THE ULTRAVIOLET ABSORPTION SPECTRA OF ORGANIC SUBSTANCES IN THE LIQUID AND SOLID STATES. IV. CHLOROTOLUENES*

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Plates XVI A, B

ABSTRACT. The ultraviolet absorption spectra of o- and m-chlorotoluene in the vapour, liquid and solid states and of p-chlorotoluene in the liquid and solid states have been investigated in order to find out the changes which may take place in the spectra with change of state. In all the cases the bands shift to longer wavelength side with liquefaction by more than 250 cm^{-1} and in the case of both ortho- and metachlorotoluene the principal o, o band shifts by about 700 cm^{-1} towards shorter wavelength side on solidification. In the case of these latter two compounds the principal band is accompanied by two fainter satellites It is pointed out that these results may indicate formation of virtual bonds between neighbouring molecules in the solid state and that similar results reported by previous workers in the case of benzene may also indicate formation of such virtual bonds.

INTRODUCTION

In a programme undertaken to study the ultraviolet absorption spectra of organic substances in the liquid and solid states in order to find out whether the electronic energy levels undergo any remarkable change with change of state, interesting results were observed in the case of the cresols and xylenes (Swamy, 1952a, 1952b), It was observed that the impact of neighbouring molecules hinders transitions to higher vibrational energy states in the liquid state. In the solid state, however, in some cases transitions to vibrational states of higher quantum numbers were observed. It was observed recently (Sirkar and Swamy, 1952) that besides the changes mentioned above, the solidification of orthodichlorobenzene at −180°C brings about a splitting up of the electronic energy level into three components. These results were interpreted on the hypothesis that formation of virtual bonds between neighbouring molecules in the solid state is responsible for these changes in the absorption spectra. In order to find out whether the relative positions of substitution groups in other disubstituted benzene compounds have any influence on the changes in the absorption spectra which take place with the solidification of the substances, the absorption spectra of

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o-, m- and p- chlorotoluenes in the vapour, liquid and solid states have been studied and discussed in the light of the hypothesis put forward in the previous papers (Swamy, 1952a 1952b) regarding the quenching of vibrational transitions in the liquid and formation of virtual bonds between neighbouring molecules in the solid state at low temperatures.

EXPERIMENTAL

The three chlorotoluenes were supplied by Eastman Kodak Company and they were distilled four times in vacuum before being used for the investigation. The absorption spectra of o- and m- chlorotoluene in the vapour state were photographed using absorption tubes of length 30 cm and of diameter 12 mm, quartz windows being fitted to the tube, using sodium silicate as cement. The liquid was contained in a small bulb attached to the tube and through another side tube the absorption tube was connected to a Cenco-Hyvac pump, After the tube had been evacuated, the stop-cock leading to the pump was closed and the vapour was allowed to fill up the tube with its saturation pressure at room temperature. An Adam Hilger E_1 quartz spectrograph having a dispersion of 3 A. U. per mm in the region of 2600° A was used and Ilford HP_3 films were used to photograph the spectra On each spectrogram iron arc lines were photographed for comparison.

Films having thickness of the order of 0.2 mm were required to produce absorption bands in the liquid state. Absorption spectra in the solid state at −180°C were photographed with the technique described previously (Swamy, 1951, 1952a). For comparison mercury arc spectrum was recorded with the help of a Hartmann diaphragm on each spectrogram.

RESULTS

Spectrograms for o-, m-, and p-chlorotoluene in the liquid state and for the solid state at −180°C and those of o- and m- chlorotoluene in the vapour state are reproduced in Plate XVIA. The bands in the liquid and solid states being broad, microphotometer records were obtained to measure the frequencies accurately. These records are reproduced in figures 4, 5 and 6 of Plate XVIB. The Hg line 2537° A included in the spectrograms served as the reference in the microphotometer records and measurements were made of the centre of the absorption peak. Only the prominent bands in the vapour state have been measured and assignments given. Measurements in this case were made of the edges of the bands. The wave numbers of the bands in the vapour, liquid and solid states are given in Tables 1—III in which wave-numbers of bands observed in solution by previous workers are included for comparison. Assignments have been made in the case of bands of o- and m-chlorotoluene in the solid state at −180°C on the assumption that the electronic energy level is split up into three components. Bands of p-chlorotoluene have been assigned to certain transitions and the assignments are given in the tables, the data for the vapour being those reported by Viswanath (1952), ·

