Free Radical Studies by Resonance Raman Spectroscopy: Phenothiazine, 10-Methylphenothiazine, and Phenoxazine Radical Cations

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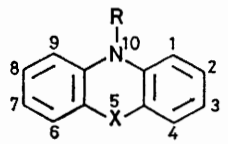
The free radical cations of phenothiazine, 10-methylphenothiazine, and phenoxazine have been formed by chemical oxidation of their parent compounds. The radicals all possess complex, intense visible absorption bands which allow excitation of their resonance Raman spectra throughout the visible region. The point-group symmetries of the parent compounds in solution have been determined as C_s for both phenothiazine and 10-methylphenothiazine, and C_{2v} for phenoxazine. A partial assignment of the Raman bands has been made for each radical cation studied. The relative intensities of Raman bands and the parent-to-radical frequency shifts observed have been interpreted in terms of the structural changes which occur on radical formation. An analysis of the phenothiazine radical cation visible absorption band, supplemented by resonance Raman data and excitation profiles, has yielded information on the excited-state geometry.

PHENOTHIAZINE (I) has been the subject of continued chemical interest during the past 50 years, initially because of the connection between it and numerous dyestuffs, and more recently because of the pharmacological properties [1] and the potential solar energy applications of substituted phenothiazines.[2] In particular,



(I) X=S, R=H
(II) X=S, R=Me
(III) X=O, R=H

much interest has been shown in the physicochemical tranquillizing ability of phenothiazine-based drugs and, despite the accumulation of a great wealth of information about the substituents necessary for neuroleptic activity, the effects of these substituents on the electronic structure of the phenothiazine molecule has not been fully resolved.

One common property of phenothiazine and its derivatives is their ease of oxidation. This has led some workers to suggest that phenothiazine tranquillizers are good electron donors and therefore might act as charge- or electron-transfer donors at drug receptor sites.[3] This idea has been supported by the discovery of many phenothiazine charge-transfer complexes.[4,5] However, others consider that the stable radical cations formed by phenothiazines may be of some importance in their biological activity.[6] Although phenothiazine itself possesses no tranquillizing properties (this action is reserved for aromatic ring-substituted phenothiazines), it is of interest to study the structural and electronic changes brought about by radical formation as manifested in its vibrational spectrum and thus to draw inferences about the behaviour in solution of the related drug molecules.

Cation radicals of the phenothiazine derivative were first obtained over 65 years ago by Pummerer and Gassner.[7] Since then, these long-lived stable free radicals have been prepared by various chemical,[8,9] photochemical,[10,11] and electrochemical routes [12] and have been subjected to extensive physicochemical studies both in solid and solution phases.

Here we present results of resonance Raman studies of the phenothiazine (I) and 10-methylphenothiazine (II) radical cations, together with the closely related phenoxazine (III) radical cation. An attempt is made to evaluate the structural changes between the parent and the radical and to unravel the complexities of the visible electronic absorption bands of the radical cations *via* plots of resonance Raman excitation profiles.

EXPERIMENTAL

Acetonitrile (Fisons S.L.R. grade) was purified and dried by the method of Forcier and Oliver.[13] It was stored over type 4A molecular sieves. Phenothiazine (Aldrich 97% purity) was recrystallized twice from benzene. Phenothiazine 5-oxide was prepared by the method of Gilman and Nelson [14] and had m.p. 242—245 °C (decomp.) (lit., 242 °C with decomp.). The phenothiazine radical cation was prepared as the perchlorate salt by chemical oxidation using the method of Billon [9] and had m.p. 174 °C (decomp.) (lit., 175 °C with decomp.).

10-Methylphenothiazine was prepared by treating the conjugate base of phenothiazine [generated in dimethyl sulphoxide (Fisons S.L.R. grade), by treatment of the parent with a slight excess of sodium hydride] [15] with an excess of methyl iodide (Fisons S.L.R. grade). The mixture was stirred under nitrogen for 1 h at 60 °C after which the solution was poured into ice–water acidified with HCl. The product was isolated and dried, then recrystallized twice from ethanol and had m.p. 102 °C (lit.,[14] 101—103 °C). 10-Methylphenothiazine 5-oxide was prepared as before,[14] as was the radical cation perchlorate.[9] Solutions of the radical cations (*ca.* 10^{-3}M) were prepared in dry acetonitrile containing *ca.* 2.5% v/v H_2SO_4.

Phenoxazine (Aldrich) was purified by vacuum sublimation. The radical cation was produced by the oxidation of the parent by the action of concentrated H_2SO_4.[16] The acid solution was then diluted using dry acetonitrile to a radical concentration of *ca.* 10^{-3}M.

