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$^{14}N/^{15}N$ and $^{12}C/^{13}C$ Equilibrium Isotope Effects on the Electron-Transfer Reaction between *N*-Methylphenothiazine and Its Radical Cation

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Appreciable equilibrium isotope effects have been observed for electron-transfer process between *N*-methylphenothiazine (MPT) and the radical cation of its ^{15}N- and/or $N-^{13}C$-methyl-substituted analogues via electron spin resonance (ESR) line-broadening effect of the radical cation perchlorates in the presence of the corresponding parent neutral molecule. The equilibrium constants for the following electron-transfer processes were determined to be $K_1 = 1.19 \pm 0.06$, $K_2 = 1.17 \pm 0.12$, $K_3 = 1.06 \pm 0.03$, $K_4 = 1.06 \pm 0.05$, and $K_5 = 1.27 \pm 0.14$ respectively, in acetonitrile at ambient temperature: $\mathrm{MPT} + [^{15}N]\mathrm{MPT}^{\bullet+} \xrightleftharpoons{K_1} \mathrm{MPT}^{\bullet+} + [^{15}N]\mathrm{MPT}$; $[^{13}C]\mathrm{MPT} + [^{13}C,^{15}N]\mathrm{MPT}^{\bullet+} \xrightleftharpoons{K_2} [^{13}C]\mathrm{MPT}^{\bullet+} + [^{13}C,^{15}N]\mathrm{MPT}$; $[^{15}N]\mathrm{MPT} + [^{13}C,^{15}N]\mathrm{MPT}^{\bullet+} \xrightleftharpoons{K_3} [^{15}N]\mathrm{MPT}^{\bullet+} + [^{13}C,^{15}N]\mathrm{MPT}$; $\mathrm{MPT} + [^{13}C]\mathrm{MPT}^{\bullet+} \xrightleftharpoons{K_4} \mathrm{MPT}^{\bullet+} + [^{13}C]\mathrm{MPT}$; $\mathrm{MPT} + [^{13}C,^{15}N]\mathrm{MPT}^{\bullet+} \xrightleftharpoons{K_5} \mathrm{MPT}^{\bullet+} + [^{13}C,^{15}N]\mathrm{MPT}$. In addition, infrared and Raman spectra of the *N*-methylphenothiazines and their radical cations were recorded and compared to assign the vibrational frequency shifts caused by the heavy-atom substitution and radical cation formation, from which the enthalpy changes of the electron-transfer processes were estimated. These results reveal that ^{15}N- and/or ^{13}C-substitution of methylphenothiazine increases the ionization potential of the molecule, making it more difficult to lose an electron to form the corresponding radical cation in solution.

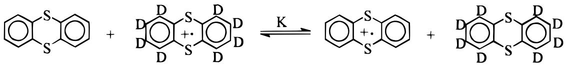
Introduction

Stevenson and co-workers[1,2] have published a series of papers since 1986 dealing with the equilibrium isotope effect (EIE) on electron-transfer processes between several radical anions and their heavy-isotope-substituted aromatic molecule precursors. They found that the equilibrium constants for the electron exchange (eq 1) deviated significantly from unity and suggested that these EIE's may serve as a basis for an efficient isotope separation:[3−5]

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

where *A represents a heavy isotope (^{2}H, ^{13}C, ^{15}N, ^{17}O, etc.) substituted aromatic molecule. Although their results, especially those dealing with $^{15}N/^{14}N$ and $^{13}C/^{12}C$ isotope effects, have been questioned from theoretical[6] and experimental standpoints,[7,8] Stevenson and co-workers[9−11] argued later that the EIE is strongly dependent on the charge and spin density in the area of isotope substitution, which is, in turn, dependent on the specific anion radical/counterion and anion radical/solvent interactions that make the statistical mechanical calculation hard to account for. The H/D isotope effects that Stevenson and co-workers initially observed via electron spin resonance (ESR) measurements[1] have been confirmed by independent cyclic voltammetric data[12,13] and theoretical calculations.[2,14]

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 molecules, which had never been studied until our previous report on the significant $^{1}H/^{2}H$ EIE on the electron exchange between thianthrene and its radical cation.[15] We found that the electron transfer between thianthrene (Th) and its radical cation ($Th^{\bullet+}$) was isotopically selective with the equilibrium constant of eq 2 being 0.62 ± 0.12 in trifluoroacetic acid/trifluoroacetic anhydride/methylene chloride mixed solvent at room temperature:[15]



This result has gotten support from NMR,[16] IR, and Raman spectroscopic studies.[17] Since this EIE is significant and, further, radical cations and their parent molecules are quite different in chemical and physical properties, thus making them easy to separate, this finding may lead to a facile approach for isotope enrichment. In fact, partial oxidation of a mixture of thianthrene and perdeuterated thianthrene followed by separation of the precipitated radical cation salts from the neutral molecules in the solution did make the isotope distribution in the neutral molecule different from that of the original mixture.[16] A similar $^{14}N/^{15}N$ EIE has been reported recently on the electron-transfer reaction between phenothiazine and its radical cation.[18] Here, we report ESR, IR, and Raman spectroscopic studies on $^{14}N/^{15}N$ and $^{12}C/^{13}C$ equilibrium isotope effects on the electron-transfer reaction between *N*-methylphenothiazine and the radical cation of its ^{15}N- and/or $N-^{13}C$-methyl-substituted analogues in solution.

Experimental Section

Materials. *N*-methylphenothiazine (MPT) was prepared according to the literature,[19] mp 100−101 °C. ^{15}N-Methylphenothiazine ($[^{15}N]$MPT) was prepared similarly, but ^{15}N-phenothiazine[18] was used instead of phenothiazine, mp 100−101 °C. MS (EI, 70 eV): 214 (M^{+}, 100%), 199 ($M^{+} - CH_3$,

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TABLE 1: ESR Parameters of Phenothiazine (PT) and *N*-Methylphenothiazine (MPT) Radical Cation Perchlorates[a]

		hyperfine splitting constants (G)							
						aromatic protons			
radical cation	*g* value	$^{14}N/^{15}N$	^{13}C	$H_{(CH_3)}$	$H_{(N)}$	2H	2H	2H	2H
$PT^{•+b}$	2.0050	6.55			7.42	1.25	2.59	0.485	0.485
$[^{15}N]PT^{•+b}$	2.0050	9.16			7.47	1.25	2.59	0.485	0.485
$MPT^{•+}$	2.0052	7.66 $(7.49)^c$		7.31 $(7.24)^c$		1.02 $(0.98)^c$	2.17 $(2.12)^c$	0.70 $(0.73)^c$	0.28 $(0.24)^c$
$[^{15}N]MPT^{•+}$	2.0052	10.73		7.31		1.02	2.17	0.70	0.28
$[^{13}C]MPT^{•+}$	2.0052	7.67	3.46	7.35		1.04	2.20	0.70	0.28
$[^{13}C,^{15}N]MPT^{•+}$	2.0053	10.81	3.45	7.32		1.03	2.20	0.70	0.28

[a] Determined in anhydrous acetonitrile solution (2.50×10^{-4} M) at room temperature. [b] Phenothiazine radical cation hexachloroantimonate, determined in acetonitrile.[18] [c] Reference 19.

TABLE 2: Equilibrium Constants and Free Energy Changes for Reactions 3−7

			reaction				
run	concentration ratio[a]	$\Delta\Delta H_{pp}{}^{b}$	3	4	5	6	7
1	1:0.4	0.015	1.28		1.06		1.20
2	1:0.8	0.03	1.18	1.24			
3	1:1.0	0.04		1.17	1.05	1.06	
4	1:1.2	0.05	1.16	1.35	1.04	1.08	1.25
5	1:1.6	0.06	1.20	1.19	1.12	1.05	1.42
6	1:2.0	0.08	1.21	1.13	1.06	1.08	1.30
7	1:3.0	0.12	1.16	1.10	1.08	1.06	
8	1:4.0	0.16	1.17	1.11	1.09	1.05	1.20
K^c			1.19 ± 0.06	1.17 ± 0.12	1.06 ± 0.03	1.06 ± 0.05	1.27 ± 0.18
K^d			1.23	1.24	1.16	1.10	1.36
$\Delta G°_{ESR}{}^{c}$ (J/mol)			−430.8	−388.8	−144.3	−144.3	−591.9
$\Delta G°_{IR}{}^{d}$ (J/mol)			−516.8	−527.6	−371.6	−228.9	−767.6

[a] $[\text{radical cation}]_0/[\text{neutral molecule}]_0$ used for ESR determinations. [b] ESR line width (in gauss) used for spectral simulation. [c] Determined by ESR spectroscopy. [d] Estimated by IR and Raman spectroscopy.

