

ELECTRON DONOR-ACCEPTOR COMPLEXES OF PHENOTHIAZINE WITH IODINE

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ABSTRACT

Electron donor-acceptor complex formation between phenothiazine (PTZ) and iodine (I_2) both in solid state and in solution are investigated by electronic, IR and high-resolution (270 MHz) FT-proton NMR spectroscopy, thermogravimetric analysis, differential thermal analysis, and mass spectral studies. PTZ forms $PTZ-I_2$, $PTZ-2I_2$, $PTZ-3I_2$ and $PTZ-4I_2$ charge-transfer complexes with iodine in solution. The study indicated that it forms only one type of complex, $PTZ-I_2$, in solid state with stoichiometry 1:1. The charge transfer interaction between PTZ and I_2 seems to be very strong. The mode of interaction appears to depend on the type of electron acceptor and the chemical environment.

INTRODUCTION

GUTMANN and Keyzer¹ noted the intensity of the ESR signal of the powdered phenothiazine-iodine system, which rose with increase in iodine content to a maximum at 2:3 ratio. It was also observed that the signal intensity at 2:3 ratio was twice as strong as that at 1:1 and a little stronger than that at 1:2. These authors, on the basis of conductivity, IR and ESR spectroscopic studies, concluded that at least three different species of complex between PTZ and I_2 are likely to exist. They have also reported that the composition 2:3 is the stable one with the probable structure $I_2^- PTZ^+$, I_2 , PTZ^+ , I_2^- . Matasunga², on the basis of IR measurements, reported that the $PTZ-I_2$ complex is dative in the ground state. Bhat and Rao³ studied the solid charge-transfer (CT) complexes of $PTZ-I_2$ in the ratios 1:1, 1:3 and 3:1. This system was found to show change in sign of the majority charge carriers with variation in donor-acceptor ratio. Chan *et al.*⁴ prepared $PTZ-I_2$ complex by grinding PTZ and I_2 together in 1:2 molar ratio and reported that the complex is generally dative in the ground state. Perissinotti *et al.*⁵ studied galvanic formation cells with β -silver iodide as electrolyte and mixtures of $PTZ-I_2$ of different compositions as cathode. From the observation of EMF plateaus of the galvanic cells they determined the existence and the limits of the four domains in the $PTZ-I_2$ system. These domains correspond to the two stoichiometric ones $(PTZ)_2-I_2$ and $(PTZ)_2-I_6$, and two non-stoichiometric ones, $(PTZ)-I_{3-x}$ and $(PTZ)-I_{7-x}$. Saksena and Aradhana⁶ measured the dielectric

constants of various compositions of the $PTZ-I_2$ system in benzene at a radio frequency of 1 MHz at 30 and 40°C. Kinetic and thermodynamic parameters indicate a 1:1 molar association between PTZ and I_2 . A literature survey reveals that studies of the CT interaction between PTZ and I_2 are scanty. It is felt that the nature of interaction between PTZ and I_2 needs some further investigation. The present study of the CT interaction of PTZ with I_2 using electronic, IR and high-resolution FT-NMR spectroscopy and thermo-analytical techniques seems to throw more light on the pharmacological action of the phenothiazine drugs.

EXPERIMENTAL

A commercially available sample of phenothiazine (Fluka AG, Switzerland) was purified by repeated crystallization from double-distilled benzene and dried over P_2O_5 under vacuum; m.p. 182°C. Iodine, BDH Analar sample, was used as received. All other reagents were of Analar grade.

A Beckman model DB spectrophotometer with 1 cm matched silica cells was used for electronic spectra. A Perkin-Elmer IR model 580 was employed to record IR spectra using KBr pellet technique. A Bruker WH-270 pulsed FT 1H -NMR spectrometer was used to obtain 1H -NMR spectra. Thermo-analytical studies were carried out using a Stanton Redcroft DTA 674 instrument. Mass spectra were recorded using a Hewlett-Packard 5995 mass spectrometer.

