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$^{14}N/^{15}N$ ISOTOPE EFFECT ON THE ELECTRON TRANSFER PROCESS BETWEEN PHENOTHIAZINE AND ITS RADICAL CATION

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An appreciable equilibrium isotope effect has been observed for electron transfer from phenothiazine (PT) to the radical cation of its ^{15}N-substituted analogue ($[^{15}N]PT^{+\cdot}$), i.e.

$$PT + [^{15}N]PT^{+\cdot} \overset{K}{\rightleftharpoons} PT^{+\cdot} + [^{15}N]PT$$

via electron paramagnetic resonance analysis of the mixed radical cations formed from mixing the $[^{15}N]$phenothiazine radical cation hexachloroantimonate and phenothiazine in acetonitrile ($K = 0{\cdot}77 \pm 0{\cdot}10$ at 25 °C), and by physical separation of the neutral phenothiazines from the radical cation salts in the equilibrium mixture ($K = 0{\cdot}83 \pm 0{\cdot}10$ at 25 °C). Infrared and Raman spectra of $[^{14}N]$- and $[^{15}N]$phenothiazines and their radical cations were measured to assign the vibrational frequency shifts caused by the heavy-atom substitution and radical cation formation, which gave an estimate of the enthalpy change of 441·7 J mol^{-1} for the electron transfer process. These results reveal that ^{15}N substitution of phenothiazine decreases appreciably the ionization potential of the molecule, making it easier to lose an electron to form the corresponding radical cation in solution. © 1997 by John Wiley & Sons, Ltd.

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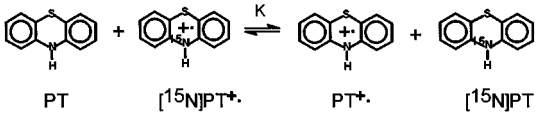
INTRODUCTION

Isotope effects and isotope enrichment have attracted much attention for a long time owing to the wide use of isotopes in a variety of scientific and technical applications. However, isotope effects on electron transfer reactions have rarely been studied. Starting in 1986, Stevenson and co-workers published a series of papers[1] dealing with the equilibrium isotope effect (EIE) on electron transfer processes between several radical anions and their heavy isotope-substituted aromatic molecule precursors, as shown in the following equation:

$$*A + A^{-\cdot} \rightleftharpoons *A^{-\cdot} + A \qquad (1)$$

where *A represents a heavy isotope (^2H, ^{13}C, ^{15}N, ^{17}O, etc.)-substituted aromatic molecule. They found that the equilibrium constants for the electron exchange [equation (1)] deviated significantly from unity, and suggested that these EIEs might be used as a basis of isotope separations. Although some of their results, especially those dealing with $^{15}N/^{14}N$ and $^{13}C/^{12}C$ isotope effects, have led to some controversy,[2] the results are supported by independent cyclic voltammetric data[3,4] and theoretical calculations.[5] Stevenson and co-workers[6–8] also pointed out that the EIE is strongly dependent upon the charge and spin density in the area of isotope substitution, which, in turn, is dependent upon the specific anion radical–counter ion and anion radical–solvent interactions. In view of these arguments, we were motivated to see if a similar EIE exists in electron transfer processes between radical cations and their neutral molecule precursors, which had never been studied before our previous reports on the significant $^1H/^2H$ and $^{32}S/^{33}S$ EIEs on the electron exchange of thianthrene and its radical cation.[9–11] Here we report electron paramagnetic resonance (EPR), IR and Raman spectroscopic studies and physical separation results on the $^{14}N/^{15}N$ isotope effect on the electron exchange reaction of phenothiazine and its radical cation of the ^{15}N-substituted analogue [equation (2)].