The Raman instrumentation, computer link,[17] and spinning-cell technique [18] have been described elsewhere. The solutions were prepared as 20 cm^3 samples which were stable over a period of at least 10 h. The sample (*ca.* 1 cm^3) in the spinning cell was replaced hourly to minimize the effects of photodecomposition. Absorption spectra measured before and after 1 h exposure to the Raman laser showed only very slight (*ca.* 2%) photodecomposition.

E.s.r. spectra were obtained at ambient temperature using a Varian E3 spectrometer. The samples were prepared as for Raman measurements. All solutions and cells were purged with nitrogen.

RESULTS

The parent phenothiazine has no absorption in the 400—700 nm region of the spectrum but its radical cation posesses a very clearly resolved yet complex absorption band with maxima, in agreement with literature values,[15] occurring at 513 (ε 7 453 dm^3 mol^{-1} cm^{-1}), 495, 478, 462, and 435 nm (4 571 dm^3 mol^{-1} cm^{-1}) as shown in Figure 1. 10-Methylphenothiazine and phenoxazine also have no absorption in the 400—700 nm region and their radical cation absorption spectra, although similar to that of the phenothiazine radical cation, are less clearly resolved. The 10-methylphenothiazine radical cation gives maxima at 511 (ε 4 560 dm^3 mol^{-1} cm^{-1}), 492, 474, and 437 nm (1 791 dm^3 mol^{-1} cm^{-1}) as shown in Figure 2 while the phenoxazine radical cation gives maxima at 525, 490, and 406 nm (Figure 3).

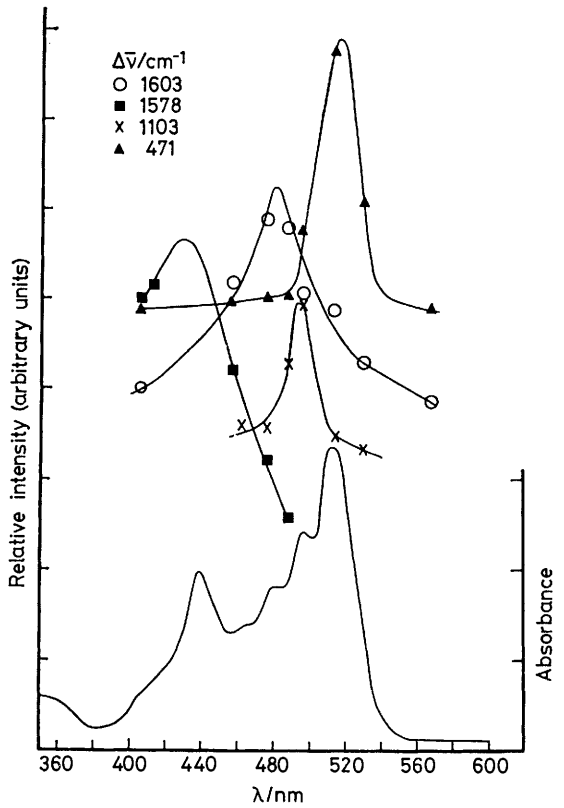


FIGURE 1 Visible absorption spectrum of the phenothiazine radical cation and excitation profiles of some prominent resonance Raman bands which have been calculated using the acetonitrile solvent 920 cm^{-1} band as an internal standard

Also shown in Figures 1—3 are excitation profiles calculated from some of the more intense resonance Raman bands, the relative intensities of which were strongly dependent upon the laser excitation wavelength. Band intensities have been fully corrected for the ν^4 scattering dependence, absorption, and the instrumental sensitivity variations. It is observed in Figure 1 that a close coincidence exists between components of the phenothiazine radical cation

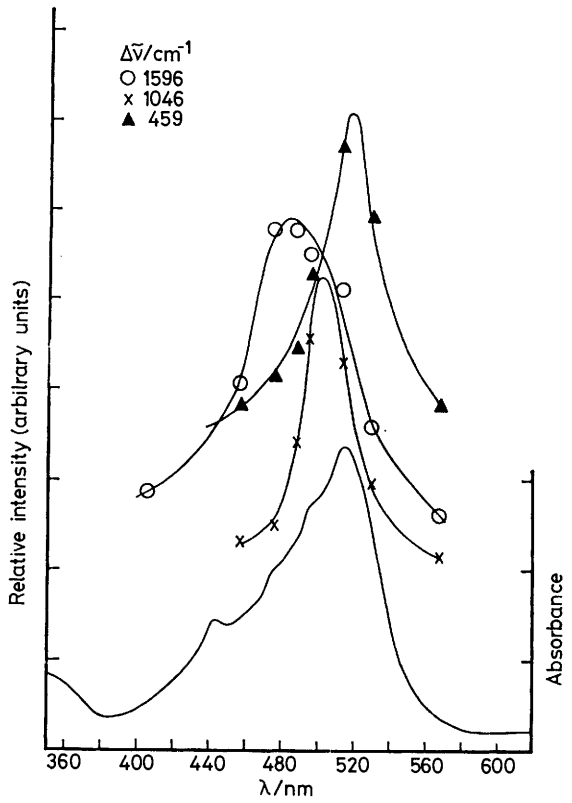


FIGURE 2 Visible absorption spectrum of the 10-methylphenothiazine radical cation and excitation profiles of some prominent resonance Raman bands which have been calculated using the acetonitrile solvent 920 cm^{-1} band as an internal standard