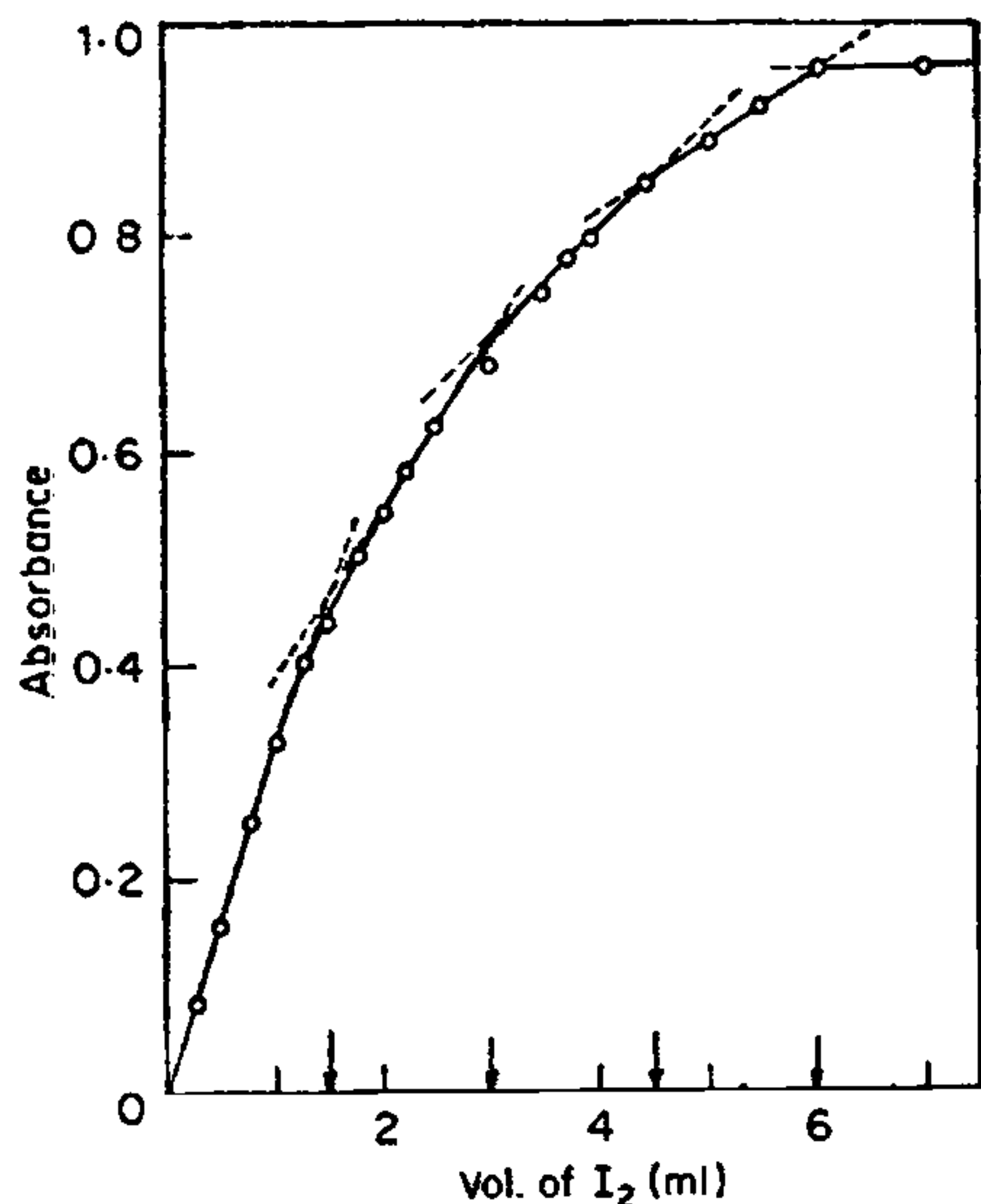


Figure 1. Mole ratio plot for phenothiazine-iodine system.

PROCEDURES

PTZ-I₂: Mole ratio method

Exactly 1.5 ml portions of 2×10^{-3} M PTZ in

ethyl alcohol were transferred into 20 separate 10 ml standard flasks. Then 0.5, 1.0, 1.5, . . . , 6.5 and 7 ml of 2×10^{-3} M iodine in ethyl alcohol were transferred to the above flasks. The solutions were made up with ethyl alcohol and mixed for uniform concentration. Percentage transmittance was recorded at the wavelength of maximum absorption λ_{\max} 650 nm. A graph of absorbance vs volume of iodine added was drawn to obtain the mole ratio curve. The linear portions of the curve were extrapolated to determine the compositions of various species of the complex (figure 1).

Preparation of solid complexes

PTZ (0.5 g) in 50 ml ethyl alcohol solution was mixed with 150 ml of a solution of 0.64 g of I₂ in ethyl alcohol. The solution was stirred for 2–3 h. The solid complex formed (PTZ-I₂) was filtered using a G4 sintered glass crucible and washed with carbon tetrachloride. The complex was dried over P₂O₅ in a vacuum desiccator.