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RESULTS AND DISCUSSION

EPR spectroscopic studies

Radical cation hexachloroantimonates of phenothiazine and its ^{15}N-substituted analogue showed well resolved EPR spectra in dilute anhydrous acetonitrile solution at room temperature that are characterized by hyperfine splitting constants (hfcs, mT) of 0·655 (^{14}N), 0·742 (1H), 0·259 (2H), 0·125 (2H), 0·0485 (4H) and 0·916 (^{15}N), 0·747 (1H), 0·259 (2H), 0·125 (2H), 0·0485 (4H) for $PT^{+\bullet}$ and $[^{15}N]PT^{+\bullet}$, respectively (Figure 1). Addition of neutral ^{15}N-substituted phenothiazine ($[^{15}N]PT$) to the acetonitrile solution of phenothiazine radical cation ($PT^{+\bullet}$) hexachloroantimonate resulted in a change of the EPR spectrum from the unique $PT^{+\bullet}$ spectrum to a superimposed one of $PT^{+\bullet}$ and $[^{15}N]PT^{+\bullet}$, together with significant line broadening of the spectrum (Figure 2). This demonstrates clearly that electron exchange had taken place between $PT^{+\bullet}$ and $[^{15}N]PT$ as depicted in equation (2). Computer simulation of EPR spectra from five independent experiments with an initial concentration ratio of $[^{15}N]PT/PT^{+\bullet}SbCl_6^-$ ranging from 0·8 to 2·3 gave an equilibrium constant $K = 0{\cdot}77 \pm 0{\cdot}10$ at 25 °C in acetonitrile for reaction (2). This result reveals that the electron is transferred preferentially to [^{14}N]phenothiazine radical cation in the electron exchange process. In other words, the heavy isotope-substituted phenothiazine, $[^{15}N]PT$, has a diminished ionization potential, or the heavy isotope-substituted phenothiazine radical cation, $[^{15}N]PT^{+\bullet}$, possesses a diminished electron affinity compared with the light isotopic analogue in solution. This is similar to what we observed previously in the electron exchange equilib-

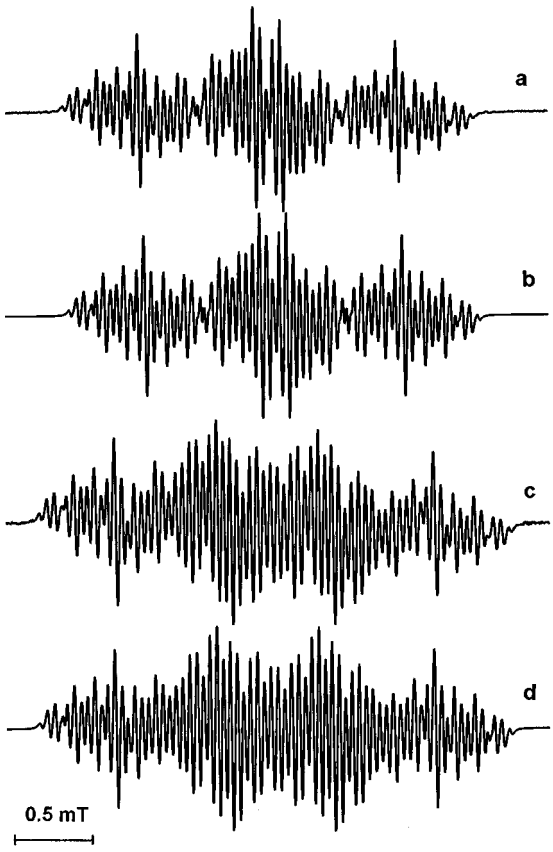

Figure 1. EPR spectra of phenothiazine radical cations recorded in acetonitrile solution at 25 °C. (a) $[^{15}N]PT^{+\bullet}$, $4{\cdot}7 \times 10^{-4}$ mol l^{-1}; (b) computer simulation of (a), linewidth $\Delta H_{pp} = 0{\cdot}020$ mT, for hfcs see text; (c) $PT^{+\bullet}$, $4{\cdot}6 \times 10^{-4}$ mol l^{-1}; (d) computer simulation of (c), $\Delta H_{pp} = 0{\cdot}024$ mT, for hfcs see text