absorption spectrum and the excitation profiles of some of the Raman bands. However, the structure in the absorption band for 10-methylphenothiazine (Figure 2) is less distinct and is still less so for phenoxazine radical cation (Figure 3). Accordingly, the coincidences with the measured excitation profiles are less evident.

Figure 4 shows some resonance Raman spectra recorded for the phenothiazine radical cation and illustrates the dependence of the relative band intensities on changes in the wavelength of the exciting line. As can be seen, the 471 cm^{-1} band dominates the spectrum when 514.5 nm excitation is used and becomes progressively weaker as excitation is systematically moved to shorter wavelength, a progression which leads to other bands dominating the radical cation spectrum. Similar dependence of the relative band intensities on changes in the exciting line is also shown by the 10-methylphenothiazine and the phenoxazine radical cations; these spectra will be published elsewhere.[19] As is apparent from the excitation profiles (Figures 1—3), however, the relative intensities of the Raman bands for the phenoxazine radical cation spectra are all maximized when either 520.8 or 514.5 nm excitation is used; this is not the case for the phenothiazine and 10-methylphenothiazine radical cations. Figure 5 shows the resonance Raman spectra of approximately equimolar solutions of each of the radical cations studied, using the same exciting line (514.5 nm). As can be seen, the phenoxazine radical cation spectrum show two very prominent bands at low wavenumber compared to only one for phenothiazine cation and none for the 10-methylphenothiazine radical cation.

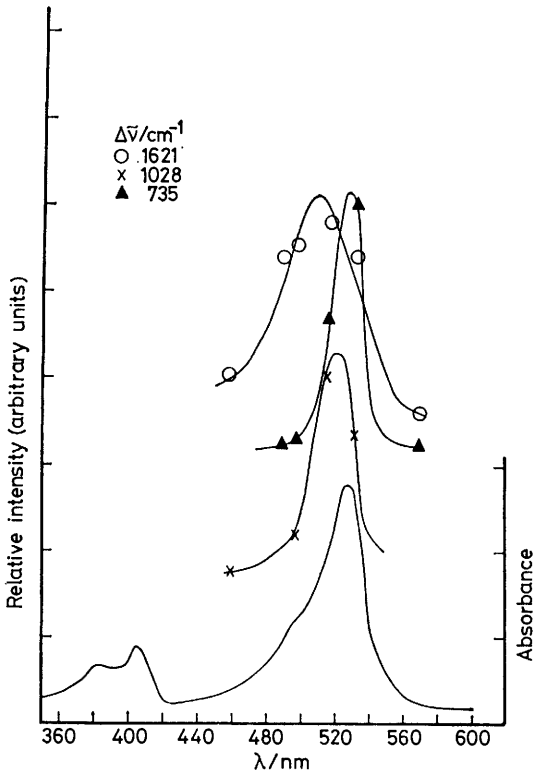


FIGURE 3 Visible absorption spectrum of the phenoxazine radical cation and excitation profiles of some prominent resonance Raman bands which have been calculated using the acetonitrile solvent 920 cm^{-1} band as an internal standard

The i.r. and Raman spectra (in solution and solid phases) of all three parent compounds were obtained in order to determine their symmetries. It was found for phenothiazine and 10-methylphenothiazine that many vibrational modes were both i.r. and Raman active, and that no major differences existed between spectra from solids and solutions. Phenoxazine showed fewer bands which were both i.r. and Raman active, but solution and solid phase spectra correlated well. Few large frequency shifts (>5 cm^{-1}) were observed upon dissolution of the parents in acetonitrile (those bands showing >5 cm^{-1} shifts are shown in Table 1); however, a marked change in the relative intensities of some low frequency bands was apparent in both the phenothiazine and 10-methylphenothiazine parent spectra, respectively (Figure 6).

Depolarization ratios have been measured for most Raman bands for each radical cation and in all cases these ratios were found to be 1/3. E.s.r. measurements have been made of all the radical cations studied and some of these data are summarized in Table 3.

DISCUSSION

The radical cations have been characterized by both their e.s.r.[20,21] and visible absorption [9,15] spectra. The e.s.r. spectra were assigned by comparison with previous work; the slight deviation in hyperfine splitting constants is attributed to either solvent effects or instrumental variations (Table 3).

