

RAMAN, INFRARED AND LUMINESCENCE SPECTRA OF
SOME TRISUBSTITUTED BENZENES

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Plate VIII

ABSTRACT. In the present paper tentative assignment of the vibrational frequencies of the molecules of 2, 4- and 3, 4-dichlorotoluenes and 1, 2, 4-trichlorobenzene has been proposed from an analysis of the Raman and infrared spectra of the compounds. The Raman spectra of the dichlorotoluenes have been investigated at -180°C and it has been observed that some of the intramolecular vibrations are affected and a few low frequency lines are exhibited by the compounds at the low temperature. Explanation of these changes has been offered in terms of association of the molecules at the low temperature. It has also been observed that in the solid state at -180°C both the compounds yield luminescence bands and the $\text{C}=\text{C}$ valence oscillation appears to be coupled with the electronic transition giving rise to these bands.

INTRODUCTION

It is known from previous investigations (Biswas, 1954, 1955a,b, Sanyal, 1953) that the Raman spectra of mono- and disubstituted benzene compounds undergo changes and new low frequency Raman lines appear in the spectra with change of state and lowering of temperature, depending on the nature and relative positions of the substituents. In the present work, such investigation has been extended to two trisubstituted benzene compounds, viz., 2, 4- and 3, 4-dichlorotoluene. In order to understand the significance of the changes, it is necessary to assign the molecular frequencies, and both infrared and Raman spectra of the compounds were studied for this purpose. As a comparison with 1, 2, 4-trichlorobenzene would be helpful in making the assignments, the infrared spectrum of this compound was also recorded in the present investigation and the data for the Raman spectra obtained by Mukherjee (1960) have been utilised. The proposed assignments of the frequencies of all the three compounds and the observed changes in the Raman spectra of 2, 4- and 3, 4-dichlorotoluene with solidification have been discussed in this paper.

EXPERIMENTAL

The liquids were supplied by Fisher Scientific and Co., U.S.A. and were repeatedly subjected to both fractional and vacuum distillation before each exposure. In the case of the dichlorotoluenes two spectrograms, one with suit-

able light filters and another without filters, were obtained both for the liquid and solid states. The experimental arrangement for recording the Raman spectra in the solid state was the same as that reported earlier (Deb, 1960). The polarisation of the Raman lines was also studied by photographing the two components simultaneously with the help of a double image prism. The Raman spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph giving a dispersion of about 11 Å per mm in the 4046 Å region.

The infrared absorption spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer with NaCl optics. Thin films of the liquids at the room temperature pressed between two rocksalt plates were used to obtain the absorption spectra.

RESULTS AND DISCUSSION

The spectrograms showing the Raman lines of 2, 4- and 3, 4-dichlorotoluene in the liquid and solid states are reproduced in Figs. 1 and 2, Plate VIII and the infrared absorption curves of the dichlorotoluenes and 1, 2, 4-trichlorobenzene are shown in Figs. 3, 4 and 5. The frequency shifts of the Raman lines and the observed infrared frequencies in cm^{-1} of the three compounds are given in Tables I, II and III, the Raman frequencies for 1, 2, 4-trichlorobenzene being taken from Mukherjee's results (Mukherjee, 1960). The state of polarisation of Raman lines are indicated by the letters 'P' and 'D' which mean 'polarised' and 'totally depolarised' respectively. The frequencies lower than 600 cm^{-1} could not be studied in the infrared because of the limitation of the NaCl optics used.

(a) *Assignment of molecular frequencies of 2, 4- and 3, 4- dichlorotoluene and 1, 2, 4- trichlorobenzene.*

