INFRARED SPECTRA OF PHENOTHIAZINES

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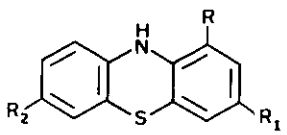
Abstract: Infrared spectra of phenothiazine including N-alkylated derivatives, sulphoxides and sulphones are reviewed with particular reference to their structural determination.

The infrared spectra of a vast number of phenothiazine derivatives have been recorded. From the data available, some general conclusions may be drawn concerning the diagnostic value of these spectra in establishing the existence and position of various substituents on the phenothiazine ring.

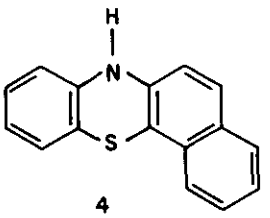
Since the phenothiazine structure is composed of two benzene rings joined in the 2-position, it would be expected that each ring should exhibit infrared absorption characteristics of the type of substitution found in that ring. For example, phenothiazine substituted in the 1-position should exhibit two absorption peaks, one in the region assigned to vicinal trisubstitution (due to the substituent in the 1-position and the adjacent nitrogen and sulphur bridges of the phencthiazine structure) and one peak in the region for ortho-disubstitution (for the 2-nitrogen and sulphur bridges). When the two rings are identical, as in the case of phenothiazine (1) itself and 3,7-difluorophenothiazine (2), two peaks very close together and in the proper region might be expected[1]. Phenothiazine shows two peaks at 735 cm^{-1} and 752 cm^{-1}, both within the region for o-disubstitution, and no other peaks at 740 cm^{-1} and 833 cm^{-1}.



1, $R_1 = R_2 = R = H$
2, $R_1 = R_2 = F$; $R = H$
3, $R_1 = R_2 = H$; $R = F$

1-Fluorophenothiazine (3) has two peaks, one at 769 cm^{-1} for the vicinal trisubstituted structure and one at the 746 cm^{-1} for the other ring, which is o-disubstituted.

It has been observed that the frequencies of the valence vibrations of the N-H bond differ considerably for the compound in the cyrstalline state and when dissolved in solvents. Hence it is possible to postulate intermolecular association by hydrogen bonding of the type-N-H....N. The frequency in the solid state is considerably higher than can be explained by peculiarities in the packing of molecules in the crystal. With 3,4-benzophenothiazine (4) and 3,4,5,7-dibenzophenothiazine (5), the frequency is shifted to the longwave part of the spectrum indica-



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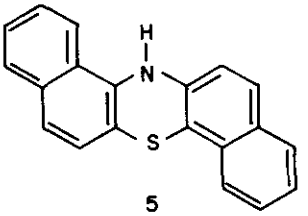

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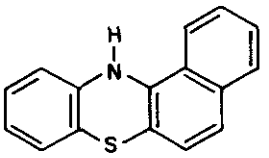
ting that association is strengthened. On the other hand, on passing 1,2-benzophenothiazine (6) and 1,2,8,9-dibenzophenothiazine (7), the frequency is shifted towards the shortwave part of the spectrum, which has been attributed to the steric hindrance arising through shielding of the N-H bond by one or two phenyl nuclei, resulting in weakening the association of the molecules[39].



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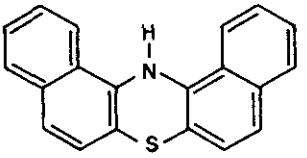

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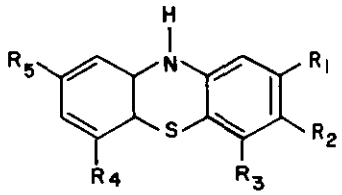
Discrepancies in the region between 813 cm^{-1} and 800 cm^{-1} for asymmetric trisubstitution are found with 2,4-difluoro- and 2,4,6,8-tetrafluorophenothiazine. Compounds containing 1,2,3, 5-tetrasubstitution absorb between 833 cm^{-1} and 820 cm^{-1} and two of them, 2,4-difluoro- (8) and 2,4,6,8-tetrafluorophenothiazines (9) have bonds corresponding to asymmetric substitution, but do not have that structure[7].

Thompson and co-workers[2,3] and Barnes[4] have reported that for substituted benzene rings, the peak at 671 cm^{-1} shifts more as a function of the relative positions than the nature of substituents. Since 2-trifluoromethylphenothiazine (10) containing an asymmetrically trisubstituted benzene ring and 4-trifluoromethylphenothiazine (11) have a vicinal structure, the two compounds should be distinguishable from their infrared spectra. Smith[5] showed that the product of the ring closure of 3-trifluoromethyldiphenylamine with sulphur had an absorption peak at 822 cm^{-1}, and on this basis called it 2-trifluoromethylphenothiazine (10)[7].

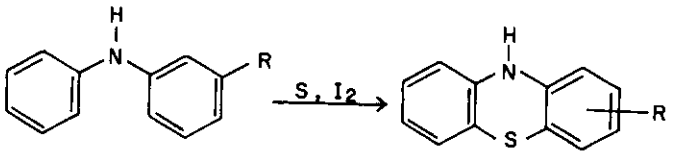


8, R_1 = R_3 = F; R_2 = R_4 = R_5 = H
9, R_1 = R_3 = R_4 = R_5 = F; R_2 = H
10, R_1 = F; R_2 = R_3 = R_4 = R_5 = H
11, R_3 = F; R_1 = R_2 = R_4 = R_5 = H
12, R_1 = F; R_5 = CF_3; R_3 = R_2 = R_4 = H
13, R_2 = CH_3; R_5 = CF_3; R_3 = R_1 = R_4 = H
14, R_2 = OCH_3; R_4 = CF_3; R_3 = R_1 = R_4 = H
15, R_3 = OCH_3; R_5 = CF_3; R_1 = R_2 = R_4 = H
16, R_1 = OCH_3; R_4 = CF_3; R_3 = R_2 = R_5 = H

Nodiff and Craig[8] have also observed that the 2- or 3-substituted phenothiazines usually have a peak between 933 cm^{-1} and 800 cm^{-1}, and the 1- or 4-substituted phenothiazines usually have a peak between 800 cm^{-1} and 763 cm^{-1}. 2-Fluoro-8-trifluoromethylphenothiazine (12) and 3-methyl-8-trifluoromethylphenothiazine (13) showed two strong bands in the region 800-833 cm^{-1}, with weak bands in the 763-800 cm^{-1} region. On the other hand, 3-methoxy-6-trifluoromethylphenothiazine (14) with one asymmetric and one vicinal trisubstituted ring has one strong peak at 803 cm^{-1} and 781 cm^{-1}. It was also observed that two isomeric phenothiazines, namely 4-methoxy-8-trifluoromethyl-(15) and 2-methoxy-6-trifluoromethylphenothiazine (16) have almost identical spectra, which include strong peaks at 813 cm^{-1} and 787 cm^{-1}. This, therefore, would seem to indicate that both these compounds have a combination of vicinal and asymmeric trisubstitution in the same molecule.

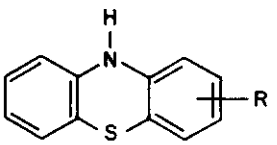
The infrared spectrum of 1-chlorophenothiazine showed a weak peak at 781 cm^{-1} and strong peaks at 763 cm^{-1} and 746 cm^{-1}. These strong peaks are characteristic of the combination of vicinal trisubstituted and o-disubstituted benzene rings, which are found in 1- or 4-substituted phenothiazines. No peaks were observed in the region 800-833 cm^{-1} [8].

Thionation of 3-substituted diphenylamines gave both the 2- and 4-substituted phenothiazines (17) depending on whether thionation takes place o or p to the substituent. Both were differentiated by their IR spectra, in which the 2-isomer gave a deep band in the region 800-833 cm^{-1} (asymmetric trisubstitution), while the 4-isomer showed a deep band in the region 741-800 cm^{-1} (vicinal trisubstituted benzenes).



17, R = OH, OCC_6H_5, SCH_3, SCF_3

Thus 2-methylmercapto, 2-trifluoromethylmercapto and 4-trifluoromethylmercaptophenothiazine showed the peaks at 806, 813 and 781 cm^{-1} respectively. However, 2-methylsulphonylphenothiazine (18) gave a very weak peak at 806 cm^{-1} but an unexpected strong peak at 769 cm^{-1}.



18, R = SO_2CH_3 19, R = SO_2CF_3

Similarly, 2-trifluoromethylsulphonylphenothiazine (19) gave a moderate peak at 866 cm^{-1} but again an unexpected peak at 769 cm^{-1} [8]. The results are summarised in Table I.

TABLE I

Infrared Spectra of Nuclear Substituted Phenothiazines

Compound	NH	800-839cm^{-1} (Asym.)	745-760cm^{-1} (Vic.)	750-760cm^{-1}	Other Peaks	Ref.
Phenothiazine	3336			750		39
	3340			735		55
	3342			739	1573, 1598[c]	56
					1500, 1477	
1,2,Benzophenothiazine	3398					39

TABLE I (Continued)

Compound	NH	800-839cm^{-1} (Asym.)	745-760cm^{-1} (Vic.)	750-760cm^{-1}	Other Peaks	Ref.
3,4-Benzo	3287					39
1,2,8,9-Dibenzo	3457					39
3,4,6,7-Dibenzo	3283					39
3,4,8,9-Dibenzo	3395					39
1-Fluorophenothiazine			770	745		77
2-Fluoro		790		740		77
2-Chloro	3326	805		748	850(s)	55
	3339	802		732,746	1570, 1595	56
					1500, 1472	
3-Chloro	3342			747	881(m), 816	55
3-Fluoro		800	752	740		7
					774(vs)	55
4-Chloro	3298			750		55
2-Trifluoromethyl		815	750	750		7
3-Trifluoromethyl		825		750		7
		810	810	750	790, 795	7
2,4-Difluoro		800[a]	795	740		7
2,7-Difluoro[6]		810	750[a]		800	7
		795				7
3,7-Difluoro[6]		825		745	780(w)	7
		815				7
3, Thiocyano	3352					7
3,7-Dithiocyano	3330	817			873, 2132[b]	55
		800			872(s), 874(s),	55
					811	
2,3,7-Trichloro	3336				872(s), 847(s),	55
					811	
2,4,8-Trifluoro		795			825, R815	7
2,4,7-Trifluoro		795			825	7
3,4,7-Trifluoro	3392				272(s), 847(s),	55
					811	
					880(s), 864, 849	55