TABLE I

Absorption bands of o-chlorotoluene. v in cm^{-1}

Present author		Wolf and Herold (1931)	Purvis (1911)	Present author				
Vapour (Prominent bands)	Assignment	Solution in heptane	Liquid	Liquid 30°C	Assignment	Solid, −180°C	Assignment	
36589 (ms)	v_0-249	36560 (s)	36340	36381	v_0	36830 (m)	B$_0$	
36677 (s)	v_0-161		(1 st	(vs,				290
36838 (vs)	v_0		wide)	broad)				
37206 (w)	v_0+368		1018			37122 (vs)	A$_0$	
37298 (m)	v_0+460		37358	37396	v_0+1015	37420 (m)	C$_0$	590
37368 (msf)	v_0+530		(f st	(s,				
37463 (vw)	v_0+625		wide)	broad)				
37518 (w)	v_0+680	37550 (m)	2036					
37651 (m)	v_0+813		38376			37840 (vs)	B$_1$	B$_0+$
37753 (ms)	v_0+915		(vw,	38413	$v_0+2\times1015$			1010
37843 (vs)	v_0+1005		wide)	(weak)		38130 (s)	A$_1$	A$_0+$
37922 (ms)	v_0+1084							1010
38030 (w)	v_0+1192					38428 (ms)	C$_1$	C$_0+$
38215 (s)	$v_0+915+460$							1008
38290 (ms)	$v_0+915+530$							
38364 (m)	$v_0+1005+530$							
38653 (m)	$v_0+1005+813$	38750 (s)						
38850 (mst)	$v_0+2\times1005$					38849 (m)	B$_2$	B$_0+$
39010 (w)	$v_0+2\times1084$							1010$\times2$
39198 (w)	$v_0+2\times915+530$	3 500 (m)						
39290 (vw)	$v_0+1005+915 +530$	40550 (w)						

TABLE II

Absorption bands of a m-chlorotoluene. v in cm^{-1}

Present author		Wolf and Herold (1931)		Purvis (1911)		Present author		
Vapour (Prominent bands)	Assignment	Solution in heptane	Assignment	Liquid	Liquid at 30°C	Assignment	Solid at −180°C	Assignment
36619 (vs)	v_0						36120 (m)	C$_0$
37037 (ms)	v_0+418	36400 (s)	v_0	36287	36315	v_0	36630 (s)	B$_0$
37095 (ms)	v_0+476			(f st,	(vs,			
37231 (w)	v_0+612			wide)	broad)			
37330 (m)	v_0+711						37015 (vs)	A$_0$
37397 (msf)	v_0+778				36742			
37470 (m)	v_0+851				(vw)	v_0+427		
37608 (s)	v_0+981	37400 (s)	v_0+1000	37302				
37830 (ms)	v_0+1211			(f st,	37310	v_0+905		
38025 (m)	$v_0+981+418$			wide)	(vs,		37150 (w)	C$_1$
38177 (m)	$v_0+2\times778$				broad)			
38580 (s)	$v_0+2\times981$							
38819 (s)	$v_0+1220+918$	38350 (m)	v_0+1950	38303	38297	$v_0+2\times995$	37656 (s)	B$_1$
39036 (m)	$v_0+2\times1211$			(vw	(m)		38040 (s)	A$_1$, A$_0$
39194 (w)	$v_0+2\times981 +612$			wide)				+1025
							38175 (m)	C$_2$
							38680 (a)	B$_2$
							39065 (s)	A$_2$ A$_0+$
39568 (m)	$v_0+3\times981$	39350 (w)	$v_0+1950 +1000$				39200 (vw)	2$\times$1025 C$_3$

