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STRUCTURE AND INFRARED SPECTRA OF SOME PHENOTHIAZINE SERIES DERIVATIVES

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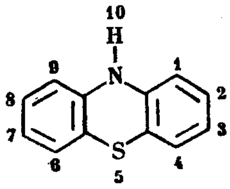
Infrared spectra of phenothiazine, isomeric benzo- and dibenzophenothiazines, and their S-oxides and -dioxides are investigated in the N–H and S → O valence bond vibration regions. On the basis of the results obtained, a hypothesis is advanced regarding intermolecular hydrogen bonding with the compounds studied, and views are put forward regarding the effect of structural factors on their formation.

Infrared spectroscopy was added to investigation of dipole moments and polarographic reduction as a means of obtaining information about structural peculiarities and properties of phenothiazine derivatives previously synthesized by the present authors.

The present paper gives results of a study of the infrared spectra of phenothiazine, its benzo and dibenzo derivatives, as well as of their S-oxides and -dioxides.



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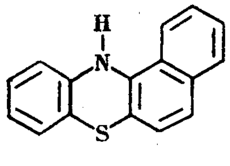

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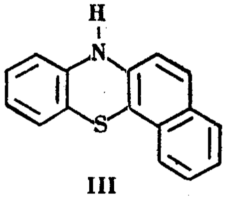

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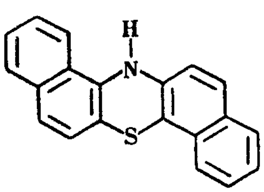

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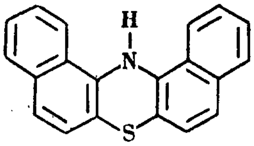

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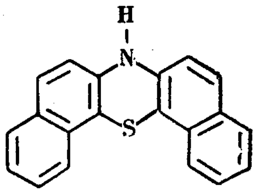


VI

A UR-10 spectrophotometer was used for measuring the spectra both of solids (paste with perfluoro hydrocarbon) or of benzene solutions (0.05 M).

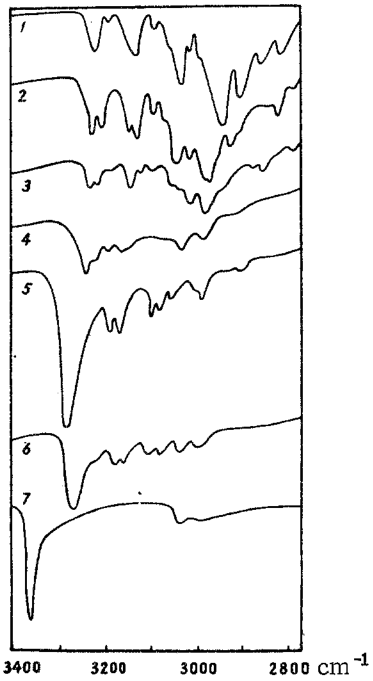
Table 1

N–H Bond Valence Vibration Frequencies of Unoxidized Phenothiazine Bases (LiF Prism)

No.	Compound	In perfluoro hydrocarbon cm^{-1}	In benzene solution, cm^{-1}	$\Delta\nu$, cm^{-1}
I	Phenothiazine....................	3340	3398	58
II	1, 2-Benzophenothiazine...........	3398	3432	34
III	3, 4-Benzophenothiazine...........	3287	3402	115
IV	3, 4, 8, 9-Dibenzophenothiazine.....	3395	3435	40
V	1, 2, 8, 9-Dibenzophenothiazine.....	3457	3464	7
VI	3, 4, 6, 7-Dibenzophenothiazine.....	3283	3402	119

The data of Table 1 for unoxidized phenothiazine bases show that the frequencies of the valence vibrations of the N–H bond differ considerably for the compounds in the crystalline state and when dissolved in solvents ($\Delta\nu$ up to 119 cm^{-1}). Hence it is possible to postulate intermolecular association by hydrogen bonding of the type $=N-H\ldots N\langle$ [1]. In the case of phenothiazine (I), 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 (III) and 3, 4, 6, 7-dibenzophenothiazine (VI), the frequency is shifted to the longwave part of the spectrum, indicating that association is strengthened. On the other hand, on passing to 1, 2-benzophenothiazine (II) and 1, 2, 8, 9-dibenzophenothiazine (V), the frequency is shifted towards the shortwave part of the spectrum. This can be explained by steric hindrance arising through shielding of the N–H bond by one or two phenyl nuclei, which correspondingly weakens association of the molecules.