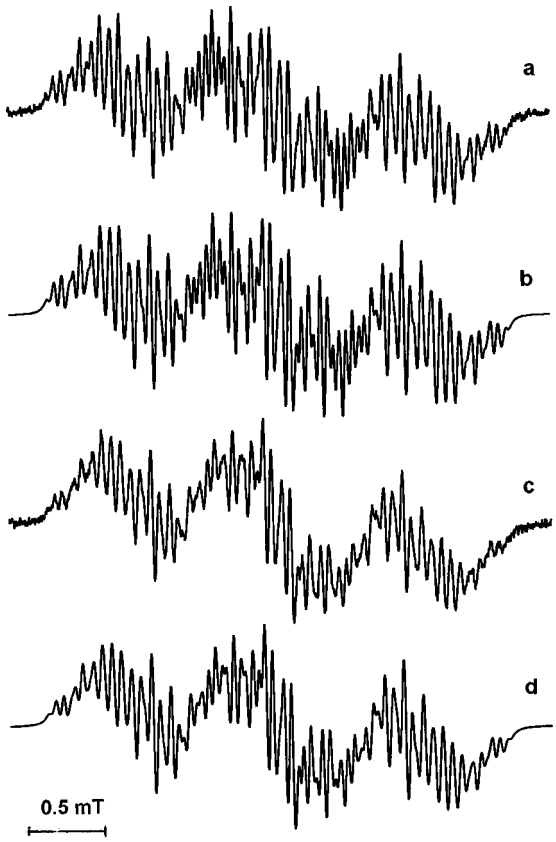

Figure 2. Representative EPR spectra obtained from a mixture of phenothiazine radical cation hexachloroantimonate and [^{15}N]phenothiazine recorded in acetonitrile solution at 25 °C. (a) $[PT^{+\bullet}]_0 = 4{\cdot}64 \times 10^{-4}$ mol l^{-1}, $[[^{15}N]PT]_0 = 3{\cdot}89 \times 10^{-4}$ mol l^{-1}; (b) computer simulation of (a) generated by using a molar ratio of $PT^{+\bullet}$ to $[^{15}N]PT^{+\bullet}$ of 1:0·94, corresponding to $K = 0{\cdot}80$ for reaction (2); (c) $[PT^{+\bullet}]_0 = 4{\cdot}59 \times 10^{-4}$ mol l^{-1}, $[[^{15}N]PT]_0 = 5{\cdot}16 \times 10^{-4}$ mol l^{-1}; (d) computer simulation of (c) generated by using a molar ratio of $PT^{+\bullet}$ to [15N]$PT^{+\bullet}$ of 1:1·28, corresponding to $K = 0{\cdot}78$ for reaction (2)

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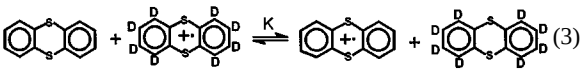
rium of thianthrene and its radical cation, in which an electron is transferred preferentially from the perdeuterated molecule to the perprotio radical cation [K=0·62 for equation (3)].[9] The result is also in general agreement with the EIEs in the electron transfer processes of radical anions and their molecule precursors reported by Stevenson and co-workers.[1, 6–8]



(3)

Isotope enrichment by physical separation

Since the equilibrium constant for equation (2) differs significantly from unity, partial oxidation of a mixture of [^{14}N]- and [^{15}N]phenothiazines should bring about different isotope distributions in the neutral molecules and radical cations. In addition, the radical cation salt of phenothiazine is persistent in anhydrous acetonitrile at room temperature and it is very easily separated from the neutral molecule precursor by precipitation. Therefore, this isotopically selective electron exchange may be used to develop a method for isotope enrichment. Thus, a 3:7 mixture of carefully weighed portions of [^{15}N]- and [^{14}N]phenothiazines was dissolved in anhydrous diethyl ether–acetonitrile mixed solvent and oxidized by a 0·5 stoichiometric amount of 2,2,6,6-tetramethyl-4-acetoxypiperidineoxoammonium hexachloroantimonate, which quantitatively oxidizes phenothiazine to its radical cation.[12] The radical cation salts precipitated completely from the solvent and were separated from the liquid phase by filtration. Removal of the solvent under reduced pressure left the unoxidized neutral phenothiazines (designated phase 1). The radical cation salts were reduced by tetra-*n*-butylammonium iodide followed by treatment with $NaHSO_3$ to eliminate traces of iodine. The pure neutral phenothiazines (phase 2) were then recovered. Phases 1 and 2 were subjected to NMR analysis. The N-proton in [^{14}N]phenothiazine appears as a singlet and that in [^{15}N]phenothiazine as a doublet with a coupling constant of 87·7 Hz, and they well resolved from each other. Therefore, the ^{14}N/^{15}N ratio can be obtained easily by integrating the two peaks (Figure 3). The solid-phase equilibrium constant is defined as the molar ratio of the heavy to light isotopic isomers in phase 1 divided by that in phase 2, and is often called the separation factor α [equation (4)].[8]

