Vol. A58 (1980) *ACTA PHYSICA POLONICA* No 4

VIBRATIONAL SPECTRA OF 2,6-DICHLOROANISOLE

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(Received October 5, 1979; final version received February 4, 1980)

The infrared absorption spectra of 2,6-dichloroanisole has been recorded by a Perkin-Elmer-521 spectrophotometer in the region 250-4000 cm^{-1} on a thin film. The spectra have been analysed assuming C_{2v} point group for the molecule. A tentative assignment of the observed bands to different fundamental modes has been made. The shift of the C-Cl and C_{aryl}-O frequencies are discussed.

1. *Introduction*

Vibrational spectra of anisole and its monosubstituted derivatives have been studied extensively by many workers [1–7], but very little work appears on di-substituted anisoles [8–10]. In order to extend this study to di-substituted anisoles and to study the effect of substitution, the molecule 2,6-dichloroanisole has been undertaken at present.

2. *Experimental*

The spec-pure chemical, 2,6-dichloroanisole, obtained from M/s FLUKA AG, Switzerland, was used as supplied without further purification. The infrared absorption spectra have been recorded by a Perkin-Elmer-521 spectrophotometer on a thin film in the region 250–4000 cm^{-1}. The spectrometer was calibrated by running the spectra of a thin sheet of polystyrene.

3. *Results and discussion*

The infrared absorption spectra of 2,6-dichloroanisole is shown in Fig. 1 and the observed frequencies along with their probable assignments are presented in Table I. Wilson's [11] notations have been followed in Table I, where *a* and *b* denotes the compo-

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TABLE I

Assignment of vibrational frequencies of 2,6-dichloroanisole

Symmetry species	Vibration number	Position of the bands along with their visual intensities* [cm^{-1}]	Description of mode
A$_1$	2	3065 (mb)	C—H stretch
	20*a*	3045 (vw)	C—H stretch
	8*b*	1590 (ms)	C—C stretch
	19*b*	1475 (vs)	C—C stretch
	13	1260 (vvs)	C$_{aryl}$ — O stretch
	9*a*	1180 (s)	C—H i.p.b.
	7*a*	1155 (s)	C—Cl stretch
	12	1002 (vvsb)	ring planar defor., trigonal bending
	1	780 792 (vvs)	C—C stretching, breathing type
	6*a*	612 (vvs)	C—C i.p.b.
	18*b*	355 (s)	C—Cl i.p.b.
B$_2$	20*b*	3005 (mw)	C—H stretch
	8*a*	1570 (vvs)	C—C stretch
	19*a*	1422 (vs)	C—C stretch
	14	1332 (s)	C—C stretch, Kékulé vib.
	7*b*	1100 (vs)	C—Cl stretch
	3	1290 (m)	C—H i.p.b.
	9*b*	1208 (vvs)	C—H i.p.b.
	6*b*	560 (s)	C—C i.p.b.
	15	410 (ms)	C—OCH$_3$ i.p.b.
	18*a*	325 (vw)	C—Cl i.p.b.
A$_2$	17*a*	820 (mb)	C—H o.p.b.
	16*a*	550 (ms)	C—C o.p.b.
	10*a*	—	—
B$_1$	4	712 (s)	C—C o.p.b.
	17*b*	910 (s)	C—H o.p.b.
	11	750 (vvs)	C—H o.p.b.
	16*b*	402 (ms)	C—C o.p.b.
	10*b*	—	—
	5	272 (m)	C—OCH$_3$ o.p.b.
OCH$_3$ group vibrations		2945 (vs)	C—H asym. stretch
		2860 (vs)	C—H asym. stretch
		2825 (s)	C—H sym. stretch
		1447 (s)	CH$_3$ asym. defor.
		1390 (sh)	CH$_3$ sym. defor.