The strong Raman lines at 705 cm^{-1} , 685 cm^{-1} and 675 cm^{-1} observed in the case of 2,4-dichlorotoluene, 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene respectively (698 , 682 and 675 cm^{-1} in the infrared) may be assigned to a C—Cl vibration arising from a_{1g} , b_{1u} , e_{2g} and e_{2u} vibrations in benzene, all of which become a' -type vibration in these compounds having C_s symmetry. The polarisation data support this assignment which is also in agreement with the results for mono- and dichlorobenzenes (Sponer and Kirby-Smith, 1941). There would also be components arising from these modes with frequencies of C—H valence oscillation of a' -type. They are likely to be represented by the lines 3062 , 3062 and 3066 cm^{-1} for the three compounds. We should also expect a corresponding C—CH₃ stretching oscillation in the case of the dichlorotoluenes and actually the Raman spectra of the two dichlorotoluenes show lines at 1203 and 1211 cm^{-1} which should represent this vibration, there being no corresponding line in the spectrum of 1, 2, 4-trichlorobenzene. The depolarised lines 2926 cm^{-1} of 2, 4-dichlorotoluene and 2938 cm^{-1} of 3, 4-dichlorotoluene have also no counter-

TABLE I
Raman and infrared spectra of 2, 4-dichlorotoluene

| Raman shift in cm^{-1} | | | Infrared bands Waveno, in cm^{-1} and intensity |
|---------------------------------|------------------------|---------------------|--|
| Liquid at 30°C: | | Solid at -180°C: | |
| Landolt-Bornstein (1951) | Present authors | | |
| | | 28 (3) | |
| | | 42 (1) | |
| | | 84 (4b) | |
| | | 101 (1) | |
| 122 (3) | 127 (2) o, k D | | |
| 181 (7) | 181 (6) \perp o, k D | 160 (1b) | |
| 202 (8) | 202 (8) \perp e, k D | 205 (4b) | |
| 265 (0) | 269 (0) k | 268 (1) | |
| 311 (5) | 312 (6) \perp e, k D | 318 (3) | |
| 378 (7) | 380 (8) \perp e, k P | 380 (3) | |
| 400 (3) | 402 (3) o, k P | 401 (1) | |
| 462 (4) | 464 (4) o, k P | 464 (2) | |
| 542 (0) | | | |
| 645 (3) | 646 (3) o, k D | 653 (1) | |
| 704 (6) | 705 (8) o, k P | 706 (6) | 698 (w) |
| | | | 799 (s) |
| 832 (6) | 834 (8) o, k P | 833 (6) | 825 (s) |
| | | | 852 (w) |
| | | | 983 (w) |
| 1046 (0) | 1049 (1) o, k | 1048 (0) | 1044 (ms) |
| | | | 1088 (mb) |
| 1105 (5) | 1108 (4) o, k P | 1107 (2) | |
| | | | 1122 (vw) |
| 1143 (3) | 1145 (4) o, k P | 1148 (0) | |
| 1203 (5) | 1204 (6) o, k P | 1210 (6) | |
| 1251 (1) | 1255 (1) o, k P | 1257 (0) | |
| | 1302 (1) o, k P | 1301 (0) | |
| 1378 (4) | 1382 (6) o, k P | 1383 (5) | 1372 (m) |
| 1437 (0) | 1438 (0) o, k | 1440 (0) | 1438 (w) |
| | | | 1460 (s) |
| | | | 1558 (vw) |
| 1590 (5b) | 1592 (6b) o, k D | 1591 (1) | 1580 (vw) |
| 2029 (1) | 2925 (4b) o, k D | 2926 (1) | |
| 3061 (0) | 3062 (1) o, k | 3060 (0) | |

