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Journal of Molecular Structure 413–414 (1997) 49–59

Journal of
MOLECULAR
STRUCTURE

# Structures and dynamics of the lowest excited triplet states and cation radicals of phenothiazine and 2-chlorophenothiazine: transient resonance Raman and absorption study[1]

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Received 29 January 1997; accepted 3 February 1997

**Abstract**

Transient resonance Raman and absorption spectra of the lowest excited triplet states $T_1$ and the cation radicals of phenothiazine and 2-chlorophenothiazine were measured. It was found that in the photoreaction of 2-chlorophenothiazine a transient exhibiting an absorption band at 556 nm was generated from the cation radical. The corresponding transient was not observed in the absorption spectrum of phenothiazine, a fact which suggests a possibility of phenothiazinyl radical generation for 2-chlorophenothiazine by photoinduced dechlorination. Vibrational assignments of the $T_1$ states and the cation radicals of the both compounds were made based on the frequency shifts on isotopic substitutions. Unusually large low-frequency shifts of the phenyl 8a and 8b modes were observed in the $T_1$ state but no appreciable shifts were detected in the cation radical, indicating that the phenyl rings are drastically weakened, and therefore, the phenyl C–C bonds are very much lengthened in the $T_1$ state. This implies that the excitation is strongly localized on the phenyl rings and the $T_1$ state has an $n-\pi^*$ character. © 1997 Elsevier Science B.V.

*Keywords:* Phenothiazine; Transient absorption; Transient Raman; Excited state structure

## 1. Introduction

The photochemistry of phenothiazine and its derivatives (Fig. 1) has been extensively investigated [1–10] because of their pharmacological interest. Phenothiazine tranquilizers, particularly chlorpromazine (2-chloro-N-[3-dimethylamino-propyl]phenothiazine), have long been used for the treatment of psychotic disorders [11]. However, they are known to cause both phototoxic and photoallergic reactions in the skin [12] and eyes [13,14] of patients receiving these drugs. While detailed mechanisms of the phototoxicity and photoallergy of these drugs are not known, it is obvious that photolytically generated excited states, radicals or the compounds derived from them play important roles in the mechanisms.

In this view, the photochemistry of phenothiazine and 2-chlorophenothiazine was investigated by means of time-resolved absorption and time-resolved resonance Raman spectroscopies in order to obtain information on the structures and dynamics of the excited states and radicals (neutral as well as cationic) which appear in the photochemical reactions of these

[1] Dedicated to Professor Kozo Kuchitsu on the occasion of his 70th birthday.

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0022-2860/97/$17.00 
*PII* S0022-2860(97)00060-4

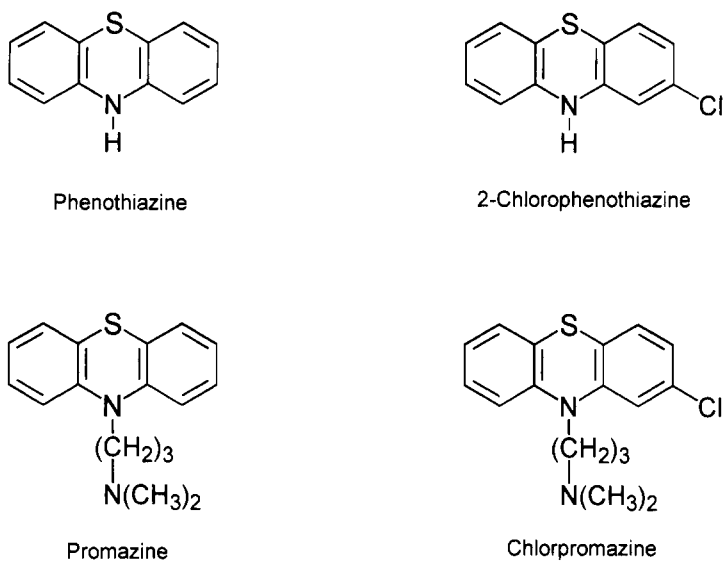


Fig. 1. Phenothiazine and its derivatives.

compounds. Due to structural similarities, these two compounds are considered to be useful models for elucidating photochemical properties, particularly the structures and dynamics of the transients involved in the photochemical reactions of the clinically important drugs, i.e. promazine and chlorpromazine.

## 2. Experimental

The experimental arrangement of our time-resolved Raman spectroscopy system has been described previously [15]. Briefly, an excimer laser (Lambda Physik LPX120i) was used as a light source for pumping, and an excimer-laser-pumped dye laser (FL3002E) was used as a light source for Raman probing. The energy of the excimer laser used for the pumping was about 100 mJ pulse$^{-1}$ at the laser head and that of the dye laser used for Raman probing was 15–10 mJ pulse$^{-1}$ at the laser head depending on the wavelength. Both lasers (pulse width, 15–20 ns) were used at the repetition rate of 20 Hz. Time-resolved absorption spectra were measured by a laser flash photolysis system constructed in our laboratory which consists of an excimer laser (Lambda Physik LPX120i) for pumping, a xenon lamp for white light, and a 30 cm spectrometer equipped with a gated multichannel detector.