PTZ-2I₂, PTZ-3I₂ and PTZ-4I₂ were prepared as above using 1.28, 1.95 and 2.6 g of I₂ in 150 ml ethyl alcohol respectively.

RESULTS AND DISCUSSION

The electronic spectra of PTZ, I₂ and PTZ-I₂ (1:1) were recorded in ethyl alcohol and are shown in figure 2 (see also table 1). There is no marked

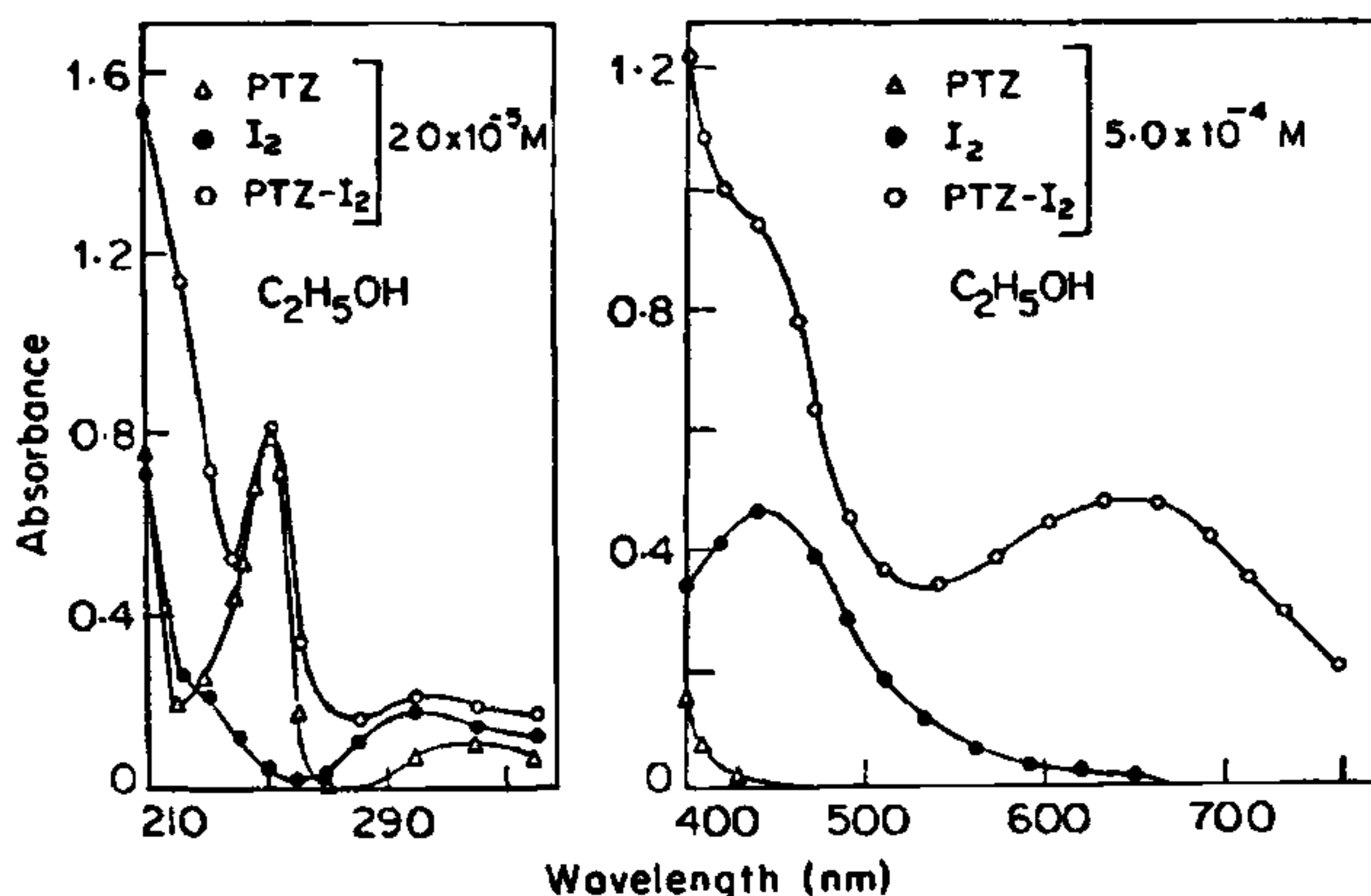


Figure 2. Electronic spectra (UV and visible) of phenothiazine, iodine and phenothiazine-iodine complex.