TABLE II

| Raman shift in cm^{-1} | | Infrared bands Wave No in cm^{-1} and Intensity |
|---------------------------------|----------------------------------|--|
| Liquid at 30°C | Solid at -180°C | |
| | 46 (1) | |
| | 76 (1) | |
| 127 (2b) + e, k D | 145 (2) | |
| 202 (6b) \pm e, D | 202 (3) | |
| 269 (0) e, k D | 269 (0b) | |
| 312 (6) \perp e, k D | 316 (1) | |
| 368 (4) \pm e, k P | 366 (2) | |
| 435 (6) \pm e, k P | 433 (4) | |
| 463 (6) \pm e, k P | 461 (3) | |
| 557 (obb) e, k | | |
| 624 (obb) e, k | | |
| 645 (ob) e, k | 646 (0) | |
| 686 (7) e, k P | 680 (8) | 682 (m) |
| | | 805 (vs) |
| | | 865 (s) |
| 870 (4) e, k P | 870 (3) | 941 (vw) |
| | | 908 (vw) |
| | | 1030 (s) |
| 1030 (4) e, k P | 1026 (2) | |
| 1101 (0) e | 1100 (0) | |
| 1135 (5) e, k P | 1146 (2) | 1130 (s) |
| | 1170 (1) | 1142 (vvw) |
| 1211 (6) e, k P | 1215 (6) | 1211 (vvw) |
| | | 1258 (w) |
| 1276 (1b) e, k D | 1276 (0) | |
| 1381 (4) e, k P | 1377 (4) | 1381 (s) |
| 1443 (1b) e | | 1420 (vvw) |
| 1457 (1b) e | | |
| 1470 (0) e | | 1469 (vs) |
| 1598 (6) e, k D | 1596 (1) | 1592 (w) |
| 2938 (5) e, k D | 2938 (0) | |
| 3062 (1) e, k P | 3062 (0) | |

TABLE III

Raman and infrared spectra of 1, 2, 4-trichlorobenzene

| Raman shift in cm^{-1} Liquid at 30°C (Mukherjee, 1960) | | Infrared bands Wave No. in cm^{-1} and Intensity |
|--|------------|---|
| 112 (2) | o, k | |
| 182 (2) | e, k | |
| 195 (4) | o, k | |
| 310 (1) | e, k | |
| 332 (3) | \pm e, k | |
| 398 (2) | o, k P | |
| 459 (2) | e, k | |
| 673 (5) | o, k | 675 (m) |
| 816 (0) | o, k | 810 (vs) |
| 868 (0)* | | 865 (s) |
| 1034 (3) | e, k P | 1052 (s) |
| 1090 (1) | o, k P | 1096 (vs) |
| 1124 (2) | o, k | 1122 (s) |
| 1158 (4) | o, k | |
| 1261 (1)* | | 1243 (m) |
| 1375 (0) | o, k | 1376 (s) |
| | | 1419 (w) |
| | | 1459 (vs) |
| | | 1490 (vw) |
| 1571 (6h) | o, k | 1566 (s) |
| | | 1620 (vvw) |
| | | 1725 (vw) |
| 3066 (5) | k | 3090 (m) |

* These frequencies are taken from Landolt-Bornstein's (1961) tables.

part in the spectrum of 1, 2, 4-trichlorobenzene and are thus expected to arise from a mode of vibration in the methyl group. From analogy with other methylated, compounds, these have been attributed to the asymmetric stretching of the C—H bond in the methyl group.

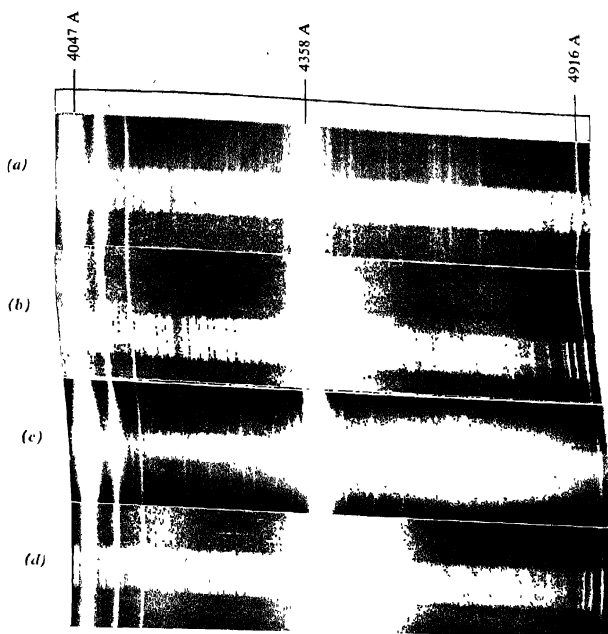
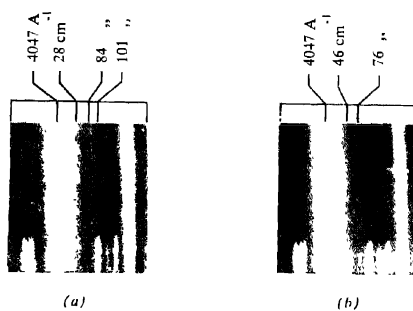


