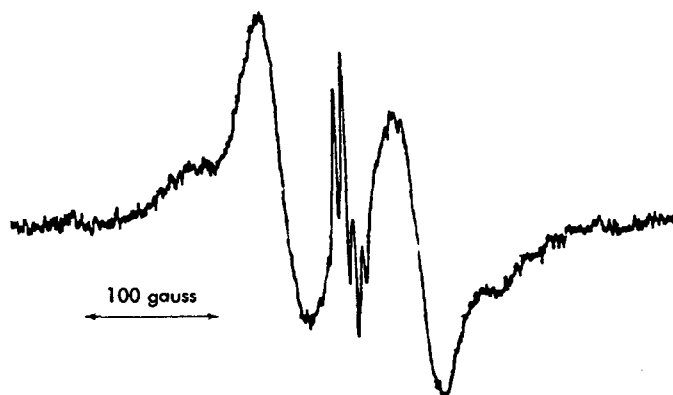
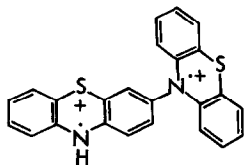


FIG. 1. The e.s.r. spectrum of the solution of II in 98% sulfuric acid at room temperature.

randomly oriented triplets (FIG. 1). The intensity of the signal was almost unchanged for several hours.

This signal is assigned to biradical cation III. The zero-field splitting parameters were determined from the spectrum by Wasserman's method (1): $D' = 138$ gauss ($D = 0.013$ cm^{-1}), $E = 0$.

The value of D' indicates that average distance between electrons in III is 5.9 \AA , which is in accordance with the distance estimated from the structure III.



III

When this solution was frozen to a rigid glass (ca. -180°C), three pairs of broad lines and one sharp line at a half field ($\Delta m = 2$) were observed (FIG. 2). The zero-parameters were also determined: $D' = 153$ gauss ($D = 0.014$ cm^{-1}), $E' = 9.3$ gauss ($E = 0.0009$ cm^{-1}).

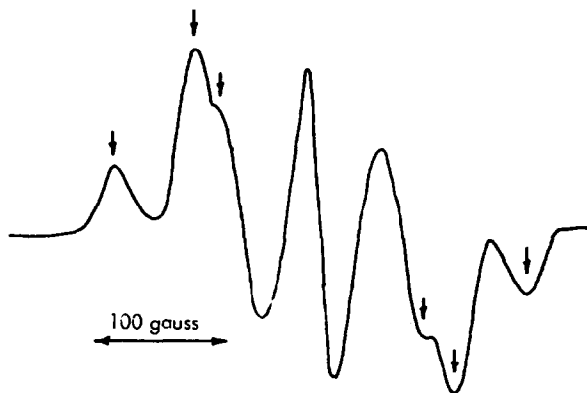


FIG. 2. The e.s.r. spectrum of III in a rigid glass (at -180°C).

Then, as the sample was slowly warmed up to room temperature again, the signal gradually returned to a similar pattern to the original one.

The changes in the signal with temperature descent may be attributed to the lowering of symmetry of III due to the restriction of free rotation about C-N bond between both phenothiazine nuclei.

Although the e.s.r. spectra of biradicals have been studied by several workers (2, 3, 4), this is the first case that biradical species of the non-rigid system with such a large D -value was detected by the e.s.r. spectroscopy.

Products studies were also carried out. II was dissolved in concentrated sulfuric acid at room temperature. The solution was initially reddish brown and then changed very slowly into dark brown in a few days, but the changes in the spectra were negligibly small for several hours (FIG. 3). The 2-hr.-old

