

ABSORPTION SPECTRUM OF 3-CHLORO-THIONAPHTHENE

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INTRODUCTION

In recent years there has been a systematic study of the electronic absorption spectra of benzene, naphthalene and their derivatives in the region about λ 3000 to λ 2400. In order to understand and interpret successfully the spectra of these compounds, it is considered beneficial to investigate the electronic spectra of bicyclic compounds containing a five-membered ring and a six-membered ring as these possess configurations intermediate between the benzene and the naphthalene molecules.

On the theoretical side, taking indene as a particular case, the electronic energy levels have been predicted from calculations applying the approximate valence bond or the atomic orbital method and by the antisymmetrized molecular orbital method by Viswanath (1953) and Ramamurty (1953). Viswanath (1952) also made an experimental study of the absorption of some molecules of this type, namely, indene, indole and thionaphthene in the vapour phase. Much information, which will be of help for a complete interpretation of the above spectra, can be obtained if the absorption of some suitable derivatives be studied. The present paper comprises an experimental investigation of the absorption of a chloro-derivative of thionaphthene, 3-chloro-thionaphthene, in the vapour phase. A preliminary report was published in *Current Science* (1953). The absorption of this molecule does not appear to have been studied by any earlier worker.

EXPERIMENTAL

The absorption spectrum of 3-chloro-thionaphthene is photographed on Hilger medium quartz spectrograph using a quartz to pyrex absorption cell of 40 cm. length. A pure specimen of the substance supplied by Light & Co. was redistilled into the absorption tube in vacuum. The amount of vapour of the substance introduced and its pressure was adjusted by varying the temperature of the reservoir containing the liquid. For recording the spectrum the temperature of the container was varied in the range -10° C. to 100° C. While working at higher temperatures the absorption tube was heated to the same temperature or maintained at a slightly higher temperature than that of the container. The windows of the absorption column were kept at a slightly higher temperature than that of the column in order to prevent the condensation of the vapour. A Hilger low voltage hydrogen arc lamp fed by a stabilized power unit supplied by the manufacturers along with the lamp was used as the source of continuous ultraviolet radiation. The spectra were recorded on Ilford special rapid photographic plates (21° Sch.). The exposure time was about 15 to 20 minutes.

DESCRIPTION

The spectrum extended from λ 3000 to λ 2755. About 90 red degraded band heads are measured. The reproduction of the spectrum photographed at 30° C.

is reproduced in Plate X. Most of the bands are sharp. The spectrum resembles closely in general appearance that of thionaphthene. It presents a typical group pattern as in thionaphthene with some overlapping at the violet end. But, whereas an alternation in the intensity of the components of each group was observed in thionaphthene, the bands in each group in the case of 3-chloro-thionaphthene shows a gradual fall in intensity from violet to red. Viewing the spectrum as a whole, there is a rapid fall in intensity of absorption from red to violet unlike the gradual fall observed in the case of thionaphthene. Table 1 records wave number and intensity data of all the bands. The intensities are, following the usual practice, expressed as v st, st, m st indicating very strong, strong, medium strong respectively; similarly vw, w, mw. The fourth column gives the difference from 0, 0 band and the last one the assignment of the bands in terms of the characteristic frequencies.

TABLE 1

Wave number	Intensity	Difference from 0, 0 cm. ⁻¹	Assignment
33319	vvw	414	
33360	vvw	373	0-2×188
33390	vvw	343	0-188-4×40?
33424	vw	309	0-188-3×40
33469	w	264	0-188-2×40
33509	m	224	0-188-40
33545	m st	188	0-188
33572	m st	161	0-4×40
33614	st	119	0-3×40
33654	st	78	0-2×40
33694	v st	39	0-40
33728	v st	5	
33733	vv st	0	0, 0
33769	vw	36	
33775	vw	42	
33802	vw	69	
33809	vw	76	
33840	vw	107	
33872	vvw	139	0+177-40
33877	vw	144	
33910	w	177	0+177
33970	w	237	
34008	w	275	
34051	w	318	
34098	w	365	
34148	w	415	0+680-188-2×40?
34178	vvw	445	
34189	vvw	456	0+680-188-40
34200	vvw	467	
34222	vvw	489	0+680-188
34256	vvw	523	0+680-4×40
34266	vvw	533	
34294	vvw	561	0+680-3×40
34301	vvw	568	0+763-188?
34331	vw	598	0+680-2×40
34372	w	639	0+680-40
34413	m st	680	0+680
34456	vvw	723	0+763-40
34463	vw	730	
34496	m	763	0+763
34543	vvw	810	
34578	vvw	845	0+1025-188
34584	vvw	851	0+680+177
34619	vvw	886	0+968-2×40

TABLE I.—Contd.