TABLE I (continued)

	1045 (ms)	C_{alkyl}—O stretch
	1072 (vvs)	CH_3 rocking
	1035 (ms)	CH_3 rocking
	260 (w)	C—O—C i.p.b.
Other vibrations	590 (mw) = 272+325, 1515 (mw) = 792+712, 1595 (mw) = 2×792, 1617 (vw) = 792+820, 1655, 1662 (m) = 1045+612 or 1100+560, 1675 (m) = 1260+410, 1692 (mw) = 910+780, 1790 (m) = 1035+750, 1802 (m) = 1045+750, 1860 (ms) = 1045+820, 1930 (ms) = 1155+780, 2060 (ms) = 2×1035, 2225 (mw) = 1155+1072, 2270 (m) = 1260+1002, 2510 (mb) = 2×1260, 2930 (mw) = 1475+1447, 3535 (m) = 2825+712.	

* Intensities are shown in parentheses against each wave number. i.p.b. → in-plane bending and o.p.b. → out-of-plane bending.

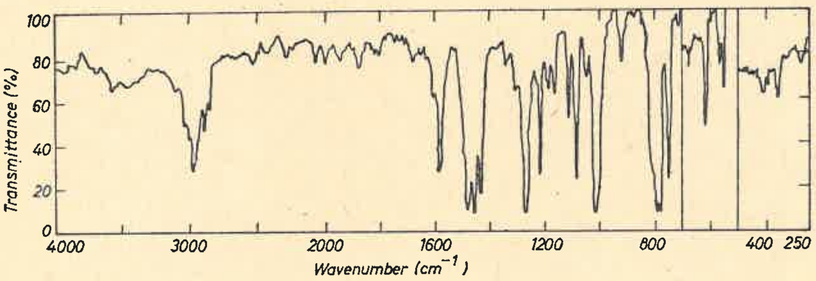

Fig. 1. Infrared absorption spectra of 2,6-dichloroanisole

nents of doubly degenerated modes which splits into their components when symmetry reduces by substitution in the benzene molecule.

Assuming the OCH_3 group to be a single mass point, the molecule 2,6-dichloroanisole would belong to the C_{2v} point group symmetry under which 30 normal modes will be distributed as $11a_1+3a_2+6b_1+10b_2$. In addition to these, there will also appear 12 vibrations due to the OCH_3 group. In the absence of Raman lines with depolarisation data and the vapour phase infrared spectra, the present assignments are made on the basis of visual intensities and data available for similar molecules. For the present case some important assignments are discussed below:

3.1. A_1 species

The present molecule, 2,6-dichloroanisole, is a tri-substituted benzene, thus, three C—H stretching vibrations, ν_2 and ν_{20a} belonging to the A_1 species and ν_{20b} belonging to B_2 species are expected in the region 3000–3100 [12]. The vibrations 2 and 20*a* have been identified at 3065 and 3045 cm^{-1} respectively in the present molecule. In tri-substituted benzenes [13] the frequency of one of the two ring modes ν_1 and ν_{12} decreases to 820 cm^{-1} while the other remains around 1000 cm^{-1}. Thus the bands observed at 780 and 1002 cm^{-1} in the present study have been assigned to the ν_1 and ν_{12} vibrations respectively. These are also in agreement with the assignments made by Goel et al. [8, 14], Srivastava [15] and Pandey and Singh [16] for chloro-substituted benzenes.

In the present case, the ν_{8b} and ν_{19b} vibrations belonging to the A_1 species and which represents the C—C stretching vibrations, have been identified at 1590 and 1475 cm^{-1} respectively. These assignments are in agreement with literature values [14, 17].

3.2. B_2 species

C—H stretching vibration ν_{20b} belonging to the B_2 species has been identified at 3005 cm^{-1} in the present molecule. The vibrations ν_{8a} and ν_{19a} corresponding to ring stretching and belonging to the B_2 species, have been identified at 1570 and 1422 cm^{-1} respectively.

As a result of substitution at positions 1, 2 and 6 of the ring, the stretching vibrations ν_{13}, ν_{7a} and ν_{7b} become X-sensitive. Bishui [18] assigned the C—Cl stretching mode in 2,6-dichloroaniline at 1050 and 1070 cm^{-1} while Scherer and Evans [19] assigned this mode at 1070 and 1152 cm^{-1} in m-dichlorobenzene. Thus the bands at 1155 and 1100 cm^{-1} have been assigned to the C—Cl stretching mode (ν_{7a} and ν_{7b} respectively) in the title compound. This also finds support from the literature values [20–22].