Phenothiazine was purchased from Kanto Chemical Co. Ltd and 2-chlorophenothiazine was synthesized by the reaction of 3-chlorodiphenylamine with sulfur in the presence of a small amount (1 wt.% of diphenylamine) of iodine [16]. Both compounds were purified by recrystallization from ethanol. Although a small amount of a by-product, 4-chlorophenothiazine, was also produced in the above reaction, it was successfully removed by recrystallization. $^{34}S$ substituted phenothiazine and 2-chorophenothiazine were synthesized by the same reaction of $^{34}S$ (Isotec Inc., 90.46 at.%) with diphenylamine for the former and with 3-chlorodiphenylamine for the latter. Diphenylamine and 3-chlorodiphenylamine were purchased from Tokyo Kasei Organic Chemicals. N–D substituted phenothiazine was obtained by an exchange reaction with $D_2O$: stirring a mixture of $CCl_4$ solution of phenothiazine and $D_2O$ under $N_2$ atmosphere, renewing $D_2O$ several times, and finally removing $CCl_4$ by evaporation.

## 3. Results and discussion

### 3.1. Time-resolved absorption spectra

Time-resolved absorption spectra of phenothiazine (PTH) in deoxygenated methanol reveal that two transients are involved in the photoreaction of this compound (Fig. 2(a)): a transient exhibiting a strong absorption band at 455 nm with a lifetime of about

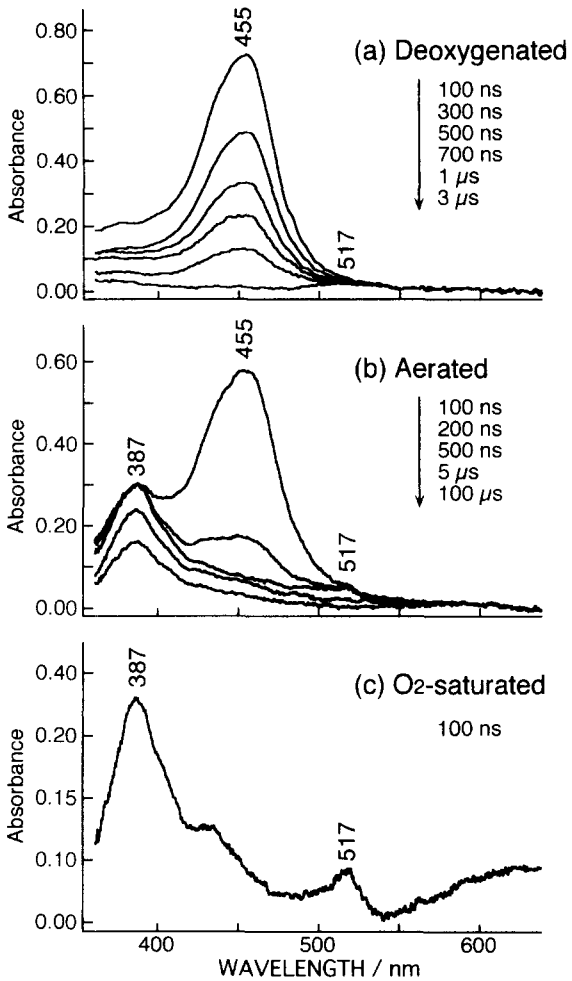


Fig. 2. Transient absorption spectra of phenothiazine: (a) in deoxygenated methanol measured at 100, 300, 500, 700 ns, 1 and 3 μs after excitation with UV (308 nm) light; (b) in aerated methanol measured at 100, 200, 500 ns, 5 and 100 μs; (c) in oxygenated methanol measured at 100 ns. Concentration is $1.0 \times 10^{-3}$ mol dm$^{-3}$.

800 ns and another transient having a very weak peak at 517 nm with a much longer lifetime. In aerated methanol solutions an additional transient exhibiting a band at 387 nm and having a long lifetime appears with a concomitant intensity decrease of the 455 nm band as shown in Fig. 2(b). In oxygen-saturated methanol solutions the 455 nm band disappears completely and the 387 nm band becomes more intense (Fig. 2(c)). These observations indicate that the transient exhibiting the 455 nm band is the $T_1$ state $^3PTH^*$ and the 387 nm band may be attributable to a compound generated from $^3PTH^*$ and $O_2$. The band at 517 nm and a shoulder around 435 nm may be assigned to the cation radical.

The above results are in good accord with the previous reports in the literature. Henry and Kasha [4] observed a band at 467 nm in both EPA and 3-methylpentane solutions at 77 K and assigned the band to $^3PTH^*$. Iwaoka et al. [5] assigned the band at 465 nm observed by flash photolysis in ethanol solutions to $^3PTH^*$. They also observed a band at about 385 nm in aerated ethanol solutions and assigned it to a charge-transfer complex PTH–$O_2$ generated through $^3PTH^*$. Shine and Mach [2] observed bands at 437 and 515 nm in aqueous acetic acid solutions irradiated with ultraviolet light and assigned them to the cation radical $PTH^{+\cdot}$. Alkaitis et al. [6] observed two bands at 460 and 520 nm and assigned the former to $^3PTH^*$ and the latter to $PTH^{+\cdot}$ which they considered to be generated through monophotonic ionization process.