Wave number	Intensity	Difference from 0, 0 cm. ⁻¹	Assignment
34660	vvw	927	0+968-40
34682	vvw	949	0+763+177?
34696	vvw	963	
34701	m	968	0+968
34726	m bd	993	0+1025-40?
34758	m bd	1025	0+1025, 0+1213-188
34799	w	1066	
34834	w	1101	
34866	vvw	1133	0+1213-2×40
34875	w	1142	
34905	w	1172	0+1213-40
34912	w	1179	
34946	m	1213	0+1213
34965	w	1232	
34982	m	1249	0+1321-2×40?
35015	m	1282	0+1321-40
35047	m	1314	
35054	m st	1321	0+1321
35088	w	1355	
35096	w	1363	0+2×680
35125	w	1392	
35132	w	1399	0+763+680-40?
35159	w	1426	
35167	vw	1434	0+763+680?
35205	vw	1472	
35274	vw	1541	
35318	vvw	1585	
35350	vvw	1417	
35414	vvw	1681	
35482	vvw	1769	
35564	vvw	1831	
35615	vvw	1882	
35640	vvw	1907	
35704	vvw	1971	
35778	vvw	2045	0+2×1025, 0+3×680
35801	vvw	2068	
35829	vvw	2096	
35904	vvw	2171	0+1213+968?
35955	vvw	2222	
36063	vvw	2330	
36131	vvw	2398	
36165	vvw	2432	0+2×1213
36234	vvw	2501	
36287	vvw	2554	

ANALYSIS

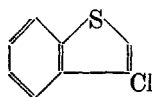
Thionaphthene, of which 3-chloro-thionaphthene is a derivative, is a molecule containing one six and one five-membered rings. It has only two symmetry elements, the plane of the molecule and the identity, characteristic of the molecules belonging to the C_s group. The spectrum corresponding to the allowed electronic transition $A'-A'$ shows conspicuous group arrangements of the bands. These arrangements are observed to differ from those found in disubstituted benzenes which also belong to the same symmetry class. This may be explained on the basis of the different electronic structures of the two types. However, in general appearance and nature, the spectra resemble each other. The spectrum of thionaphthene extends from λ 3000 to λ 2685. The 0, 0 band is located at ν 34060. The bands in the 0, 0 group

are almost equispaced and exhibit a distinct alternation in intensity. These are analysed assuming a number of difference frequencies. This entire pattern repeats itself with the bands at characteristic upper state frequencies to a greater or a smaller degree depending upon the intensity of the main head. The following prominent frequencies are identified in the upper state:—

672, 736, 936, 1181 and 1331.

Of these 1331 is weak, whereas the rest are of higher intensity. 936 and 1181 are assigned to C—C ring frequencies. 1331 is suggested to probably represent a characteristic vibration of the five-membered ring, since frequencies of this order have not been identified in the ultraviolet spectra of benzene and its derivatives. No frequencies smaller than 672 are reported in this molecule.

3-chloro thionaphthene is a derivative obtained by replacing the hydrogen atom in position three of the five-membered ring by a chlorine atom; and has the structure



In spite of this substitution it retains the two symmetry elements, the minimum possible in the case of plane molecules. However, this substitution results in an effective reduction in the spectroscopic symmetry character of the molecule. The spectrum corresponds to an allowed electronic transition A'-A'. Though the spectrum is expected to possess the general appearance of those of the molecules belonging to the same symmetry class, it should show the characteristics of an allowed transition to a much greater degree than thionaphthene. The structure of groups may be different. The number of frequencies that occur in this spectrum are expected to be larger.