In the infrared spectra of aryl and alkyl ethers, several workers [1, 4, 8] have reported two stretching vibrations involving the oxygen atom, viz., C_{aryl}—O and C_{alkyl}—O stretching vibrations. The C_{aryl}—O stretching mode was observed at 1266 ± 6 cm^{-1}, but in anisole due to the hyper-conjugation effect of the methyl group, it is observed at a higher frequency. The C_{alkyl}—O stretching vibration occurs at 1035 ± 10 cm^{-1} in anisoles. In the present molecule the band observed at 1045 cm^{-1} has been assigned to the C_{alkyl}—O stretching while the ν_{13} vibration corresponding to C_{aryl}—O stretching has been identified at 1260 cm^{-1}. These also find support from the literature values [5, 6, 10].

ν_3 and ν_{9b} vibrations which correspond to the C—H in-plane bending modes have been identified at 1290 and 1208 cm^{-1} in the title compound, while C—C in-plane bending mode ν_{6b} (corresponding to e_{2g}608 mode of benzene) have been identified at 560 cm^{-1}.

3.3. A_2 species

The out-of-plane C—Cl stretching mode ν_{10a} of the A_2 species and ν_{10b} of the B_1 species lie below the region under study, thus they could not be observed. Since the vibrations belonging to the A_2 species are infrared inactive, they will either be absent or appear weakly. Thus a band with medium intensity at 820 cm^{-1} has been assigned to the ν_{17a} mode and that at 550 cm^{-1} to the ν_{16a} mode belonging to the A_2 species.

3.4. B_1 species

The band corresponding to the b_{2g} (703) mode of benzene (ν_4 vibration) has been identified at 712 cm^{-1}. The ν_{17b} and ν_{11} vibrations corresponding to C—H out-of-plane bending modes have been assigned at 910 and 750 cm^{-1} in the present case.

3.5. OCH_3 group vibrations

There are three C—H stretching vibrations in the methyl group, one of these is symmetric while the other two are asymmetric. The C—H asymmetric stretching vibrations have very nearly the same magnitudes and usually appear with varying intensity in the region 3000–2900 cm^{-1}. In view of this, the bands observed at 2945 and 2860 cm^{-1} have been assigned to the C—H asymmetric stretching and that at 2825 cm^{-1} to C—H symmetric stretching vibrations. This finds support from the work of Mooney [21] on halogenated toluenes and the work of Goel et al. [8, 10] and Dwivedi and Sharma [5] on substituted anisoles. Further, for one methyl group attached to the benzene ring, two rocking modes are expected. Wilmshurst and Bernstein [23] have assigned these modes in toluene at 1040 and 1080 cm^{-1}. In view of this, the CH_3 rocking modes in the present case have been assigned at 1035 and 1072 cm^{-1}. This is also in agreement with the values suggested in the literature [5, 10, 24].

3.6. Shift of C—Cl and C—OCH_3 frequencies

It is interesting to note the shift of C—Cl and C_{aryl}—O stretching frequencies in the present case compared to that in 2,3-dichloroanisole [10]. The two C—Cl stretching frequencies and C_{aryl}—O stretching mode were observed at 1171, 1119 and 1273 cm^{-1} in 2,3-dichloroanisole while in the present case at 1155, 1100 and 1260 cm^{-1} respectively. In 2,6-dichloroanisole both chlorine atoms are nearer to the OCH_3 group than in 2,3-dichloroanisole. Since chlorine is electronegative, both Cl atoms, which are nearer to the OCH_3 group in 2,6-dichloroanisole, may perturb the OCH_3 group and C—OCH_3 frequencies more than in 2,3-dichloroanisole. According to Nakanishi and Solomon [25] such a perturbation may arise from mesomeric and inductive effects. In turn, this also explains the shift of C—Cl stretching frequencies. This finds support from the similar shift observed in 2,4- and 2,6-dibromophenols [26].

The authors are thankful to Dr. S. P. Gupta, Principal, D. N. College, Meerut for providing the necessary facilities and one of the authors (RKG) to the University Grants Commission, New Delhi for financial assistance.

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