$$K=\frac{([[^{15}\mathrm{N}]\mathrm{PT}]/[\mathrm{PT}])_{\text{phase 1}}}{([[^{15}\mathrm{N}]\mathrm{PT}]/[\mathrm{PT}])_{\text{phase 2}}}=\alpha \qquad (4)$$

Four independent separation experiments gave a solid-phase equilibrium constant of 0·83±0·10 at room temperature, in good agreement with the EPR result reported above.

IR and Raman spectroscopic studies

Stevenson and co-workers[1b, h] suggested that the diminished electron affinity of perdeuterobenzene compared with that of protiobenzene stemmed from the zero-point vibrational energy effect (ZPE) upon the substitution. We also found that significant low-frequency shifts took place in some of the IR and Raman peaks of thianthrene upon deuteration and radical cation formation, which may explain the diminished ionization potential of perdeuterated thianthrene.[10] Therefore, IR and Raman spectra of phenothiazine, [^{15}N]phenothiazine and their radical cation hexachloroantimonates were recorded, as shown in Figures 4 and 5. Since phenothiazine is known to be folded about the S—N axis with a dihedral angle of *ca* 158·5° between the two phenylene rings,[13] the two phenylene rings are nearly independent and the spectrum can be interpreted in terms of substituted benzene spectra, whose symmetry assignments are well established.[14] Such an approach has been successfully used to assign IR and Raman spectra of thianthrene by using *o*-dichloro- and *o*-dibromobenzenes as reference compounds.[10, 14] Therefore, the same approach was used for the spectral assignment of phenothiazine.

Phenothiazine with 23 atoms and C_s symmetry has 63 fundamental frequencies, i.e. $33A'+30A''$. The complete IR

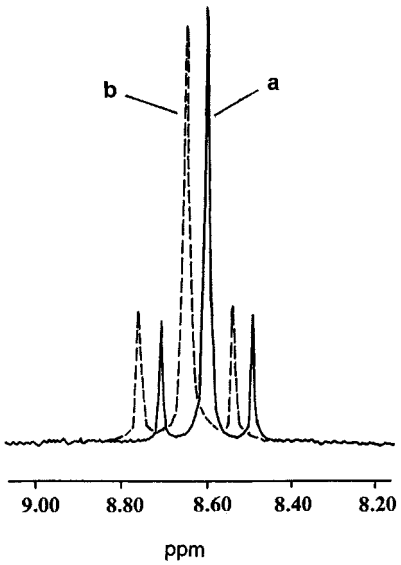


Figure 3. Representative ^{1}H NMR spectra of the N-protons of PT and [^{15}N]PT recorded in acetone-d_6. The samples were obtained by partial oxidation of a mixture of 35 mg of PT and 15 mg of [^{15}N]PT and then separation of the neutral molecules (phase 1) and radical cations (phase 2). The latter was reduced to neutral molecules for NMR determination (see Experimental section for details). (a) Spectrum of phase 1 which shows a molar ratio of PT to [^{15}N]PT of 1:2·54; (b) spectrum of phase 2 which shows a molar ratio of PT to [^{15}N]PT of 1:2·16. Spectrum (b) is shifted downfield for clarity. K=0·85 for reaction (4) is obtained from this particular experiment

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and Raman spectral assignments are listed in Table 1. The Raman spectral assignment of phenothiazine is in accordance with those reported previously.[13, 15] The assignment for [^{15}N]phenothiazine is straightforward since it showed similar IR and Raman spectra to those of its ^{14}N analogue and some low-frequency shifts are obvious due to the heavy isotope substitution.