Table 1 UV-visible absorption data (in ethyl alcohol) for PTZ, I_2 and PTZ- I_2

Compound	$\lambda_{\max} (\epsilon, \text{l mol}^{-1} \text{cm}^{-1})$	
	Ultraviolet	Visible
PTZ	225.0 sh (1.05×10^4)	
	252.0 (2.68×10^4)	
	318.0 (4.36×10^3)	
I_2	225.0 sh (1.20×10^4)	
	298.0 (9.35×10^3)	440.0 (9.5×10^2)
PTZ- I_2	225.0 sh (4.68×10^4)	430.0 sh (3.88×10^3)
	250.0 (3.90×10^4)	634.0 (1.92×10^3)
	304.0 (1.05×10^4)	

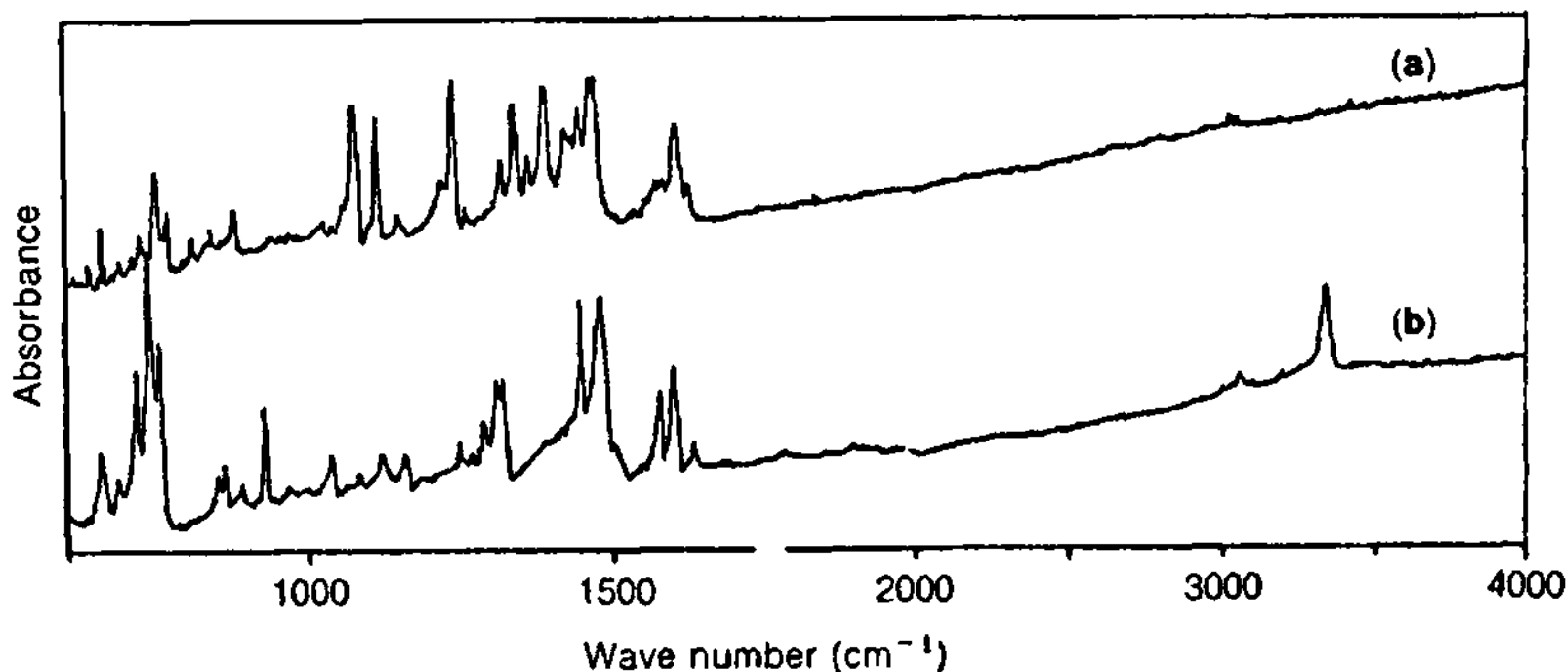
sh, shoulder.