TABLE I (Continued)

Compound	NH	800-839cm^{-1} (Asym.)	745-760cm^{-1} (Vic.)	750-760cm^{-1}	Other Peaks	Ref.
2-Chloro-3,7-dithiocyano	3310				2143[b], 2125[b]	55
4-Chloro-3,7-dithiocyano	3313				874(m), 811, 2134[b]	55
2,4,6,8-Tetrafluoro		790[a]				7
8-Fluoro-2-trifluoromethyl		825, 800			865, 840, 755	8
8-Methyl-3-trifluoromethyl		815, 800			865, 760(w)	8
8-Methyl-2-trifluoromethyl		815, 800			885(w), 865 790(w)	8
3-Methoxy-8-trifluoromethyl		800	780		885(w), 865 845, 700	8
					885(w), 865, 845	8
2-Chloro-7-fluoro		800, 795			865, 840, 795	8
3-Methoxy-6-trifluoromethyl		825, 815			858(w), 860 785(w), 740	8
2-Chloro-8-trifluoromethyl		825, 815				

a. Structure corresponding to this bond not present in molecule

b. Peak due to SCN

c. NH deformation

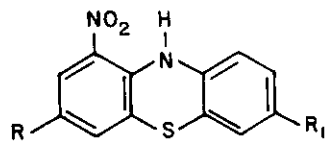
2,7-Disubstituted phenothiazines incorporate two asymmetrically trisubstituted benzene rings each of which contains a single isolated hydrogen atom and a pair of adjacent hydrogen atoms. The presence of isolated hydrogen is manifested by three peaks between 909 cm^{-1} and 840 cm^{-1}. One to three additional maxima between 833 cm^{-1} and 781 cm^{-1} (most frequently two peaks between 833 cm^{-1} and 794 cm^{-1}) can be attributed to the presence of the adjacent hydrogen pairs. The aromatic rings are also evidenced by a peak at 3125 cm^{-1} (=CH stretch), a trio between 1613 cm^{-1} and 1493 cm^{-1} (C = C skeletal in plane vibration) and a consistent quartet at 1124-1149, 1087-1111, 1031-1053, and 926-943 cm^{-1} (in plane C - H bending)[54].

Although O - H stretching at 3333 cm^{-1} is one of the most characteristic of the group frequencies, it is most often very weak, absent or obscured in the hydroxyphenothiazines.

The region 1176-1333 cm^{-1} contains four to seven bonds of varying intensity absorption in the low wavelength, half of this range can be assigned to C - N stretch while the peaks in the other half are indicative of CO stretch[54].

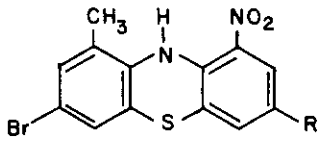
The infrared patterns are characteristic of but not unique for, 3,7-disubstituted phenothiazines. Normal peaks arising from N - H stretching vibrations in the secondary amino group appear at 3450 cm^{-1} and from C - N stretching vibrations in the amino group in the region 1310-1370 cm^{-1}. These two peaks at 1600 cm^{-1} and 1590 cm^{-1}, which may also be assigned to the aromatic system, are characteristic of many phenothiazines with an unsubstituted nitrogen atom. Two peaks arising from C -O -C stretching vibrations in alkylaryl ethers and appearing in the regions 1220-1230 cm^{-1} and 1030-1050 cm^{-1} have no direct connection with 3,7-disubstitution. Sharp peaks in the region 760-685 cm^{-1} arise from C-X (halogen) stretching vibrations, but they have also been found in the spectra of many phenothiazines which do not even contain halogen. A wide band was observed in the region 810-850 cm^{-1} assignable to -CH out of plane deformation vibrations in a 1,2,4-trisubstituted benzene ring i.e. in 3,7-disubstituted phenothiazines. Only in the case of 3-bromo-7-methoxyphenothiazine were two peaks observed at 950 cm^{-1} and at 815 cm^{-1} [15]. The presence in other 3,7-disubstituted phenothiazines of a single broad peak or two peaks, close together, near 825 cm^{-1}, has been reported earlier [12,7]. However, the same peaks are also found in other phenothiazines, which contain two asymmetrically trisubstituted benzene rings (2,7- and 2,8-disubstitution) [8,10,13].

Infrared spectra of 3-alkoxy-1-nitro-7-substituted phenothiazines (20) gave a single peak



20, R = OCH_3, OC_2H_5; R_1 = NO_2, $ClCH_2$, NO_2

in the region 3300-3380 cm^{-1} due to secondary amino groups. Two other peaks in the region 1565-1576 cm^{-1} and 1330-1350 cm^{-1} were also observed and were attributed to the asymmetric and symmetric valence vibrations of the nitro group [17]. On the other hand, 1-nitro-9-methyl-3-substituted phenothiazines (21) exhibited a sharp peak at 3000-3250 cm^{-1}, characteristic of the N-H stretching vibration. The shift to a lower frequency mainly suggests the formation of a six membered chelate of high stability through a strong N-H---O = N bonding between the nitro group at 1-position and the secondary amino group of the phenothiazine. Two other peaks in the region



21, R = NO_2, Cl

1563-1575 cm^{-1} and 1330-1350 cm^{-1} corresponding to the asymmetric and symmetric valence vibrations of the nitro group were also exhibited[18]. The results are summarised in Table II.

The absorption of the 3-sulphonylphenothiazines in the 885-893 cm^{-1} region attributed to the isolated C-H bond in 4-position of the phenothiazine nucleus is absent from the spectrum of the 2-methylsulphonyl derivative, although there is an isolated C-H bond in the 1-position of this phenothiazine derivative. The 3-phenothiazinyl sulphones have moderately strong absorption bands in the 820 cm^{-1} region. These are absent from the spectrum of 2-methylsulphonylphenothiazine, which instead shows a weak band in the 795-820 cm^{-1} region. The absorption of the various sulphones in the 795-820 cm^{-1} region is attributed to the two aromatic C-H bonds in the series at the 1,2-position for the 3-phenothiazinyl sulphones and the 3,4-positions of 2-methylsulphonylphenothiazine. In addition, the normal 1,2,4-trisubstituted benzene absorption pattern is observed for all the 3-phenothiazinyl sulphones and not the 1,2,3-trisubstituted pattern, which would be present if the sulphonylation products were 1- or 4-sulphonylphenothiazines[13].

IR spectrum of the 10-p-tolylsulphonyl derivative does not show any absorption at 895 and 800 cm^{-1}. In the case of 3,7-diphenylsulphonylphenothiazine, the band at 900nm was stronger than that in the spectra of any of the 3-phenothiazinyl sulphones, as expected, because of the presence of two isolated aromatic C-H bonds at the 4- and 6-positions of this disulphone[13].

Scapini and Gardini[21] have concluded from their study of the infrared dpectra of nitrosulphonaminophenothiazines (22) and their N-acetyl derivatives that the stretching frequency of each functional group is easily assignable in the spectrum, but it is not possible to use the absorption bands in the region 740-833 cm^{-1} to determine their structure.

In the case of phenothiazinyl ketones (22a) it was shown that the nature of the acyl group has no effect on the N-H stretching frequency and very little on the carbonyl stretching frequency[51].

TABLE II

Compound	N-H	C-N	C-O-C	1,2,4-Trisubst.	C-X	o-Disubst.	Other Frequencies	Ref.
3,7-Diethoxyphenothiazine	3450	1340	1050 1230	830	-	-	1077,1270,1470,2900	15
3-Methoxy-7-methoxy	3450	1340	1040 1230	825	-	-	1077,1270,1480,2850	15
3-Chloro-7-ethoxy	3450	1340	1040 1230	840	750	-	1077,1270,1455,1480 2900	15
3-Bromo-7-methoxy	3450	1310	1030 1230	850	745	-	1050,1250,1450,1470 1400,2850	15
3-Bromo-7-methoxy	3450	1370	1030 1220	820	750	-	1280,1435,1470,2845	15
3-Bromo-7-chloro	3450	1310	-	810	750,685	-	1280,1440,1470,2845	15
3-Methoxy	3450	-	1230 1250	825	-	735,750	-	16
3-Ethoxy	3445	-	1230 1040	820	-	745	-	16
7-Chloro-3-ethoxy	3450	-	1230 1040	810	750	-	-	16
7-Chloro-3-methoxy	3450	-	1230 1030	815,840	750	-	-	16
7-Chloro-3-nitro	3450	-	-	875	-	735	-	16
7-Chloro-3-bromo	3450	-	-	810	-	733,765	-	16

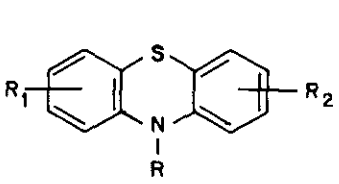
TABLE II (Continued)

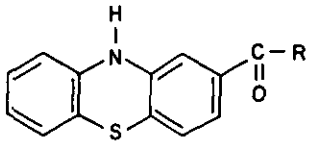
Compound	N-H	C-N	C-O-C	1,2,4-Trisubst.	C-X	o-Disubst.	Other Frequencies	Ref.
3-Nitro	3450	-	-	825	-	735,710	-	20,16
	3335	-	-	826	-		-	
3,7-Dinitro	3455	-		815,840	-	743,735	-	20,16
				831				
2-Trifluoromethyl-7-hydroxy-8-methoxy	3280[b]	-	1060	-	-	-	-	57
2-Trifluoromethyl-7,8-dimethoxy	3330	-	1060	-	-	-	-	57
10-(2-Cyanoethyl)-7,8-dimethoxy-2-trifluoromethyl		-	1045	-	-	-	-	57
10-(2-ethoxycarboxyethyl)-7,8-dimethoxy-2-trifluoromethyl			1035	-	-	-	1705[a]	57
10-(2-ethoxycarbonylethyl)-7,8-dimethoxy-2-trofluoromethyl			1050	-	-	-	1710[a] ,1010[c]	57
Phenothiazine-5-oxide	-		1125					
10-Phenothiazinylacetaldehyde acetal								

a. C = O stretching

b. The location, shape and intensity of this band suggest a zwitterion structure involving the amino and phenolic groups.

c. S---> O stretching



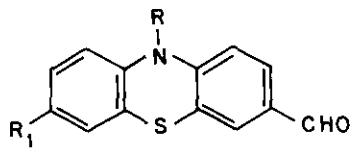


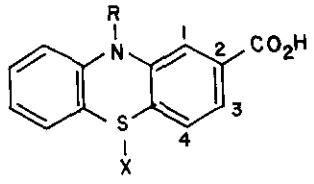
22, R = H, $COCH_3$ 22a, R = CH_3, C_5, $ClCH_2$, Cl CH

On the other hand, Ojah et al.[20] have observed a single peak at 3000-3280 cm^{-1} due to NH stretching vibrations in the case of ethoxynitrophenothiazines. The nitro group exhibited a sharp and intense band at 1500-1495 cm^{-1}. A strong band between 820-825 cm^{-1} and 870-925 cm^{-1} due to 1, 2,4-trisubstitution, i.e. adjacent to free hydrogen atoms were also observed. Bands between 1050-1120 cm^{-1} were attributed to C-O-C stretching[20]. The results are summarised in Table III.