Phenothiazine radical cation possesses the same symmetry as its parent molecule, but the dihedral angle of the two phenylene rings increases to 172·2°.[16] The two radical cations showed IR and Raman spectra similar to those of their parent molecules except that a very strong new peak of hexachloroantimonate appeared at 846 cm^{-1} in their Raman spectra. It can be seen from Table 1 that although change in mass is relatively small, replacement of a ^{14}N atom by ^{15}N brings about low-frequency shifts of not only N—H and N—C stretchings, but also some of C—C and C—H vibrations. Transformation of phenothiazines into their radical cations also produces significant frequency shifts. Therefore, isotope substitution and radical cation formation should result in a non-zero enthalpy change for reaction (2). Vibrational bands which are effective for the enthalpy change are summarized in Table 2. The remaining vibra-

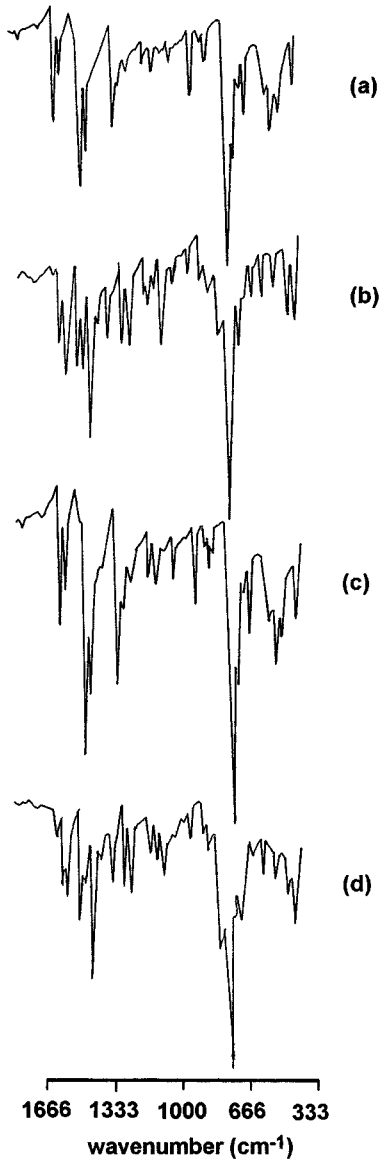

Figure 4. IR spectra of (a) PT, (b) PT$^{+\cdot}$SbCl$_6^-$, (c) [^{15}N]PT and (d) [^{15}N]PT$^{+\cdot}$SbCl$_6^-$