difference in the UV spectrum of PTZ- I_2 complex in comparison to the summation spectrum of PTZ and I_2 except that an increased intensity of the shoulder at 225 nm is observed in the complex. In the visible region the complex shows a shoulder with higher intensity corresponding to the absorption of I_2 at 440 nm with a slight blue shift (~ 10 nm); in addition, a broad band at 634 nm is observed in the spectrum of the complex, which may be assigned to the CT band. The absorption at 440 nm in the I_2 spectrum may be assigned to the transition $\dots (\sigma_g 5P)^2 (\pi_u 5P)^4 (\pi_g 5P)^4 \rightarrow \dots (\sigma_g 5P)^2 (\pi_u 5P)^4 (\pi_g 5P)^3 (\sigma_u 5P)$. This transition has been found to be slightly affected in the complex. Investigations of the stoichiometry of the PTZ and I_2 complex using the principle of the mole ratio method⁷ indicated that there are four types of complexes in solution with the stoichiometry 1:1, 1:2, 1:3 and 1:4 (PTZ- I_2 , PTZ-2 I_2 , PTZ-3 I_2 and PTZ-4 I_2).

The IR spectra of the CT complex of PTZ- I_2

along with the spectrum of PTZ are presented in figure 3. The IR spectra corresponding to the ratios 1:1, 1:2, 1:3 and 1:4 (PTZ- nI_2) are identical in appearance. Remarkable changes are observed in the spectra of the complexes in comparison with the spectrum of PTZ. The new intense vibrational bands observed are 1070, 1110, 1335 and 1395 cm^{-1} , which indicate strong interaction between PTZ and I_2 . The N-H stretching frequency at 3330 cm^{-1} of PTZ is absent in the spectra of the complexes. The bands around 1300-1310 cm^{-1} due to C-N stretching and the C-H out-of-plane bending around 710-748 cm^{-1} are shifted to higher energy regions in the spectra of the complexes. The IR spectra of the complexes show strong CT interaction between PTZ and I_2 , which seems to affect the N-H stretching frequency of the electron system of the PTZ molecule.

Proton NMR spectra of PTZ, PTZ- I_2 , PTZ-2 I_2 , PTZ-3 I_2 and PTZ-4 I_2 were recorded in DMSO- d_6 . All the four compounds gave qualitatively identical NMR spectra. The data indicate that PTZ and I_2 form only one type of complex corresponding to the composition 1:1 in the solid state unlike in solution. High-resolution proton NMR spectra of PTZ and PTZ- I_2 are shown in figure 4. The N-H proton of PTZ undergoes shielding in the process of CT interaction between PTZ and I_2 . All the aromatic protons 1, 2, 3, 4, 6, 7, 8 and 9 ($\delta = 6.6665$ -7.0185 ppm) of PTZ are deshielded in the spectra of the complexes. The signals corresponding to these protons appear in the range 7.5819-7.0794 ppm. Greater hyperfine structure is observed for the aromatic protons of PTZ. This may be due to the presence of long-range coupling and the different influences of the S and N