In the case of phenothiazine aldehydes (23) the carbonyl stretching frequencies were shown to fall in the range 1665-1700 cm^{-1}. These frequencies are also characteristic for benzaldehydes with electron releasing substituents[27] pointing out the same effect exhibited by the 3-position of the phenothiazine ring. Electron withdrawing groups, such as Cl, CHO, or NO_2 at 7-position gave higher values as compared to 3-formylphenothiazine, which clearly points out that the electron attracting nature of these groups is felt in 3-position[23].

In the case of phenothiazine-2-carboxylic acids, (24) the presence of a methyl group in position 10 was shown to lower the electron density in the phenothiazine ring. This has been attributed to the folded structure of the phenothiazine molecule[24,26], which for sterical rea-





23, R_1 = H, Cl, CHO, NO_2
R = CH_3

24, R = H, CH_3
25, R = CH_3 ; X = O

sons imposes the methyl group at position outside the dihedron. This indicates that the conjugation possibility for the unshared electron pair of the nitrogen atom with the electrons of the benzene ring is restricted. In the case of sulphones (25), the values obtained indicate a lower

TABLE III

Compound	NH	CO	SO_2 Asymm.	SO_2 Symm.	NO_2 Aysmm.	NO_2 Symm.	1,2,4-Tri- subst.	1,2,3-Tri subst.	o-Di- subst.	O-C	Ref.
10-Acetylphenothiazine	-	1670	-	-	-	-	-	-	763,740	-	21
10-Acetyl-3-sulphonamido	-	1645	1330	1170	-	-	835,803	-	763,740	-	21
3-Sulphonmido-8-nitro	3355	-	1330	1160	1515	1330	826,810	-	767,737	-	21
10-Acetyl-8-nitro-3-sulphonamido	3345	-	1350	1170	1485	1330	830,810	-	741	-	21
10-Acetyl-3-nitro-8-sulphonamido	-	1700	1350	1350	1165	1530	830,806	-	765,746	-	21
3-Nitro-7-sulphonamido	-	1670	1350	1170	1520	1340	826,813	-	760,751	-	21
10-Acetyl-3-nitro-7-sulphonamido	-	1670	1350	1170	1520	1340	830,803	-	760,751	-	21
10-Acetyl-1-nitro	-	1680	-	-	1531	1360	807	-	773,757	-	21
10-Acetyl-2-nitro	-	1685	-	-	1520	1345	-	-	755,739	-	21
10-Acetyl-3-nitro	-	1685	-	-	1515	1350	-	-	765,750	-	21
10-Acetyl-3,8-dinitro	-	1700	-	-	1525	1350	831	-	769,743	-	21
10-Acetyl-3,7-dinitro	-	1690	-	-	1525	1350	832	-	748	-	21
2-Acetyl-9-methyl	3370	1660	-	-	-	-	795,893	705,755	-	-	22
2-Acetyl-7-methyl	3330	1663	-	-	-	-	805,889	-	-	-	22
							815,880				
2-Acetyl-6-methyl	3340	1655	-	-	-	-	810,882	705,763	-	-	22
							800,880				
2-Acetyl-7-ethoxy	3340	1660	-	-	-	-	810,875	712,760	-	2825,1230	22
		1680								1040	43
2-Acetyl-9-methoxy	3330	1675	-	-	-	-	777,880	712,760	-	2825,1250	22
2-Acetyl-7-methylthio	3340	1660	-	-	-	-	805,880	-	-	1040	22

TABLE III (Continued)

Compound	NH	CO	SO_2 Asymm.	SO_2 Symm.	NO_2 Aysmm.	NO_2 Symm.	1,2,4-Tri- subst.	1,2,3-Tri subst.	o-Di- subst.	O-C	Ref.
2-Acetyl-7-chloro	3330	1665	-	-	-	-	800,880	-	-	-	22
							808.871	-	-	-	22
2-Acetyl-9-chloro	3360	1670	-	-	-	-	798,888	710,762	-	-	22
2-Acetyl-8-methyl	3340	1660	-	-	-	-	795,882	-	-	-	22
2-Acetyl-8-chloro	3350	1668	-	-	-	-	812,853	-	-	-	22
							793,872				
2-Chloro-8-acetyl	3355	1669	-	-	-	-	810,865	-	-	-	22
							792,810				
2-Acetyl-6-methoxy	3340	1665	-	-	-	-	860,875	-	-	-	56
							795,840				
2-Acetyl	3348	1670	-	-	-	-	820,880	-	-	-	22
	3340	1667	-	-	-	-	824,890	-	-	2825,1240	56
2-Propinoylphenothiazine	3300	1678	-	-	-	-	-	-	-	1040	51
2-Chloroacetylphenothiazine	3340	1683	-	-	-	-	-	-	-	-	51
2-Dichloroacetylphenothiazine	3340	1680	-	-	-	-	-	-	-	-	51
2-Nitro	3355	-	-	-	1470	1330	826,812	-	-	752,839	21
3-Nitro-10-methyl	3325	-	-	-	-	-	-	-	-	-	23
1-Nitro	3355	-	-	-	1490	1342	-	-	-	765,754	21
3-Nitro	3335	-	-	-	1470	1330	820	-	-	744,735	21
3,7-Dinitro	3345	-	-	-	1510	1340	830,815	-	-	743,735	21
2-Methylsulphonylphenothiazine	-	-	1315	1132	-	-	805	-	-	-	13
			1300								

TABLE III (Continued)

Compound	SO_2 Asymm.	SO_2 Symm.	1,2,4-Tri-subst.	o-disubst.	Ref.
2-Methylsulphonyl	1370	1130	820,895	780	13
3-Phenylsulphonyl	1370	1150	820,895	760,750	13
3-p-Tolysulphonyl	1370	1150	820,895	760,755 740,710	13
3,7-Dipheny-sulphonyl	1335	1150	895,820	760,750 715,700	13
10-Phenylsulphonyl	1350	1155	815	765,760 755,720,715	13
10-p-Tolylsulphonyl	1350	1155	815,800	765,730	13
10-Methylsulphonyl	1350	1150	-	765,785,750	13
Phenothiazinebenzenesulphonylimine	1132	1035,1200	-	-	38
Promethazine	1138	1045,1199	-	-	38
Mepazine	1137	1042,1200	-	-	38
Phenothiazine-p-toluene-sulphonylimine	1132	1035,1200	-	-	38
Promethazine-p-toluene-sulphonylimine	1136	1040,1196	-	-	38
Mepazine-p-toluene-sulphonylimine	1135	1035,1205	-	-	38
Phenothiazine-p-ethyl-benzene sulphonylimine	1135	1035,1205	-	-	38

TABLE III (Continued)

Compound	NH	NH_2	CO	SO_2 Asymm.	SO_2 Symm.	Ref.
10-Methyl-7-chloro-3-aminophenothiazine	3305	3450	-	-	-	38
10-Ethyl-7-chloro-3-amino	3384	3480	-	-	-	38
10-Methyl-7-chloro-3-aminophenothiazine hydrochloride	3480(NH_2)	-	-	-	-	38
10-Ethyl-7-chloro-3-aminophenothiazine hydrochloride	-	2610($\overset{+}{N}H_3$)	-	-	-	38
10-Methyl-7,9-dichloro-3-aminophenothiazine hydrochloride	-	2625($\overset{+}{N}H_3$)	-	-	-	38
1-Aminomethylphenothiazine (film)	3350	3230,3160	-	-	-	77
N,N'-bis((1-Phenothiazinyl))methyl urea	3400 3280	-	1675	-	-	77
1-Tosylaminomethylphenothiazine	3380 3260	-	-	1325	1150	77
2-Tosyl-1,3-dihydro-2H-Pyrimido(5,6,1-Kl)-phenothiazine	-	-	-	1340	1160	77
1,3-Dihydro-2H-pyrimido(5,6,1-Kl)-phenothiazine	3160	-	-	-	-	77
1,2-Dihydro-3H-pyrazino(3,2,1-Kl)-phenothiazine-1,2-dione	3440	-	1715 1695	-	-	77
1-Tosylaminophenothiazine	3370	-	1155	1323	1155	77

TABLE III (Continued)