Time-resolved absorption spectra of 2-chlorophenothiazine (CPTH) are a little more involved. At 200 ns after irradiation with UV (308 nm) light three bands are observed at 438, 458 and 517 nm. These bands decrease in intensity with time while a new band appears at 556 nm as shown in Fig. 3. Corresponding with the spectra of phenothiazine the band at 458 nm can be assigned to the $T_1$ state $^3CPTH^*$, and the bands at 517 and 438 nm can be attributed to the cation radical $CPTH^{+\cdot}$. We have confirmed that the 458 nm band was quenched by oxygen. The new band at 556 nm appears to be generated from the cation radical because the rise time of this band is approximately the same as the decay time of the 517 nm band, and besides, there exists an isosbestic point

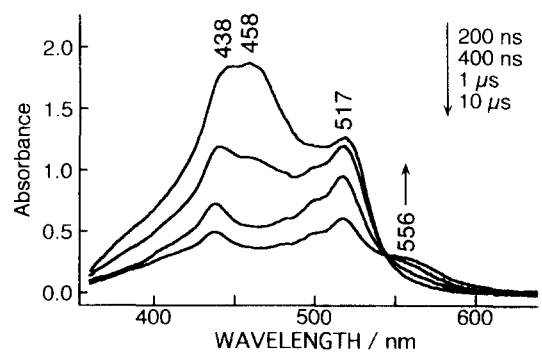


Fig. 3. Transient absorption spectra of 2-chlorophenothiazine in deoxygenated methanol: measured at 200, 400 ns, 1 and 10 μs after UV (308 nm) excitation. Concentration is $5.0 \times 10^{-4}$ mol dm$^{-3}$.

between this band and the 517 nm band; the 458 nm band decays much faster. It is interesting to note that the 517 nm band is much more intense, and therefore, the yield of the cation radical is much larger in 2-chlorophenothiazine than in phenothiazine. This may suggest that the ionization potential of CPTH is much lower than that of PTH.

The assignment of the 556 nm band could not be determined unambiguously in the present investigation. We call the transient exhibiting this band "X". Since the transient X is not involved in the photoreaction of phenothiazine, its generation must be related to the chlorine substituent. Therefore, it seems probable that the 556 nm band arises from the phenothiazinyl neutral radical generated by dechlorination with UV light. Transient absorption spectra of 2-chlorophenothiazine were not reported previously.

### 3.2. Transient resonance Raman spectra

The Raman spectrum of the ground state $S_0$ of phenothiazine in acetone and resonance Raman spectra of $^3PTH^*$ and $PTH^{+\cdot}$ in methanol are compared in Fig. 4. One feature of interest in these spectra is that the phenyl ring stretch modes 8a and 8b (Wilson vibration number [17]) observable at 1603 and 1575 $cm^{-1}$ in the $S_0$ spectrum are both very drastically down-shifted to 1507 $cm^{-1}$ in the $T_1$ state spectrum, while they do not exhibit appreciable frequency-shifts in the spectrum of the cation radical. Since the low-frequency shifts of the 8a and 8b modes (phenyl ring stretch modes) on