99%). ^{13}C-methylphenothiazine ([^{13}C]MPT) and $^{15}N,^{13}C$-methylphenothiazine ([$^{15}N,^{13}C$]MPT) were prepared similarly from iodomethane-^{13}C with phenothiazine and ^{15}N-phenothiazine, respectively, mp 100−101 °C. Both of them have similar ^1H NMR spectra (acetone-d_6, ppm): 3.38 (d, 137.3 Hz), 7.05 (t). MS (EI, 70 eV) of [^{13}C]MPT: 214 (M^+, 99%), 198 ($M^+ - {}^{13}CH_3$, 100%). MS (EI, 70 eV) of [$^{13}C,^{15}N$]MPT: 215 (M^+, 99%), 199 ($M^+ - {}^{13}CH_3$, 100%). The radical cation perchlorates, $MPT^{•+}ClO_4^-$, $[^{15}N]MPT^{•+}ClO_4^-$, $[^{13}C]MPT^{•+}ClO_4^-$, and $[^{13}C,^{15}N]MPT^{•+}ClO_4^-$, were prepared by oxidizing the corresponding parent molecules with 2,2,6,6-tetramethyl-4-acetyloxypiperidine oxoammonium perchlorate in methylene chloride/carbon tetrachloride mixed solvent as described previously,[20] mp 180 °C (dec). The *g* values of the ESR spectrum were 2.0052, 2.0052, 2.0052, and 2.0053, respectively.

Methylene chloride, carbon tetrachloride, and acetonitrile were purified as usual and dried over P_2O_5 before use.

ESR Measurements. Carefully weighed portions of ^{15}N- and/or ^{13}C-substituted methylphenothiazine radical cation perchlorate and the corresponding neutral molecule were dissolved in anhydrous acetonitrile. The initial concentration of the radical cation was ca. 2.5×10^{-4} M, and the concentration ratio of the neutral molecule/radical cation ranged from ca. 0.4 to 4.0. The solution was placed in a 2 mm glass capillary and degassed by a freeze-and-thaw procedure, then sealed for ESR determinations.

ESR spectra were recorded on a Bruker ER-200D spectrometer using a standard TE_{102} rectangular cavity, operating in the X-band with 100 kHz modulation and a modulation amplitude of 0.1 G and time constant of 200 ms. All measurements were carried out at ambient temperature.

Spectral simulation was performed with a homemade software that is based on the Bloch equations and rigorously accounts for the line broadening caused by electron exchange between the radical and the nonparamagnetic species in solution.[21] Hyperfine splitting constants were obtained from the spectrum of the isotopically pure radicals by computer simulation. Then the simulated spectra of the two radical cations with different isotopes were computationally superimposed with the concentration ratio as a new variable to match the experimental spectrum of the mixed radical cations. Line widths of both species were adjusted in the simulation by reference to lines that are relatively free of overlap. The equilibrium constants evaluated from the concentration ratios of the two radical cations are reproducible over several experiments with different initial concentration ratios of the radical cation/neutral molecule.

IR and Raman Measurements. IR spectra were recorded on a Nicolet 170SX IR spectrometer using KBr pellets. Raman spectra were recorded on a Spex 1403 laser Raman spectrometer with an argon-ion laser excitation at 514.5 nm at room temperature using KBr pellets.

Results

A. ESR Spectroscopic Studies. *N*-methylphenothiazine radical cation perchlorate ($MPT^{•+}ClO_4^-$) showed a well-resolved ESR spectrum in carefully degassed dilute anhydrous acetonitrile at room temperature (Figure 1a) that is characterized by a triplet of ^{14}N splitting of 7.66 G and proton splittings from N-methyl and aromatic protons as listed in Table 1. The ^{15}N-substituted analogue ($[^{15}N]MPT^{•+}ClO_4^-$) showed similar proton splittings, whereas the ^{14}N splitting was replaced by a doublet of ^{15}N splitting of 10.73 G (Figure 1c, Table 1). When ^{15}N-substituted methylphenothiazine ([^{15}N]MPT) was added to the solution of $MPT^{•+}ClO_4^-$, the unique ESR spectrum of $MPT^{•+}$ was replaced by a superimposed spectrum of $MPT^{•+}$ and $[^{15}N]MPT^{•+}$, together with significant line broadening as illustrated in Figure 2. This demonstrates unambiguously that electron transfer takes

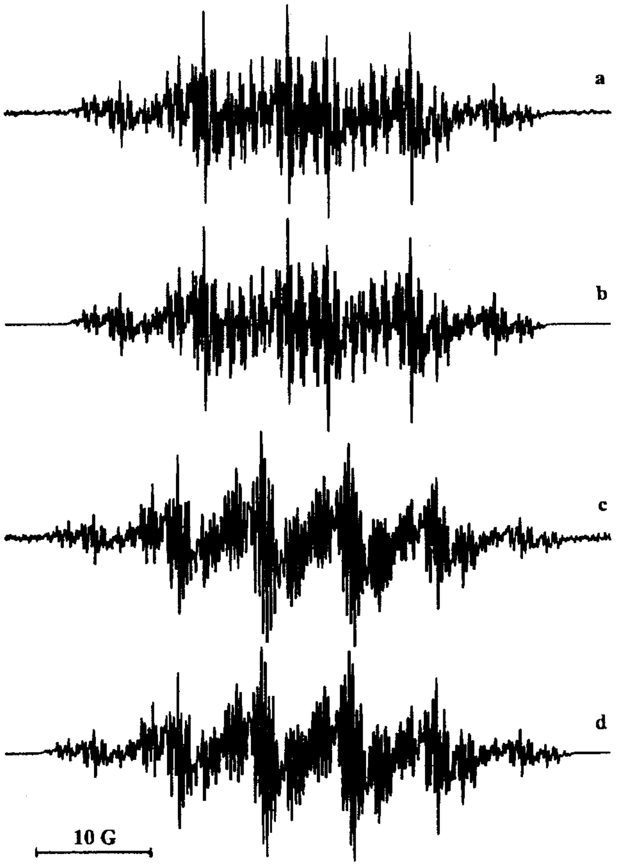
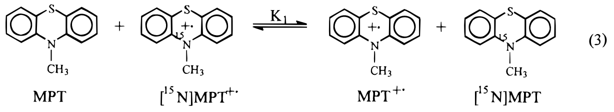


Figure 1. ESR spectra of *N*-methylphenothiazine radical cations recorded in acetonitrile solution at 25 °C: (a) [^{15}N]MPT$^{\bullet+}$, 2.50 × 10^{-4} M; (b) computer simulation of (a), line width $\Delta H_{pp} = 0.18$ G (for hyperfine splitting constants (hfcs) see text); (c) MPT$^{\bullet+}$, 2.50 × 10^{-4} M; (d) computer simulation of (c), line width $\Delta H_{pp} = 0.18$ G (for hfcs see text).

place between [^{15}N]MPT$^{\bullet+}$ and MPT as depicted in eq 3:



(3)

where the equilibrium constant K_1 can be calculated by

$$K_1 = \frac{[[^{15}\text{N}]\text{MPT}][\text{MPT}^{\bullet+}]}{[[^{15}\text{N}]\text{MPT}^{\bullet+}][\text{MPT}]} = \frac{(1-\alpha)\{[[^{15}\text{N}]\text{MPT}]_0 - \alpha[\text{MPT}^{\bullet+}]_0\}}{\alpha^2[\text{MPT}^{\bullet+}]_0}$$

where α represents the fraction of [^{15}N]MPT$^{\bullet+}$ in the total concentration of radical cations in the equilibrium, which was obtained by computer simulation of the ESR spectrum by adding the pure spectra of MPT$^{\bullet+}$ and [^{15}N]MPT$^{\bullet+}$ with different ratios, taking into account the line-broadening effect due to the electron exchange. The line-broadening due to the electron exchange, $\Delta\Delta H_{pp}$, can be calculated[22] by $\Delta\Delta H = 6.58 \times 10^{-8}k(1 - P_j)[c]$, where $\Delta\Delta H$ is the increment in peak-to-peak line width due to the electron exchange (in Gauss), [*c*] is the concentration of the diamagnetic parent molecule (in mol/L) and P_j is the intensity fraction of the *j*th line in the total intensity of the spectrum. The electron exchange rate constant, *k*, for eq 3 has been determined to be 2.20 × 10^9 mol^{-1} s^{-1}.[23] Seven independent experiments with an initial concentration ratio of [^{15}N]-MPT/MPT$^{\bullet+}$ ranging from 0.4 to 4.0 gave the equilibrium constant $K_1 = 1.19 \pm 0.06$. The results are listed in Table 2.

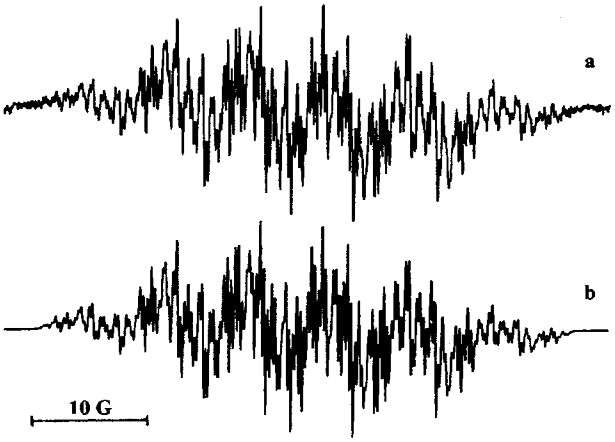
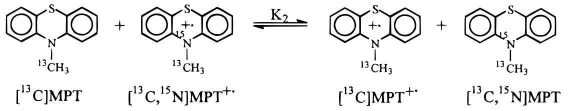


Figure 2. Representative ESR spectrum obtained from a mixture of methylphenothiazine radical cation perchlorate and ^{15}*N*-methylphenothiazine recorded in acetonitrile solution at 25 °C: (a) [MPT$^{\bullet+}$]$_0$ = 2.46 × 10^{-4} M, [[^{15}N]MPT]$_0$ = 1.98 × 10^{-4} M; (b) computer simulation of (a) generated by using a molar ratio of MPT$^{\bullet+}$/[^{15}N]MPT$^{\bullet+}$ of 1:0.75, corresponding to $K_1 = 1.16$ for reaction 3.

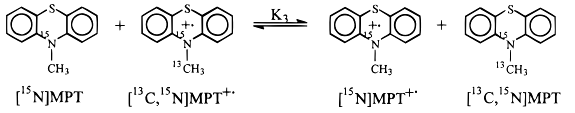
^{13}C-substitution of the methyl carbon in either MPT$^{\bullet+}$ or [^{15}N]-MPT$^{\bullet+}$ produced a new doublet of ^{13}C-splitting together with appreciable change on nitrogen and proton splittings in the ESR spectrum (Figure 3 and Table 1). Similarly, addition of neutral [^{13}C]MPT molecule to the acetonitrile solution of [^{13}C,^{15}N]-MPT$^{\bullet+}$ClO$_4^-$ changed the unique spectrum of [^{13}C,^{15}N]MPT$^{\bullet+}$ to a superimposed spectrum of [^{13}C,^{15}N]MPT$^{\bullet+}$ and [^{13}C]MPT$^{\bullet+}$ as illustrated in Figure 4, demonstrating the occurrence of the electron exchange as shown in eq 4.



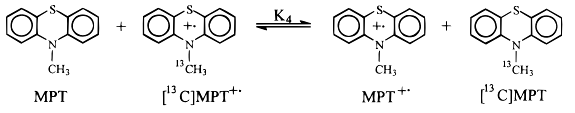
(4)

The K_2 was determined to be 1.17 ± 0.12 (Table 2).

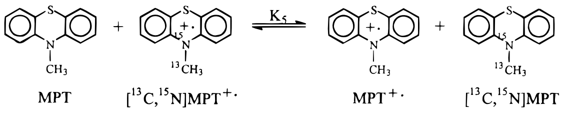
Similar ESR determinations for mixtures of [^{15}N]MPT and [^{13}C,^{15}N]MPT$^{\bullet+}$ (Figure 5), MPT and [^{13}C]MPT$^{\bullet+}$ (Figure 6), and MPT and [^{13}C,^{15}N]MPT$^{\bullet+}$ (Figure 7) gave equilibrium constants for reactions 5, 6, and 7 being $K_3 = 1.06 \pm 0.03$, $K_4 = 1.06 \pm 0.05$, and $K_5 = 1.27 \pm 0.14$, respectively (Table 2).



(5)



(6)



(7)

Free energy changes derived from the equilibrium constants are also listed in the table.

B. IR and Raman Spectroscopic Studies. Stevenson and co-workers[1b] have suggested that the EIE between benzene and perdeuteriobenzene radical anion stems from the zero-point vibrational energy effect (ZPE) upon the isotope substitution

TABLE 3: Fundamental Vibrational Frequencies (cm^{-1}) of MPT, MPT$^{\bullet+}$ClO$_4^-$, [^{15}N]MPT, and [^{15}N]MPT$^{\bullet+}$ClO$_4^-$ [a]