**Figure 3.** IR spectra of (a), phenothiazine and (b), phenothiazine-iodine complex.

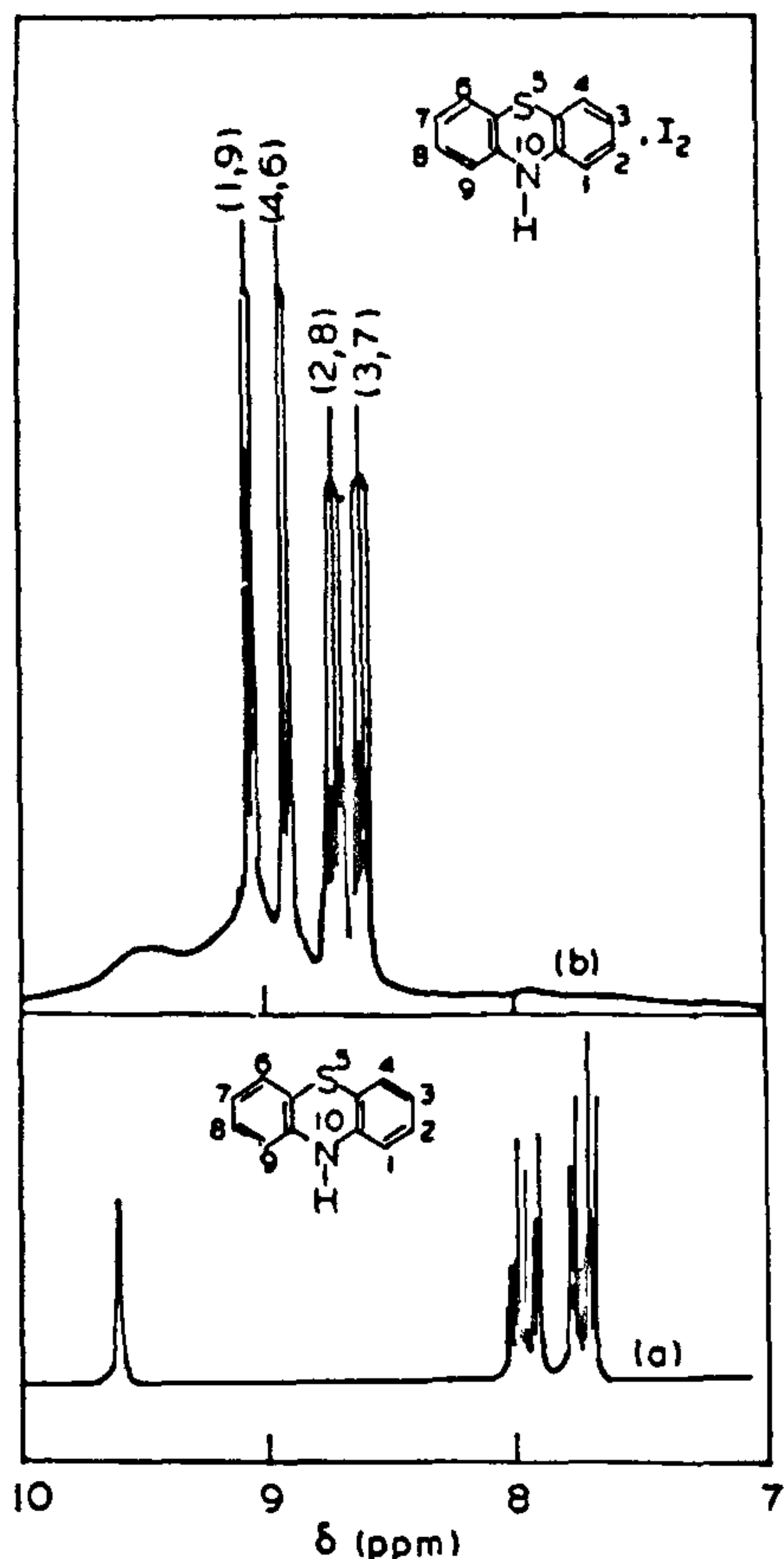


Figure 4. High-resolution (270 MHz) proton FT-NMR spectra of (a), phenothiazine and (b), phenothiazine-(iodine)₂ complex.

atoms at positions 5 and 10 on the protons (4, 6) and (1, 9). The CT interaction between PTZ and I₂ seems to make the above effects less on the chemical environment of the protons 1, 4, 6 and 9, with the result that simpler splittings corresponding to the aromatic protons of PTZ are observed in the complex. The two doublets at 8.0483–8.0777 ppm and 7.9068–7.9353 ppm may be assigned to the protons (1, 9) and (4, 6) of the PTZ-I₂ complex respectively. The two triplets at 7.6976–7.7529 ppm

and 7.5838–7.6494 ppm may be assigned to the protons (2, 8) and (3, 7) of the complex respectively. The assignments seem to be confirmed by the ortho coupling constant values (9–10 Hz). The long-range couplings are absent in the complex.

The thermogravimetric analysis curves, mass spectral data and differential thermal analysis (DTA) curves also support the above conclusions regarding the stoichiometry. The complex starts to degrade at 200°C and is found to lose weight of about 60% over the temperature range 200–500°C. The complex degrades in two steps. The first weight loss may be due to the loss of iodine and the second weight loss could be due to loss of iodine as well as degradation of the PTZ structure. The DTA curve of complex PTZ-I₂ shows a sharp endothermic peak at 232°C due to the melting. The compound seems to be stable up to the melting point and decomposes above this temperature. A mass spectral study at 200°C of the PTZ-I₂ complexes gave identical mass spectra. The *m/e* peaks from 40 to 800 have been scanned. Only two peaks are observed, the base peak *m/e*=127 and another peak *m/e*=254 with 60% intensity of the base peak. These peaks are due to atomic iodine and molecular iodine respectively.

ACKNOWLEDGEMENTS

The authors thank Prof. C. L. Khetrapal and Mr Nagana Gowda, Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, for the NMR spectroscopic data. One of the authors (MVK) is grateful to UGC, New Delhi, for a fellowship.

3 December 1988

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