Fig. 1



Raman spectra

- Fig. 1. (a) 2,4 - dichlorotoluene, liquid at 30°C
 (b) " " " " solid at -180°C
 (c) 3,4 - dichlorotoluene, liquid at 30°C
 (d) " " " " solid at -180°C
- Fig. 2. (a) Low-frequency Raman lines of 2,4 - dichlorotoluene at -180°C
 (b) Low-frequency Raman lines of 2,4 - dibromotoluene at -180°C

The frequencies 1145 and 1108 cm^{-1} of 2, 4-dichlorotoluene, 1136 and 1101 cm^{-1} of 3, 4-dichlorotoluene, and 1158 and 1098 cm^{-1} of 1, 2, 4-trichlorobenzene

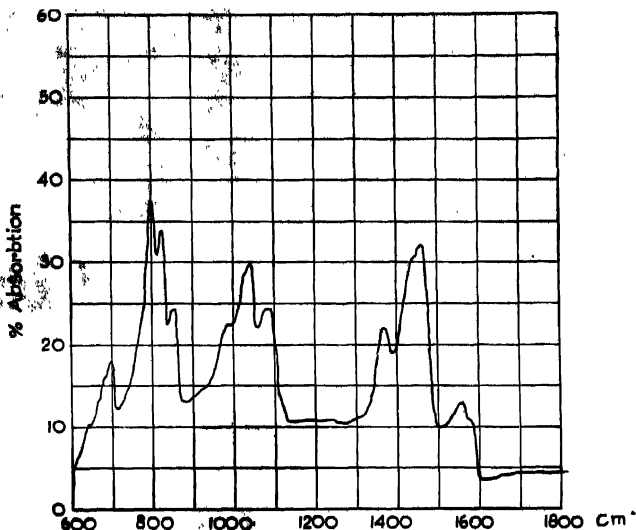


Fig. 3. Infrared spectrum of 2,4-dichlorotoluene (liquid at 26°C)

are probably due to a' -type vibration originating from e_{2g} and b_{2u} modes in benzene, the frequencies representing C—H in-plane deformation vibration. It may be noted that these lines are all polarised and the frequencies are only weakly active in the infrared. The Raman lines 1049, 1030 and 1052 cm^{-1} respectively of the two dichlorotoluenes and the trichlorobenzene may be due to a component of the e_{1u} (1035 cm^{-1}) mode of benzene.

As can be seen from the tables, that 2, 4- and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene show strong infrared bands at 1460, 1469 and 1459 cm^{-1} respectively, which are either absent or very weak in the Raman effect, and also bands at 1372, 1381 and 1376 cm^{-1} respectively. It is well known that within the methyl group in methyl substituted benzenes there are bands due to asymmetric and symmetric C—H bending oscillation falling in the 1450 and 1381 cm^{-1} regions. But the presence of strong bands at 1459 and 1376 cm^{-1} in the infrared spectrum of 1, 2, 4-trichlorobenzene clearly indicates that the similar frequencies observed in the dichlorotoluenes cannot be uniquely assigned to vibrations in the CH_3 group, for they may be due to some other suitable modes of vibration of the molecules themselves. From the discussions of previous workers, the 1460, 1469 and 1459 cm^{-1} bands due to the three compounds appear to represent a

component of the ϵ_{1u} mode of frequency 1485 cm^{-1} in benzene. The frequencies 1372 , 1381 and 1376 cm^{-1} may represent another component of the same mode. In the case of the dichlorotoluenes the bending modes of methyl group may be superposed on these frequencies. The bands near 1430 cm^{-1} due to the dichlorotoluenes may be attributed to a second component of the asymmetric bending in the methyl group usually observed in the methyl substituted compounds (Sheppard *et al.*, 1953). The Raman lines 1592 cm^{-1} of 2, 4-dichlorotoluene, 1598 cm^{-1} of 3, 4-dichlorotoluene and 1591 cm^{-1} of 1, 2, 4-trichlorobenzene correspond in all probability to a component of ϵ_{2g} mode in benzene of frequency 1596 cm^{-1} . The observed infrared frequencies are 1580 , 1592 and 1566 cm^{-1} respectively, the other components in infrared are probably the frequencies 1558 , 1564 and 1550 cm^{-1} respectively.