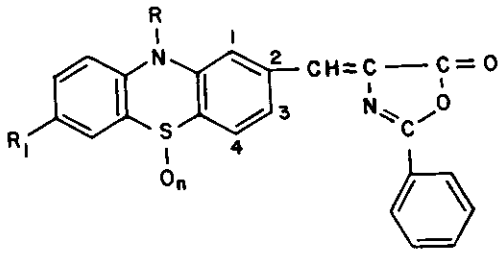
Compound	NH	CO	SO_2 Asymm.	SO_2 Symm.	O-C	C=N	Ref.
3-Tosyl-1,2-dihydro-3H-pyrazino(3,2,1-Kl)-phenothiazine	-	-	1355	1165	-	-	77
1-(N-Tosyl-N(2-bromoethyl)aminophenothiazine	3370	-	1350	1158	-	-	77
1,2-Dihydro-3H-pyrazino (3,2,1-Kl)phenothiazine	3400	-	-	-	-	-	77
2-Tosyl-1,2-dihydroamidazo(4,5,1-Kl)phenothiazine	3320	-	1255	1168	-	-	77
Imidazo(4,5,1-Kl)-phenothiazine	-	-	-	-	-	1625	77
1,2-Dihydroimidazo(4,5,1-Kl)phenothiazine	3250	-	-	-	-	-	77
10-(1-oxopyridyl)phenothiazine dioxide	-	-	1160	1140	-	-	76
10-(2-pyridyl)phenothiazine dioxide	-	-	1160	1140	-	-	76
8-Trifluoromethylphenothiazine-1-carboxylic acid chloride	3320	1710	-	-	-	-	76
8-Trifluoromethylphenothiazine-1-carboxylic acid isothiocynate	3320	1710	-	-	-	-	76
10-Trifluoromethyl-2,3-dihydro-1H-pyrimido-	3220	1710	-	-	-	-	76
(5,6,1-Kl)phenothiazine	3120						
10-Trifluoromethyl-2,3-dihydro-1H(5,6,1-Kl)-	3.12	5.80	-	-	-	-	76
phenothiazine-1,3-dione	3.3	5.95	-	-	-	-	76
1-Methylmercapto-10-trifluoromethyl-3H-pyrimido-	-	5.91	-	-	-	-	76
(5,6,1-Kl)phenothiazine-3-one							
2-Ethyl-10-trifluoromethyl-2,3-dihydro	-	5.82	-	-	-	-	76
1H-pyrimido(5,6,1-Kl)phenothiazine-1,3-dione	-	5.95	-	-	-	-	76
2-(2,3-Dihydroxypropyl)-10-trifluoromethyl-2,3-	2.95	5.82	-	-	-	-	76
pyrimido-1H-pyrimido(5,6,1-Kl)phenothiazine-1,3-dione	3.06						
8-Trifluoromethylphenothiazine-1-carboxylic acid	3.2	5.71	-	-	-	-	76
3,13-bis(Trifluoromethyl)-6H,16H,(1,5)diazocine-							

TABLE III (Continued)

Compound	NH	CO	SO_2 Asymm.	SO_2 Symm.	O-C	C=N	Ref.
(3,2,1-Kl)7,6,5-Kl)diphenothiazine-6,16-dione	-	6.90	-	-	-	-	76
10-(2-N,N'-Dimethylhydrazinomethyl)phenothiazine	3180	-	-	-	-	-	48
10-(2-N,N'-Pentamethylenehydrazinoethyl)phenothiazine	3320	-	-	-	-	-	48
10-(2-(1-methylpiperazine-4-amino)ethyl)phenothiazine	3180	-	-	-	-	-	48
2-Chloro-10-(2,N,N'-dimethylhydrazinoethyl)-phenothiazine	3220	-	-	-	-	-	48
2-Chloro-10-(2-N,N'-pentamethylenehydrazinoethyl)-phenthiazine	3220	-	-	-	-	-	48
2-Chloro-10-(2-(1-methylpiperazine-4-amino)ethyl)-phenothiazine	3220	-	-	-	-	-	48
10-Phenothiazine acetadehyde diethyl acetal	-	-	-	-	1125	-	48
2-Chloro-10-phenothiazineacetaldehyde diethyl acetal	-	-	-	-	1130	-	48
10-Phenothiazineacetaldehyde	-	1715	-	-	-	-	48
2-Chloro-10-phenothiazinylacetadehyde	-	1720	-	-	-	-	48
Phenothiazine-10-acetonitrile	-	-	-	-	-	2240	78
Phenothiazine-10-acetamide	3475,3190(NH_2)	1660	-	-	-	-	78
Pyrrolo(3,2,1-Kl)phenothiazine-2-carboxyldehyde	-	1666	-	-	-	-	78

electron density in 3-position.

The azlactones are characterised by a band at 1780-1850 cm^{-1} described as a CO stretching vibration [27-33]. This range is characteristic also for the carbonyl group of β,γ -unsaturated γ-lactones [34].



26, R = CH_3, H; R_1 = H, Cl, n = o

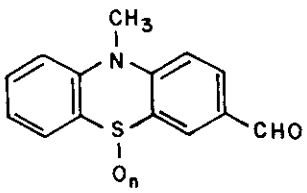
27, R = CH_3; R_1 = NO_2, Cl, n = o

The single absorption band expected for the stretching vibration of the azlactone carbonyl compounds (26,27) is replaced by two bands (A and B). The stronger band A is most sensitive to the nature of the phenothiazine ring. It was also observed that the position of band A and the relative intensities of the two bands are sensitive to the solvent polarity. However, the position of the C = N band was found unchanged under the same conditions. It may be mentioned that Jones et al. [35,36] had observed a similar behaviour for α,β -unsaturated γ-lactones and explained the presence of the two "carbonyl" bands by a Femi type resonance between the true CO stretching vibration, possibly an overtone of a low fundamental frequency [23].

The C = O stretching frquencies of phenothiazine aldehydes, carboxylic acids and azlactones are given in Tables IV, V, and VI.

TABLE IV

C = O Stretching Frequencies of Phenothiazine Aldehydes



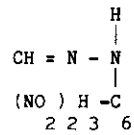
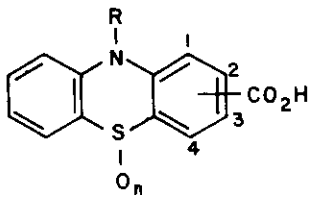
Compound No.	R	n	VCO cm^{-1}
1	H	0	1665
2	Cl	0	1696
3	CHO	0	1685
4		0	1690
5	NO_2	1	1700
6	H	2	1690

TABLE V

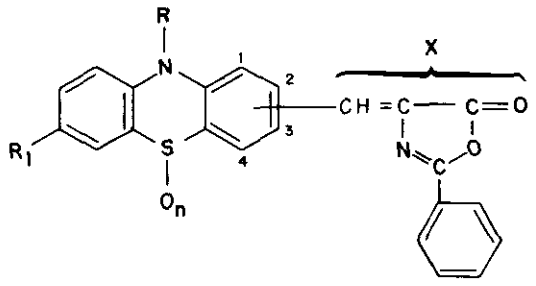
C = O Stretching Frequencies of Phenothiazine Carboxylic Acids



Compound No.	R	Position of the COOH group	n	CO cm^{-1}
1	H	2	0	1685
2	H	2	2	1710
3	CH_3	2	0	1690
4	CH_3	2	2	1720
5	CH_3	3	2	1700

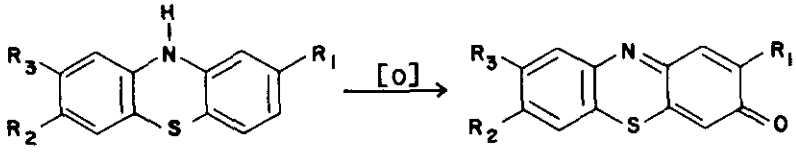
TABLE VI

C = O Stretching Frequencies of Phenothiazine Azlactones



Compound No.	R	R1	n	Position of x	CO cm^{-1} Band A	Band B
1	CH_3	H	0	3	1790	1770
2	CH_3	H	2	3	1800	1760
3	CH_3	H	0	2	1796	1770
4	H	H	0	2	11790	1775
5	CH_3	Cl	0	3	1813	1787
6	CH_3	NO_2	1	3	1795	1760
7	CH_3	Cl	2	3	1799	1770
8	CH_3	NO_2	2	3	1805	1769

The oxidation product of 2-nitrophenothiazine (28) exhibited an absorption peak at 1633 cm^{-1}, which has also been observed in the case of other phenothiazines[41,42]. The product was identified as 2-nitrophenothiazone-7 (29) by comparing its spectra with that of an authentic specimen isolated from the oxidation of 2-nitro-7-chlorophenothiazine (30). Similarly, the structure of 2,8-diacetylphenothiazone-3 (31), an oxidation product of 2,8-diacetylphenothiazine (32) was deduced from IR spectrum[43]



28, R_1 = NO ; R_2 = R_3 = H

29, R_1 = H; R_2 = NO , R_3 = H

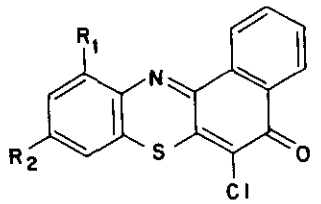
30, R_1 = NO ; R_2 = Cl, R_3 = H

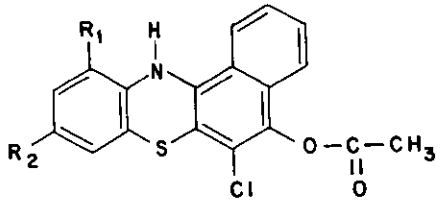
31, R_1 = R_2 = $COCH_3$, R_3 = H

32, R_1 = R_3 = $COCH_3$, R_2 = H

In halogenophenothiazones, the C = O stretching frequencies were observed in the region 1638-1647 cm^{-1}, which with the introduction of the nitro group at 4-position increased the frequency slightly from 1647 to 1657 cm^{-1}. The nitro group showed its characteristic band at 1560-1475 cm^{-1} and 1375-1300 cm^{-1}. Reduction of the NO_2 group with Zn/CH_3COOH resulted in the formation of the corresponding aminophenothiazones which were characterised by IR absorption spectra[45]. The results are sumarised in Table VII.

The reductive acetylation of the substituted 5H-benzo(a)phenothizine-5-ones (33) gave two series of benzo(a)phenothiazine derivatives in which the degree of acetylation depends upon the reaction conditions. Under mild conditions, substitued 5-acetoxy-12H-benzo(a)phenothiazines (34) are obtained, whereas under less mild conditions, the products were 5-acetoxy-6-chloro-9-methoxy-12H-benzo(a)phenothiazines (35) and 5-acetoxy-6-chloro-9-ethoxy-12-H-benzo(a)phenothiazine (36) from 37 and 38 respectively. The structures of these compounds were established on the basis of IR absorptions at 1742 - 1779 cm^{-1} (aromatic acetate) and at 3398-3470 cm^{-1} (NH)[44].





33, R_1 = H, Br, Ch
R_2 = H, Cl, Br, F, CH_3, OCH_3, OC_2H_5

34, R_1 = R_2 = H

35, R_1 = OCH_3; R_2 = H

36, R_1 = H; R_2 = OC_2H_5

37, R_2 = OCH_3, R_1 = H

38, R_2 = OC_2H_5, R_1 = H

The results are summarised in Table VIII.