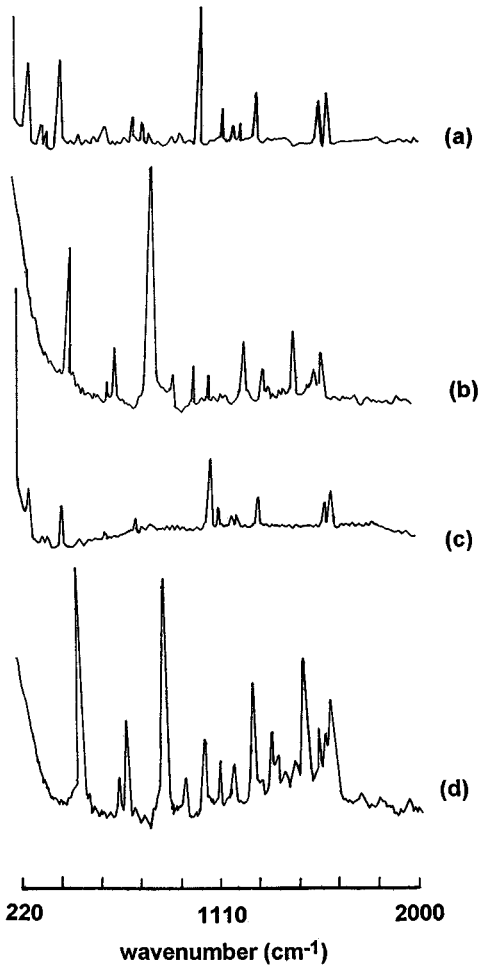

Figure 5. Raman spectra of (a) PT, (b) PT$^{+\cdot}$SbCl$_6^-$, (c) [^{15}N]PT and (d) [^{15}N]PT$^{+\cdot}$SbCl$_6^-$

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tions showed very small effects and are not included in the table. On the basis of these 10 vibrations, the zero-point energy effect results in an enthalpy change of 441·7 J mol^{-1} for reaction (2). Since electron transfer between two structurally similar species would not bring about the entropy change,[17] thus giving identical free energy and enthalpy changes, this value should correspond to an equilibrium constant of 0·84 for reaction (2), which is in reasonable accordance with the EPR and NMR results given above.

In conclusion, this work demonstrates that an electron moves in an isotopically selective manner between phenothiazine and its radical cation in solution. ^{15}N substitution decreases the ionization potential of phenothiazine and the electron affinity of phenothiazine radical cation. This equilibrium isotope effect can be rationalized by zero-point energy differences caused by the heavy isotope substitution.

Table 1. Fundamental vibrational frequencies (cm^{-1}) of PT, $PT^{+\cdot}SbCl_6^-$, [^{15}N]PT and [^{15}N]$PT^{+\cdot}SbCl_6^-$[a]

Mode symmetry	PT		$PT^{+\cdot}SbCl_6^-$		Normal coordinate	[^{15}N]PT		[^{15}N]$PT^{+\cdot}SbCl_6^-$		Normal coordinate
	IR	Raman	IR	Raman		IR	Raman	IR	Raman	
A′	3339(s)	3345(m)			ν(NH)	3331(s)	3339(m)			ν(^{15}NH)
	3183(w)		3192(m)		ν(NH)	3177(w)		3177(m)		ν(^{15}NH)
	3099(w)		3104(w)		ν(CH)	3092(w)		3093(m)		ν(CH)
	3053(w)		3031(m)		ν(CH)	3050(w)		3028(s)		ν(CH)
		1601(s)		1598(s)	ν(CC)		1600(s)		1599(s)	ν(CC)
	1596(s)		1594(s)		ν(CC)	1596(s)		1585(s)		ν(CC)
	1571(s)		1559(s)		ν(CC)	1570(s)		1562(s)		ν(CC)
				1480(s)	ν(CC)				1480(s)	ν(CC)
	1472(vs)		1471(s)		ν(CC)	1468(vs)		1475(s)		ν(CC)
	1442(s)		1442(s)		ν(CC)	1442(s)		1441(vs)		ν(CC)
	1280(m)		1282(s)		ν(CC)	1281(m)		1283(s)		ν(CC)
				1262(s)	β(CH)	1259(m)			1258(vs)	β(CH)
		1250(s)			ν(CN)		1245(s)			ν(C^{15}N)
	1242(m)		1256(s)		ν(CN)	1239(m)		1248(s)		ν(C^{15}N)
		1160(m)		1155(m)	β(CH)		1156(m)		1157(s)	β(CH)
	1153(m)		1151(m)		β(CH)	1153(s)		1152(m)		β(CH)
		1132(m)		1125(w)	β(CH)		1130(m)			β(CH)
	1118(m)		1122(m)		ν(CN)	1120(s)		1122(s)		ν(C^{15}N)
			1089(s)					1086(s)		
		1083(s)		1100(s)	ν(CN)		1082(s)		1100(s)	ν(C^{15}N)
	1078(w)			1071(w)	ν(CS)	1077(w)			1070(w)	ν(CS)
	1033(m)	1035(vs)	1027(m)	1031(s)	γ(CS)	1033(vs)	1034(vs)	1029(w)	1032(s)	γ(CS)
	855(s)		850(m)		ν(CN)	858(s)		863(m)		ν(C^{15}N)
		845(w)		846(vs)	ν(CN)	840(m)	837(w)		852(vs)	ν(C^{15}N)
	683(m)	684(m)	681(w)	683(s)	γ(CC)	682(m)	682(m)		683(vs)	γ(CC)
	655(s)		643(m)		ν(CS)	653(s)		642(m)	645(s)	ν(CS)
		658(m)		648(m)	ν(CS)	653(s)			645(s)	ν(CS)
			595(s)		δ(CCC)	612(m)		594(s)		δ(CCC)
	493(m)	495(w)			δ(CSC)	492(m)	490(w)			δ(CSC)
		258(s)		375(m)	δ(CNC)		251(m)		364(m)	δ(C^{15}NC)
A″	964(vw)		985(w)		γ(CH)	964(w)		988(w)		γ(CH)
	923(s)		951(m)		γ(CH)	923(s)		953(m)		γ(CH)
				942(m)	δ(CNC)				945(s)	δ(C^{15}NC)
	884(m)	888(m)	887(m)		γ(CH)	876(m)	878(w)	883(w)		γ(CH)
	735(vs)		749(vs)		γ(CH)	735(vs)		749(vs)		γ(CH)
		756(s)			γ(CH)		751(w)			γ(CH)
	715(s)		711(s)		γ(CC)	715(s)		712(s)		γ(CC)
		539(m)					537(m)			
	530(s)		531(m)		γ(CC)	529(s)		531(s)		γ(CC)
		430(m)					431(m)			
	426(s)		434(s)		γ(CS)	426(s)		436(s)		γ(CS)
		347(vs)	468(s)	473(vs)	δ(CNC)		345(vs)	469(m)	472(vs)	δ(C^{15}NC)
		281(s)		283(w)			277(m)			
		189(vs)		226(s)	δ(CSC)		186(s)		225(s)	δ(CSC)