In all these three molecules with C_s symmetry, the 606 cm^{-1} ϵ_{2g} vibration in benzene splits up into two a' components and these may be identified with

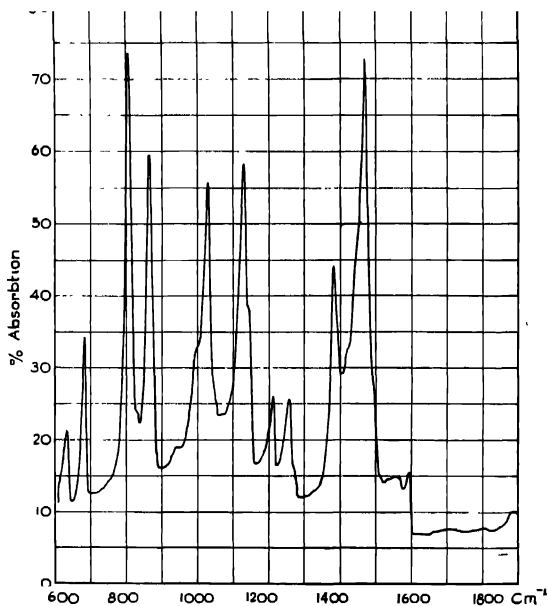


Fig. 4. Infrared spectrum of 3,4-dichlorotoluene (liquid at 26°C)

the polarised Raman lines 380 and 464 cm^{-1} of 2, 4-dichlorotoluene, 368 and 463 cm^{-1} of 3, 4-dichlorotoluene and 332 and 459 cm^{-1} of 1, 2, 4-trichlorobenzene.

In each case, the lower of the two frequencies would correspond to the mode in which all the atoms are displaced.

As discussed above, there are four bending modes in the plane of the benzene molecule viz., a_{2g} (1298 cm^{-1}), b_{2u} (1170 cm^{-1}), e_{2g} (1178 cm^{-1}) and e_{1u} (1035 cm^{-1}). These become a' -type vibrations in the case of C_2 symmetry and are expected to give rise to frequencies corresponding to chlorine bending vibration. The three polarised Raman lines at 402 , 435 and 395 cm^{-1} in the case of the three compounds may correspond to one such mode. At least another component of low frequency should be found near 200 cm^{-1} (Sponer and Kirby-Smith, 1941) but the depolarisation of the observed lines in this region presents difficulty in assignment of this mode.

Out of the four hydrogen bending vibrations (a_{2u} , b_{2g} , e_{2u} and e_{1g}) perpendicular to the plane of the ring in benzene, there should result a'' type bending vibrations

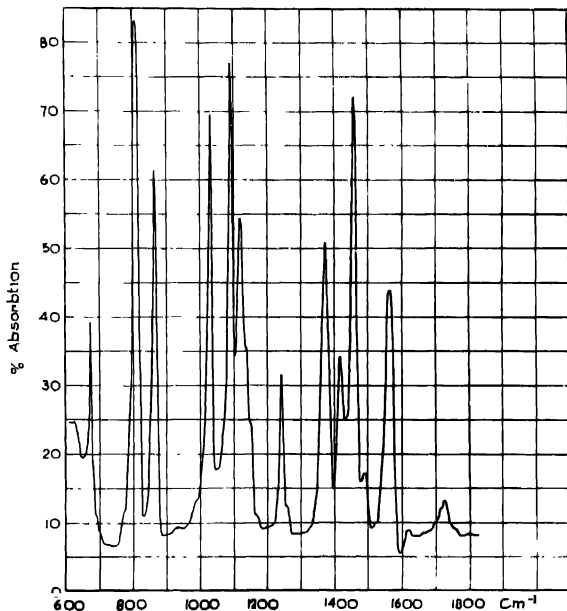


Fig. 5. Infrared spectrum of 1,2,4-trichlorobenzene (liquid at 26°C)