Table III

Absorption bands of p-chlorotoluene. v in cm^{-1}

Viswanath (1952)		Wolf and Herold (1931)	Present author			
Vapour (Prominent bands)	Assignment	Solution in heptane	Liquid, 30°C	Assignment	Solid, −180°C	Assignment
36299 (v st)	ν_0	36030 (s)	36059 (vs, broad)	ν_0	36224 (vs)	ν_0
36843 (m st)	ν_0+544					
37038 (m st)	$\nu_0+762-26$				36992 (s)	ν_0+768
37061 (m st)	ν_0+762	36930 (s)	37071 (vs, broad)	ν_0+1012		
37343 (m st)	ν_0+1044				37282 (s)	ν_0+1058
37351 (m st)	ν_0+1052	37400 (w)				
37488 (m si)	ν_0+1189	37990 (s)			37756 (w)	$\nu_0+2\times768$
38114 (m st)	$\nu_0+1052+762$		38075 (m)	$\nu_0+2\times1008$		
38399 (m st)	$\nu_0+2\times1052$	38760 (s)			38148 (s)	$\nu_0+1058+768$
39172 (w)	$\nu_0+2\times1052$				38344 (m)	$\nu_0+2\times1058$
	$+796-26$	39650 (w)			39118 (m)	$\nu_0+2\times1058+768$

DISCUSSION

There are some general features in the changes which take place in the absorption spectra with change of state. Along the series o-, m-, and p-chlorotoluene, the position of the o-o transition moves towards lower frequencies. The number of bands diminishes when the vapour is liquefied and instead of sharp bands characteristic of vapour, only broad bands are observed in the liquid state. In the solid state at −180°C more bands appear, and the bands become narrower, but the edges are not sharp, as can be seen from the microphotometric records. The principal band and its companions shift towards longer wavelengths on liquefaction of the vapour and they shift again to shorter wavelengths on solidification of the liquid. The formation of broad bands and the diminution in the number of bands with liquefaction were ascribed by the author (Swamy, 1952a) to the influence of translational motion of the molecules in the liquid in the state of aggregation. The constant impact of molecules hinders transitions to higher vibrational energy states. The considerable shift towards longer wavelengths may be due to the lowering of the electronic energy state due to the association of molecules through virtual bonds.

