

ABSORPTION SPECTRA OF SUBSTITUTED THIANAPHTHENES

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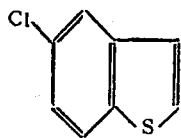
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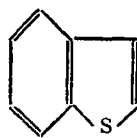
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INTRODUCTION

THE near ultraviolet spectrum of thianaphthene has been recently investigated by a number of workers.^{1, 2} Such a study is important from the point of view of isosteric substitution of $-S-$ in place of $-CH=CH-$. The derivatives of thianaphthene have been studied by Desai and Padhye³ in solution phase. The vapour absorption of thianaphthene does not seem to have received much attention except for 3-chlorothianaphthene.⁴ In the present studies it is proposed to investigate the vapour spectra of thianaphthene derivatives from the point of view of effect of substitution at different positions in thianaphthene nucleus. The substituents in the phenyl part of the thianaphthene nucleus are expected to be more interesting from the point of view of comparison with corresponding naphthalene derivatives. Absorption spectra of 5-chlorothianaphthene (I) and 7-bromothianaphthene (II) are reported here.



(I)



Br (II)

EXPERIMENTAL

The substances were obtained from Dr. Tilak of this Department and were analytically pure. An all-quartz absorption cell 33 cm. of length was used. A drop of the substance under investigation was put into the cell which was evacuated until the liquid practically disappeared when the cell was sealed off under vacuum. Spectra were photographed on a Hilger medium quartz spectrograph using a hydrogen arc as the source of continuous radiation and Kodak B-10 plates. Spectra were recorded for a range of temperatures of the cell between 30° C. and 120° C. The temperatures were increased in steps of 10° and absorption spectra were recorded until the

discrete absorption bands merged into a continuum with a cut off on a longer wavelength side. The time of exposure varied between 30 m. and 1 hour. Three plates were measured for each of two substances on a Hilger Comparator with least count $\cdot 0001$ cm. Hartman's formula was used to calculate the wavelengths of the bands employing copper lines as standards.

RESULTS

5-Chlorothianaphthene.—The spectrum of 5-chlorothianaphthene resembles closely in general appearance that of thianaphthene. The longest wavelength region of bands lies between 3050 and 2800 Å corresponding to longest wavelength absorption region of thianaphthene vapour (3000 and 2700 Å). The bands represent a typical group pattern as in thianaphthene, due possibly to a small difference frequency arising out of ν - ν transitions. The bands in each group show, however, a gradual fall in intensity from violet to red end as against alternation of intensity of components of each group observed in the case of thianaphthene. The second region of absorption starts at about 2700 Å and extends upto 2500 Å corresponding to second region of absorption of thianaphthene between 2650 and 2450 Å. It consists of a few broad diffuse bands. Figure 1 c gives reproduction of a typical plate.

The longest wavelength system consists of a number of discrete bands degraded towards the red. Some twenty prominent bands have been measured and the intense ones are given in Table I. The strongest band on the long wavelength side at 33053 cm.^{-1} has been taken as the 0-0 band. The spectra recorded at higher temperatures confirm this choice since there is no reversal of intensity in the first two bands and no further bands are developed on the longer wavelength side. The electronic transition giving rise to the bands thus shows a red shift of 1009 cm.^{-1} from that in thianaphthene. The vibrational assignments of these bands are given in Table I. The bands separated by 714, 1029 and 1192 from the 0-0 on the shorter wavelength side mark the beginning of separate groups and represent excited state frequencies of the prominent vibrations excited. Other vibrations involved are 626, 995 in the excited state but the bands corresponding to these lie in the groups following the bands in the previous group. It is important to note that the vibrations which are prominently excited are those which give rise to diffuse bands or (') series in thianaphthene.³ Excited state frequencies in thianaphthene which give sharp bands and start a group are not so prominent in the spectrum of 5-chlorothianaphthene. The bands near the 0-0 band show that one or possibly two fundamentals are excited in the ground state namely 80 and 138 cm.^{-1} . The bands, involving these

TABLE I
5-Chlorothianaphthene

Band heads of prominent bands

Wavelength A.U.	Wavenumber in cm.^{-1}	Intensity visual	Assignment	
			Ground state	Excited state
3037.2	32915	8	138	..
3031.9	32973	8	80	..
3024.6	33053	10	..	0-0
2974.3	33611	6	..	558
2968.3	33679	6	..	626
2960.6	33767	7	..	714
2936.2	34048	6	..	995
2933.2	34082	7	..	1029
2919.3	34245	5	..	1192
2888.1	34615	2	..	1562
2874.6	34777	2	..	1724

vibrations in the ground state at 32973 and 32915 cm.^{-1} , show a type of appearance distinctly different from the bands belonging to the group following the strong band. The group character in the spectrum of 5-chlorothianaphthene has not been well developed and hence small frequency differences for consecutive bands in each group cannot be established.