Detailed assignments of vibrational modes for molecules of this complexity are at best approximate. In making band assignments we have made use of the previous Raman work on phenothiazines,[22] although we are not everywhere in agreement with this. Additionally, we have made use of data on diphenyl sulphide,[23]

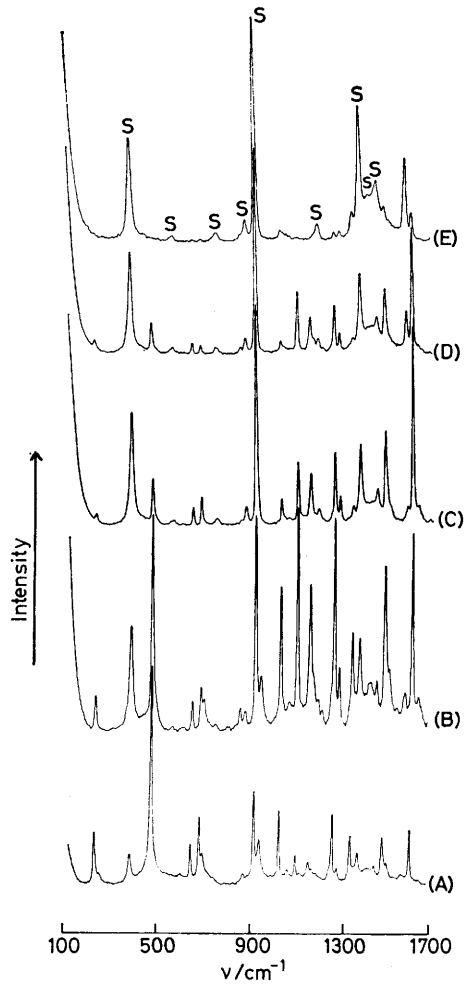


FIGURE 4 Resonance Raman spectra of the phenothiazine radical cation recorded between 100 and 1 700 cm^{-1} using (A) 514.5 nm, (B) 496.5 nm, (C) 476.8 nm, (D) 457.9 nm, Ar^+ excitation and (E) 406.7 nm Kr^+ excitation. All spectra have been digitally smoothed and backgrounds subtracted where necessary. Solvent bands marked S

phenazine,[24] and other simple sulphur and amino-compounds.[25] Use also was made of the intensities of the Raman bands, those of highest intensity being assigned to modes involving sulphur, consistent with its large polarizability. Due to the complexity of the molecules and in the absence of any isotopically substituted molecules, only a partial assignment of the spectra is offered (Table 2) for the radical cations.

The bands of particular interest are those showing the largest shifts from the corresponding parent, namely those assigned to the δ_d(CNC) and δ_d(CSC) skeletal deformation modes [see (IV)]. These band frequencies are given explicitly in Table 1 and assigned in Table 2.

TABLE 1

Comparison of Raman band wavenumbers (cm^{-1}) for phenothiazine (PTZ), 10-methylphenothiazine (10-MePTZ), and phenoxazine (phenox) and their radical cations