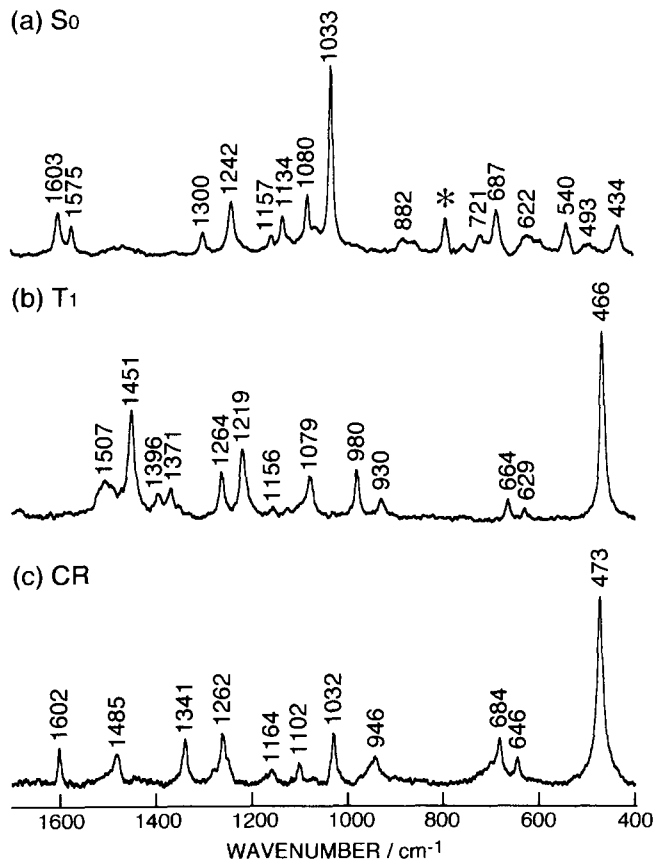


Fig. 4. The Raman spectrum of phenothiazine in the $S_0$ state and transient resonance Raman spectra of $^3PTH^*$ and $PTH^{+\cdot}$: (a) nearly saturated solution of $S_0$ in acetone. Probe wavelength: 581 nm; (b) $^3PTH^*$ in deoxygenated methanol measured at 150 ns after the pumping with 308 nm light. Probe wavelength: 456 nm. Concentration: $2.0 \times 10^{-3}$ mol $dm^{-3}$; (c) $PTH^{+\cdot}$ in oxygenated methanol measured at 100 ns after the pumping with 308 nm light. Probe wavelength: 517 nm. Concentration: $2.0 \times 10^{-3}$ mol $dm^{-3}$. The asterisk (*) denotes solvent bands.

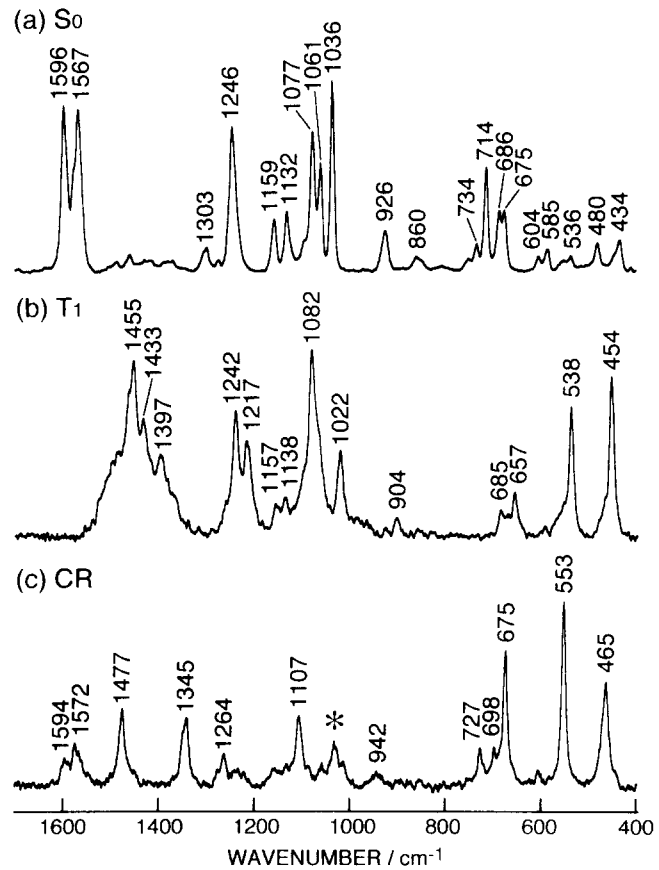


Fig. 5. The Raman spectra of 2-chlorophenothiazine in the $S_0$ state and transient resonance Raman spectra of $^3$CPTH* and CPTH$^+$: (a) nearly saturated solution of $S_0$ in acetone. Probe wavelength: 1064 nm; (b) $^3$CPTH* in deoxygenated methanol measured at 150 ns after the pumping with 308 nm light. Probe wavelength: 456 nm. Concentration: $2.0 \times 10^{-3}$ mol dm$^{-3}$; (c) CPTH$^+$ in oxygenated methanol measured at 100 ns after the pumping with 308 nm light. Probe wavelength: 517 nm. Concentration: $2.0 \times 10^{-3}$ mol dm$^{-3}$. The asterisk (*) denotes solvent bands.

going from the $S_0$ state to $T_1$ state are usually around 20–30 cm$^{-1}$ [18,19], the down-shift of 96 cm$^{-1}$ in phenothiazine is unusually large. This suggests that the excitation is strongly localized on the phenyl rings and that the phenothiazine phenyl rings are drastically weakened in the $T_1$ state. This point will be discussed later.

The Raman spectrum of the $S_0$ state of 2-chlorophenothiazine (CPTH) in acetone and resonance Raman spectra of $^3$CPTH* and CPTH$^+$ in methanol are shown in Fig. 5. Like phenothiazine the phenyl 8a and 8b modes at 1596 and 1567 cm$^{-1}$ are also drastically down-shifted to around 1510 cm$^{-1}$ in the spectrum of the $T_1$ state, whereas they do not exhibit appreciable shifting in the spectrum of the cation radical. The localized excitation on the phenyl rings is considered to be operative also in this compound. Comparison of the spectra of phenothiazine and 2-chlorophenothiazine reveals that in the spectra of phenothiazine the bands corresponding to the bands of 2-chlorophenothiazine at 585 cm$^{-1}$ of the $S_0$ state, at 538 cm$^{-1}$ of the $T_1$ state, and at 553 cm$^{-1}$ of the cation radical are not observed. These bands can be assigned to the C–Cl stretching mode of CPTH, $^3$CPTH* and CPTH$^+$, respectively.