7-Bromothianaphthene—The absorption spectrum of 7-bromothianaphthene shows a characteristic difference in appearance from that of 5-chlorothianaphthene and thianaphthene itself. The longest wavelength region lies between 3050 and 2850 Å corresponding to longest wavelength absorption region of thianaphthene vapour between 3000 and 2700 Å. The second region of absorption starts at 2700 Å and extends upto 2350 Å,

corresponding to second region of absorption of thianaphthene (2650 to 2450 Å). It consists of a few broad diffuse bands.

The long wavelength system consists of a number of discrete bands degraded towards the red. Some thirty bands were measured and the prominent strong bands are recorded in Table II. The strongest band at 33493 cm^{-1} has been chosen as 0-0 band on the same grounds as in 5-chloro-thianaphthene. This shows red shift of 369 cm^{-1} from the 0-0 band in thianaphthene spectrum. The vibrational assignment of these bands is given in Table II. Figure 1 *b* gives a reproduction of a typical plate.

TABLE II

7-Bromothianaphthene

Band heads of prominent bands

Wavelength A.U.	Wavenumber in cm^{-1}	Intensity visual	Assignment
2984.8	33493	10	0-0
2971.6	33642	0	149
2938.7	34019	5	526
2918.6	34253	6	760
2900.6	34465	9	972
2895.1	34529	4	1036
2881.7	34692	8	1199
2875.5	34766	7	1273
2865.6	34886	3	1393

The band at 34465 cm^{-1} on the shorter wavelength side is the next prominent band in the spectrum after the 0-0 band. This involves frequency of 972 cm^{-1} in the excited state. The other excited state frequencies which could be easily identified are 760, 526 and 1273 cm^{-1} . The three other frequencies which seem to be involved are 1199, 1036 and 1393 cm^{-1} . In thianaphthene the difference in intensity of the $v-v$ bands from the superposed 0-1 bands, which follow them, is quite marked and hence the excited state frequencies can be easily identified. In the present case the

whole spectrum looks like a series of bands of nearly equal intensity and hence bands arising out of 0-1 transition involving excited state frequency of some particular vibrations cannot be identified on intensity considerations alone. The identification of such bands in the present case is therefore based on the analysis, and comparison of spectra of other thianaphthenes. The difference in diffuse and sharp bands in the spectrum of 7-bromothianaphthene is not very marked. The small difference frequency possibly arising out of $\nu-\nu$ transition giving rise to consecutive bands in each group in the present case is of the order $39 \pm 2 \text{ cm.}^{-1}$. There are two bands at 33642 and 33345 cm.^{-1} separated by 148 cm.^{-1} from the 0-0 band on either side. These possibly represent the fundamental frequencies in the ground and the excited state.

DISCUSSION

5-Chlorothianaphthene and 7-bromothianaphthene are the derivatives of thianaphthene obtained by replacing hydrogen at 5th and 7th positions in the phenyl part of the thianaphthene molecule by chlorine and bromine atom respectively. In spite of this substitution the molecules retain the two symmetry elements of thianaphthene namely the plane of the molecule and the identity characteristic of a molecule belonging to a Cs group. The spectra therefore correspond to an allowed electronic transition A^1-A^1 .

It has not been possible to give a complete vibrational analysis of all the bands measured for lack of adequate Raman and Infra-red data. Yet, a comparison of the prominent excited state frequencies involved in the spectra of these two molecules with those of 3-chlorothianaphthene and thianaphthene will be of interest. The results are tabulated in Table III.