Raman wavenumbers (cm^{-1})								
PTZ [a]	$PTZ^{+\cdot}$ [b]	$PTZ^{+\cdot}$ − PTZ [c]	10-MePTZ [a]	$10\text{-MePTZ}^{+\cdot}$ [b]	$10\text{-MePTZ}^{+\cdot}$ − 10-MePTZ [c]	Phenox [a]	$Phenox^{+\cdot}$ [b]	$Phenox^{+\cdot}$ − Phenox [c]
1 633vw	1 630w	−3	1 623w			1 644m (sh)		
1 598s	1 603s	+4	1 592m	1 596s	+4	1 632s		
1 569s	1 578s	+9	1 570s	1 573m-s	+3	1 623m (sh)	1 621s	−1
	1 570m [d]	or −1		1 538w		1 586s	1 592m-w	+6
1 552vw	1 535w	−17	1 492w	1 495m	+3		1 587m-w	or +1
	1 501m (sh)			1 485m			1 563w	
1 489w	1 482s	−7	1 470w	1 474m	+4	1 511m		
1 464w			1 361w	1 344m	−17	1 500m	1 498s	−2
	1 418m		1 333w	1 337m	+4	1 466w	1 472w	+6
1 341vw	1 342s	+1	1 306m			1 405m	1 399w	−6
1 302w	1 332m (sh)	+30	1 290w (sh)	1 291s	+1	1 343m	1 345s	+2
1 281w	1 285m	+4	1 260s	1 252s	−8		1 315m	
1 259m (sh)	1 263s	+4	1 231w			1 335m (sh)		
1 247s	1 248m (sh)	+1		1 189m		1 298w	1 295w-m	−3
1 193vw	1 208w	+15	1 166m	1 163m	−3	1 260s	1 243w	−17
	1 171m (sh)		1 141m-w			1 239w (sh)	1 230m	−9
1 155m	1 157s	+2	1 124m			1 195m-s		
1 130m	1 125vw	−5	1 108s	1 118s	+10	1 182w (sh)	1 181w (sh)	−1
1 083s	1 103s	+20	1 075w	1 095w	+20	1 154m	1 159m	+5
1 063w	1 066w	+3	1 053m (sh)				1 134m	
1 033vs	1 030s	−3	1 038vs	1 046s	+8		1 102w	
	944m (sh)			1 034m (sh)		1 031vs	1 028m-s	−3
883w			973w			1 020m (sh)	1 017m-s	−3
854w	854m-w	0	862w				981m-w	
750w			757m-w	678m-s	+11	898m-w		
716w	697m	−19	728m	715w	−13		822w	
681m	684m	+3	698w		or +17		801w	
652w	646m	−6	673m-s	666s	−5	719m (sh)		
595w	561w	−34	570w	571w-m	+1	734m-s	735vs	+1
537w		or +24	540m	545w	+5	666w	661m-s	−5
492w			496w			589m (sh)		
430m	447w	+15	442w	451m (sh)	+9	576m	579vs	+3
343s	471vvs	+128	355w	343m	−12	534m-w		
(291m) [a]			331s	459s	+128	520m-w		
277m			298w			395s	401m-s	+6
254m			264vw			278m-s	287w	−1
240w	244m	+4	243w			268m (sh)		
184s	224m	+40	185s	245m	+60	240w	238w-m	−2
[171 (sh)] [a]				195w				

[a] Wavenumbers listed are for parents in the solid phase; these showed little change (+5 cm^{-1}) upon dissolution. Wavenumbers in parentheses are taken from solution phase and show >5 cm^{-1} shift. [b] Band intensities are strongly dependent upon excitation wavelength used. [c] Differences are calculated between the radical cations and the parent wavenumbers recorded from the solid phase. [d] Only apparent with blue excitation (see excitation profiles, Figure 1).

Key: v = very, s = strong, m = medium, w = weak, (sh) = shoulder.

These provide the most significant information concerning the structural changes in the phenothiazines brought about by radical formation.

The geometry of the phenothiazine and phenoxazine radical cations in the solid state and of their parent compounds has been established previously, as has the structure of the parent 10-methylphenothiazine. The structural geometry of the phenothiazine parent is as represented in (IV), with a dihedral angle of 158.5°.[26] This angle increases on radical formation to 172°.[27] The dihedral angle for the 10-methyl salt has been measured as 143.7° in the parent [28] and we assume this too will open out to some degree on radical formation.

Crystal structure studies have shown that phenoxazine [29] is planar, as is its radical cation.[27]

The geometry of these molecules in solution has not been established with certainty. However, e.s.r. studies [20] have assumed the presence of a large dihedral angle [small degree of fold along the S–N axis (IV)] for the phenothiazine radical cation, which decreases upon methylation (larger degree of fold). Accordingly, the i.r. and Raman data for the parent phenothiazine compounds and those for the radical cations may be interpreted in terms of the point group symmetries of both the parents and radicals in solution being C_s. The close similarity of solid and solution phase spectra indicates that there is no gross change in overall symmetry in solution. The number of resonance-enhanced Raman bands is consistent with this. The phenoxazine parent and radical cation have both been taken to be planar (C_{2v}) in solution, consistent with the fact that fewer of the Raman bands are resonance-enhanced as compared with the phenothiazines.

The decrease observed (Figure 6) in the relative intensities of the δ_d(CNC) and δ_d(CSC) skeletal deformation bands upon dissolution of the phenothiazine parent in acetonitrile can be interpreted in terms of a lessening in the degree of fold along the S–N axis. The possibility of this being due to pre-resonance was investigated;

TABLE 2

Assignments of major resonance Raman bands for phenothiazine ($PTZ^{+\cdot}$), 10-methylphenothiazine (10-$MePTZ^{+\cdot}$) and phenoxazine ($phenox^{+\cdot}$) radical cations