mode symmetry	MPT		MPT$^{+\bullet}$		normal coordinate	[^{15}N]MPT		[^{15}N]MPT$^{+\bullet}$		normal coordinate
	IR	Raman	IR	Raman		IR	Raman	IR	Raman	
A′	3052 (m)		3049 (m)		ν(CH)	3050 (m)		3047 (m)		ν(CH)
		1592 (s)		1601 (s)	ν(CC)		1594 (m)		1598 (s)	ν(CC)
	1590 (vs)		1592 (w)		ν(CC)	1590 (vs)		1586 (m)		ν(CC)
		1571 (vs)		1579 (m)	ν(CC)		1570 (vs)		1568 (vs)	ν(CC)
	1565 (vs)		1536 (vs)		ν(CC)	1565 (vs)		1535 (vs)		ν(CC)
	1488 (m)				ν(CC)					
	1449 (vs)		1459 (vs)		ν(CC)	1452 (vs)		1440 (s)		ν(CC)
			1440 (s)							
		1332 (w)		1344 (m)			1324 (w)		1337 (s)	
	1328 (vs)		1328 (s)		methyl twisting	1317 (vs)		1319 (s)		methyl twisting
		1304 (s)		1309 (w)			1304 (s)		1306 (w)	
	1285 (s)		1291 (m)		ν(CC)	1283 (s)		1290 (m)		ν(CC)
				1280 (m)	ν(CC)		1283 (w)		1286 (w)	ν(CC)
	1265 (vs)									
		1260 (vs)		1262 (s)	ν(CN)		1253 (vs)		1256 (s)	ν(C^{15}N)
	1243 (m)			1246 (m)	ν(CN)	1249 (vs)			1243 (m)	ν(C^{15}N)
		1165 (m)		1163 (m)	β(CH)		1165 (m)		1159 (m)	β(CH)
	1161 (m)		1175 (s)		β(CH)	1154 (m)		1175 (m)		β(CH)
		1143 (m)		1139 (w)	β(CH)		1249 (vs)		1243 (m)	β(CH)
	1132 (vs)				β(CH)	1135 (vs)				β(CH)
		1126 (m)		1117 (w)	β(CH)		1124 (m)		1126 (w)	β(CH)
		1108 (vs)		1099 (m)	ν(CS)		1103 (s)		1099 (s)	ν(CS)
	1106 (m)		1086 (vs)		ν(CS)	1099 (m)		1086 (vs)		ν(CS)
	1035 (s)	1037 (s)		1031 (m)	γ(CS)	1036 (vs)	1036 (vs)		1032 (s)	γ(CS)
	858 (vs)		875 (m)		ν(CN)	852 (vs)		870 (m)		ν(C^{15}N)
		846 (m)		855 (vs)	ν(CN)		850 (s)		845 (m)	ν(C^{15}N)
		674 (vs)		684 (m)	δ(CCC)		674 (s)		680 (m)	δ(CCC)
	673 (w)				ν(CS)	669 (w)				ν(CS)
	601 (w)		622 (vs)		δ(CCC)	600 (w)		622 (vs)		δ(CCC)
		580 (s)		598 (s)						
	578 (s)				δ(CCC)	575 (s)		597 (s)		δ(CCC)
		496 (m)			δ(CCC)		496 (m)			δ(CCC)
	491 (s)		494 (m)		δ(CSC)	491 (s)				δ(CSC)
		332 (vs)	474 (w)	473 (s)	δ(CNC)		329 (vs)		470 (s)	δ(C^{15}NC)
A″	975 (m)		956 (w)		γ(CH)	961 (w)		954 (m)		γ(CH)
		947 (m)		944 (m)			948 (s)		937 (m)	
	934 (m)					931 (m)				
		760 (m)		778 (w)	γ(CH)		759 (m)		785 (w)	γ(CH)
									746 (w)	
	752 (vs)		755 (vs)		γ(CH)	752 (vs)		756 (vs)		γ(CH)
	725 (s)	728 (s)		728 (w)	γ(CC)	726 (s)	730 (m)		727 (w)	γ(CC)
	693 (w)	697 (m)	709 (m)		γ(CC)	693 (m)	694 (m)	710 (w)		γ(CC)
	539 (s)	540 (s)	546 (w)		γ(CC)	536 (w)	539 (s)	540 (w)		γ(CC)
		443 (m)					442 (m)			
	431 (m)		449 (w)		γ(CS)	434 (m)		448 (m)		γ(CS)
	411 (w)		414 (w)		γ(CS)	416 (m)		401 (w)		γ(CS)
		355 (m)		353 (m)			377 (m)		390 (m)	
		296 (m)					290 (m)			
		246 (m)					249 (m)			
		187 (vs)		249 (m)	δ(CSC)		186 (vs)		239 (w)	δ(CSC)
		142 (s)		194 (vs)			140 (s)		195 (vs)	

[a] s = strong, vs = very strong, m = medium, w = weak, ν = stretching, δ = bending, β = in-plane deformation, γ = out-of-plane deformation.

and estimated the free energy change of the electron exchange process from the IR frequency shifts upon deuteration and radical anion formation. We[17,18] also found that significant low-frequency shifts took place in some of the IR and Raman bands of thianthrene upon deuteration and radical cation formation and of phenothiazine upon ^{15}N substitution and radical cation formation, which may explain the isotope effect. Therefore, IR and Raman spectra of *N*-methylphenothiazine, ^{15}*N*-methylphenothiazine, *N*-methyl-^{13}C-phenothiazine, ^{15}*N*-methyl-^{13}C-phenothiazine, and their radical cation perchlorates were recorded, as shown in Figures 8−11. Since *N*-methylphenothiazine is known to be folded about the S−N axis with a dihedral angle between the two phenylene rings of ca. 143.7°,[24] 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.[25] Such an approach has been successfully used to assign IR and Raman spectra of thianthrene and phenothiazine by using *o*-dichloro- and *o*-dibromobenzenes as reference compounds.[16,18,25] Therefore, the same approach was used for the spectral assignment of *N*-methylphenothiazine.

N-methylphenothiazine with 26 atoms and C_s symmetry has 72 fundamental frequencies, i.e., 38A′ + 34A″. Here A′ is the symmetric vibration and A″ is the antisymmetric vibration. The complete IR and Raman spectral assignments of the all-isotope-substituted methylphenothiazines and their radical cations are listed in Tables 3 and 4. The Raman spectral assignments of *N*-methylphenothiazine and its radical cation are in accordance with those reported previously.[26,27] The assignments for the heavy-atom-substituted methylphenothiazines are straightfor-

TABLE 4: Fundamental Vibrational Frequencies (cm^{-1}) of [^{13}C]MPT, [^{13}C]MPT$^{\bullet+}$ClO$_4^-$, [^{15}N,^{13}C]MPT, and [^{15}N,^{13}C]MPT$^{\bullet+}$ClO$_4^-$ [a]

mode symmetry	[^{13}C]MPT		[^{13}C]MPT$^{+\bullet}$		normal coordinate	[^{15}N,^{13}C]MPT		[^{15}N,^{13}C]MPT$^{+\bullet}$		normal coordinate
	IR	Raman	IR	Raman		IR	Raman	IR	Raman	
A′	3052 (m)		3050 (m)		ν(CH)	3051 (m)		3053 (m)		ν(CH)
		1592 (s)		1598 (s)	ν(CC)		1591 (s)		1600 (s)	ν(CC)
	1591 (vs)		1592 (w)		ν(CC)	1590 (vs)		1594 (w)		ν(CC)
		1570 (vs)		1577 (m)	ν(CC)		1569 (vs)		1568 (vs)	ν(CC)
	1565 (vs)		1536 (vs)		ν(CC)	1565 (vs)		1534 (vs)		ν(CC)
	1489 (s)		1487 (w)		ν(CC)	1487 (s)		1487 (w)		ν(CC)
		1490 (m)		1494 (m)	ν(CC)		1488 (w)		1487 (s)	ν(CC)
	1452 (vs)	1455 (w)	1459 (m)	1436 (m)	ν(CC)	1444 (vs)	1442 (w)	1459 (m)		ν(CC)
	1439 (vs)		1437 (s)					1437 (s)		
		1331 (m)		1330 (m)					1340 (s)	
	1326 (vs)		1326 (s)		methyl twisting	1315 (vs)	1315 (w)	1318 (s)	1318 (w)	methyl twisting
		1305 (m)					1302 (m)			
	1285 (vs)		1293 (s)		ν(CC)	1282 (s)		1289 (m)		ν(CC)
		1288 (w)		1292 (w)	ν(CC)		1283 (w)		1286 (w)	ν(CC)
	1251 (vs)	1256 (s)		1255 (m)	ν(CN)		1249 (vs)		1253 (s)	ν(C^{15}N)
	1244 (vs)		1245 (s)	1242 (w)	ν(CN)	1241 (vs)		1242 (s)		ν(C^{15}N)
		1164 (m)		1160 (m)	β(CH)		1164 (m)		1161 (m)	β(CH)
	1161 (m)		1176 (s)		β(CH)	1162 (m)		1175 (s)		β(CH)
		1138 (w)		1138 (w)	β(CH)	1241 (w)				β(CH)
	1132 (vs)				β(CH)	1132 (vs)				β(CH)
				1121 (m)	β(CH)				1125 (m)	β(CH)
		1104 (s)		1103 (m)	ν(CS)		1099 (s)		1100 (s)	ν(CS)
	1103 (w)		1085 (vs)		ν(CS)	1097 (s)		1083 (vs)		ν(CS)
	1035 (vs)	1035 (vs)		1033 (s)	γ(CS)	1035 (s)	1034 (m)		1032 (s)	γ(CS)
	859 (vs)									
	843 (s)		863 (m)		ν(CN)	851 (vs)		852 (m)		ν(C^{15}N)
		840 (w)		853 (w)	ν(CN)		854 (m)		847 (w)	ν(C^{15}N)
		673 (s)		678 (m)	δ(CCC)		672 (s)		667 (m)	δ(CCC)
	668 (s)		667 (w)		ν(CS)	668 (s)		661 (w)		ν(CS)
	600 (m)		622 (vs)		δ(CCC)	600 (m)		622 (vs)		δ(CCC)
	575 (vs)	575 (w)	598 (s)		δ(CCC)	574 (s)	574 (m)	597 (vs)		δ(CCC)
		492 (m)		490 (w)	δ(CCC)		496 (m)			δ(CCC)
	490 (vs)				δ(CSC)	488 (s)		488 (w)		δ(CSC)
		332 (vs)		473 (s)	δ(CNC)		328 (vs)		471 (s)	δ(C^{15}NC)
A″	974 (s)		955 (m)		γ(CH)	975 (s)		953 (m)		γ(CH)
		935 (w)		940 (m)						
	935 (s)					935 (s)				
		757 (w)		760 (w)	γ(CH)		765 (m)		761 (m)	γ(CH)
	761 (vs)		755 (vs)		γ(CH)	761 (vs)		754 (vs)		γ(CH)
	755 (vs)					760 (vs)				
	724 (vs)	726 (s)	722 (w)	721 (w)	γ(CC)	725 (vs)	727 (s)	721 (w)		γ(CC)
	693 (s)		709 (s)		γ(CC)	693 (s)		708 (s)	704 (w)	γ(CC)
	539 (vs)	539 (vs)	544 (m)	532 (w)	γ(CC)	536 (s)	537 (s)	541 (m)	538 (m)	γ(CC)
	448 (w)	439 (w)	448 (m)	453 (w)	γ(CS)	442 (w)	440 (m)	448 (s)		γ(CS)
	430 (s)				γ(CS)	429 (s)				γ(CS)
	411 (s)					412 (m)				
		355 (m)		346 (m)			352 (m)		367 (m)	
		295 (m)					290 (m)		321 (m)	
		245 (m)					244 (m)			
		186 (vs)		242 (w)	δ(CSC)		185 (vs)		250 (m)	δ(CSC)
		153 (s)		200 (vs)			152 (s)		196 (vs)	

