

## Infrared absorption spectra of 2,3- and 3,5-dichloroaniline

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MS received 7 June 1978; revised 16 August 1978

**Abstract.** The infrared absorption spectra of 2,3- and 3,5-dichloroanilines have been recorded in the region  $250-4000\text{ cm}^{-1}$ . The spectra of the latter are recorded in solid phase (KBr and Nujol mull) and in  $\text{CS}_2/\text{CCl}_4$  and  $\text{CHCl}_3$  solutions while that of the former in thin film only. The spectra have been analysed assuming  $\text{C}_s$  and  $\text{C}_{2v}$  point group symmetry respectively and a tentative assignment of the observed bands to different fundamental modes has been made.

**Keywords.** Infrared absorption spectra; vibrational analysis infrared bands.

### 1. Introduction

The vibrational spectra of aniline have been studied in detail by Evans (1960). The infrared spectra of a large number of mono-, di-, tri- and tetra-substituted anilines have also been studied by many workers (Fuson *et al* 1952; Flett 1948; Venkateshwaran and Pandya 1942; Green 1970; Ferguson *et al* 1953; Verma 1968, Singh and Singh 1969; Tripathi *et al* 1975a,b; Sanyal *et al* 1978; Sharma and Dwivedi 1976; Tewari and Upadhyay 1968; Srivastava 1967 and Singh *et al* 1966). So far no work seems to have been carried out on the infrared spectra of 2,3 and 3,5-dichloroanilines. Thus the present investigation aims at giving the vibrational analysis and assignment of infrared bands of these molecules. In order to check the assignment of specially C—Cl stretching frequencies, the spectrum of 3,5-dichloroaniline has also been studied in  $\text{CS}_2/\text{CCl}_4$  and chloroform solutions along with the solid phase (KBr and Nujol mull) spectra.

### 2. Experimental details and results

Pure chemicals, 2,3-dichloroaniline and 3,5-dichloroanilines (hereafter referred to as 2,3 DCA and 3,5 DCA) obtained from Tokyo Kasei Kogyo Co., Tokyo, in liquid and solid phases respectively, were used as such. The infrared absorption spectra were recorded in thin film (2,3 DCA) and of 3,5 DCA in KBr pellet, Nujol mull and  $\text{CS}_2/\text{CCl}_4$  and  $\text{CHCl}_3$  solutions on a Perkin Elmer Spectrophotometer model-521 in the region  $250-4000\text{ cm}^{-1}$ . The spectra are shown in figure 1. The observed bands have been corrected by calibrating the spectrometer using the spectrum of a thin sheet of polystyrene. The fundamental frequencies along with their probable assignments are given in table 1.

**Table 1.** Assignments of fundamental vibrational frequencies of 2,3- and 3,5-dichloroaniline\* (All values in  $\text{cm}^{-1}$ ).