Comparison of various excited state frequencies shows that all the substituted thianaphthenes show frequencies corresponding to 735, 938, 1012 and 1180 of thianaphthene. The spectrum of 5-chlorothianaphthene does not show any frequency corresponding to 1336 of thianaphthene and that of 7-bromothianaphthene possibly has the corresponding one as 1273 cm.^{-1} . Similarly the frequencies corresponding to 672 cm.^{-1} in thianaphthene do not seem to be present in the spectra of 5-chloro- and 7-bromothianaphthene. These two frequencies seem to be predominately perturbed by substitution in phenyl part and hence possibly involve vibrations involving the phenyl part of the molecule. Hence, it seems unlikely that the 1331 cm.^{-1} frequency of thianaphthene is either a C-S or C-C five-membered ring vibration. It is likely that such a mode may be associated with the frequency 1012 cm.^{-1} in thianaphthene and corresponding ones in the derivatives. The frequencies

714 in 5-chlorothianaphthene and 760 in 7-bromothianaphthene correspond to the totally symmetric a_{1g} vibration 710 in naphthalene. The totally symmetric C-C vibration frequencies 938 and 1180 in thianaphthene are modified to 968 and 1213 in 3-chloro thianaphthene, 995 and 1192 in 5-chlorothianaphthene and 972 and 1199 in 7-bromothianaphthene.

The excited state frequency 626 cm.^{-1} in 5-chlorothianaphthene may be due to a totally symmetric C-Cl vibration. The corresponding frequency in *para*-chloroanisole has been identified by Rao⁵ as 621 in the excited state.

TABLE III

Identified frequencies in thianaphthene and its derivatives

Thianaphthene	3-Chloro-thianaphthene	5-Chloro-thianaphthene	7-Bromo-thianaphthene
..	..	80	..
165	177	138	149
236
..	526
..	..	626	..
672	680
735	763	714	760
938	968	995	972
1012	1025	1029	1036
1180	1213	1192	1199
1336	1321	..	1273
1410	1393

The excited state frequency 526 in 7-bromo possibly represents totally symmetric C-Br vibration. The C-Br stretching frequency has been identified by Krishnamachari⁶ in *ortho*-, *meta*-, and *para*-fluorobromobenzene as 599, 607, 513 respectively. The frequency 149 represents C-Br planar bending vibration.

TABLE IV
Comparison of positions of 0-0 bands

Molecule	Wavenumber of 0-0 band in cm.^{-1}	Shift towards Red in cm.^{-1}
Thianaphthene	34062	..
3-Chlorothianaphthene ..	33733	329
7-Bromothianaphthene ..	33493	369
5-Chlorothianaphthene ..	33053	1009

The characteristic difference in the relative importance of the different vibration in 5-chloro- and 7-bromothianaphthene as compared to thianaphthene is rather significant. The 5-chloro prominently shows the vibrations responsible for (') series in thianaphthene whereas 7-bromo shows those for the inprimed ones. The primed bands in thianaphthene were explained as due to those vibrations which become totally symmetric under the reduced C_s symmetry of thianaphthene (from the D_{2h} of naphthalene). It may be noted that 5-chloro corresponds to β -substitution in naphthalene and 7-bromo to α -substitution. It would be interesting to investigate the relative importance of the totally and the non-totally symmetric vibrations in the vapour absorption spectra of α and β halogenated naphthalenes.

The shift in the 0, 0 band in the spectra of substituted thianaphthenes are tabulated in Table IV. It is observed that in 3-chloro and 7-bromo thianaphthene the shift of the 0, 0 band is small and of the same order. 5-Chlorothianaphthene, however, shows a pronounced long wavelength shift. This observation substantiates the finding in the case of solution spectra of these compounds by Desai.⁷ As already mentioned, position 5 in thianaphthene corresponds to β -position in naphthalene, whereas position 7 and possibly position 3, in thianaphthene, correspond to the α position in naphthalene. That β -substituted naphthalenes principally shift the long wavelength band is well recognised and hence in an isosteric molecule like thianaphthene a similar behaviour is observed. It seems, however, that the 2500 Å band system of 7-bromothianaphthene does not show the enhanced shift over 5-chlorothianaphthene as the α -substituted naphthalene would do against a β -substituted one. Hence it seems that as far as the effect of

substitution on individual transitions in the spectra is concerned, thianaphthene and naphthalene show differences and each molecule has to be treated independently.

SUMMARY

The near ultraviolet absorption spectra of 5-chlorothianaphthene and 7-bromothianaphthene have been investigated in the region 3050 to 2800 Å and 3050 to 2850 Å respectively—corresponding to longest wavelength system. The tentative vibrational assignments are put forward for the prominent bands. The assignment of certain frequencies are discussed with respect to the effect of substitution (Cl or Br) in the phenyl part of the thionaphthene nucleus.