[a] s = strong, vs = very strong, m = medium, w = weak, ν = stretching, δ = bending, β = in-plane deformation, γ = out-of-plane deformation.

ward, since they showed similar IR and Raman spectra relative to their ^{14}N- and/or ^{12}C-analogues, and frequency shifts due to the heavy-atom substitution are obvious.

The spectral assignments of the *N*-methylphenothiazine radical cation and its isotope-substituted analogues were performed by using a similar approach with reference to the Raman spectral assignment of the *N*-methylphenothiazine radical cation reported by Hester et al.[26] The four radical cations showed additional strong IR bands of perchlorate at 1080 and 630 cm^{-1} with respect to their parent molecules. All the IR and Raman assignments are listed in Tables 3 and 4.

It can be seen from Tables 3 and 4 that transformation of the *N*-methylphenothiazines to their radical cations brings about significant changes in their IR and Raman spectra. For instance, the 1565 cm^{-1} A′ C−C stretching in MPT is 29 cm^{-1} higher than the corresponding vibration in MPT$^{\bullet+}$ClO$_4^-$ (1536 cm^{-1}). The 187 cm^{-1} C−S−C and 332 cm^{-1} C−N−C skeletal deformation bands in MPT move to remarkably higher frequencies (249 and 473 cm^{-1}, respectively) in MPT$^{\bullet+}$ClO$_4^-$. These shifts reveal a significant structural change upon radical cation formation, i.e., a lessening on the degree of folding along the S−N axis,[26] which has been proved by X-ray single-crystal diffraction.[28] It is also shown that although the change in mass is relatively small, replacement of a ^{14}N atom by ^{15}N and/or ^{12}C by ^{13}C brings about appreciable frequency shifts of not only the N−C and C(methyl)−H stretching but also some of the ring C−C and C−H vibrations. Therefore, it is clear that radical cation formation and isotope substitution may result in a nonzero enthalpy change for reactions 3−7. Vibrational bands that are effective for the enthalpy change of eqs 3−7 are summarized in Tables 5−9. The remaining vibrations showed very small effects and are not included in the tables. On the basis of these

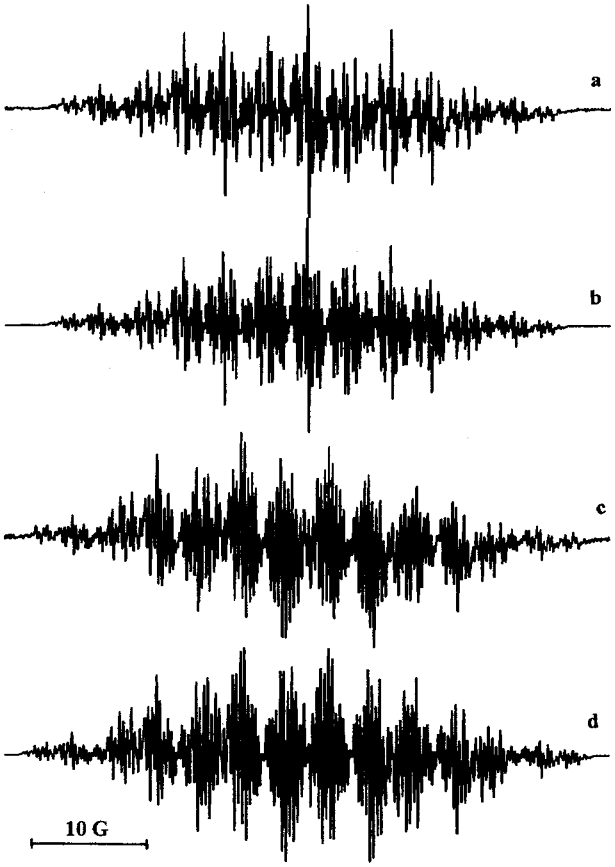


Figure 3. ESR spectra of ^{13}C-substituted methylphenothiazine radical cations recorded in acetonitrile solution at 25 °C: (a) $[^{13}C,^{15}N]MPT^{•+}$, 2.75×10^{-4} M; (b) computer simulation of (a), line width $\Delta H_{pp} = 0.18$ G (for hfcs see text); (c) [13C]MPT$^{•+}$, 2.55×10^{-4} M; (d) computer simulation of (d), line width $\Delta H_{pp} = 0.18$ G (for hfcs see text).

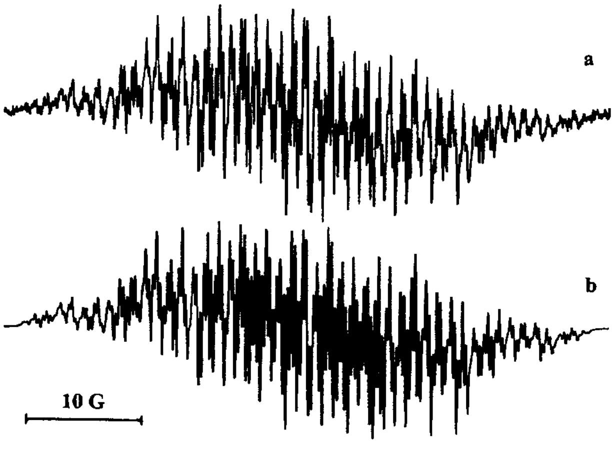


Figure 4. Representative ESR spectrum obtained from a mixture of $^{15}N,^{13}C$-methylphenothiazine radical cation perchlorate and N,^{13}C-methylphenothiazine recorded in acetonitrile solution at 25 °C: (a) $[[^{13}C,^{15}N]MPT^{•+}]_0 = 2.75 \times 10^{-4}$ M, $[[^{13}C]MPT]_0 = 3.28 \times 10^{-4}$ M; (b) computer simulation of (a) generated by using a molar ratio of $[^{13}C,^{15}N]MPT^{•+}/[^{13}C]MPT^{•+}$ of 1:1.35, corresponding to $K_2 = 1.24$ for reaction 4.

vibrations, the enthalpy change for reactions 3−7 due to the zero-point energy effect can be calculated. Since the electron transfer between two structurally similar species would not bring about an entropy change,[29] thus giving an identical free energy and enthalpy change, the equilibrium constants for reactions 3−7 can be estimated from the IR and Raman frequency shifts and listed in Table 2.