2,3-Dichloroaniline	3,5-Dichloroaniline				Assignment
	KBr	Nujol mull	$\text{CS}_2/\text{CCl}_4$	$\text{CHCl}_3$	
3484(sb)	—	3514(s)	3512(vs)	3514(vs)	$\nu(\text{N—H})$ asym.
3394(vs)	3421(vs)	3414(vs)	3419(vvs)	3419(vvs)	$\nu(\text{N—H})$ sym.
—	3330(vs)	—	3299(ms)	—	$\nu(\text{N—H})$
3194(ms)	3214(vw)	—	3225(mw)	3219(mw)	$\nu(\text{N—H})$
—	3104(mw)	3099(vw)	3099(vw)	3104(vw)	$\nu(\text{C—H})$ , $e_{1u}$ (3099)
3060(vs)	3094(vvw)	—	3069(vw)	—	$\nu(\text{C—H})$
1606(vs)	1616(ms)	—	—	—	$\text{NH}_2$ scissoring.
1581(ms)	1587(vs)	1587(ms)	1587(vsb)	1588(s)	$\nu(\text{C—C})$ , $e_{2g}$ (1595)
1556(vw)	1571(s)	1566(m)	—	1564(s)	$\nu(\text{C—C})$ , $e_{2g}$ (1595)
1465(vs) } 1447(s) }	1445(vs)	1440(vs)	1450(vvs)	1450(vs)	$\nu(\text{C—C})$ , $e_{1u}$ (1485)
—	—	1370(sb)	1421(ms)	—	?
1312(s)	1302(s)	1299(ms)	1303(vs)	1305(vvs)	$\nu(\text{C—N})$
1297(s)	1272(ms)	1272(vw)	1287(s)	—	$\nu(\text{C—C})$ , $b_{2u}$ (1310)
1202(s)	—	—	1253 (ms)	—	$\beta(\text{C—H})^{a,b}$
1162(ms)	—	—	—	—	$\beta(\text{C—H})^{a,b}$ , $e_{2g}$ (1178)
1097(vs)	1107(vs)	1107(vs)	1105(vs)	—	$\beta(\text{C—H})^{a,b}$ , $e_{1u}$ (1037)
1032(vs)	1062(mw)	1067(s)	1065(s)	—	$\text{NH}_2$ twisting.
997(s)	989(s)	988(vs)	990(vs)	991(vs)	C—C—C trigonal bending <sup>c,d,e</sup> $b_{1u}$ (1010)
957(m)	936(vs)	936(vvs)	—	935(vvs)	$\gamma(\text{C—H})$
905(vs)	842(vs)	837(s)	—	—	$\gamma(\text{C—H})$ , $e_{1g}$ (848-9)
—	821(vs)	818(vs)	819(s)	—	C—C ring breathing <sup>c,d,e</sup> $a_{1g}$ (995)
767(vs)	797(vs)	793(vs)	793(s)	—	$\delta(\text{C—H})$ , $a_{2u}$ (671)
737(s)	—	717(vs)	—	—	$\nu(\text{C—Cl})$
697(s)	702(sb)	—	—	—	$\delta(\text{C—C})$
667(m)	658(vs)	657(vs)	663(vs)	—	$\nu(\text{C—Cl})$ , $\text{NH}_2$ wagging
582(s)	578(ms)	567(msb)	—	569(s)	$\beta(\text{C—C})$ , $e_{2g}$ (608)
—	529(m)	527(ms)	—	527(s)	$\beta(\text{C—C})$ , $e_{2g}$ (608)
419(ms)	427(s)	422(mw)	420(mw)	424(s)	$\delta(\text{C—C})$ , $e_{2u}$ (404)
397(ms) } 385(m) }	397(mw) } 382(vw) }	392(mw)	—	385(vw)	$\delta(\text{C—C})$ , $e_{2u}$ (404)
365(ms)	367(vw)	372(vw)	—	375(vw)	$\beta(\text{C—NH}_2)$
325(w)	325(w)	322(ms)	325(vvw)	325(vw)	$\beta(\text{C—Cl})$
312(w)	312(mw)	312(vvw)	—	315(vvw)	$\gamma(\text{C—NH}_2)$
299(vw)	—	297(vw)	299(vvw)	300(vw)	$\beta(\text{C—Cl})$

\*Intensities are shown in parentheses against each wave number.

s=strong, vs=very strong, vvs=very-very strong, m=medium,

mw=medium weak, w=weak, vw=very weak, b=broad.

$\nu$ =stretching,  $\beta$ =in-plane bending and  $\gamma$  or  $\delta$ =out-of-plane bending.

(a) Values in agreement with that of Mooney (1964) and (b) Joshi and Singh (1966, 1967)

(c) Sharma and Dwivedi (1975), (d) Tripathi *et al* (1975) (e) Sanyal *et al* (1978).