TABLE VII

Compound	C = O (KBr)	C = O (CCl_4)	N-H (KBr)	N-H (CCl_4)	Ref.
4-Bromophenothiazone-3	1638	-	-	-	45
4-Nitro	1647	-	-	-	45
4,7-Dibromo	1672	-	-	-	45
7-Bromo-4-nitro	1653	-	-	-	45
4,7-Dichloro	1646	-	-	-	45
7-Chloro-4-nitro	1653	-	-	-	45

TABLE VII (Continued)

Compound	C = O (KBr)	C = O (CCl_4)	N-H (KBr)	N-H (CCl_4)	Ref.
1,4,7,9-Tetrabromo	1642	-	-	-	45
1,7,9-Tribromo-4-nitro	1652	-	-	-	45
1,4,7,9-Tetrachloro	1644	-	-	-	45
1,7,9-Trichloro-4-nitro	1653	-	-	-	45
1,2,4,7,8,9-Hexabromo	1647	-	-	-	45
1,2,7,8,9-Pentabromo-4-nitro	1657	-	-	-	45
4-Amino	1648	1748	3324	3466	50
			3370	3375	
4-Amino-7-bromo	1635	1642	3314	3411	50
			3367	3470	
4-Amino-2-chloro	1632	1640	3314	3394	50
			3368	3370	
1-Amino-7-chloro	1644	1639	3320	3368	50
			3410	3470	
4-Amino-2-bromophenothiazone-3	1631	1640	3308	3353	50
			3392	3448	
2-Chloro-4-nitro	1640	1660	-	-	50
2-Bromo-4-nitro	1633	1658	-	-	50
4-Acetylamino	1627	1630	3248	-	50
	1700	1706	3374	-	
	(acetyl)	(acetyl)			
2,8-Diacetyl	1630	-	-	-	43
4-Benzylideeamino	1685(acetyl)	-	-	-	50
	1624	1629			
3-Acetoxy-4-diacetylamino	1717	1729	-	-	50
2-Nitrophenothiazone-7	1633	-	-	-	43
2-Acetylphenothiazone-7	1633	-	-	-	43
	1680 (acetyl)				
8-Methoxy-2-trifluoromethylphenothiazone-7	1640	-	-	-	57
2-Anilinophenothiazone-3	1627	-	3267	-	52
2-Anilino-4-bromo	1623	-	3281	-	52

TABLE VII (Continued)

Compound	C = O (KBr)	C = O (CCl_4)	N-H (KBr)	N-H (CCl_4)	Ref.
2-Anilino-4-chloro	1627	-	3264	-	52
2-Anilino-1-bromo	1621	-	3136	-	52
2-Anilino-7-bromo	1626	-	3331	-	52
2-Anilno-7-chloro	1627	-	3264	-	52

TABLE VIII

Infrared Spectral Data of 5-H-Benzo(a)phenothiazine-5-ones

Compound	C=O	N-H	Aromatic C-H	C=N	Ph-N	1,2,4-Trisub.	1,2-Disub.
1,2-Benzophenothiazine-5-one	1645	3264	3040	1520	1289	-	750
6,9-Dichloro-1,2-benzophenothiazine-5-one	1645	3050	3050	1520	1304	815	770
6-Chloro-9-fluoro	1645	3050	3050	1529	1300	822	774
6-Chloro-9-methyl	1645	3100	3100	1520	1300	820	745
6-Chloro-9-methoxy	1645	3050	3050	1529	1300	820	775
6-Chloro-9-ethoxy	1645	3100	3100	1520	1295	825	775
6-Chloro-9-methyl-11-bromo	1645	3050	3050	1520	1300	-	775
6-Chloro-9,11-dimethyl	1645	3050	3050	1520	1300	-	770
6-Chloro-9-bromo	1645	3050	3050	1520	1305	825	775

IR Data of 12H-Benzo(a)phenothiazine-5-ols

Compound	NH/OH	Aromatic	C-N	C-O	Isolated ring H.atom	Vicinal pair of H.atom	1,2-Di-subst.
1,2-Benzophenothiazine-5-ol	3425[a]	3040	1302	1030	-	-	751
6,9-Dichloro-1,2-benzopheno-thiazine-5-ol	3448[a]	3058	1292	1031	882	882	752
					868		731
6-Chloro-9-bromo	3425[a]	3040	1299	1031	883	820	755
					860		725
6-Chloro-9-fluoro	3413[a]	3049	1292	1030	883	828	775
						813	752

IR Data of 12H-Benzo(a)phenothiazine-5-ols (Continued)

Compound	NH/OH	Aromatic	C-N	C-O	Isolated ring H.atom	Vicinal pair of H.atom	1,2-Di-subst.
6-Chloro-9-methyl	3049[a]	3360	1290	1029	880	840	772
						820	775
6-Chloro-9-methoxy	3040[a]	3360	1299	1066	880	846	772
						820	753
6-Chloro-9-ethoxy	3410	-	1299	1049	885	847	773
					886	828	730
6-Chloro-9-methyl-11-bromo	3413	-	1289	1075	883	-	752
							725
6-Chloro-9,11-dimethyl	3435	-	1305	1006	892	-	753
							725

IR Data of 5-Acetoxy-12H-Benzo(a)phenothiazines

Compound	C=O	NH	C-O	Isolated ring H.atom	1,2,4-Tri-subst.	1,2-Di-subst.
5-Acetoxy-12H-benzo(a)phenothiazine	1762	3400	1210	-	-	757
						750
						721
5-Acetoxy-6,9-dichloro	1779	3470	1205	907	855	743
					810	710
5-Acetoxy-6-Chloro-9-bromo	1748	3410	1200	906	855	746
					806	710
5-Acetoxy-6-chloro-9-fluoro	1742	3450	1209	893	833	760
				885	825	745
5-Acetoxy-6-chloro-9-methyl	1750	3415	1200	885	845	750
					825	720
						700
5-Acetoxy-6-chloro-9-methoxy	1764	3428	1206	909	830	741
				873	792	724
5-Acetoxy-6-chloro-9-ethoxy	1745	3450	1217	910	791	741
				866		719

IR Data of 5-Acetoxy-12H-Benzo(a)phenothiazines (Continued)

Compound	C=O	NH	C-O	Isolated ring H.atom	1,2,4-Tri-subst.	1,2-Di-subst.
5-Acetoxy-6-chloro-9,11-dimethyl	1762	3398	1200	910	-	770
						750
5-Acetoxy-6-chloro-9-methyl-11-bromo	1767	3448	1196	909	-	746
				879		719

IR Data of 5-Acetoxy-12-Acetyl-12H-Benzo(a)phenothiazines

Compound	NH	C=O (Arom. acetate)	C=O (N-acetyl	C-O	Isolated ring H. atom	1,2,4-Tri-subst.	1,2-Di-subst.
5-Acetoxy-12-acetyl-12H-	-	1778	1682	1180	-	-	749
benzo(a)phenothiazine							690
5-Acetoxy-6,9-dichloro	-	1779	1689	1190	891	835	768
					870	820	762
						794	735
5-Acetoxy-6-chloro-9-bromo	-	1783	1695	1190	890	820	762
					867		735
5-Acetoxy-6-chloro-9-fluoro	-	1757	1667	1206	908	859	755
					871		746
							717
5-Acetoxy-6-chloro-9-methyl	-	1742	1669	1196	905	833	758
					886	806	741
							719
5-Acetoxy-6-chloro-9-methoxy	-	1773	1684	1190	892	838	761
					867	827	742
5-Acetoxy-6-chloro-9-ethoxy	-	1786	1681	1189	866	826	758
						793	741
							722

Compound	C=O (N-acetyl-one)	N-H	Ref.
2-Acetylphenothiazine	1667	3340	51
2-Chloroacetylphenothiazine	1683	3340	51
2-Dichloroacetylphenothiazine	1680	3340	51
2-Propinoylphenothiazine	1678	3300	51

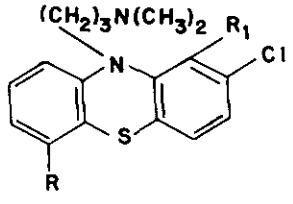
2,10-Disubstituted phenothiazines have a characteristic and unique pattern in the infrared spectrum. There are four bands in the region 1000-700 cm^{-1} which are common to all. These bands occur at 915-928 cm^{-1}, 840-870 cm^{-1}, 785-800 cm^{-1} and 730-755 cm^{-1}. The band at 785-800 cm^{-1} exhibits some splittings in certian cases, but it is steady in location [59].

Phenothiazines with no substituents in the 2-position all show very strong absorption in the 720-700 cm^{-1} range which is assignable to the out-of-plane bending vibrations of the four adjacent hydrogens of the phenothiazine ring system [59].

Two other characteristic bands for the phenothiazine system are found at 1590-1560 cm^{-1}. These bands are quite consistent in location, although they vary as to which is the most intense. They may also be assigned to the aromatic system.

In the case of phenothiazine amine salts, a strong broad band centered between 2300-2500 cm^{-1} is characteristic of the R_3NH^+ ion combined with x^-. The relatively small negative ion x^- can approach the amine cation R_3NH^+ from only one direction, forming the ion pair $R_3NH^+X^-$ with the hydrogen atom bonded strongly to the negative ion. Water of hydration tends to raise the frequency and lower the intensity of the absorption. Thus in the case of anhydrous chloropromazine hydrochloride, the R_3NH^+ absorption band is strong and broad and centered at 2390 cm^{-1}. The hemihydrate of chloropromazine hydrochloride shows a splitting of the broad band into two peaks located at 2400 and 2550 cm^{-1}. The spectrum of the hydrate shows a weaker R_3NH^+ absorption located at 2600 cm^{-1}. This unusual behaviour exhibited by the hydrate and hemihydrate is due to the reduction of hydrogen bonding of H^+ to X^- by the presence of water [59,60].

The structure of one of the metabolite of chloropromazine, namely 6-hydrochloropromazine (39) was established by its IR spectrum, which showed a strong hydroxyl absorption at 3420 cm^{-1}.



39, R_1 = H; R = OH 40, R_1 = OH; R=H

The strong band at 1235 cm^{-1} confirmed the expected phenolic character of the hydroxyl group. Additional broad absorption in the 2300-2700 cm^{-1} spectral region suggested significant zwitterion contribution. IR bands at 854, 807 and 773 cm^{-1} indicated isolated two adjacent and three adjacent aromatic ring protons thus confirming the position of substituents on the phenothiazine nucleus[61].

Similarly, the structure of 1-hydroxychlorpromazine (40) was established. This showed a band at 3510 cm^{-1} and strong absorption in the 1200-1250 cm^{-1} region which confirms the presence of phenolic hydroxyl group. Absorption in the 200-2600 cm^{-1} region indicated zwitterion contribution. The aromatic out of plane bending bands at 787 and 741 cm^{-1} were consistent with those of aromatic rings substituted at 1,2,3,4 and 1,2-position respectively.