The absorption of 3-chloro-thionaphthene presents a distinct group pattern, which is most marked in association with the 0, 0 band, and there is some overlapping at the violet end of the spectrum. The intensity of the groups falls very rapidly from red to violet end of the spectrum. The most intense group is at the red end with the head at ν 33733. This head is taken as the 0, 0 band since in an allowed case the vibrationless electronic transition should be strong. This is accompanied on the red side by a number of almost equispaced bands with a gradual fall in intensity of the individual components, as distinct from the alternation in intensity observed in thionaphthene. This pattern is also prominent at

ν 33910, ν 34413, ν 34496, ν 34701, ν 34758, ν 34946 and ν 35054.

The number of component heads and the intensities of these fall off rapidly towards the violet end. The pattern is partially observed in association with the comparatively weaker frequencies. Only two distinct frequencies 40 and 188 could be suggested from an analysis of the component heads in the different groups. Of these 40 forms long progressions in all the groups. It also occurs as a progression superposed on 188. The gradual reduction in intensity of the components lends support for assuming only one difference frequency of value 40 to explain the group pattern. 188 may be thought of either as a ν - ν transition or as one of the ground state frequencies. Most probably it is the latter since 177 occurs in the upper state which may correspond to 188. A confirmation has to be obtained from Raman and Infra-red data.

Taking the head of each group as representing a distinct vibration the following upper state frequencies are obtained:

177, 680, 763, 968, 1025, 1213 and 1321.

Of these 680 is most intense next to the 0, 0. It forms a progression as can be seen from the last column of Table 1. Next in order of intensity are the bands 1321 and 1213 and 968; 177 has the smallest intensity, the rest of the frequencies fall in between. In the absence of any data on the ground state frequencies, no assignment of these frequencies could be made, though 680 presents the characteristics of and probably represents a totally symmetric vibration.

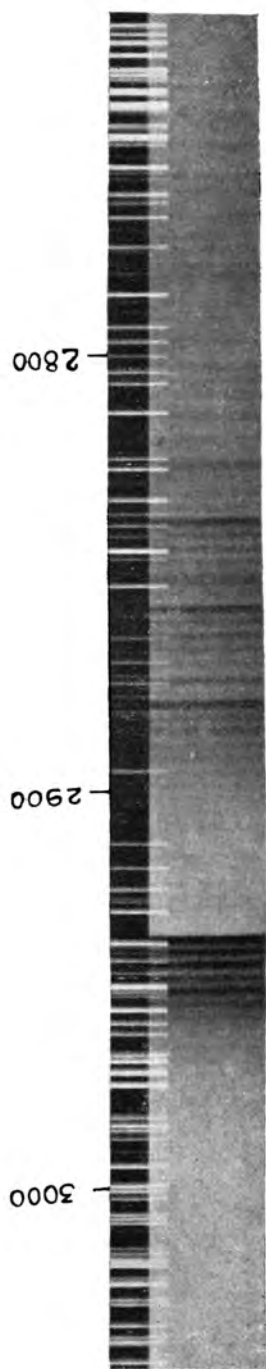
COMPARISON WITH THIONAPHTHENE

3-chloro-thionaphthene is a molecule in which the substitution is in the five-membered ring. Vibrations in this ring should be appreciably affected by this substitution by the chlorine atom while all the frequencies characteristic of vibrations in the six-membered ring may not be influenced. Chlorine is strongly electronegative as a substituent for hydrogen in C-H and can supply migration electrons into the five-membered ring direct, modifying the character and magnitude of the vibrations of the C-H type and those of the ring. A comparison between the vibrational frequencies in both these molecules, should yield interesting information about the nature of the vibrations. They are listed in Table 2. The spectra of the two molecules are presented in juxtaposition in the Plate X. The values given for thionaphthene are those reported by Viswanath. Excepting 1321 and 1331 the rest are slightly and uniformly larger in magnitude and smaller in intensity in the substituted molecule than in thionaphthene. This suggests that these represent frequencies which are not materially affected by the substitution. The indirect effect of the substituent, perhaps manifested itself as a small alteration in magnitude and intensity. These are to be associated with the phenyl ring. On the other hand, 1321 (in 3-Cl-thionaphthene) is stronger than 1331 (in thionaphthene) and is, obviously, influenced by the substitution. The very small change in magnitude suggests that it probably has rather small contribution from the hydrogen atoms. It may either be a C-S vibration (common in both molecules) or a C-C five-membered frequency. The occurrence of a vibration of smaller magnitude than 680, viz., 177 should also be noted. The intensity of the suggested C-C ring frequencies of the phenyl ring, 936 and 1181, is much reduced in the substituted molecule (968, 1213). The 0, 0 band is shifted toward the red by 327 cm^{-1} . The length and the total intensity of the transition has diminished in the substituted molecule. There is a rapid fall in the intensity of the bands from red to violet in this as against the gradual fall in thionaphthene.