[a] s = Strong; v = very; m = medium; w = weak; ν = stretching; δ = bending; β = in-plane deformation; γ = out-of-plane deformation.

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Table 2. Selected IR and Raman frequencies (cm^{-1}) of PT, $PT^{+\bullet}SbCl_6^-$, [^{15}N]PT and [^{15}N]$PT^{+\bullet}SbCl_6^-$ which contribute to $\Delta H°$ for reaction (2)

Assignment	PT	$PT^{+\bullet}SbCl_6^-$	[^{15}N]PT	[^{15}N]$PT^{+\bullet}SbCl_6^-$	Contribution to ΔH^0 ($J\ mol^{-1}$)[a]
A′ C—C stretch	1596	1594	1596	1585	−107·4
A′ C—C stretch	1571	1559	1570	1562	47·6
A′ C—C stretch	1472	1471	1468	1475	95·7
A′ C—N stretch	1242	1256	1239	1248	−59·8
A′ C—H in-plane deformation	1160	1155	1156	1157	71·5
A″ C—H out-of-plane deformation	964	985	964	988	35·9
A″ C—H out-of-plane deformation	923	951	923	953	23·8
A″ C—H out-of-plane deformation	884	887	876	883	47·7
A′ C—N stretch	855	850	858	863	119·5
A′ C—N stretch	845	846	837	852	167·2

[a] Total contribution to $\Delta H^0 = 441{\cdot}7\ J\ mol^{-1}$.