In order to obtain information on the structural changes on-going from the $S_0$ state to the $T_1$ state and to the cation radical, it is necessary to make more detailed vibrational assignments of their Raman bands. For this purpose we have synthesized isotopically substituted analogues, viz. $^{34}$S substituted analogue (PTH–$^{34}$S and CPTH–$^{34}$S) and N–D

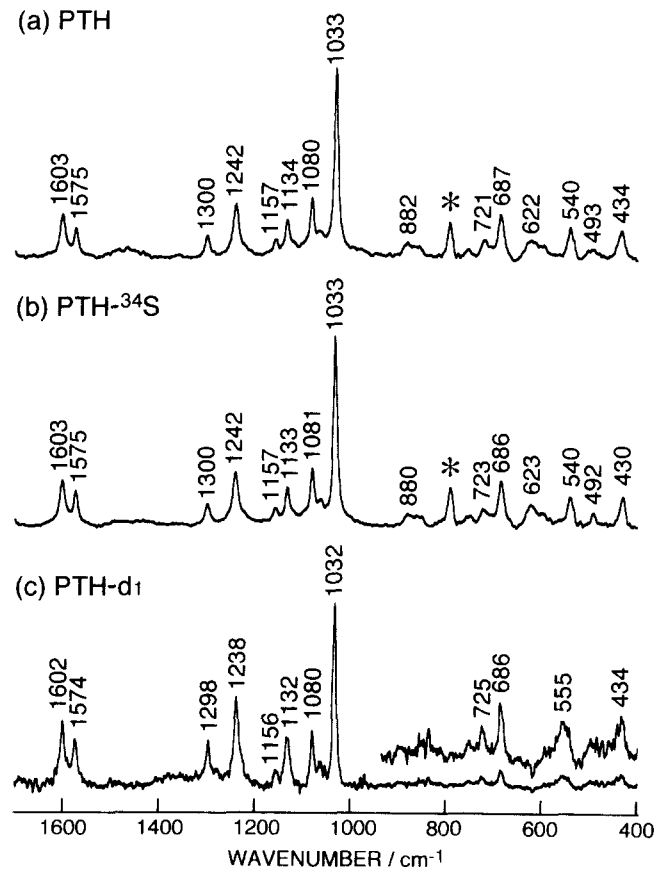


Fig. 6. Comparison of Raman spectra of the $S_0$ states of phenothiazine and its isotopically substituted analogues: (a) PTH normal species in acetone (nearly saturated solution) measured with 581 nm light; (b) PTH–$^{34}$S in acetone (nearly saturated solution) measured with 581 nm light; (c) PTH-$d_1$ in methanol-$d_1$ (saturated solution) measured with 532 nm light. The asterisk (*) denotes solvent bands.

substituted analogue (PTH-$d_1$), and measured the Raman or resonance Raman spectra of their $S_0$ and $T_1$ states and cation radicals.

Raman spectra of phenothiazine and its isotopically substituted analogues in the $S_0$ state, i.e. PTH, PTH–$^{34}$S and PTH-$d_1$ are compared in Fig. 6. It is seen that only one band exhibits an appreciable shifting on each of the $^{34}$S and N–D substitutions: the band at 434 $cm^{-1}$ of PTH is down-shifted to 430 $cm^{-1}$ in the spectrum of PTH–$^{34}$S and the band at 1242 $cm^{-1}$ of PTH is down-shifted to 1238 $cm^{-1}$ in the spectrum of PTH-$d_1$. The 434 $cm^{-1}$ band can be assigned to a vibrational mode involving the largest contribution of the C–S symmetric stretch (for simplicity hereafter we call this mode "C–S symmetric stretch") and the 1242 $cm^{-1}$ band is assignable to a mode in which the contribution of the C–N symmetric stretch is the largest (hereafter "C–N symmetric stretch"). The frequency 434 $cm^{-1}$ appears to be considerably lower than the usual C–S stretching frequencies which are expected to lie around 580–750 $cm^{-1}$ [20]. The lower frequency of the C–S symmetric stretch of PTH is considered to be ascribed to the mixing with skeletal deformation of the ring. Although in this figure the PTH spectrum measured in acetone is compared with the PTH-$d_1$ spectrum measured in methanol-$d_1$, this comparison is justified because the frequency difference between the spectrum of PTH in acetone and that in methanol is negligibly small.

Resonance Raman spectra of phenothiazine and its isotopically substituted analogues in the $T_1$ state, i.e. $^3$PTH*, $^3$PTH*–$^{34}$S and $^3$PTH*–$d_1$ are shown in Fig. 7. A strong band at 466 $cm^{-1}$ of the $S_0$ state is