It is observed that in the case of both o- and m- chlorotoluene the electronic energy level is split up into three components in the solid state at −180°C. In o-chlorotoluene, the components are on either side of the principal band, while in meta both the compononts are on the longer wavelength side. In p- chlorotoluene, the electronic energy level does not appear to be split up. It has to be concluded on the basis of these results that the splitting depends on the position of the substituent groups and that
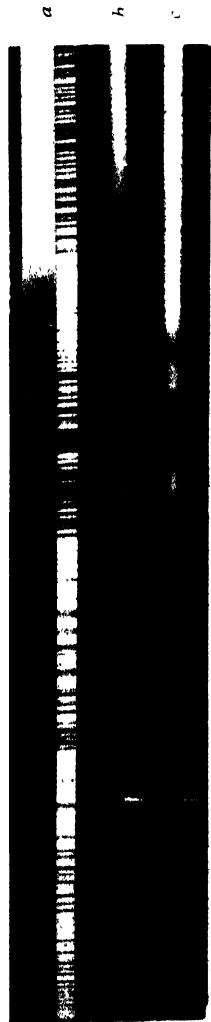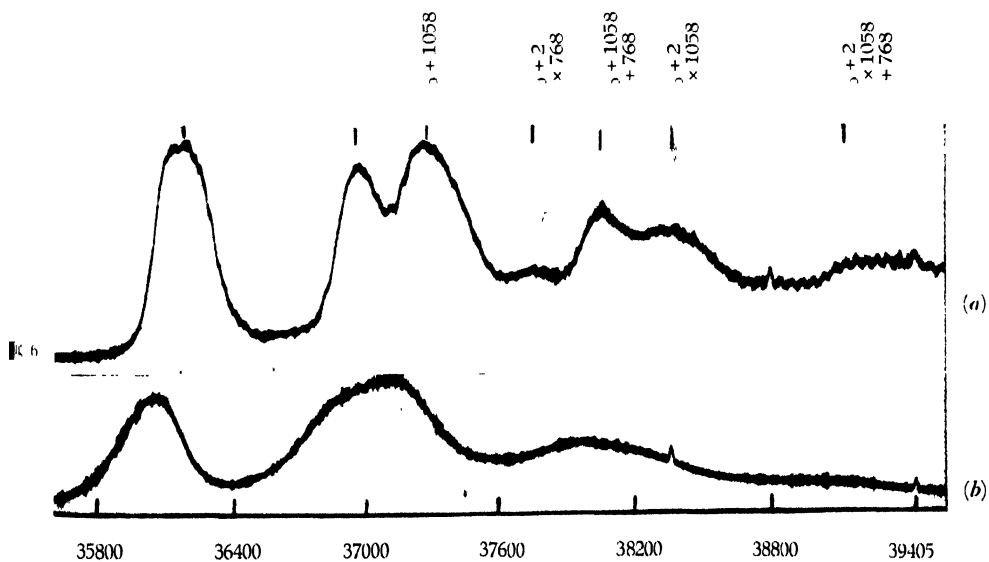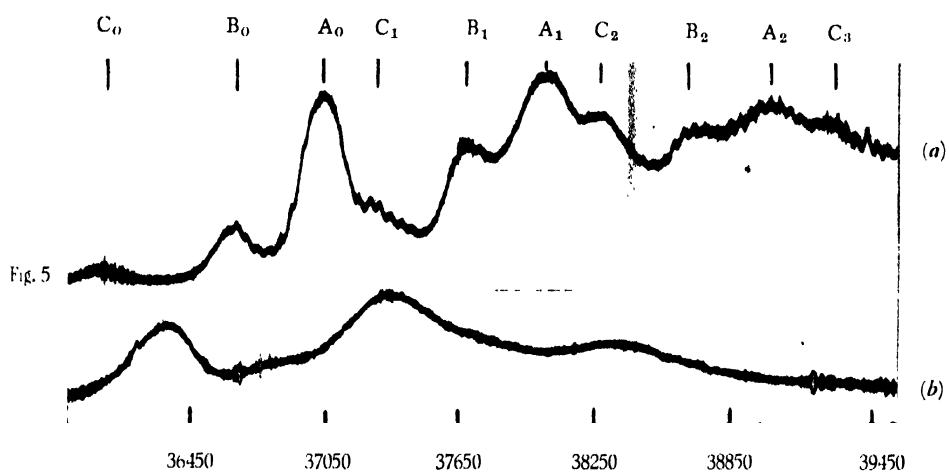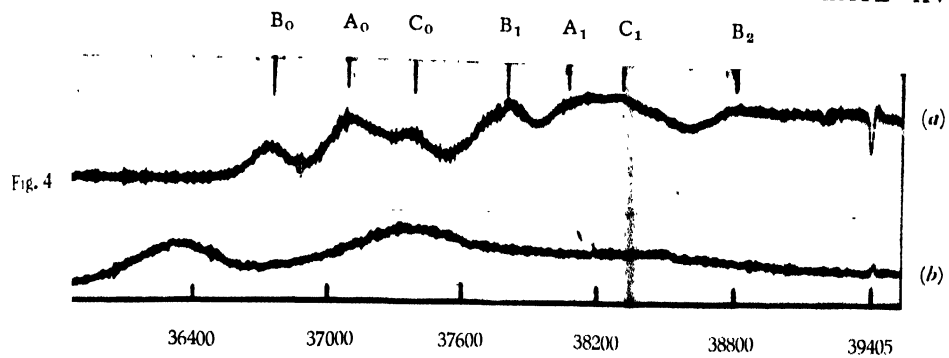
PLATE XVI A

Fig. 1

Fig 2

Fig. 3.