On the other hand, 7-hydroxyclorpromazine which incorporates two asymmetrically tri-substituted benzene rings each of which contains a single isolated hydrogen atom and a pair of adjacent hydrogen atoms, gave three peaks between 815-910 cm^{-1}. These bands were attributed to the isolated hydrogens, one to three maxima between 835-760 cm^{-1} were attributed to the presence of adjacent hydrogen pairs. The aromatic rings exhibited a weak band at 3120 cm^{-1} (=C-H stretch), a trio between 1495-1610 cm^{-1} (C=C) skeletal in-plane vibrations) and a quartet at 1150, 1120, 1100, 1088, 1050, 1030, 1010, 940 and 920 cm^{-1} (in-plane C-H bending)[62]. The results are summarised in Table IX.

TABLE IX

Compound	Amine & amide N - H	Aromatic = CH	Amide C = O	Arocmatic C = C	Sulphoxide S - O	Aromatic in-plane deformation C = H
2-Chloro-7-hydroxy-10-(3 dimethylaminopropoyl) phenothiazine	(a)	-	-	1587(s)ml563(s), 1493(m)	-	1124(m),1099(m) 1053(m), 943(m)
10-(3)-Aminopropyl)-2-chloro 7-hydroxyphenothiazine oxalate	(f)	3125(w)	-	1613(m),1563(m) 1493(m),	-	1124(w),1087(w) 1042(w), 926(w)
10-(3-Aminopropyl)-2-chloro- 7-hydroxyphenothiazine *sulphoxide hemi-oxalate*	(f)	3125(w)	-	1587(s),1538(s 1493(w)	962 (s)(h)	1149(w),1111(w)

TABLE IX Continued)

Compound	Amine & amide N - H	Aromatic = CH	Amide C = O	Arocmatic C = C	Sulphoxide S - O	Aromatic in-plane deformation C = H
10-(3-Aminoprpyl)-2-chloro-7-hydroxyphenothiazine sulphoxide hydroiodide	(f)	-	-	1587(s),1538(s) 1493(s)	980	1149(w),1111(w) 1042(w), 935(m)
2-Chloro-10-(3-formamidopropyl)-7-hydroxyphenothiazine-5-oxide	3333(w)	3125 (w)	1667 (s)	1587(m),1538(m) 1493(w)	980 (s)	1149(w),1111(m) 1042(m), 943(w)
2-Chloro-10-(3-formamidopropyl)-7-formylphenothiazine	3333(m)	3125 (w)	1639 (s)	1587(w),1538(m) 1493(m)	-	1136(w),1099(s) 1042(w), 926(w)
2-Chloro-10-(3-formamidopropyl-7-hydroxyphenothiazine	3333(w)	-	1639 (s)	1587(w),1563(m) 1493(m)	-	1124(w),1099(w) 1053(w), 926(w)
7-Acetoxy-2-chloro-10-(3-formamidopropyl)phenothiazine-5-oxide	3333(m)	3125 (w)	1639 (s)	1587(w),1538(s) 1493(m)	-	1124(m),1099(w) 1053(s), 943(m)
7-Acetoxy-2-chloro-10-(3-formamidopropyl)phenothiazine-5-oxide	3326(m)	3125 (w)	1667(s) 1639(s)	1587(m),1538(w) 1493(m)	1010 (s)	1124(w),1099(w) 1053(s), 935(m)
10-(3-Acetamidopropyl)-7-acetoxy-2-chlorophenothiazine-5-oxide	3326(m)	3125 (w)	1667(s) 1639(s)	1613(s),1563(s) 1493(m)	1020 (s)	1136(w),1111(w) 1053(s), 935(m)
10-(3-Acetamidopropyl)-2-chloro-7-hydroxyphenothiazine-5-oxide	3326(w)	3125 (w)	1639 (s)	1587(s),1538(s) 1493(w)	990 (s)	1124(w),1099(w) 1042(m), 943(m)
10-(3-Acetamidopropyl)-2-chloro-7-(perhydro-2-pyranyloxy)phenothiazine	3333(m)	-	1639 (s)	1563(m),1538(m) 1493(m)	1000 (s)	1111(b-s) 1111(m),1042(m) 935(w)

TABLE IX Continued)

Compound	Amine & amide N - H	Aromatic = CH	Amide C = O	Arocmatic C = C	Sulphoxide S - O	Aromatic in-plane deformation C = H
10-3-Acetamidopropyl)-2-chloro-7-(perhydro-2-pyranyloxy)phenothiazine-5-oxide	3333(m)	-	1667 (s)	1563(m),1538(m) 1493(m)	1000	1111(b-s) 1042(s), 935(w)
2-Chloro-7-(perhydro-2-pyranyloxy)phenothiazine	3333(w)	-	-	1613(m),1563(m) 1493(m)	-	1124(m),1099(m) 1031(s), 935(m)
2-Chloro-10-(N-methylformamido)propyl)-7-(perhydro-2-pyranyloxy)phenothiazine	-	3125 (w)	1667 (s)	1613(m),1587(m) 1493(s)	-	1124(m),1111(m) 1031(m), 926(m)
2-Chloro-10-(3-(N-methylformamido)-propyl)-7-(perhydro-2-pyranyloxy)phenotiazine-5-oxide	-	-	1695 (s) 1493 (m)	1613(m), 1563(m)	980 (b-m)	1124(w),1099(m) 1053(s), 935(m)
2-Chloro-7-hydroxy-10-(3-methylaminopropyl)phenothiazine-5-oxide	3326(m)	3125 (w)	-	1587(s),1538(m) 1493(s)	1010 (s)	1124(w),1099(m) 1042(m), 926(w)

Compound	Isolated H	2 Adjacent H	Miscellaneous
2-Chloro-7-hydroxy-10-(3-dimethyl aminopropyl)phenothiazine	877(m), 862(m) 847(s)	813(s), 800(s) 781(m)	2564(b-w)(c)
10-(3-Aminopropyl)-2-chloro-7-hydroxyphenothiazine oxalate	901(s), 862(w), 847(w)	833(w), 800(s)	3571(w-sharp) (g)
10-(3-Aminopropyl)-2-chloro-7-hydroxy-phenothiazine sulphoxide hemi-oxalate	893(m), 862(w) 847(w)	820(w) 126(m)	-
10-(3-Aminopropyl)-2-chloro-7-hydroxy-phenothiazine sulphoxide hydroiodide	901(s) 847(m)	813(m), 800(m)	-

Aromatic C-H out of plane deformation

Compound	Isolated H	2 Adjacent H	Miscellaneous
2-Chloro-10-(3-formamidopropyl)-7-hydroxyphenothiazine-5-oxide	901(m),870(w) 840(w)	833(w), 794(m)	-
2-Chloro-10-(3-formamidopropyl)-7-formylphenothiazine	893(m),870(w), 847(s)	826(w),806(s) 794(m)	1724(s)(j)
2-Chloro-10-(3-formamidopropyl)-7-hydroxyphenothiazine	901(m),870(w), 847(m)	806(b-s)	-
7-Acetoxy-2-chloro-10-(3-formamidopropyl)phenothiazine	893(m),877(w), 847(m)	813(m),794(s)	1754(s)(j)
7-Acetoxy-2-chloro-10-(3-formamidopropyl)phenothiazine-5-oxide	901(w),870(w), 847(m)	820(w),806(m) 794(w)	1754(s)(j)
10-(3-Acetamidopropyl)-7-acetoxy-2-chlorophenothiazine-5-oxide	909(m),877(m), 847(s)	806(w),800(s), 775(w)	1754(s)(j)
10-(3-Acetamidopropyl)-2-chloro-7-hydroxyphenothiazine-5-oxide	901(m),870(m)	833(m),806(s)	-
10-(3-Acetamidopropyl)-2-chloro-7-(perhydro-2-pyranyloxy)phenothiazine	901(m),877(w) 855(m)	820(s),806(s)	961(s)(k)
10-(3-Acetamidopropyl)-2-chloro-7-(perhydro-2-pyranyloxy)phenothiazine-5-oxide	909(m),885(w), 847(m)	820(m),806(m) 775(m)	961(m)(k)
2-Chloro-7-(perhydro-2-pyranyloxy)-phenothiazine	893(w),870(m)	826(w),800(m)	961(s)(k)
2-Chloro-10-(3-(N-methylformamido)propyl)--7-(perhydro-2-pyranyloxy)phenothiazine	893(w),970(m)	820(m),806(m)	961(s)(k)
2-Chloro-10-(3-(N-methylformamido)-propyl)-7-(perhydro-2-pyranyloxy)-phenothiazine-5-oxide	901(w),885(m) 862(w),840(w)	826(w),806(m) 794(m)	980(b-m)(i-k)

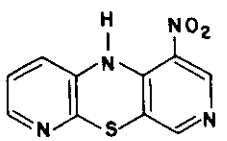
Aromatic C-H out of plane deformation (Continued)

Compound	Isolated H	2 Adjacent H	Miscellaneous
2-Chloro-7-hydroxy-10-(3-methyl-aminopropyl)phenothiazine-5-oxide	901(m),855(b-s)	806(m),800(m)	2500(b-w)(e)

w = Weak; m = Medium; s = Strong; b = Broad

(c) The reason for this apparent band split is not clear. (d) This spectrum contains a weak doublet at 3333-3448 cm^{-1} attributed to the symmetric and asymmetric stretching vibrations at a primary amine. (e) The location, shape and intensity of this band are suggestive of a zwitterionic structure involving the amino and phenol group. (f) The primary amine salts all exhibit three peaks between 2500-2941 cm^{-1} and a broad slightly stronger peak at 2000 cm^{-1}. (g) Unassociated OH stretching. (h) The few other peaks between 952-1220 cm^{-1} are all quite weak. (i) This broad band (2500 cm^{-1} wide) is probably an overlap of the S = O (sulphoxide) and C = O (tetrahydropyranyloxy) stretching bands. (j) Ether C - O stretching vibration. (k) Ether C-O stretch arising from the tetrahydropyranyloxy group. (l) Film (crude).