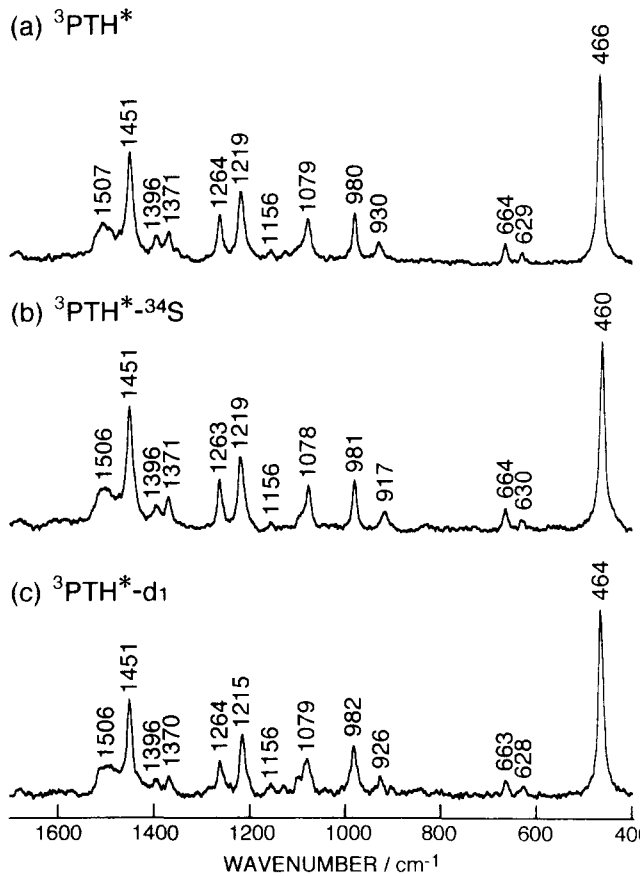


Fig. 7. Transient resonance Raman spectra of the $T_1$ state of phenothiazine and its isotopically substituted analogues in deoxygenated methanol: (a) $^3$PTH* normal species; (b) $^3$PTH*–$^{34}$S; (c) $^3$PTH* – $d_1$. Pump wavelength: 308 nm; probe wavelength: 456 nm. Concentration: $2.0 \times 10^{-3}$ mol dm$^{-3}$. (For the measurement of $^3$PTH* – $d_1$, methanol-$d_1$ was used to avoid the exchange of N–D deuterium with methanol O–H hydrogen.)

down-shifted to 460 cm$^{-1}$ on the $^{34}$S substitution. The 466 cm$^{-1}$ band can be assigned to the C–S symmetric stretch. The band at 930 cm$^{-1}$ is also down-shifted to 917 cm$^{-1}$ on the $^{34}$S substitution. This band is assignable to the first overtone of the 466 cm$^{-1}$ band. This assignment is supported by the observation that the frequency decrease 13 cm$^{-1}$ of the 930 cm$^{-1}$ band is about twice as large compared to the frequency decrease 6 cm$^{-1}$ of the 466 cm$^{-1}$ band. The band at 1219 cm$^{-1}$ of the normal species $^3$PTH* is down-shifted to 1215 cm$^{-1}$ on deuteration of the N–H group. The 1219 cm$^{-1}$ band can be assigned to the C–N symmetric stretch.

Resonance Raman spectra of 2-chlorophenothiazine and its $^{34}$S substituted analogue in the $T_1$ state, i.e. $^3$CPTH* and $^3$CPTH*–$^{34}$S are shown in Fig. 8. The bands at 454 and 904 cm$^{-1}$ of the normal species $^3$CPTH* are down-shifted to 449 and 895 cm$^{-1}$, respectively on the $^{34}$S substitution. The 454 cm$^{-1}$ band can be assigned to the C–S symmetric stretch and the 904 cm$^{-1}$ band to the first overtone of the 454 cm$^{-1}$ band.

Resonance Raman spectra of the cation radicals of phenothiazine and its isotopically substituted analogues, i.e. PTH$^{+\cdot}$, PTH$^{+\cdot}$–$^{34}$S and PTH$^{+\cdot}$-$d_1$ are shown in Fig. 9. It is seen that the bands at 473 and 946 cm$^{-1}$ of the normal species PTH$^{+\cdot}$ are down-shifted to 466 and 932 cm$^{-1}$, respectively on the $^{34}$S substitution. The 7 cm$^{-1}$ magnitude of the down shift on the $^{34}$S substitution indicates that the 473 cm$^{-1}$ is assignable to the C–S symmetric stretch. The 946 cm$^{-1}$ band exhibiting the down shift of 14 cm$^{-1}$ is considered