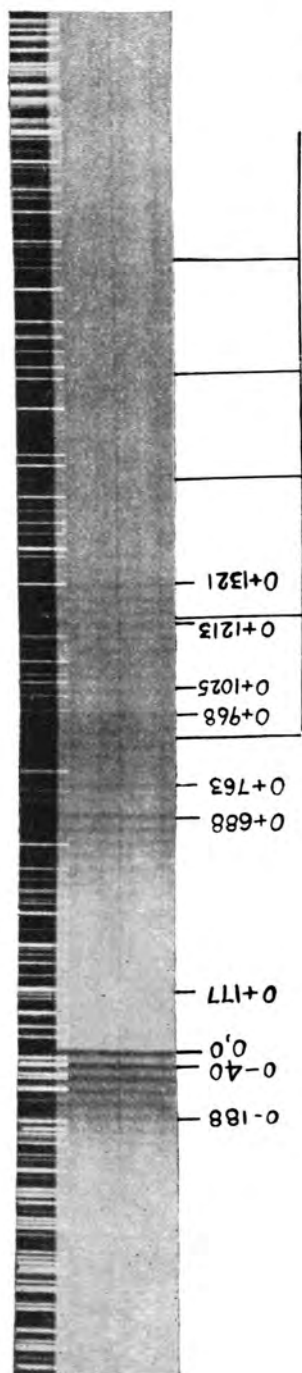
TABLE 2

Thionaphthene (Viswanath)	3-Cl-thionaphthene (Present work)
	177 (w)
672 (m st)	680 (m st)
736 (m st)	763 (m)
936 (st)	968 (m)
	1025 (m bd)
1181 (m st)	1213 (m)
1331 (w)	1321 (m st)

A special feature noteworthy in this case is the occurrence of a sequence of continuous patches superposed at the violet end. Measurements of the wavelengths could not be made because of the low intensity and diffuseness. These are indicated in Plate X. The estimated wavelength data is given in Table 3. They are almost equi-spaced with an average separation of 331 cm^{-1} . The one at $\nu\ 34640$ is most intense and lies at the extreme red end of the sequence. It may be a separate system of weak intensity.



a



b

Diffuse patches.

(a) Absorption spectrum of Thionaphthene.
 (b) Absorption spectrum of 3-(3-Thionaphthene).

TABLE 3

Estimated wavelength	Intensity	Wave number	Difference between two consecutive patches in cm.^{-1}
2886	st	34640	339
*2858	m st	34979	321
2832	m	35300	340
2805	w	35640	346
2778	vw	35986	340
2752	vw	36326	

* Overlapped by the discrete absorption bands.

SUMMARY

The absorption of 3-Cl-thionaphthene, a derivative of thionaphthane in the region λ 3000 to λ 2755 is investigated. About 90 red degraded bands are measured. An analysis of these bands is presented using the following upper state frequencies 177, 680, 763, 968, 1025, 1213, 1321. The assignment of certain frequencies have been discussed taking into consideration the possible effect of substitution of the Cl atom on the vibrations. 1321 may be a C-S or C-C five-membered ring frequency. The 0,0 band is shifted towards red by 327 cm.^{-1} from that of thionaphthene. Estimated wavelengths of the sequence of diffuse patches which occur superposed on this system at the violet end are listed.

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