In 1-nitro-3,6-diazaphenothiazine (41), the proximity of the N-10 proton to the 1-nitro group resulted in the formation of a six-membered chelate (42) of high stability through strong NH-ON hydrogen bonding[63-65]. This was shown in the infrared spectrum in which the single NH-stretching frequency is shifted from 3310-3500 to 3295 cm^{-1}[66]. The shift in the N = O frequency from 1316-1340 cm^{-1} confirms the chelation and the assigned structure (42)[67]. The infrared spectra of 3-azaphenothiazine (43) anhydronium base (44) and quaternary iodide (45) provided an interesting confirmation of the structural assignments. Compound 43 has an intense band at 824, which has been attributed to the out of plane vibrations of two adjacent hydrogens on the



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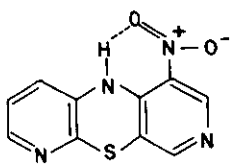
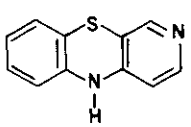


42

pyridine ring[68]. This band is absent from the spectrum of 44 and is replaced in the spectrum of 45 by a weak, broad band at 832 cm^{-1}[70].



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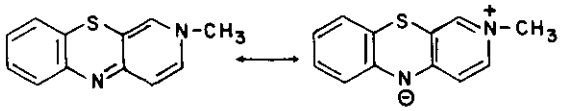

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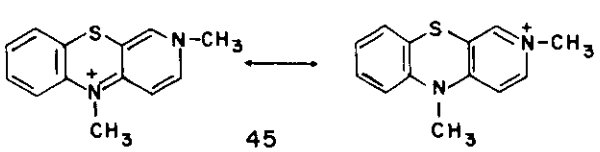

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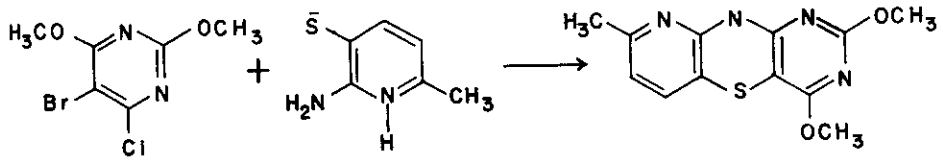
On the other hand, the spectrum of 44 has the characteristic intense band at 1645 cm^{-1} expected for the conjugated ethylene and imine double bonds [69], and although this band is absent in the spectrum of 43, it occurs in the spectrum of 45 as a band of medium intensity at 1634 cm^{-1} [70].

The product 2,4-dimethoxy-8-methyl-1,3,9-triazaphenothiazine (47) obtained from 5-bromo-4-chloro-2,6-dimethoxypyrimidine and 46 in acidic medium exhibited bands at 3400 (NH) 1650 (NH) deformation, 1200 (C-O-C) and 830 cm^{-1} (6CH, 7-CH). On the other hand, an alternate structure (48) should have exhibited a stronger intramolecular hydrogen bonding due to chelation between the oxygen of the methoxy group and the 10-NH proton leading to a five-membered ring of high stability [71].



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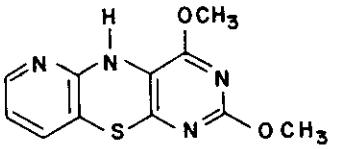
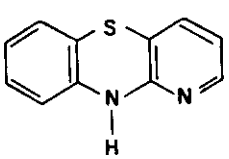


48

Chloroacetylation product of 1-azaphenothiazine (49) did not exhibit any absorption characteristic to N-H stretching or of protonated ammonium $N^{+}H$ stretching (2300-2500 cm^{-1}). This observation indicated that both the N-1 and the N-10 positions of the azaphenothiazine nucleus



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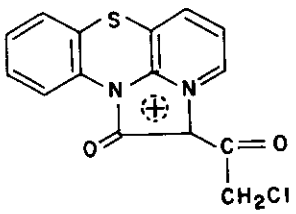


50

must be substituted and that there must be a cationic site, on the basis of which the product was assigned to be 50 [70]. The results are summarised in Table X.

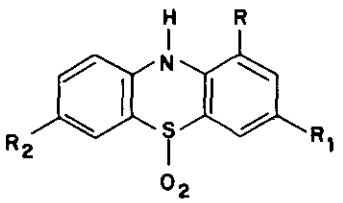
TABLE X

Compound	Absorption Bonds	Ref.
2,4-Diamino-8-methyl-1,3,4-triazophenothiazine	3430, 3430, 3380, 3340, 3180, 1630, 1614, 1580, 1550, 1455, 1428, 1400, 1370, 1341, 1273, 1260, 1190, 1150 1143, 1090, 1050, 1022, 984, 892, 814, 787, 748 cm^{-1}	73
2-Amino-4,8-dimethyl-1,3,9-triazaphenothiazine	3400, 3270, 3100, 1650, 1591, 1530, 1280, 1218, 1047 1020, 940, 865, 840,781 cm^{-1}	
2-Amino-4-chloro-8-methyl-1,3,9-triazaphenothiazine	3360, 3300, 3105, 2890, 1652, 1600, 1528, 1495, 1452, 1390, 1370, 1324, 1250, 1190, 1160, 1100, 1050, 944, 862, 823, 800, 765 cm^{-1}	
4-Amino-8-methyl-2-methylthio-1,3,9-triazaphenothiazine	3300, 3100, 1670, 1630, 1600, 1545, 1340, 1260, 1173, 1080, 1050, 986, 830, 710 cm^{-1}	
4-Amino-7-methoxy-1,3,6-triazaphenothiazine	3490, 3160, 1605, 1670, 1647, 1585, 1525, 1508, 1493 1410, 1396, 1310, 1284, 1271, 1256, 1214, 1200, 1180 1137, 1112, 1080, 1070, 1055, 1028, 1010, 982, 892 870, 854, 805, 790, 783 cm^{-1}	
2-Amino-7-chloro-4-hydroxy-1,3,6-triazaphenothiazine	3500, 3270, 3140, 1680, 1643, 1600, 1575, 1430, 1390, 1328, 1280, 1258, 1228, 1130, 1112, 1030, 876, 829, 754 cm^{-1}	
4-Amino-7-chloro-1,3,6-triazaphenothiazine	3373, 3075, 1650, 1630, 1596, 1570, 1485, 1390, 1354, 1346, 1274, 1253, 1188, 1174, 1130, 1070, 978, 890, 820, 804, 790 cm^{-1}	
2,4-Dichloro-7-methyl-1,3,6-triazaphenothiazine	3373, 3075, 1650, 1596, 1570, 1485, 1390, 1354, 1346, 1224, 1253, 1188, 1174, 1139, 1070, 978, 890, 858 820, 804, 790 cm^{-1}	
2-Amino-4-hydroxy-7-methoxy-1,3,6-triazaphenothiazine	3220, 1675, 1640, 1600, 1415, 1318, 1260, 1250, 1216, 1123, 1078, 1020, 910, 853, 818 cm^{-1}	
2,4,7-Trichloro-1,3,6-triazaphenothiazine	3300, 3062, 1680, 1567, 1548, 1518, 1402, 1350, 1258, 1202, 1107, 1065, 982, 968, 832 cm^{-1}	
2-Amino-4-chloro-7-methoxy-1,3,6-triazaphenothiazine	3350, 3200, 1660, 1550, 1260, 1128, 1018, 882, 817 cm^{-1}	
2,4-Dimethoxy-1,3,9-triazaphenothiazine	3400, 1650, 1200, 830 cm^{-1}	74

nucleus. Similarly, 3-chloro-acetamido-10-ethylphenothiazine exhibited a band at 1660 cm^{-1}, which was shifted to a higher frequency (1715 cm^{-1}) in the corresponding sulphone. It seems that the more strongly the lone pair of the nitrogen is drawn towards the ring, the less effectively can it conjugate with the carbonyl group and the higher will be the (CO) frequency. This large shift must be due to the combined -I effect and the mesomeric effect as both are operating in the same direction [37].

With the substituents, the sulphone frequency is only poorly affected, but the sulphonyl group itself produces quite large changes in the absorption pattern of the parent compounds [49]. 2-Acetylphenothiazine exhibited a sharp intense peak at 1672 cm^{-1} due to C = O stretching vibrations. This band is shifted to higher frequency 1685 cm^{-1} in the corresponding sulphone. The withdrawal of electron from the benzene ring must be only due to -I effect, which results in a decreased conjugation of the exocyclic C = O group with the aromatic nucleus. 2-Acetylphenothiazine oxime exhibited a band at 1600 cm^{-1} due to exocyclic C = N stretching mode which was shifted to higher frequency 1642 cm^{-1} in the corresponding sulphone. Both are examples of an electron acceptor ability of the heteroaromatic nucleus in the sulphone as compared to the parent nucleus [49].

There seems to be no correlation between the substitution pattern and the frequencies of the C-H in-plane deformation bands but the frequencies of C - H out-of-plane deformation bands in the region 700-900 cm^{-1} are related to the number of adjacent hydrogen atoms on the heteroaromatic ring. A sharp intense peak in compounds (54-56) at 785-790 cm^{-1} owing to out-of-plane bending vibration of three adjacent hydrogen atoms is shifted to higher frequencies (805-810 cm^{-1}) in the sulphone. Also in compound (57,58) the peak at 735-758 is shfted to higher frequencies (740-770 cm^{-1}) in the corresponding sulphones [37].