of hydrogen, chlorine and probably of methyl group, giving rise to depolarised Raman lines. It is known from previous results that 1,2,4-trisubstituted benzene compounds usually exhibit infrared band corresponding to a C—H out of plane deformation near 800 cm^{-1} (Bellamy, 1954). Accordingly, the bands 799 , 805

and 810 cm^{-1} observed in the infrared spectra of 2, 4- and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene may be taken to correspond to this vibration, but the absence of any corresponding Raman line in the case of all the three compounds is difficult to interpret as no line is expected to be forbidden in the Raman effect of compounds with C'_s symmetry. The two depolarised low frequency Raman lines 181 cm^{-1} and 202 cm^{-1} for 2, 4-dichlorotoluene, and 182 and 195 cm^{-1} for 1, 2, 4-trichlorobenzene correspond in all probability to components of out of plane chlorine bending modes. The value of 181 cm^{-1} is probably a little higher in the case of 3, 4-dichlorotoluene as is evident from the broadness of the 202 cm^{-1} line. Biswas (1958) has proposed the alternative assignment for line near 202 cm^{-1} observed in chlorotoluenes, that these may be due to dimeric type of associated molecules present in the liquid. This will be taken up while discussing the Raman effect at low temperatures. In both 2, 4- and 3, 4-dichlorotoluene, a depolarised line at 269 cm^{-1} is observed, while there is no corresponding line in 1, 2, 4-trichlorobenzene. This may indicate that this frequency originates from a motion of the methyl group and we propose to associate it with $C-CH_3$ out of plane deformation.

The b_{2g} and e_{2u} modes of out of plane carbon vibration in benzene will produce a'' type vibrations giving depolarised Raman lines. One of the components of the e_{2u} mode which will be only slightly affected is probably the 312 cm^{-1} line in the dichlorotoluenes and 310 cm^{-1} in 1, 2, 4-trichlorobenzene. The other lower component may be detected in the 127 cm^{-1} line in the dichlorotoluenes and probably the 112 cm^{-1} line in 1, 2, 4-trichlorobenzene. The 645 cm^{-1} line may be the contribution of the b_{2g} mode.

In the Raman spectra of dichlorotoluenes two strong polarised lines at 834 and 870 cm^{-1} have been observed (825 and 865 cm^{-1} in the infrared). These may be a' vibration originating from a_{1g} , b_{1u} , e_{2g} and e_{1u} modes in benzene, though it is difficult to propose any definite interpretation of these bands.

(b) *Changes in the intramolecular oscillations of 2, 4- and 3, 4-dichlorotoluene in the solid state at -180°C .*

In the Raman spectra of both 2, 4- and 3, 4-dichlorotoluene a line at 127 cm^{-1} is observed which is found to disappear in the spectra of the solids. Further, in the case of 2, 4-dichlorotoluene the 181 cm^{-1} line is also absent and a new line at 160 cm^{-1} is observed at -180°C . In the case of 3, 4-dichlorotoluene the broad band at 202 cm^{-1} becomes sharp while a new line at 145 cm^{-1} appears when the compound is solidified. These changes probably indicate that in the solid state at -180°C , the molecules of the compounds become associated resulting in restriction of some vibrations of the single molecules. This probably causes the $C-Cl$ out of plane bending vibration of frequency 181 cm^{-1} in the case of 2, 4-dichlorotoluene and one component of the mode of frequency 202 cm^{-1} of 3, 4-dichlorotoluene to shift

to lower energies and the lower component of C—C out of plane deformation vibration of frequency 127 cm^{-1} to disappear. The absence of any appreciable shift of the 202 cm^{-1} line due to 2, 4-dichlorotoluene and the other component of 202 cm^{-1} line due to 3, 4-dichlorotoluene may be due to the fact that these lines have their origin in a motion of dimeric molecules present in the liquid state as proposed by Biswas (1958) in the case of monochlorotoluenes.