Ultraviolet absorption spectra

Fig. 1. Orthochlorotoluene
(a) Vapour at 30°C
(b) Liquid at 30°C
(c) Solid at −180°C

Fig 2. Metachlorotoluene
(a) Vapour at 30°C
(b) Liquid at 30°C
(c) Solid at −180°C

Fig. 3. Parachlorotoluene
(a) Liquid at 30°C
(b) Solid at −180°C

Microphotometer records of the absorption spectra of chlorotoluenes.

Fig. 4. (*a*) *o*—Chlorotoluene   solid at   −180°C
        (*b*)   ,.   liquid at   30°C

Fig. 5. (*a*) *m*—Chlorotoluene   solid at   −180°C
        (*b*)   ,.   liquid at   30°C

Fig. 6. (*a*) *p*—Chlorotoluene   solid at   −180°C
        (*b*)   ,,   liquid at   30°C

splitting of electronic energy levels does not take place when the permanent electric moment is small, as in the case of *p*- chlorotoluene. The results will now be discussed for the three substances separately.

(a) *o-Chlorotoluene.* The absorption spectra of *o*-chlorotoluene in the vapour state was studied previously by Purvis ('1911) and Tintea (1939). The data reported by Purvis give only the positions of some of the bands without giving any assignments. The data reported by Tintea were not available to the author and hence the absorption spectra of *o*- chlorotoluene in the vapour state were photographed by the author. A large number of bands are observed, but measurements of only the principal bands produced in the excited state are made and assignments are given in column 2 of Table I. The vapour spectrum resembles that of *o*-fluorotoluene (Cave and Thompson, 1950). The o,o band is at 36838 cm^{-1}. But just to the lower frequency side of this position there are several intense bands, the principal ones being at 36677 and 36589 cm^{-1} respectively. These represent transitions o – 161 and o – 249 cm^{-1} respectively and may be correlated with the strong Raman frequencies 163 and 247 cm^{-1} (Magat, 1936), The principal frequencies are $v_0 + 530$, $v_0 + 813$, $v_0 + 915$, $v_0 1005$, $v_0 + 1084$ and their harmonics and combinations. Strong bands seem to appear at intervals of about 1000 cm^{-1}. The C-Cl vibration appears to be weak.

In the present investigation only three bands are observed in the case of *o*-chlorotoluene in the liquid state, the frequency difference being 1015 cm^{-1}. The bands are broad and the v_0 band is shifted by about 450 cm^{-1} towards longer wavelength from its position in the vapour state probably due to formation of virtual bonds. The principal v_0 band shifts from 36381 cm^{-1} in the liquid state to 37122 cm^{-1} in the solid state at −180°C and splits up into three bands in the solid state. So, in place of the three bands in the liquid state there are altogether seven bands. The bands also become sharper in the solid state. There are two intense bands marked A_0 and A_1 accompanied by less intense bands on either sides. The band on the longer wevelength side of the principal bands is at a distance of 290 cm^{-1} and the distance on the shorter wavelength side is 590 cm^{-1}. The former band cannot be due to a $v \rightarrow o$ transition, as the distance between the two bands is large enough to make the number of molecules present in the excited state of this mode of vibration negligible. There is no strong band even in the vapour state corresponding to this transition.

The feebleness of the two companions of the principal absorption band may be explained on the assumption that the virtual bond is formed only at some point in the molecule, the other carbon atoms remaining unaffected. The large shift of the principal band may be due to change of the energy of the whole molecule, *i.e* , of all the carbon atoms caused by the formation of the virtual bond.