53, $R_1 = R_2 = H$

54, $R_1 = R_2 = NO$; $R_2 = H$

55, $R_1 = H$; $R_2 = NO$; $R_2 = Cl$

56, $R_1 = R_2 = NO$, $R_2 = Br$

57, $R_1 = H$; $R_2 = NO$; $R_2 = CH$

58, $R_1 = R_2 = NO$; $R_2 = Cl$

59, $R_1 = R_2 = NO$; $R_2 = CH$

60, $R_2 = NO$; $R_2 = H$

61, $R_2 = NO$; $R_2 = Cl$; $R_2 = H$

62, $R_2 = NO$; $R_2 = Cl$; $R_2 = Br$

63, $R_2 = NO$; $R_2 = Cl$; $R_2 = CH$

64, $R_2 = NO$; $R_2 = R_2 = Cl$

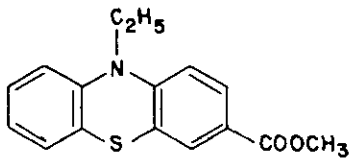
TABLE X (Continued)

Compound	Absorption Bonds	Ref.
4-Amino-8-methyl-1,3,9-triaza-phenothiazine	3390, 3100, 1650, 1603, 1250, 1180, 1136, 1019, 980, 895, 794 cm^{-1}	74
1-Acetyl-3-methyl-2,3-diaza-phenothiazine	1675, 1635 cm^{-1}	67
3-Methyl-2,3-diazaphenothiazine-4	1620, 3240 cm^{-1}	67
10-Acetyl-3-hydro-2,3-diazapheno-thiazone-4	1675, 1635, 2860 cm^{-1}	
3-Hydro-2,3-diazaphenothiazone-4	1615, 3240, 3100, 2800 cm^{-1}	
1-Nitro-7-methoxy-3,6-diazapheno-thiazone-4	3295, 3025, 1605, 1570, 1510, 1440, 1425, 1395 1316, 1300, 1275, 1250, 1225, 1195, 1175, 1150, 1130, 1100, 1025, 906, 880, 835, 820, 763, 740 cm^{-1}	
1-Nitro-7-chloro-3,6-diazapheno-thiazone-4	3270, 3030, 1590, 1575, 1545, 1506, 1326, 1280, 1234, 1182, 1135, 1095, 920, 905, 860, 760 cm^{-1}	

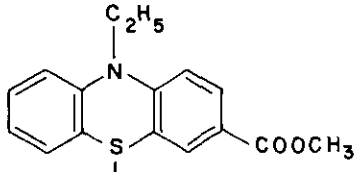
Phenothiazine Sulphoxides and Sulphones

The symmetric stretching vibration gives rise to a sharp intensity doublet in solution at 1185-1138 cm^{-1} and in the crystalline state at 1185-1140 cm^{-1}. In the low frequency region the phenothiazine sulphones exhibited a weak to medium absorption at 55-580 cm^{-1}, which appears mostly as a doublet or sometimes as a single band with an inflection.

10-Ethyl-3-methoxycarbonylphenothiazine (51) exhibited a sharp intense peak at 1690cm^{-1}, which was ascribed to C = O stretching vibrations. This band is shifted to a higher frequency



51



52

(1715 cm^{-1}) in the corresponding sulphone (52). This is in agreement with an increased electron-acceptor ability of the heteroaromatic nucleus in the sulphone as compared with the parent

In the case of phenothiazine sulphone (53) and 3,7-dinitrophenothiazine sulphone (54), a sharp N - H stretching peak was observed at 3450 cm^{-1} indicating a free NH group. On the other hand, the corresponding band in the spectra of 1-nitrophenothiazines (55-64) was observed at 3270-3350 cm^{-1} suggesting mainly OH-N intramolecular hydrogen bonding. The sharp peaks occurring at 1510-1560 and 1270-1350 cm^{-1} are attributed to the aromatic nitro group as usual. A weak medium band at 1070-1095 cm^{-1} which may be due to the asymmetric C - S stretching vibration increases in intensity and is slightly shifted to higher frequencies for the sulphones.

The spectra of the sulphones exhibited an intense absorption band in the range 3200-2400 cm^{-1}, characteristic of the N-H bond. Intermolecular hydrogen bonding of S-dioxides are weakened because of peculiarities in the 3-dimensional structure of the SO_2 group not present in SO.

Another fairly strong absorption between 812 and 820 cm^{-1} which is due to the same out-of-plane bending vibration of the two adjacent hydrogen atoms, ie. 1,2,4-trisubstitution again shows a marked shift to higher frquencies (820-835 cm^{-1}) in the corresponding sulphones (55-59, 63, 64). A similar shift is also observed in case of compounds containing a lone hydrogen atom i.e. 1,2,3,5-tetrasubstitution [49].

In general phenothiazine sulphones exhibit three characteristic intense absorption bands, both in the crystalline state and in carbon tetrachloride solution. In dilute solutions a sharp intense peak is obtained in the region 1332-1349 cm^{-1}, which has been ascribed to the antisymetric stretching mode of the sulphonyl group. In the solid state this absorption appears split into three bands between 1260-1350 cm^{-1},

In sulphoxide the absorption band in the region 3300-3450 cm^{-1}, characteristic of the N-H band vanishes and series of bands of various intensities appear in the region 3050-3000 cm^{-1}. This has been attributed to the formation of a strong intermolecular hydrogen bond >S-->O--N-H<. The bond appears more strongly in the spectrum of phenothiazine S-oxide probably due to the absence of steric hinderance [39]. Also the vibration frequencies for the S---> O bond have been observed in the region 1000-1100 cm^{-1} [75]. An additional intense band at 975-985 cm^{-1} has been ascribed to hydrogen bond formation [40]. Replacement of the hydrogen atom in the N-H group by methyl or acetyl resulted in the disappearnce of the longwave band and an increase in intensity of the shortwave band. The latter was ascribed to vibrations of the S---> O bond. The results are summaried in Tables XI, XII and XIII.

TABLE XI

S---> O Bond Valence Vibration Frequencies for Sulphoxides

Compound	(In Vaseline) cm^{-1}	Ref.
Phenothiazine-S-oxide	1075, 976	39
1,2-Benzophenothiazine-S-oxide	1072,986	39
3,4-Benzophenothiazine-S-oxide	1074,977	39
3,4,6,7-Dibenzophenothiazine-S-oxide	1053,985	39
10-Acetylphenothiazine-S-oxide	1044	39
10-Acetyl-1,2-benzophenothiazine-S-oxide	1074	39
10-Methyl-3,4-benzophenothiazine-S-oxide	1023	39

TABLE XII

Characteristic Vibrations (cm^{-1}) of the Sulphonyl Group in Phenothiazine Sulphones

Compound	ν_1 (SO_2)		ν_2 (SO_2)		ν_3 (SO_2)		Unassigned Bands		
	CCl_4	KBr	CCl_4	KBr	CCl_4	KBr	KBr	CCl_4	Ref.
Phenothiazine sulphone	1170	1172	559	568	1335	1350	485	489	37
	1150	1150	555	560	1344	1300			
7-Chloro-1-nitrophenothiazine sulphone	1185	1180	560	563		1350	488	485	37
	1160	1160	550	550		1290			
						1260			
7-Methyl-1-nitrophenothiazine sulphone	1180	1180	565	568	1336	1348	485	477	37
	1155	1152	565	568	1285	1285			
						1270			
7-Bromo-1-nitrophenothiazine sulphone	1180	1185	570	572	1340	1350	490	495	37
	1160	1165	565	560		1290			
						1260			

TABLE XII (Continued)

Characteristic Vibrations (cm^{-1}) of the Sulphonyl Group in Phenothiazine Sulphones

Compound	ν_1 (SO_2)		ν_2 (SO_2)		ν_3 (SO_2)		Unassigned Bands		Ref.
	CCl_4	KBr	CCl_4	KBr	CCl_4	KBr	KBr	CCl_4	
7-Chloro-1,3-dinitrophenothiazine sulphone	1175 1140	1175 1140	570 560	570 560	1349	1350 1260 1300	482	490	37
7-Methyl-1,3-dinitrophenothiazine sulphone	1180 1145	1180 1140	580 560	575 555	1345	1348 1300 1260	500	498	37
1,3-Dinitrophenothiazine sulphone	1170 1150	1170 1150	560 560	563 560	1340	1335 1295 1260	490	493	37
3-Chloro-1-nitrophenothiazine sulphone	1165 1140	1155 1142	577 565	575	1348	1350 1260	488	493	37
7-Bromo-3-chloro-1-nitrophenothiazine	1180 1138	1185 1140	560 560	558 550	1345	1350 1290 1265	480	488	37
3-Chloro-7-methyl-1-nitrophenothiazine	1185 1140	1182 1140	575 560	578 555	1345	1345	485	485	37
3,7-Dichloro-1-nitrophenothiazine	1185 1140	1180 1140	560 550	555 550	1348	1350 1290 1270	490	493	37
8-Chloro-1,3-dinitrophenothiazine	1185 1165	1180 1160	580 555	575 555	1345	1350 1285 1260	487	482	37
2,4-Dibromo-7-methyl-1-nitrophenothiazine	1175 1150	1172 1148	570 552	570 555	1340	1340 1280 1265	499	498	37
3,7-Dinitrophenothiazine	1172 1155	1170 1153	556 556	554 554	1332	1344 1297 1278	485	479	37
2,8-bis(ethylamino)	1130				1460	1230			47

TABLE XII (Continued)

Characteristic Vibrations (cm^{-1}) of the Sulphonyl Group in Phenothiazine Sulphones

Compound	ν_1 (SO_2)		ν_2 (SO_2)		ν_3 (SO_2)		Unassigned Bands		Ref.
	CCl_4	KBr	CCl_4	KBr	CCl_4	KBr	KBr	CCl_4	
2,8-bis(methylamino)	1125				1430	1230			47
1-Tosylamino		1165			1325				47
1-Tosylaminomethyl		1150			1323				47
2-Tosyl-1,3-dihydro-2H-pyrimido-(5,6,1-Kl)phenothiazine sulphone		1160			1340				47
bis(N-Tosyl-N-(1-phenothiazinyl)-amino)methane sulphone		1168			1355				47

TABLE XIII

N - H and C- H out-of-plane bending vibrations (cm^{-1}) of phenothiazine sulphones in KBr

Compound	N-H	disubst.	1,2,3-trisubst.	1,2,4-trisubst.	1,2,3,5-tetra-	(C-S) Asym.	Ref.
Phenothiazine sulphone	3450	765	-	-	-	1078	37,49
7-Chloro-1-nitro	3350	-	805	835	-	1082	34,49
7-Methyl-1-nitro	3320	-	805	820	-	1085	34,49
7-Bromo-1-nitro	3330	-	810	830	-	1070	34,49
7-Chloro-1,3-dinitro	3300	-	-	835	900	1086	34,49
7-Methyl-1,3-dinitro	3300	-	-	835	895	1090	34,49
1,3-Dinitro	3300	770	-	-	895	1087	34,49
3-Chloro-1-nitro	3310	760	-	-	900	1075	34,49
7-Bromo-3-chloro-1-nitro	3350	-	-	-	870	1095	34,49
3-Chloro-7-methyl-1-nitro	3350	-	-	825	900	1072	34,49
3,7-Dichloro-1-nitro	3300	-	-	830	870	1070	34,49
8-Chloro-1,3-dinitro	3280	-	-	830	880	1090	34,49
2,4-Dibromo-7-methyl-1-nitro	3348	-	-	820	890	1084	34,49
			820			1089	
3,7-Dinitro	3345	-	-	829	-	1083	34,49

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