When 2, 4-dichlorotoluene is solidified and cooled to -180°C the lines 312 , 646 and 1204 cm^{-1} are shifted to 318 , 653 and 1210 cm^{-1} respectively without any appreciable changes in the relative intensity. Thus the component of C—C out of plane deformation vibrations of frequencies 312 and 646 cm^{-1} which are largely unaffected by substitution are found to be only slightly influenced by association of the molecules in the solid state. In the case of 3, 4-dichlorotoluene, the lines 686 and 1030 cm^{-1} are shifted to 680 and 1026 cm^{-1} respectively. Further, the strong line at 1135 cm^{-1} splits up into two lines at 1146 and 1170 cm^{-1} respectively. It is also observed that the relative intensities of lines 1592 and 2926 cm^{-1} of 2, 4-dichlorotoluene and 1598 and 2938 cm^{-1} of 3, 4-dichlorotoluene are reduced in the solid state at -180°C . The diminution in intensity of the lines of frequencies 1592 and 1598 cm^{-1} due to a mode involving stretching of the C—C bond may indicate that in the case of both these molecules formation of associated groups takes place at the expense of the C—C bond.

(c) *Low frequency Raman lines in 2, 4- and 3, 4-dichlorotoluene*

In the solid state at -180°C , the 2,4-dichlorotoluene exhibits Raman lines at 28 , 42 , 84 and 101 cm^{-1} in the low frequency region, the lines at 28 and 84 cm^{-1} being relatively stronger. On the other hand, 3, 4-dichlorotoluene under similar condition yields only two low frequency Raman lines at 46 and 76 cm^{-1} respectively. Probably the number of types of associated groups in the case

TABLE IV
Luminescence spectra of 2, 4- and 3, 4-dichlorotoluene in the solid state at -180°C

| 2, 4-Dichlorotoluene at -180°C | | 3, 4-Dichlorotoluene at -180°C | |
|--|--|--|--|
| Position of bands in cm^{-1} and Intensity | Separation in cm^{-1} from the first band | Position of bands in cm^{-1} and Intensity | Separation in cm^{-1} from the first band |
| 22717 (ms) | 0 | 24180 (w) | 0 |
| 21197 (ms) | 1520 | 22556 (s) | 1632 |
| | | 21197 (ms) | 2983 |
| | | 20889 (ms) | 3291 |

of 3,4-dichlorotoluene is smaller than that in 2,4-dichlorotoluene because of proximity of the chlorine atoms in the 3- and 4 positions in the former molecule.

(d) *Luminescence spectra of 2,4- and 3,4- dichlorotoluene at -180°C*

When 2,4-dichlorotoluene is frozen and cooled to -180°C , two strong and very broad luminescence bands with centres at about 22717 and 21197 cm^{-1} are observed and the separation 1520 cm^{-1} between the components approximates to C=C vibrational frequency. In the case of 3,4-dichlorotoluene, four broad bands are observed at 24180, 22556, 21197 and 20889 cm^{-1} respectively. The separation of the last three bands from the first one are 1632, 2983 and 3291 cm^{-1} respectively. In this case also the C=C vibration is prominent as the 1632 cm^{-1} frequency, the 3291 cm^{-1} frequency being approximately the first harmonic of 1632 cm^{-1} . The other frequency separation 2983 cm^{-1} may represent a C-H valence oscillation. It may be mentioned here that in the case of other chloro and bromo substituted toluenes, Biswas (1954, 1955) and Sanyal (1953) observed similar broad luminescence bands with a frequency separation approximating to C=C vibrational frequency. Further, in all these compounds the associated groups in the solid state at -180°C are apparently formed at the expense of the C=C bond as is evident from diminution in intensity of this vibrational frequency at the low temperature. It is, therefore, interesting to note that this particular mode is coupled with the electronic transition giving rise to the luminescence spectra exhibited by these compounds in the solid state at low temperature.

A C K N O W L E D G M E N T

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