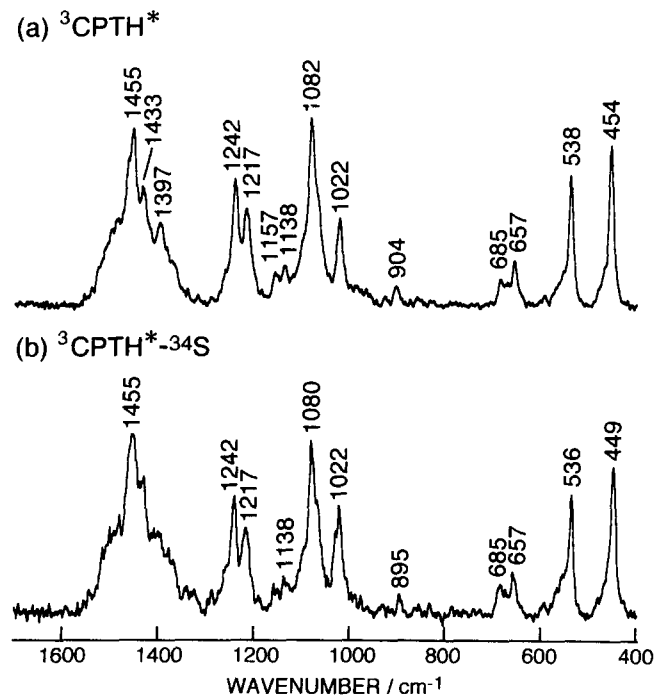


Fig. 8. Transient resonance Raman spectra of the $T_1$ state of 2-chlorophenothiazine and its $^{34}S$ substituted analogue in deoxygenated methanol: (a) $^3$CPTH* normal species; (b) $^3$CPTH–$^{34}$S. Pump wavelength: 308 nm and probe wavelength is 456 nm. Concentration: $2.0 \times 10^{-3}$ mol dm$^{-3}$.

to arise from the first overtone of the 473 cm$^{-1}$ band. We note that the C–S symmetric stretch of PTH$^{+\cdot}$ is quite harmonic. The band at 1262 cm$^{-1}$ of PTH$^{+\cdot}$ is down-shifted to 1257 cm$^{-1}$ on the deuteration of the N–H group. This band is assignable to the C–N symmetric stretch.

Resonance Raman spectra of the cation radicals of 2-chlorophenothiazine and its $^{34}S$ substituted analogue, i.e. CPTH$^{+\cdot}$ and CPTH$^{+\cdot}$–$^{34}$S, are shown in Fig. 10. The band at 465 cm$^{-1}$ is down-shifted to 459 cm$^{-1}$ on the $^{34}S$ substitution. This band can be assigned to the C–S symmetric stretch. The first overtone bands of the 465 and 459 cm$^{-1}$ bands are not clearly detectable due to overlapping by nearby bands.

### *3.3. Structures and dynamics of the $T_1$ state and the cation radical*

We have shown by time-resolved resonance Raman spectroscopy that in both phenothiazine and 2-chlorophenothiazine the 8a and 8b modes (phenyl ring stretch mode) of the phenyl rings are drastically down-shifted in the $T_1$ state, whereas they do not exhibit appreciable frequency shifts in the cation radical. In contrast the C–S symmetric stretch is up-shifted considerably both in the $T_1$ state and cation radical. These observations imply that (1) the phenyl rings of both PTH and CPTH are drastically weakened and therefore the C–C bonds of the phenyl rings are lengthened in the $T_1$ state, but these structural changes do not occur in the cation radical, and (2) the C–S bonds of PTH and CPTH are strengthened and therefore the C–S bonds are shortened both in the $T_1$ state and in the cation radical.

Since the $T_1$ state can be represented by the electron configuration in which an electron is elevated from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital), while the electronic state of the cation radical is most adequately expressed by the electron configuration in which an electron is removed from the HOMO as depicted in Fig. 11, the weakening of the phenyl rings only in the $T_1$ state and strengthening of the C–S bonds both in the $T_1$ and in the cation radical indicate that the LUMO is an anti-bonding $\pi$-orbital strongly localized on the phenyl rings, and the

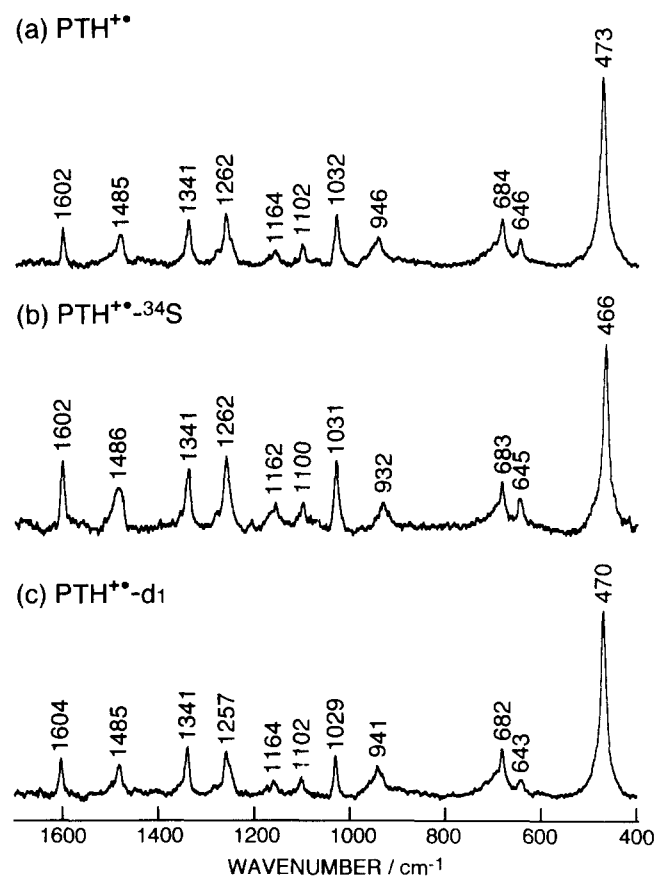


Fig. 9. Transient resonance Raman spectra of the cation radical of phenothiazine and its isotopically substituted analogues in methanol: (a) $PTH^{+\bullet}$ normal species; (b) $PTH^{+\bullet}$–$^{34}S$; (c) $PTH^{+\bullet}$-$d_1$. Pump wavelength: 308 nm and probe wavelength is 517 nm. Concentration: $2.0 \times 10^{-3}$ mol $dm^{-3}$. (For the measurement of $PTH^{+\bullet}$-$d_1$ methanol-$d_1$ was used to avoid the exchange of N–D deuterium with methanol O–H hydrogen.)