EXPERIMENTAL

Materials. Phenothiazine was synthesized according to the literature method,[18] m.p. 176–178 °C. [^{15}N]Phenothiazine was synthesized similarly from [^{15}N]diphenylamine, m.p. 176–178 °C; ^{1}H NMR (acetone-d_6, ppm) 6·68 (m, 8H), 7·85 (d, J=87·7 Hz, 1H); MS (FAB, m/z, %), 201 (M^++1, 70), 200 (M^+, 100). $Na^{15}NO_3$ (99·5 atom% ^{15}N) (Shanghai Institute of Chemical Engineering) was used to prepare [^{15}N]nitrobenzene and [^{15}N]diphenylamine according to the literature.[18, 19] The radical cation hexachloroantimonates were prepared by oxidizing the corresponding parent molecules with 2,2,6,6-tetramethyl-4-acetoxypiperidine-oxoammonium hexachloroantimonate in anhydrous acetonitrile.[12] They are deep-blue crystals, m.p. 150 °C (decomp.); EPR g-values 2·0050.

EPR measurements. Carefully weighed portions of phenothiazine radical cation hexachloroantimonate ($PT^{+\bullet}SbCl_6^-$) and [^{15}N]phenothiazine ([^{15}N]PT) were dissolved in anhydrous acetonitrile. The initial concentration of $PT^{+\bullet}SbCl_6^-$ was *ca* $5\times10^{-4}\ mol\ l^{-1}$ and $PT^{+\bullet}\ SbCl_6^-$/[^{15}N]PT concentration ratio ranged from *ca* 0·8 to 2·3. The solution was placed in a 2 mm quartz capillary and deaerated by bubbling nitrogen through, then sealed for EPR determinations. EPR spectra were recorded on a Bruker ER 200D spectrometer using a standard TE_{102} rectangular cavity and operating in the X-band with 100 kHz modulation and a modulation amplitude of 0·01 mT. All measurements were carried out at an ambient temperature.

Spectral simulation was performed with laboratory-written software that is based on the Bloch equations and rigorously accounts for the line broadening caused by electron exchange between the radical and the non-paramagnetic species in solution.[8, 20] Initially, hyperfine splitting constatns were obtained from the spectrum of the isotopically pure radical. The experimental and simulated spectra were superimposed on a computer screen and hyperfine splitting constants and linewidths were adjusted until the two spectra completely matched each other. Then the simulated spectra of the two isotopic radical cations were computationally superimposed with the concentration ratio as a new variable to match the experimental spectrum. The linewidths of both species were adjusted in the simulation of mixtures by reference to lines which are relatively free of overlap. The equilibrium constants evaluated from the concentration ratios of the two radical cations were reproducible over several experiments with different initial $PT^{+\bullet}$/[^{15}N]PT concentration ratios.

Isotope enrichment experiment. A carefully weighed mixture of 35 mg of phenothiazine and 15 mg of [^{15}N]phe-

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nothiazine was dissolved in 25 ml of dry diethyl ether. A small portion of the mixture was removed for NMR analysis as a standard, and the remainder was oxidized by 60 mg (*ca* 0·5 stoichiometric amount) of 2,2,6,6-tetramethyl-4-acetoxypiperidineoxoammonium hexachloroantimonate dissolved in 2 ml of anhydrous acetonitrile. The radical cation salts of phenothiazines precipitated rapidly after mixing the two solutions and were separated by filtration from their neutral molecule precursors. The unoxidized phenothiazines were purified by column chromatography for NMR analysis and the solid radical cation salts were reduced to neutral phenothiazines by addition of an excess of tetra-*n*-butylammonium iodide in acetonitrile and then treated with aqueous $NaHSO_3$ to eliminate the traces of iodine produced. The recovered phenothiazines were then purified by column chromatography for NMR analysis.

^{1}H NMR spectra were recorded on a Bruker AM 400 NMR spectrometer operating at 400 MHz. The molar ratio of phenothiazine to [^{15}N]phenothiazine was obtained by integrating the singlet and doublet peak areas of ^{14}N–H and ^{15}N–H, respectively, and each spectrum was integrated three times to ensure that the deviation was within 10%. The NMR result was checked with a standard sample, which gave the expected PT/[^{15}N]PT molar ratio.

IR and Raman spectroscopy

IR spectra were recorded on a Nicolet 170 SX IR spectrometer using KBr pellets. Raman spectra were recorded on a Spex 1403 laser Raman spectrometer with argon-ion laser excitation at 514 nm at room temperature using KBr pellets.

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