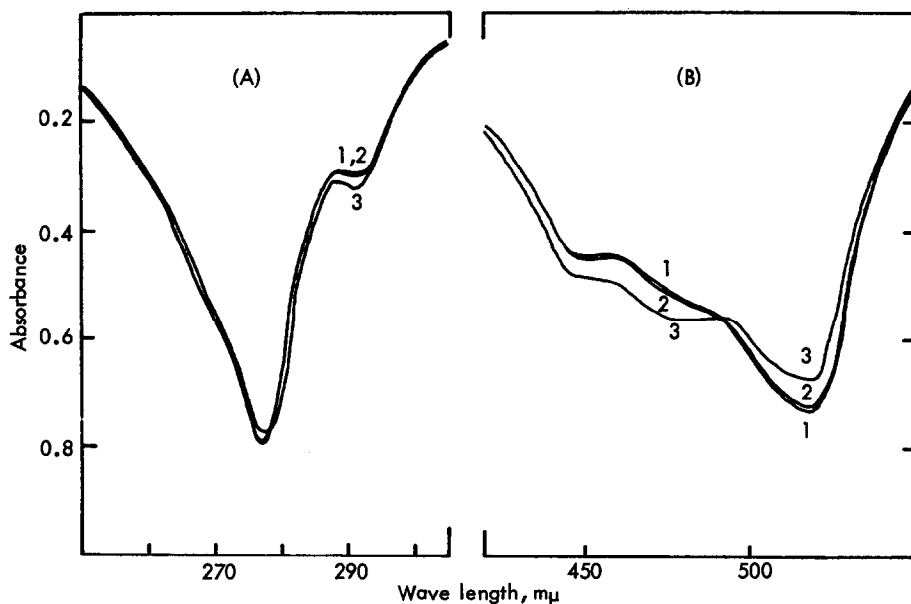
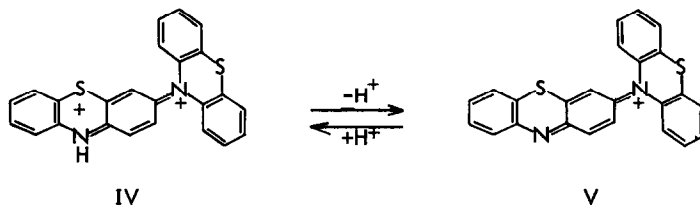


FIG. 3. Absorption spectra of 1.08×10^{-3} M solution of II in 98% sulfuric acid after period of (1) 5 min. (2) 2 hr. and (3) 20 hr. Measurements were made after diluting with the acid to (A) 1.08×10^{-5} M and (B) 4.32×10^{-5} M.

solution was diluted with sulfuric acids containing different concentrations of water. The solutions became green according to the acidities as shown in FIG. 4. The spectra of the less acidic solutions resemble that of blue substance V whose structure was proposed by Jackson et al. (5).

The dependence of the absorbance at 516 and 640 $m\mu$ on the H_0 -acidity function of solutions was shown in FIG. 5. These results can be explained by a rapid equilibrium between dication IV and blue



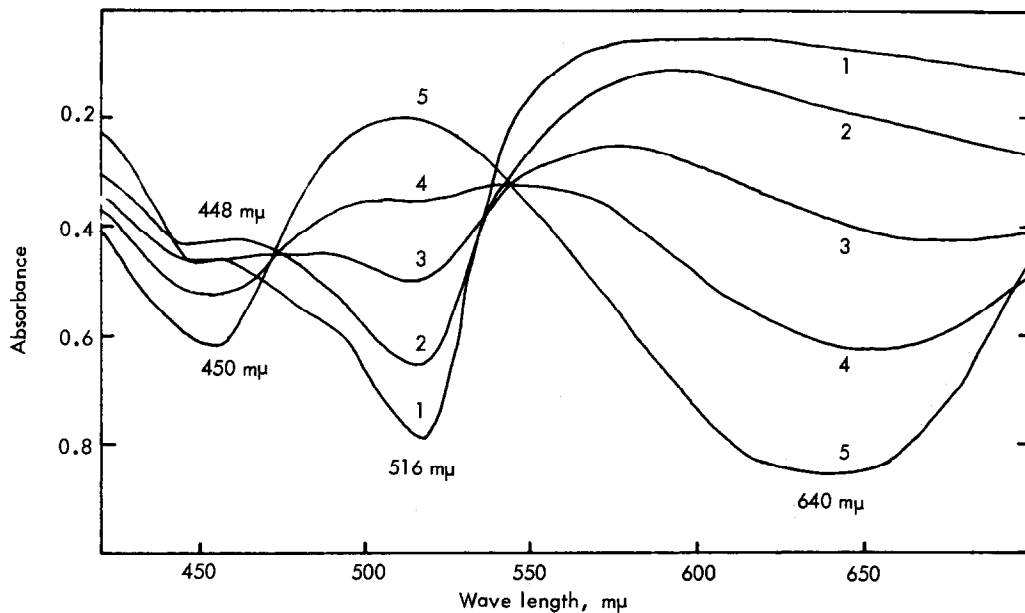


FIG. 4. The visible spectra of the solutions (4.6×10^{-5} M of II) obtained on diluting the 2 hr.-old solution (1.15×10^{-3} M of II in 98% sulfuric acid) to (1) 98% (2) 55% (3) 45% (4) 40% and (5) 6% sulfuric acid.