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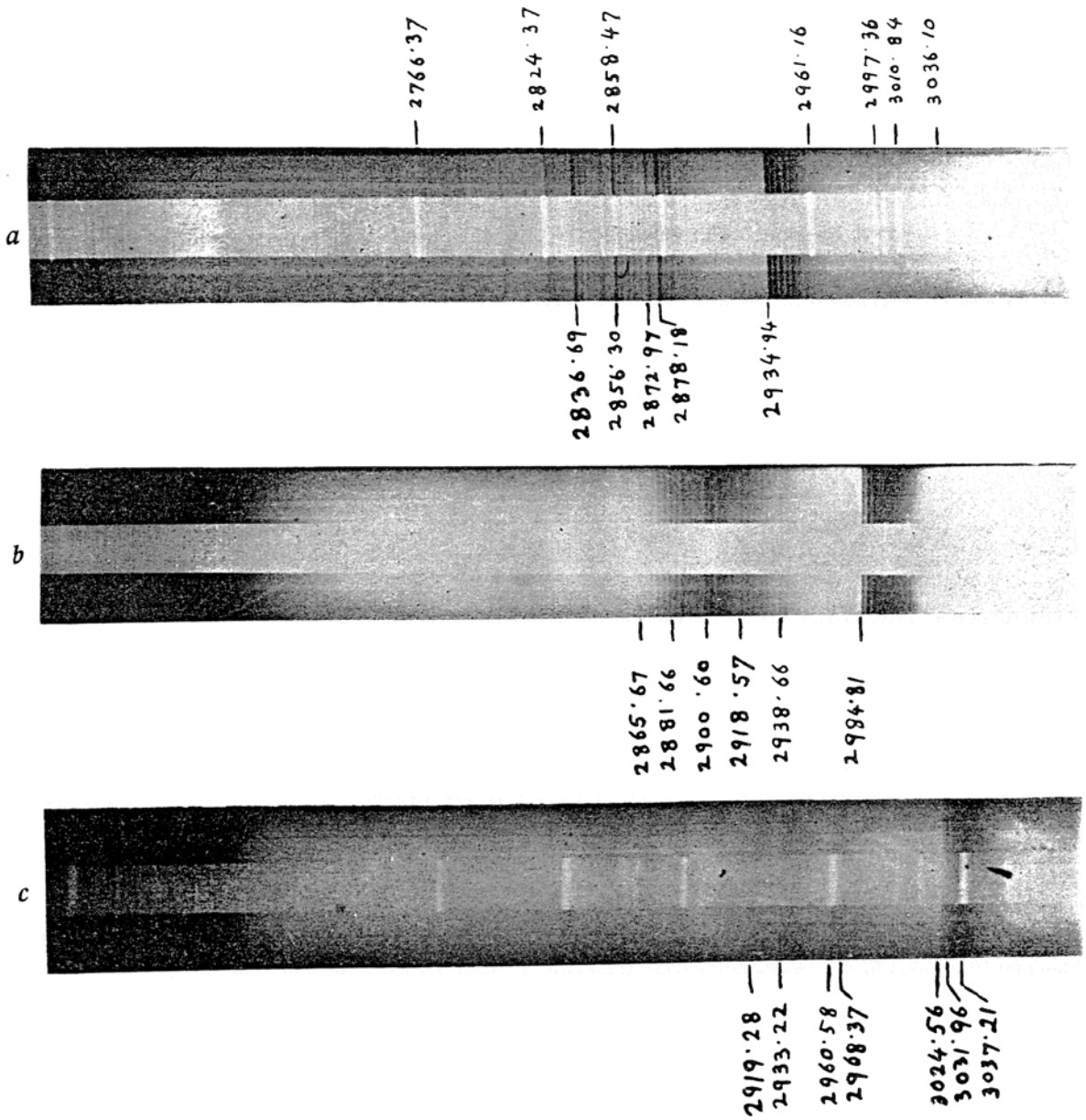


FIG. 1. (a) Absorption Spectrum of Thianaphthene, (b) Absorption Spectrum of 7-Bromothianaphthene, (c) Absorption Spectrum of 5-Chlorothianaphthene.