$PTZ^{+\cdot}$	10-$MePTZ^{+\cdot}$	$Phenox^{+\cdot}$	Assignment *
1 630			
1 603	1 596	1 621	} Ring C–C str.
1 578	1 573	1 592	
1 570		1 587	
1 535	1 538	1 563	
1 501	1 495		
1 482	1 485	1 498	Ring C–C str.
		1 472	735 × 2
	1 474		$\delta(CH_3)$
1 418			471 × 3
		1 399	
1 342	1 344	1 345	Ring C–C str.
		1 315	735 + 579
1 332	1 337		
1 285	1 291	1 295	β(CH)
1 263			
1 248	1 252	1 243	
1 208		1 230	
1 171	1 189	1 181	β(CH)
1 157	1 163	1 159	β(CH)
		1 134	735 + 401
1 125		1 102	
1 103	1 118	1 017	Ring C–N str.
1 066	1 095		
1 030	1 046	1 028	Ring C–S str./ Ring C–O str.
	1 034		$\nu_{as}(N–CH_3)$
		981	579 + 401
944			471 × 2
854		822	
		801	401 × 2
	768		$\nu_s(N–CH_3)$
697	715		
		735	δ(CNC)/δ(COC) i.p. skel. def.
684	666		$\nu_s(C–S)$
646		661	
		579	δ(CCC) i.p. skel. def.
561	571		
	545		
471	459		δ_d(CNC) skel. def.
447	451	401	δ(CCC) i.p. skel. def.
	343		
224	245		δ_d(CSC) skel. def.
		287	
244	195	238	

* Key: approx. description, only major contribution listed. ν or str. = stretching (s = symmetric, as = asymmetric), β = in-plane bending, i.p. = in plane, δ = bending, skel. def. = skeletal deformation.

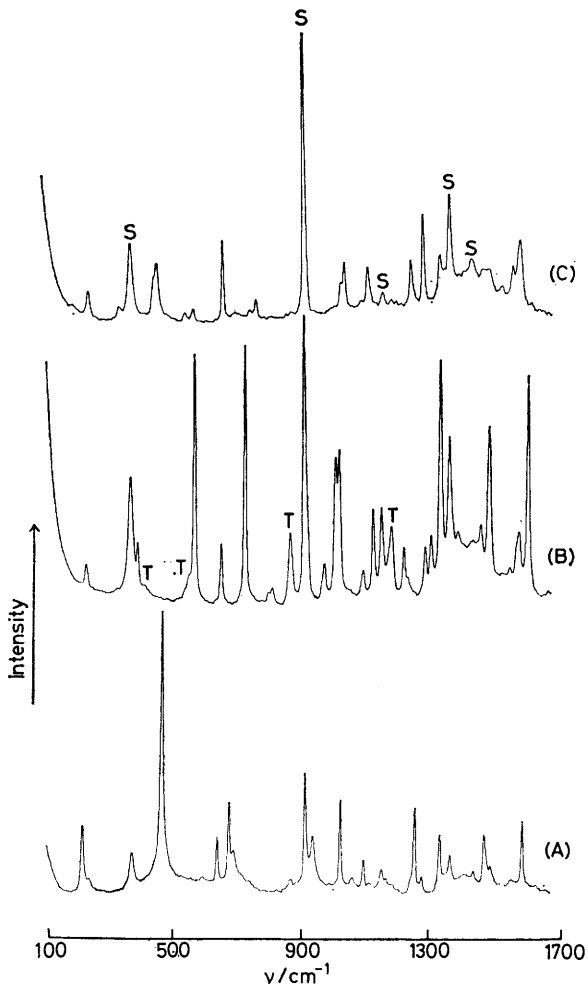


FIGURE 5 Resonance Raman spectra of (A) phenothiazine, (B) phenoxazine, and (C) 10-methylphenothiazine radical cations recorded between 100 and 1 700 cm^{-1} using 514.5 nm Ar^+ excitation. All spectra have been digitally smoothed and backgrounds subtracted. Solvent bands common to all spectra are marked S. Sulphuric acid bands marked T. Intensity changes relative to the solvent bands are due to changing resonance effects from (A) to (C)

however, the same phenomenon was observed when 647.1 nm excitation was used.

An increase in the dihedral angle [see (IV)] leads to better π-orbital overlap between the ring C and N atoms and also the ring C and S atoms and thus greater aromatic resonance stabilization of the structure. The band intensities (Figures 4 and 5) and frequency shifts (Table 1) observed in the phenothiazine and 10-methylphenothiazine radical spectra are consistent with the dihedral angle becoming greater than in the parents. The lack of frequency shifts (Table 1) observed in the case of the phenoxazine radical cation supports the view that very little structural change occurs upon radical formation,

TABLE 3

E.s.r. hyperfine splitting constants for the phenothiazine and 10-methylphenothiazine radical cations and phenoxazine radical cation in acetonitrile

Radical	a_N/mT	a_{H_2}/mT	a_{H_3}/mT	$a_N : a_{H_2}$	$a_N : a_{H_3}$
Phenothiazine	0.650	0.050	0.257	13.000	2.529
	(0.634)	(0.050)	(0.249)	(12.680)	(2.546)
10-Methylphenothiazine	0.755	0.072	0.213	10.49	3.545
	(0.749)	(0.073)	(0.212)	(10.260)	(3.533)
Phenoxazine	0.775	0.065	0.325		
	(0.790)	(0.072)	(0.330)		

Values in parentheses, see refs. 20 and 21.