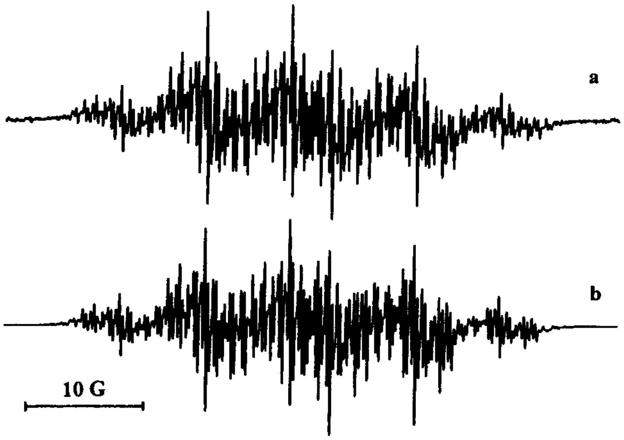


Figure 5. Representative ESR spectrum obtained from a mixture of ^{15}N-methylphenothiazine radical cation perchlorate and $^{15}N,^{13}C$-methylphenothiazine recorded in acetonitrile solution at 25 °C: (a) $[[^{15}N]MPT^{•+}]_0 = 2.50 \times 10^{-4}$ M, $[[^{13}C,^{15}N]MPT]_0 = 1.00 \times 10^{-4}$ M; (b) computer simulation of (a) generated by using a molar ratio of $[^{13}C,^{15}N]MPT^{•+}/[^{13}C]MPT^{•+}$ of 1:0.39, corresponding to $K_3 = 1.06$ for reaction 5.

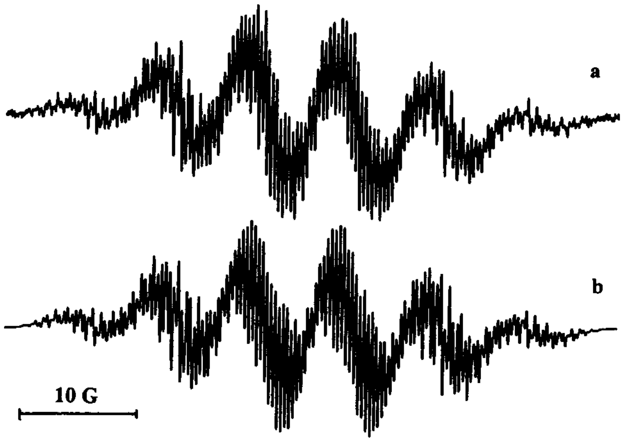


Figure 6. Representative ESR spectrum obtained from a mixture of *N*-methyl-^{13}C-phenothiazine radical cation perchlorate and *N*-methylphenothiazine recorded in acetonitrile solution at 25 °C: (a) $[[^{13}C]MPT^{•+}]_0 = 2.55 \times 10^{-4}$ M, $[MPT]_0 = 2.54 \times 10^{-4}$ M; (b) computer simulation of (a) generated by using a molar ratio of $[^{13}C]MPT^{•+}/MPT^{•+}$ of 1:1.02, corresponding to $K_4 = 1.06$ for reaction 6.

Discussion

It is clearly seen from Table 2 that the electron transfer from *N*-methylphenothiazine to its ^{15}N- and/or ^{13}C-substituted radical cations is isotopically selective. The electron transfers preferentially from the light-isotope-substituted molecule to its heavy-isotope-substituted radical cation. In other words, it is easier for the neutral light-isotope-substituted molecule to lose an electron than it is for the heavy-isotope-substituted molecule to form the corresponding radical cation. ^{15}N substitution significantly increases the ionization potential of the neutral *N*-methylphenothiazine molecule and the electron affinity of its radical cation. ^{13}C substitution behaves similarly but to a lesser extent. These results are in general agreement with the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ equilibrium isotope effects in the nitrobenzene/nitrobenzene radical anion system and in the fluorenone/fluorenone radical anion systems, respectively, reported previously by Stevenson and co-workers.[1c,e] Electron-transfer reactions 3−7 can construct two reaction cycles as shown in Scheme 1. In the scheme the arrow designates the electron transfer from the neutral molecule to its isotope-substituted radical cations and the number in the parentheses marks the reaction involved.

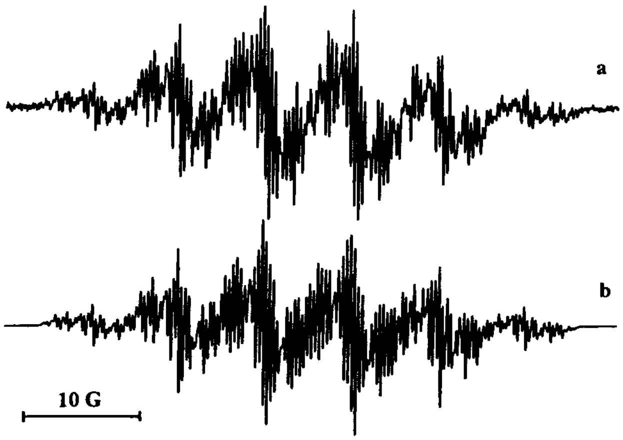
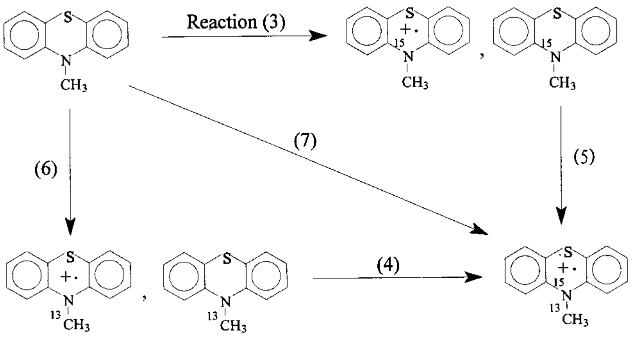


Figure 7. Representative ESR spectrum obtained from a mixture of *N*-methylphenothiazine radical cation perchlorate and ^{15}N-methyl-^{13}C-phenothiazine recorded in acetonitrile solution at 25 °C: (a) $[MPT^{\bullet+}]_0 = 2.48 \times 10^{-4}$ M, $[[^{13}C,^{15}N]MPT]_0 = 1.00 \times 10^{-4}$ M; (b) computer simulation of (a) generated by using a molar ratio of $MPT^{\bullet+}/[^{13}C,^{15}N]MPT^{\bullet+}$ of 1:0.37, corresponding to $K_5 = 1.30$ for reaction 7.

SCHEME 1



With the data listed in Table 2 it can be seen that the free energy changes for these reactions are additive. That is, the $\Delta G°_{ESR}$ of −591.9 J/mol for reaction 7 is reasonably consistent with the sum of the $\Delta G°_{ESR}$ for reactions 3 and 5, i.e., $-430.8 + (-144.3) = -575.1$ J/mol, and with that for reactions 4 and 6, i.e., $-144.3 + (-388.8) = -533.1$ J/mol. A similar additive effect on the EIE has been reported previously in electron-transfer processes between the benzene radical anion and its perdeuterated and per-^{13}C-substituted molecules.[1h,9,30]

The EIE caused by heavy-isotope substitution in the benzene/perdeuteriobenzene radical anion system has been rationalized by the zero-point energy effect (ZPE) upon the isotope substitution.[1b,h] We have compared IR and Raman spectra of thianthrene, perdeuterated thianthrene, their radical cations[17] and those of phenothiazine, and ^{15}N-substituted phenothiazine and its radical cation.[18] It was found that significant low-frequency shifts took place upon the heavy-isotope substitution and radical cation formation and that the free energy change evaluated from the frequency shifts was in good agreement with that determined by ESR spectroscopy.[17,18] In the present work the free energy