HOMO is a non-bonding orbital strongly localized on the S atom. This implies that the $T_1$ state is of $n$–$\pi^*$ character.

The generation of the transient X in the photoreaction of 2-chlorophenothiazine is of interest. Since the corresponding transient is not generated in the photoreaction of phenothiazine, the production of the transient X must be closely related to the chlorine substituent. Chlorpromazine, a clinically important drug for psychotic disorders, has a chlorine substituent at the same position (2-position) of the phenothiazine skeleton and is known to be an order of magnitude more phototoxic as well as photoallergic than promazine which has no chlorine substituent. Therefore, it is not wholly improbable that the corresponding transient X of chlorpromazine is one of the prime cause of phototoxicity and photoallergy of chlorpromazine. The identity of the transient X is not clarified as yet, but it seems probable that it is the phenothiazinyl neutral radical generated by photo-induced dechlorination.

## Acknowledgements

The present work is partly defrayed by the Grant-in Aid for Science Research on Priority-Area-Research "Photoreaction Dynamics" from the ministry of Education, Science, Sports, and Culture of Japan, and by Waseda University Grant for Special Research Projects. The authors are grateful to Advanced Research Institute for Science and Engineering Waseda University for financial assistance. The measurement of time-resolved Raman spectra were

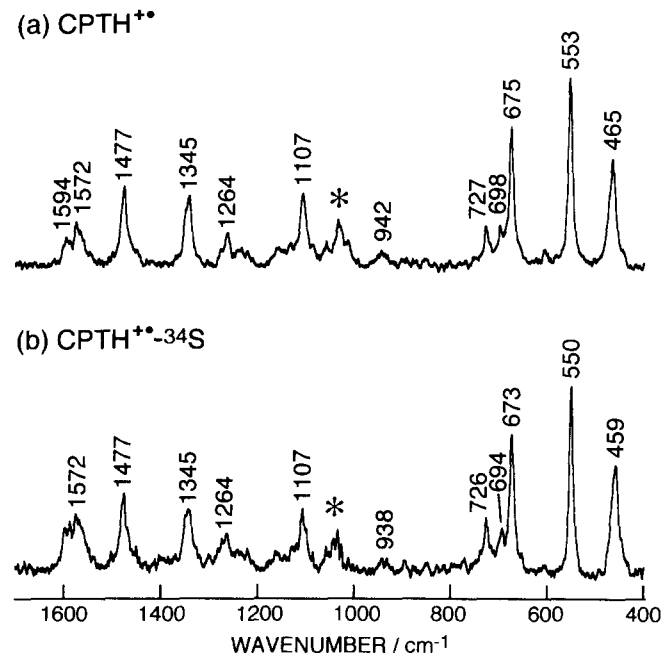


Fig. 10. Transient resonance Raman spectra of the cation radical of 2-chlorophenothiazine and its $^{34}S$ substituted analogue in methanol: (a) $CPTH^{+\cdot}$ normal species; (b) $CPTH^{+\cdot}$–$^{34}S$. Pump wavelength: 308 nm and probe wavelength is 517 nm. Concentration is $2.0 \times 10^{-3}$ mol dm$^{-3}$. The asterisk (*) denotes solvent bands.

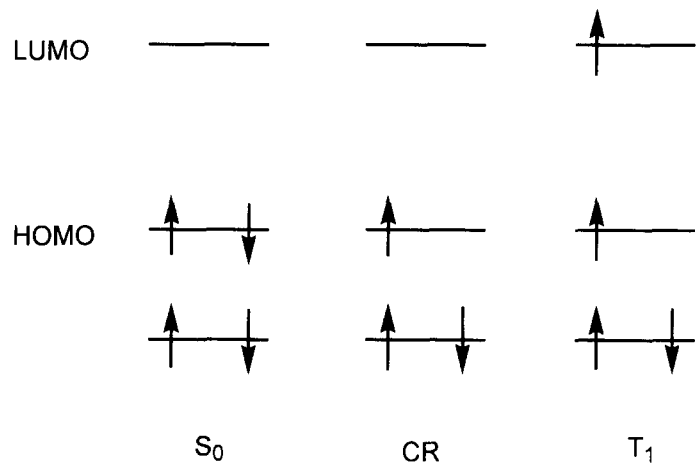


Fig. 11. Electronic configurations of the $T_1$ state and cation radical.

performed using the apparatus at the Materials Characterization Central Laboratory, Waseda University.

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