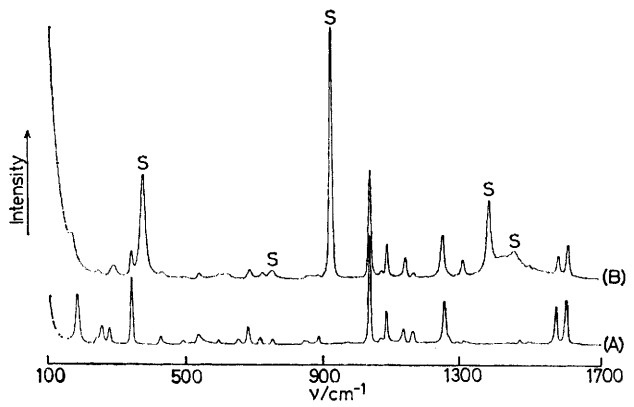
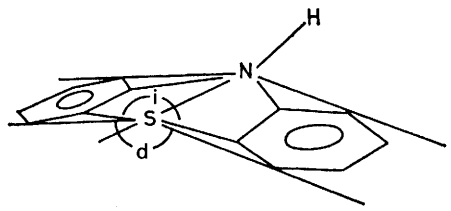


FIGURE 6 Raman spectra of phenothiazine recorded as (A) solid, (B) solution in acetonitrile, between 100 and 1 700 cm^{-1} using 514.5 nm Ar^+ excitation. Both spectra have been digitally smoothed and scaled on the 1 033 cm^{-1} band. Solvent bands marked S

since both the parent and radical cation are planar in solution as in the solid state. In the phenothiazine radical cation spectrum the most enhanced band is that at 471 cm^{-1}, assigned to the δ_d(CNC) skeletal deformation mode. This represents a large positive shift of 128 cm^{-1}

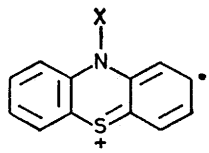


(IV)

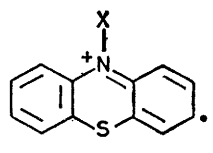
i = internal CSC angle
d = dihedral angle
(i.e. 158·5°)

from the parent, consistent with a lessening in the degree of fold along the S–N axis (*i.e.* increase in the dihedral angle). The δ_d(CSC) and ring C–N stretch bands (see Table 2) show positive wavenumber shifts of 40 and 20 cm^{-1}, respectively, on radical formation, which again is consistent with a more planar radical configuration.

The 10-methylphenothiazine radical cation spectra show no band which is singularly dominant. The differences observed in the frequency shifts and relative band intensities for the structurally important bands, compared with the phenothiazine radical cation spectra, indicate that somewhat different structural changes occur on radical formation. The bands from which structural changes may be inferred, again, are those principally involving the δ_d(CNC) and δ_d(CSC) modes (Table 2). The lack of enhancement of the δ_d(CNC) band implies a greater degree of non-planarity around the C–N–C moiety than for the phenothiazine radical cation, consistent with the *X*-ray crystallographic data of the parent compounds (discussed previously). However, the large positive wavenumber shift observed (128 cm^{-1}, Table 1) is similar to that seen for the phenothiazine radical cation. Supporting the interpretation of greater non-planarity around the C–N–C moiety for the 10-methylphenothiazine radical cation is the smaller shift observed in the ring C–N stretch mode (+10 cm^{-1}) compared with that observed for the phenothiazine system (+20 cm^{-1}). The methyl substituent at the N atom appears to hinder the conjugation of the N p_π-orbital with the aromatic carbons so that the preferred electronic structure then favours increased involvement of the S-atom in the conjugated aromatic system, as in (V). One consequence of this is the increase observed in the enhancement of the ν_s(C–S) band intensity (see Figure 5 and Table 2). In addition, the δ_d(CSC) band shift (parent-to-radical) is increased from +40 cm^{-1} for phenothiazine to +60 cm^{-1} for 10-methylphenothiazine (see Table 1).