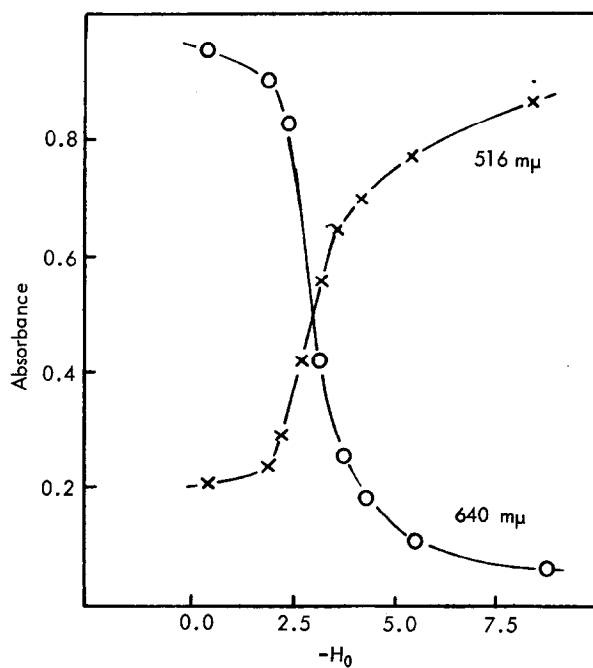
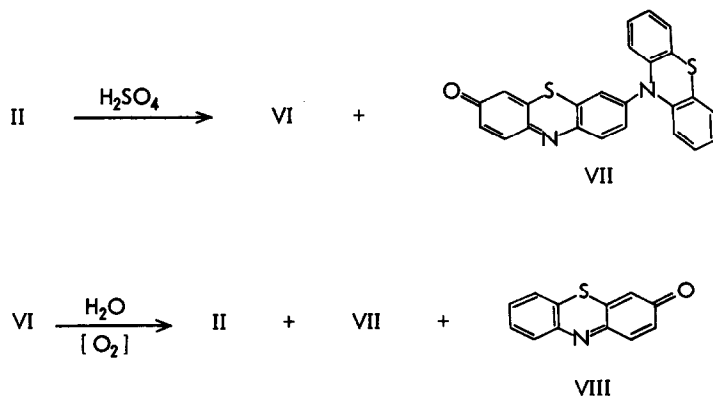


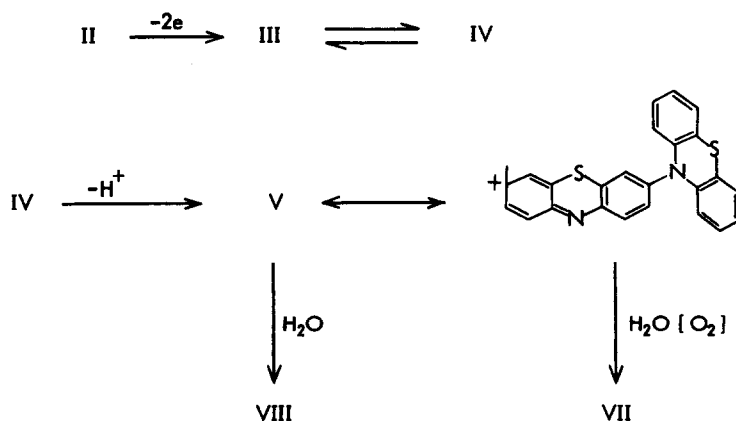
FIG. 5. Plots of the absorbance at 516 and 640 μ against acidity function (H_0) (4.85×10^{-5} M solution of II)

substance V: the absorption peaks 448 and 516 m μ are assigned to the former, and 450 and 640 m μ to the latter, respectively.

From the solution of II in concentrated sulfuric acid, fine copper-red crystals (VI) and a small amount of 7-(phenothiazinyl-10)-phenothiazone-3 (VII) were obtained. VI also gave the same spectrum in acetone solution as Jackson had observed. However, further purification of VI was unsuccessful because of its instability. Refluxing VI in aqueous methanol solution gave II, VII and a small amount of phenothiazone (VIII). Therefore, VI might be a molecular complex between V and II.



In conclusion, the transformations of II could be formulated below (6). Almost no changes with time in the spectra described above suggest the presence of an equilibrium between triplet (III) and singlet species (IV).



Further works are now in progress on behaviors of dimers obtained from phenothiazines, phenoxazines and phenoselenazines in concentrated sulfuric acid.

Acknowledgements. The author thanks Professor I. Moritani, Osaka University, for his helpful discussions, and Dr. K. Takeda, Director of this Laboratory, for his encouragement.

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