3, 4, 8, 9-Dibenzophenothiazine (IV) occupies an intermediate position.



Infrared spectra of S-oxides and S-dioxides of the phenothiazine series in the region of N–H bond valence vibrations: 1) Phenothiazine S-oxide; 2) 3, 4-benzophenothiazine S-oxide; 3) 3, 4, 6, 7-dibenzophenothiazine S-oxide; 4) 1, 2-benzophenothiazine S-oxide; 5) Phenothiazine S-dioxide; 6) 3, 4-benzophenothiazine S-dioxide; 7) 1, 2-benzophenothiazine S-dioxide.

Consideration of the absorption bands in the N–H link valence vibrations region leads to interesting conclusions regarding the S-oxides and S-dioxides of the above-mentioned phenothiazine bases (see figure).

The figure shows that with S-oxides the absorption band in the region 3450-3300 cm^{-1}, characteristic of the N–H bond, vanishes, and a series of bands of various intensities appears in the region 3300-3050 cm^{-1}. It must be assumed that this is connected with formation of a strong intermolecular hydrogen bond $>S \rightarrow O \ldots H-N<$. Furthermore, because of the absence of steric hindrance, it appears most strongly in the spectrum of phenothiazine S-oxide. The spectra of the S-dioxides of the same bases, again, exhibit an intense absorption band in the range 3400-3200 cm^{-1}, characteristic of the N–H bond. Evidently the intermolecular hydrogen bonds of S-dioxides are weakened because of peculiarities in the 3-dimensional structure of the SO_2 group not present in SO.

Unfortunately, because the compounds were almost completely insoluble in nonpolar solvents, it was difficult to draw any conclusion about the degree of polarization of the N–H link in the oxidized derivatives of phenothiazine.

Not only were the valence vibrations of the N–H link in phenothiazine derivatives studied, but those of the S→O bond in sulfoxides and sulfones were, too.

The spectra of all the S-oxides and S-dioxides of the phenothiazine series show the S→O absorption bands in the solid state (paste with vaseline). Table 2 gives data for sulfoxides.

There are indications in the literature [2] that for sulfoxides the vibration frequencies for the S→O bond lie in the range 1100-1000 cm^{-1}. In the present case not only were absorption bands found in that region, but an additional intense band at 985-975 cm^{-1} was also observed, which several authors [3] ascribe to formation of a hydrogen bond.

Replacement of the hydrogen atom in the N–H group by methyl or acetyl lead to disappearance of the longwave band, and an increase in intensity of the shortwave band. Consequently the latter was ascribed to vibrations of the S→O bond. Apparently appearance of the 985-975 cm^{-1} bands is connected with formation of a strong intermolecular hydrogen bond.

Table 2

S→O Bond Valence Vibration Frequencies for Sulfoxides of the Phenothiazine Series (NaCl Prism)

Compound	ν in vaseline cm^{-1}
Phenothiazine S-oxide	1075 976
10-Acetylphenothiazine S-oxide	1044
1, 2-Benzophenothiazine S-oxide	1072 986
10-Acetyl-1, 2-benzophenothiazine S-oxide	1074
3, 4-Benzophenothiazine S-oxide	1074 977
10-Methyl-3, 4-benzophenothiazine S-oxide. . . .	1023
3, 4, 6, 7-Dibenzophenothiazine S-oxide	1053 985

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3. E. D. Amstutz, I. Hunsberger, and J. J. Chessick, J. Am. Chem. Soc., 73, 1220, 1951.

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