(b) *m-Chlorotoluene.*—Column (2) of Table II shows the tentative assignments for the absorption bands of *m*-chlorotoluene in the vapour

state. Here again only the prominent bands have been measured. The spectrum is entirely different from that of o-chlorotoluene and resembles that of m-fluorotoluene reported by Cave and Thompson (1950). The ν_0 band is at 36619 cm^{-1} and is at about 220 cm^{-1} on the longer wavelength side of the ν_0 band for o-chlorotoluene. The principal frequencies are ν_0+418, ν_0+476, ν_0+778, ν_0+981, ν_0+1211 and their harmonics and combinations. The C-Cl vibration is more prominent in this isomer than in the ortho form. Strong bands appear at intervals of about 980 cm^{-1}. In the liquid state the substance produces four bands, the frequencies being represented by ν_0, ν_0+427, ν_0+995 and $\nu_0+2\times995$. The bands are broad and the principal band is shifted by about 300 cm^{-1} towards longer wavelengths from the corresponding position in vapour. This large shift of the ν_0 band towards longer wavelength in the liquid state may be again due to the association of molecules which lower the electronic energy state. In the case of the solid state at $-180°$ C, the ν_0 band shifts to 37015 cm^{-1} and the four bands in the liquid state are replaced by ten bands The most intense band is at 37015 cm^{-1} with two fainter companions at 36630 and 36120 cm^{-1} marked B_0 and C_0 respectively. The principal bands are at a distance of about 1025 cm^{-1} from one another and this is greater than the principal frequency 981 observed in the vapour state. It can, therefore, rightly be assumed that the electronic energy level in this case also splits up into three components, both the components lying on the longer wavelength side of the main band. This splitting is entirely diffeient from Davydov splitting (1948) as the split components are far away from the principal band. On comparing the spectra of the two isomers o- and m-chlorotoluene in the solid state, it is observed that the nature of splitting of the electronic energy level depends on the position of the substituent gioups.

It may be pointed out in this connection that even in the case of benzene in the solid state at $-259°$ C Kronenberger (1930) observed new series of bands and also the forbidden o, o band was observed by him. This appearance of the o, o band may be due to the destruction of the six fold symmetry of the benzene molecule by the formation of virtual bonds among neighbouring molecules and the appearance of the new series of bands may be actually a case of splitting up of the energy level owing to the formation of the virtual bonds. These facts may lend additional suppoit to such hypothesis put forward by Sirkar (1936) earlier and by Sirkar and Ray (1950) recently.

(c) *p-Chlorotoluenc.*—The absorption spectra of p-chlorotoluene in the vapour state was studied very recently (Viswanath, 1952). The ν_0 band has been located at 36299 cm^{-1}. The prominent bands represent frequencies, ν_0 ν_0+762, ν_0+1044, ν_0+1052, ν_0+1189 and their harmonics and combinations. The spectrum resembles that of p-dichloiobenzene, the main bands appearing at intervals of 1052 cm^{-1}. The band at 37061 representing ν_0+762 is strong, which indicates the presence of fairly strong C-Cl vibration. In the present investigation only three bands are observed in the liquid state of the subs-

tance, the frequency-difference being 1012 cm^{-1}. The bands are broad and the ν_0 band is shifted by about 240 cm^{-1} towards longer wavelengths from its position in the vapour state.

When the liquid is solidified and cooled to $-180°C$ the ν_0 band shifts by about 165 cm^{-1} towards shorter wavelength and altogether seven bands are observed. They may represent frequencies $\nu_0 + 768$, $\nu_0 + 1058$ and their combinations and harmonics. The C-Cl vibration which is not prominent in the liquid state appears prominently at $-180°C$. Assignments of the bands are given in terms of the vibrational frequencies observed. It is observed that the electronic energy level is not split up in this case. The molecule of p-chlorotoluene has a symmetric structure, the methyl and chlorine atoms being in diametrically opposite positions in the benzene ring. This makes the permanent electric moment almost zero. Freedom of rotation of the molecule is amply facilitated and the packing of the molecules may be loose in the para compound. This makes transitions to higher harmonic states possible.

The investigations are being continued with other substances and the results will be reported shortly.

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