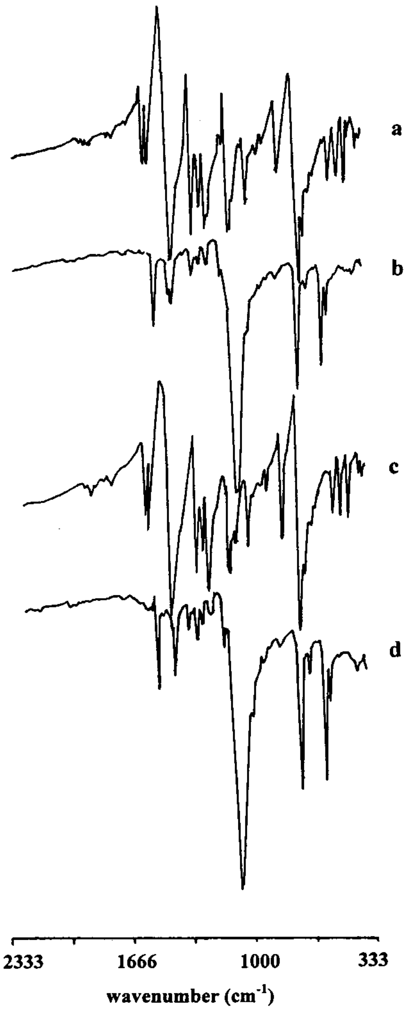


Figure 8. IR spectra of MPT (a), $MPT^{\bullet+}ClO_4^-$ (b), $[^{15}N]MPT$ (c), and $[^{15}N]MPT^{\bullet+}ClO_4^-$ (d).

TABLE 5: Selected IR and Raman Frequencies (cm^{-1}) of MPT, $MPT^{\bullet+}ClO_4^-$, $[^{15}N]MPT$, and $[^{15}N]MPT^{\bullet+}ClO_4^-$ That Contribute to $\Delta H°$ for Reaction 3[a]

assignment	MPT	$MPT^{\bullet+}$	$[^{15}N]MPT$	$[^{15}N]MPT^{\bullet+}$	contribution to $\Delta H°$ (J/mol)
A′ C−C stretching	1592	1601	1594	1598	−59.8
A′ C−C stretching	1590	1592	1590	1586	−72.0
A′ C−C stretching	1571	1579	1570	1568	−120.1
A′ C−H stretching	1449	1459	1452	1440	−145.2
A′ C−H in-plane deformation	1165	1163	1165	1159	−48.1
A′ C−H in-plane deformation	1161	1163	1165	1159	−48.1
A′ C−H in-plane deformation	1143	1139	1140	1140	48.1
A′ C−N stretching	1108	1099	1103	1099	59.8
A′ C−S stretching	1106	1086	1099	1086	84.1
A′ C−N stretching	846	855	850	845	−167.8
A′ C−S stretching	674	684	674	680	84.1
A″ C−H out-of-plane deformation	975	956	961	954	143.9
A″ C−N−C bending	947	944	948	937	−95.8
A″ C−H out-of-plane deformation	760	778	759	785 746	−143.9
A″ C−C out-of-plane deformation	728	728	730	727	−36.0

[a] Total contribution to $\Delta H° = -516.8$ J/mol.

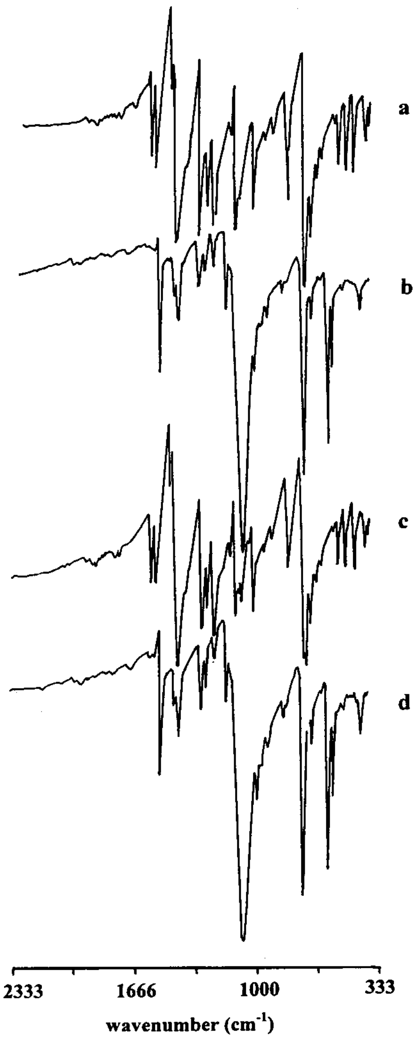


Figure 9. IR spectra of [^{13}C]MPT (a), [^{13}C]MPT$^{\bullet+}ClO_4^-$ (b), [^{15}N,^{13}C]-MPT (c), and [^{15}N,^{13}C]MPT$^{\bullet+}ClO_4^-$ (d).

changes for reactions 3−7 deduced from the IR and Raman spectra are in acceptable agreement with those obtained from the ESR determination (Table 2), demonstrating that the zero-point energy effect plays an important role in the isotope effect.

Marx et al.[6] have questioned the $^{15}N/^{14}N$ and $^{13}C/^{12}C$ isotope effects of unprecedented magnitude reported by Stevenson and co-workers, on the basis of statistic mechanical calculations of force constants using a cutoff model. Stevenson and co-workers[9−11] pointed out later that the isotope effect is strongly dependent on the specific anion radical/counterion ion-paring interaction and anion radical/solvent interactions that make the statistic mechanical calculation hard to account for. The present IR and Raman results indicate that an appreciable frequency shift takes place not only on bonds connected to the substituted isotope and next to the isotope but also on bonds far away from the isotope-substituted atoms. In addition, the molecular configuration of the radical cation is appreciably different from that of the parent molecule, as evidenced by the X-ray diffraction.[28] Therefore, it seems insufficient to evaluate the isotope effect by using the cutoff model that calculated only two bonds removed from the position of the isotope substitution and assumed the same molecular configuration for the neutral molecule and its ionic analogue.

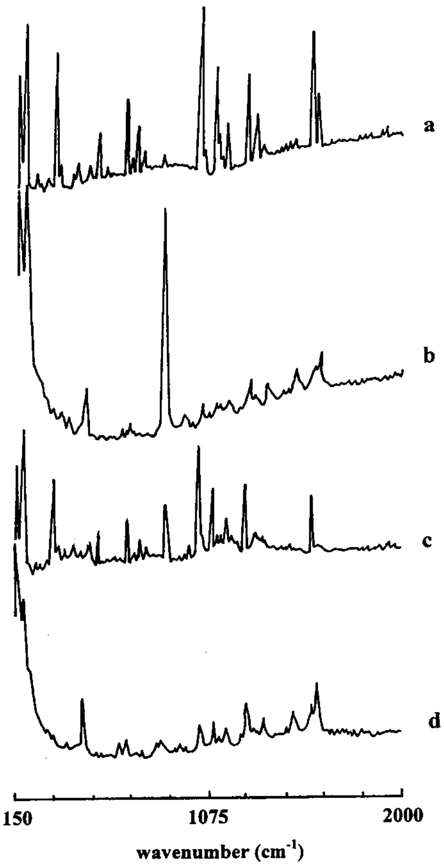


Figure 10. Raman spectra of MPT (a), MPT$^{\bullet+}ClO_4^-$ (b), [^{15}N]MPT (c), and [^{15}N]MPT$^{\bullet+}ClO_4^-$ (d).