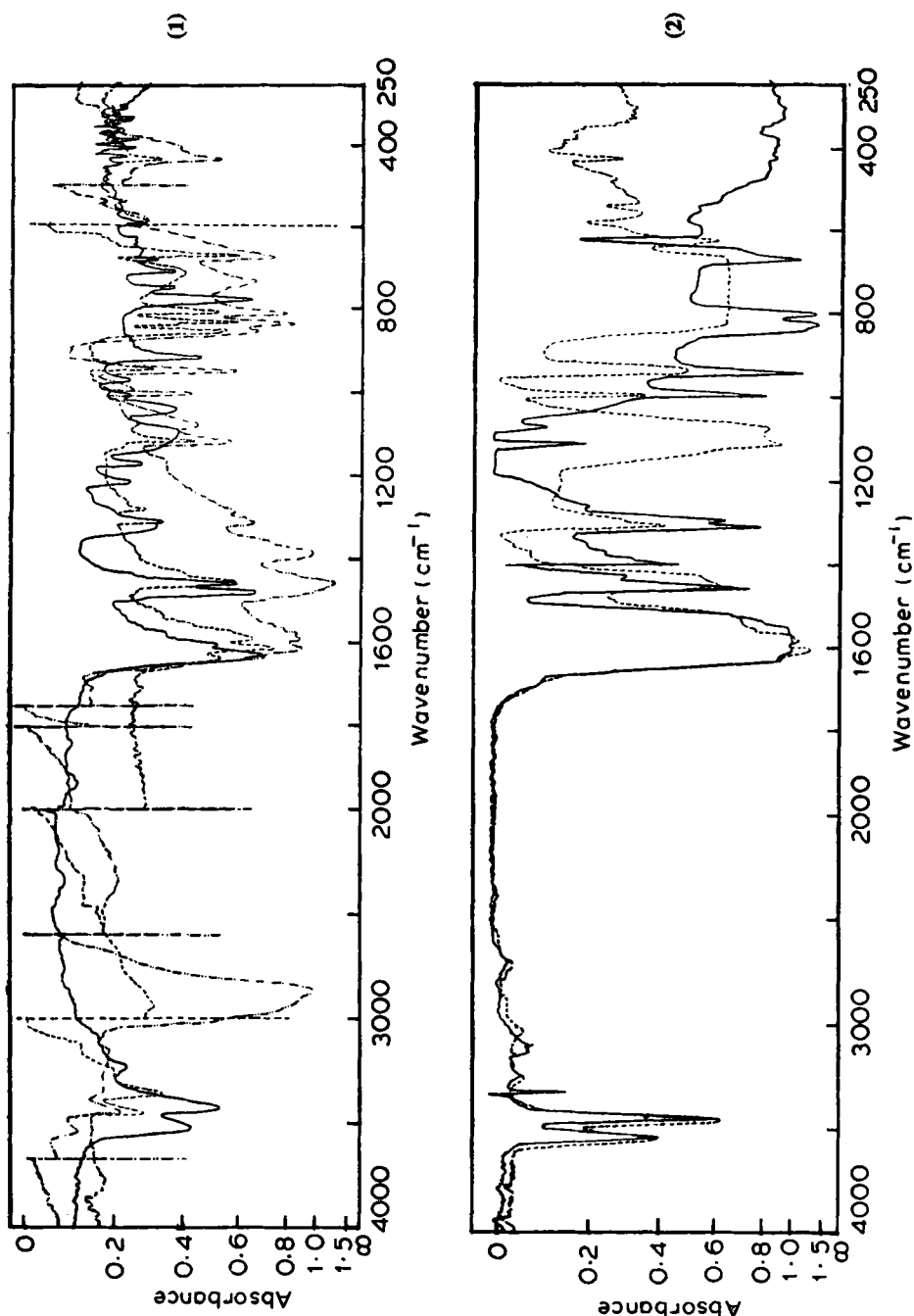


Figure 1. Infrared absorption spectra of 2,3-dichloroaniline (—) and 3,5-dichloroaniline in KBr (---) and Nujol mull (-.-.-)

Figure 2. Infrared absorption spectra of 2,3-dichloroaniline in CS<sub>2</sub>/CCl<sub>4</sub> (—) and CHCl<sub>3</sub> (-.-.-) solutions

### 3. Discussion

It is assumed that the  $\text{NH}_2$  substituent behaves as a single mass point and lies in the plane of the ring, thus the molecules 2,3 DCA and 3,5 DCA would belong to  $C_s$  and  $C_{2v}$  point group symmetry respectively. Under reduced symmetry  $C_s$  the 30 normal modes will be distributed as 21 planar ( $a'$ ) and 9-non-planar ( $a''$ ), while under  $C_{2v}$  symmetry the 30 normal modes may be classified into  $11a_1 + 3a_2 + 6b_1 + 10b_2$  type. Apart from these, there will also appear 6 additional vibrations due to  $\text{NH}_2$  group. In the absence of Raman lines with depolarisation data and type of contours in the infrared spectra in vapour phase of these molecules, the vibrational assignments have been qualitatively made essentially on the basis of magnitudes and relative intensities of the observed infrared bands and the data available for similar molecules.

#### 3.1. Skeleton vibrations

The molecules 2,3 DCA and 3,5 DCA are trisubstituted benzenes. Therefore, there are three hydrogen atoms left around the ring which may give rise to three C—H stretching, three C—H in-plane bending and three C—H out-of-plane bending vibrations. The C—H valence oscillations lie in the region  $3030$  to  $3070\text{ cm}^{-1}$  (Bellamy 1959). These vibrations in their respective regions have been identified in table 1 and the related literature has been cited therein.