(V)



(VI)

The arguments above concerning the solution structures of the phenothiazine and 10-methylphenothiazine radical cations are further supported by the e.s.r. data measured by us and previously by others [20] (Table 3). The ratios of the hyperfine splitting constants $a_N : a_{H_3}$ and $a_N : a_{H_1}$ have been calculated for each radical. The ratio of $a_N : a_{H_3}$ has been interpreted [20] in terms of the change in the dihedral angle of the radical cations studied. It may also be used, together with the ratio $a_N : a_{H_1}$, to discriminate between alternative canonical forms for both the phenothiazine and 10-methylphenothiazine radical cations, respectively. The lower ratio of $a_N : a_{H_1}$ for the 10-methylphenothiazine radical cation indicates that the canonical form (V) is of relatively greater importance than for the phenothiazine radical cation, for which (VI) is relatively more prominent. More recent analysis of the e.s.r. data,[30] also supporting our interpretations, has made use of Hückel–McLachlan calculations to obtain a reasonable theoretical fit with the experimental values observed for the 10-methylphenothiazine radical cation. This fit was only achieved by decreasing the k_{CN} and increasing k_{CS} overlap integrals, thus supporting the greater relative importance of (V) among the possible resonance structures for the 10-methylphenothiazine radical cation.

A small number of bands dominate the low wavenumber region in the spectrum of the phenoxazine radical cation. Those at 401, 579, and 735 cm^{-1} have been assigned, on the basis of previous work on phenazine,[24] the 5,10-dihydrophenazine radical cation (to be published),[19] and by comparison with the vibronic spacings observed in the phenothiazine radical cation absorption spectrum (see later), to δ(CCC) in plane and δ(CNC)/

(COC) skeletal deformation modes (see Table 2). The vibrational frequencies and relative band intensities of these modes support the assumption of a planar radical cation and that little structural change for the parent is brought about upon radical formation. As noted previously, no large frequency shifts (parent-to-radical) were observed with this system.

The resonance Raman spectra and the excitation profiles (Figures 1—3) have been used in an attempt to interpret the complex nature of the visible absorption bands obtained from the radical cations. The most interesting and informative absorption spectrum, by virtue of its relatively well resolved vibronic fine structure, is that of the phenothiazine radical cation. It is not uncommon with resonance Raman scattering to observe one dominant vibration in the spectrum which most efficiently couples the ground to the excited state. As is apparent from the phenothiazine radical cation spectra this vibration is assigned to the δ_d(CNC) skeletal deformation mode.

In a recent photoelectron study [31] of the phenothiazine parent molecule it was established that the first ionization band has substantial N lone-pair character. It was suggested, from the shape of the first band, that the amine portion of the phenothiazine molecule is pyramidal in the neutral ground state, and planar in the radical cation ground state. The first of these suggestions is in accord with our spectroscopic data, although the latter, *i.e.* a planar ground state for the radical cation, is not in agreement with our spectroscopic analysis. However, distinguishing between planar and near-planar geometries is notoriously difficult on the basis of spectroscopic data and we believe the combined evidence of our vibrational and electronic data to be the more conclusive. A substantial N lone-pair contribution to the electronic transition is consistent with the large enhancement observed in the δ_d(CNC) band intensity.

The vibronic spacing has been measured from the phenothiazine radical cation absorption spectrum and found to be (710 ± 20 cm^{-1}). The δ(CNC) mode, which is believed most effectively to link the electronic ground and excited states,[32] occurs at 471 cm^{-1} and there is no ground state (*i.e.* Raman-active) band at 710 cm^{-1}. This large discrepancy is attributed to the increase in the force constant associated with the δ(CNC) mode in the excited state, and we associate this in turn with a change of geometry to a fully planar configuration with increased aromatic resonance stabilization. Owing to the fact that the vibronic fine structures for the 10-methylphenothiazine and phenoxazine radical cations are poorly resolved, it is impractical to draw any meaningful conclusion concerning their excited state configuration.

Figures 1—3 show that the δ_d(CNC) Raman band excitation profile is maximal at the wavelength of maximum absorption for each of the three systems studied. Most other resonance-enhanced Raman bands also show this behaviour but, as is seen from the Figures, this is not always the case. For example, the peaks of the excitation profiles for the Raman bands of the phenothiazine radical cation at 1 603, 1 578, and 1 103 cm^{-1} are distinguished by having their maxima significantly to shorter wavelength. The 1 578 cm^{-1} band is different from the other two in that its excitation profile maximum coincides with that of the quite separate and distinct absorption band at 435 nm. This we assign to a second electronic transition. The apparent coincidence of the other bands with what we have assigned as vibronic components of the first electronic transition may be fortuitous. The potential energy surfaces defining the vibronic states of complex polyatomic molecules of this type are, of course, multidimensional. Thus, Franck–Condon coupling between ground and excited states may be achieved by several different routes. The 471, 1 103, and 1 603 cm^{-1} modes would appear to represent three such routes in this case. This appears to be the first observation of this effect but it illustrates well the potential of resonance Raman spectroscopy in elucidating electronic structures.

We are grateful for technical assistance by Mr. R. B. Girling, for e.s.r. spectra to Mr. W. J. Isham, for helpful discussions both with Dr. P. Hanson and W. J. I., and for financial support by the S.R.C.

[0/1735 *Received*, 10*th November*, 1980]

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