It is worth noting that the present $^{15}N/^{14}N$ EIE of *N*-methylphenothiazines is remarkably different from that of phenothiazine reported previously.[18] Electron transfer from phenothiazine to the ^{15}N-substituted phenothiazine radical cation was found to possess a positive free energy change ($\Delta G° = 441.7$ J/mol) and an equilibrium constant of less than unity ($K = 0.77$). This may be caused by the significantly different

TABLE 6: Selected IR and Raman Frequencies (cm^{-1}) of [^{13}C]MPT, [^{13}C]MPT$^{\bullet+}ClO_4^-$, [^{15}N,^{13}C]MPT, and [^{15}N,^{13}C]MPT$^{\bullet+}ClO_4^-$ That Contribute to $\Delta H°$ for Reaction 4[a]

assignment	[^{13}C]MPT	[^{13}C]MPT$^{\bullet+}$	[^{15}N,^{13}C]MPT	[^{15}N,^{13}C]MPT$^{\bullet+}$	contribution to $\Delta H°$ (J/mol)
A′ C−C stretching	1592	1598	1591	1600	36.0
A′ C−C stretching	1591	1592	1590	1594	36.0
A′ C−C stretching	1570	1571	1569	1568	−95.8
A′ C−S stretching	1103	1085	1097	1083	48.1
A′ C−N stretching	840	853	854	847	−239.7
A′ C−N stretching	859	863	851	852	−131.8
A′ C−S stretching	673	678	672	667	−120.1
A″ C−H out-of-plane deformation	974	955	975	953	−36.0
A″ C−H out-of-plane deformation	757	760	765	761	−84.1
A″ C−C out-of-plane deformation	726	721	727	727	59.8

[a] Total contribution to $\Delta H° = -527.6$ J/mol.

TABLE 7: Selected IR and Raman Frequencies (cm^{-1}) of [^{15}N]MPT, [^{15}N]MPT$^{\bullet+}$ClO$_4^-$, [^{15}N,^{13}C]MPT, and [^{15}N,^{13}C]MPT$^{\bullet+}$ClO$_4^-$ That Contribute to Δ*H*° for Reaction 5[a]

assignment	[^{15}N]MPT	[^{15}N]MPT$^{\bullet+}$	[^{15}N,^{13}C]MPT	[^{15}N,^{13}C]MPT$^{\bullet+}$	contribution to Δ*H*° (J/mol)
A′ C−C stretching	1590	1586	1590	1594	95.8
A′ C−C stretching	1452	1440	1444	1459 1437	192.0
A′ C−H in-plane deformation	1165	1159	1164	1161	36.0
A′ C−H in-plane deformation	1154	1175	1162	1175	−95.8
A′ C−N stretching	1103	1099	1099	1100	59.8
A′ C−N stretching	852	870	851	852	−203.8
A′ C−S stretching	674	680	672	667	−131.8
A″ C−H out-of-plane deformation	961	954	975	953	−179.9
A″ C−H out-of-plane deformation	759	785 746	765	761	−120.1
A″ C−H out-of-plane deformation	752	756	761 750	754	−59.8
A″ C−C out-of-plane deformation	730	727	727	727	36.0

[a] Total contribution to Δ*H*° = −371.6 J/mol.

TABLE 8: Selected IR and Raman Frequencies (cm^{-1}) of MPT, MPT$^{\bullet+}$ClO$_4^-$, [^{13}C]MPT, and [^{13}C]MPT$^{\bullet+}$ClO$_4^-$ That Contribute to Δ*H*° for Reaction 6[a]

assignment	MPT	MPT$^{\bullet+}$	[^{13}C]MPT	[^{13}C]MPT$^{\bullet+}$	contribution to ΔH° (J/mol)
A′ C−C stretching	1592	1601	1592	1598	−36.0
A′ C−C stretching	1449	1459 1440	1459 1439	1459 1437	36.0
methyl twisting	1332	1344	1331	1330	−156.1
A′ C−H in-plane deformation	1143	1139	1138	1138	48.1
A′ C−N stretching	1108	1099	1104	1103	95.8
A′ C−S stretching	1106	1086	1103	1085	36.0
A″ C−S out-of-plane deformation	1037	1031	1035	1033	48.1
A′ C−N stretching	846	855	840	853	48.1
A′ C−N stretching	858	875	859 843	863	−71.9
A′ C−S stretching	674	684	673	678	−59.8
A″ C−N−C bending	947	944	935	940	95.8
A″ C−H out-of-plane deformation	760	778	757	760	−181.2
A″ C−H out-of-plane deformation	752	755	761 755	755	−72.0
A″ C−C out-of-plane deformation	728	728	726	721	−59.8

[a] Total contribution to Δ*H*° = −228.9 J/mol.

TABLE 9: Selected IR and Raman Frequencies (cm^{-1}) of MPT, MPT$^{\bullet+}$ClO$_4^-$, [^{15}N,^{13}C]MPT, and [^{15}N,^{13}C]MPT$^{\bullet+}$ClO$_4^-$ That Contribute to Δ*H*° for Reaction 7[a]

assignment	MPT	MPT$^{\bullet+}$	[^{15}N,^{13}C]MPT	[^{15}N,^{13}C]MPT$^{\bullet+}$	contribution to Δ*H*° (J/mol)
A′ C−C stretching	1571	1579	1569	1568	−107.9
A′ C−C stretching	1449	1459	1444	1459	48.1
A′ C−N stretching	1108	1099	1099	1100	120.1
A′ C−S stretching	1106	1086	1097	1083	72.0
A″ C−S out-of-plane deformation	1037	1034	1031	1032	48.1
A′ C−N stretching	846	855	854	847	−192.0
A′ C−N stretching	858	875	851	852	−192.0
A′ C−S stretching	674	684	672	667	−179.9
A″ C−H out-of-plane deformation	975	956	975	953	−36.0
A″ C−H out-of-plane deformation	760	778	765	761	−264.0
A″ C−H out-of-plane deformation	752	755	761 750	754	−84.1

[a] Total contribution to Δ*H*° = −767.6 J/mol.

distribution of spin and charge densities on the two radical cations. It is well-known that methyl substitution on the nitrogen atom of phenothiazine increases the spin and charge density on the nitrogen atom in its radical cation.[19,20,31] In the phenothiazine radical cation the spin and charge densities are predominantly localized on the sulfur atom, while in the *N*-methylphenothiazine radical cation they are predominantly localized on the nitrogen atom.[20] As a matter of fact, *N*-methyl substitution in phenothiazine causes a ∼17% of increase of the ESR ^{14}N and ^{15}N hypersplitting constants (see Table 2). Therefore, the counterion perchlorate anion would more strongly interact with the nitrogen atom of *N*-methylphenothiazine than with phenothiazine, forming an ion pair. Obviously, ^{15}N substitution would enhance this ion-paring interaction, leading to an increase of the electron affinity of the radical cation. It has been proved that the isotope effect on radical anion/neutral molecule systems strongly depends on the charge and spin densities in the area of isotope substitution[11] and on the ion-pairing interaction.[1c,f,i,25]

In conclusion, this work demonstrates that electron transfers in an isotopically selective manner between *N*-methylphenothiazine and its radical cation in solution. The ^{15}N- and/or ^{13}C-methyl substitution increases the ionization potential of *N*-methylphenothiazine and the electron affinity of its radical cation. These equilibrium isotope effects can be rationalized by a zero-

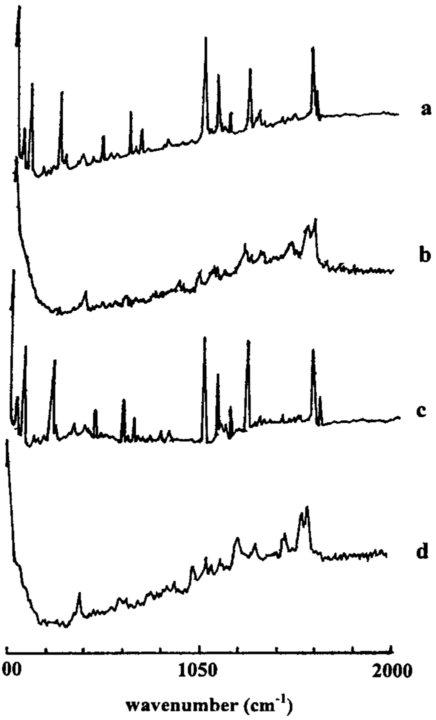


Figure 11. Raman spectra of [^{13}C]MPT (a), [^{13}C]MPT$^{\bullet+}$ClO$_4^-$ (b), [^{15}N,^{13}C]MPT (c), and [^{15}N,^{13}C]MPT$^{\bullet+}$ClO$_4^-$ (d).

point energy effect, an electronic effect, and ion-pairing interactions caused by isotope substitution and radical cation formation.

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