The appearance of a group of six bands in the region  $1000$ – $1650\text{ cm}^{-1}$  in the spectra of substituted benzenes, represent the C—C stretching modes, represented by  $e_{2g}$  (1595) and  $e_{1u}$  (1485);  $b_{2u}$  (1310) and  $a_{1g}$  (995). Except for the ring breathing vibration of benzene  $a_{1g}$  (995), all these frequencies are known to remain practically unaffected by substitution. The bands observed in this region have been assigned to correspond to these modes in table 1. The  $b_{2u}$  (1310) mode occurs in trisubstituted benzenes in the region  $1240$ – $1290\text{ cm}^{-1}$  (Varsanyi 1969). In the present molecules, the bands observed at  $1297$  and  $1272\text{ cm}^{-1}$  in 2,3 DCA and 3,5 DCA respectively have been assigned to this mode. As pointed out by several other workers the C—C ring breathing  $a_{1g}$  (995) and C—C—C trigonal bending  $b_{1u}$  (1010) vibrations of benzene give rise to combined modes in molecules belonging to reduced symmetry. As a result of this, one of the modified modes reduces to about  $800\text{ cm}^{-1}$ , while the other keeps itself around  $1000\text{ cm}^{-1}$  in trisubstituted benzenes (Tripathi 1973). These modes assigned at present in the case of 2,3 DCA and 3,5 DCA are in agreement with the literature (table 1) available for substituted anilines. The ring breathing mode could not be identified clearly in the case of 2,3 DCA. One of the bands observed in the expected regions at  $905\text{ cm}^{-1}$  is too high for ring breathing mode and is identified as C—H out-of-plane bending mode. However, the band observed at  $767\text{ cm}^{-1}$  is strong and identified as C—H out-of-plane bending mode and might have a contribution from C—C ring breathing mode. The remaining two C—C in-plane bending and three out-of-plane bending modes have been clearly identified and correlated with the corresponding modes of benzene in table 1.

3.1.1. C-X vibrations: In substituted anilines, the strong C— $\text{NH}_2$  stretching vibration appears near  $1300\text{ cm}^{-1}$  (Singh *et al* 1966; Srivastava 1968 and Tripathi 1966). In view of this, the bands observed at  $1312$  and  $1302\text{ cm}^{-1}$  in 2,3 DCA and 3,5 DCA respectively have been attributed to this mode.

Many workers have assigned the C—Cl stretching modes in the region 550–750  $\text{cm}^{-1}$  in the various chloro substituted phenols and anilines (Sanyal and Pandey 1973; Sanyal *et al* 1978; Srivastava 1970; Pandey and Singh 1975; Sharma and Dwivedi 1976). The C—Cl stretching modes assigned at present in the case of 2,3 DCA and 3,5 DCA are given in table 1. Attempts were made to check the assignments of C—Cl stretching frequency by taking the spectra in different solutions and looking for any frequency shift as was done by Nabumi Oi and Coetzee (1969), but the evidence is not conclusive.

### 3.2. Group vibrations

The  $\text{NH}_2$  group will involve the symmetric and asymmetric N—H stretching vibrations. In the case of nearly all the primary aromatic amines, two bands occur in the region 3300–3500  $\text{cm}^{-1}$  (Bellamy 1959). The bands around 3500  $\text{cm}^{-1}$  has been assigned by a large number of workers as asymmetric and that appearing around 3400  $\text{cm}^{-1}$  as symmetric stretching vibration. Thus the bands observed at 3484 and 3514  $\text{cm}^{-1}$  in 2,3 DCA and 3,5 DCA respectively have been assigned to N—H asymmetric stretching vibration and those at 3394 and 3421  $\text{cm}^{-1}$  in two molecules respectively to N—H symmetric stretching vibration. It has been pointed out by Bellamy (1959) that, in N-octamide in  $\text{CHCl}_3$  solution, the  $\text{NH}_2$  free absorption occurs at 3530 and 3415  $\text{cm}^{-1}$ , but it also shows additional bands at 3498, 3345, 3300 and 3182  $\text{cm}^{-1}$ , suggesting different types of simultaneous association of free and bonded NH bonds. In view of this the bands observed at 3194  $\text{cm}^{-1}$  in 2,3 DCA and at 3330 and 3214  $\text{cm}^{-1}$  in 3,5 DCA have been assigned to additional N—H stretching modes.

The  $\text{NH}_2$  scissoring frequency has been suggested to lie in the region 1590–1650  $\text{cm}^{-1}$  in nearly all primary aromatic amines (Bellamy 1959; Rao 1963). The bands observed at 1606  $\text{cm}^{-1}$  in 2,3 DCA and at 1616  $\text{cm}^{-1}$  in 3,5 DCA have been assigned to this mode which find support from the literature values (Tripathi and Pandya 1975; Sanyal *et al* 1978).

### Acknowledgement

One of the authors (RKG) is thankful to University Grants Commission, for financial assistance.

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