

Electronic absorption spectra of some trisubstituted benzenes and their dipole moments in the first excited electronic states

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In continuation of the work on the various aspects on the spectra of trisubstituted benzenes (Rao *et al* 1989, 1990, Aralakkanavar *et al* 1989, 1990), the present note reports the electronic spectra of 1,3-dichloro-2- and 1,3-dichloro-4-fluorobenzenes (hereafter referred to as compounds I and II respectively) and also estimated their electric dipole moments in their first excited electronic states. The infrared absorption spectrum of compound I is available in literature (Green *et al* 1971) and so we have recorded and analysed the infrared spectrum of compound II in the pure liquid state in the region $200\text{-}4000\text{ cm}^{-1}$ using a Perkin-Elmer Model double beam automatic spectrophotometer and the accuracy of the positions of the bands is a little better than $\pm 5\text{ cm}^{-1}$ in the range $200\text{-}2000\text{ cm}^{-1}$ and $\pm 10\text{ cm}^{-1}$ in the range $2000\text{-}4000\text{ cm}^{-1}$.

The samples of compound I and II used in the work, were obtained from Aldrich Chemical Co, USA and were stated to be of 99% purity. Their near ultraviolet absorption spectra in vapour were photographed using a large quartz spectrograph on Kodak analysis photographic plates at various temperatures in the range -10°C to 75°C for different path lengths varying from 5 cm to 50 cm. (For temperatures below the room temperature the absorption tube is held in position by retort stands and the container tube is immersed in a Dewar flask having ice-cooled water, ice, ice-salt mixture and ice-acetone mixture. For temperatures higher than the room temperature it is necessary to maintain the main portion of the absorption tube at a slightly higher temperature than the container in order to prevent condensation of vapour on the windows. The uniform heating of the cells is done by coating the cells with asbestos papers and a nichrome wire is wound over this maintaining 8 mm distance between consecutive turns. To account for the heat loss due to radiation near the ends of the cell, the number of turns per cm is increased at the places. The current through the nichrome wire is regulated by a variac and was controlled by using a temperature indicator control unit followed by a copper-constantan thermocouple supplied by Audiotronics,

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New Delhi and with this arrangement the temperature was found to be stable in the range $\pm 0.5^\circ\text{C}$ during the course of photographing the spectra for a specified temperature). The accuracy of the band positions is a little better than $\pm 5\text{ cm}^{-1}$

Table I. Infrared absorption (fundamental frequencies (in cm^{-1}) of 1,3-dichloro 4-fluorobenzene.

Wavenumber and intensity	Symmetry species (C_{2v})		Assignment
225 w	a''	ν_1	X-sensitive
270 w	a'	ν_2	X-sensitive
350 m	a'	ν_3	X-sensitive
400 m	a''	ν_4	X-sensitive
440 s	a'	ν_5	X-sensitive
480 w	a''	ν_6	C - C out-of-plane bend
510 s	a'	ν_7	X-sensitive
560 s	a'	ν_8	C - C in-plane bend
650 vs	a'	ν_9	X-sensitive
700 ms	a''	ν_{10}	C - C out-of-plane bend
720 vs	a'	ν_{11}	X-sensitive
805 vs	a'	ν_{12}	X-sensitive
840 ms	a''	ν_{13}	C - H out-of-plane bend
855 s	a''	ν_{14}	C - H out-of-plane bend
930 m	a''	ν_{15}	C - H out-of-plane bend
1060 vs	a'	ν_{16}	X-sensitive
1095 s	a'	ν_{17}	C - H in-plane bend
1140 s	a'	ν_{18}	C - H in-plane bend
1225 ms	a'	ν_{19}	X-sensitive
1250 s	a'	ν_{20}	C - H in-plane bend
1305 mw	a'	ν_{21}	C - C stretch
1380 s	a'	ν_{22}	C - C stretch
1480 s	a'	ν_{23}	C - C stretch
1580 s	a'	ν_{24}	C - C stretch
1615 m	a'	ν_{25}	C - C stretch
3040 m	a'	ν_{26}	C - H stretch
3100 ms	a'	ν_{27}	C - H stretch
3150 sh	a'	ν_{28}	C - H stretch

for sharp bands and $\pm 10\text{ cm}^{-1}$ for broad and diffuse bands. The electronic absorption spectra of the compounds were also recorded in solution of different

Table 2. Correlation of the fundamental vibrational frequencies of 1,3-dichloro-2- and 1,3-dichloro-4-fluorobenzenes

IR*	1,3-dichloro-2-fluorobenzene		1,3-dichloro-4-fluorobenzene		Mode
	Ground state	Excited state	Ground state	Excited state	
256	—	245	350	308	ν_5
270	276	163	270	148	ν_8
401	403	339	440	338	ν_5
570	563	456	510	424	ν_7
600	—	{564 {556	805	662	ν_{13}
660	—	516	650	596	ν_9
705	701	644	720	695	ν_{11}
1058	—	791	1060	848	ν_{16}
1112	—	975	1095	1045	ν_{17}
1154	—	{1054 {1043	1140	1109	ν_{19}
1205	—	1102	1225	1191	ν_{19}
1310	—	1232	1305	1246	ν_{21}
—	—	—	560	487	ν_8

* Green J H S et al (1971).

solvents of spectroscopic grade purity using Hitachi U-3200 UV/VIS Spectrophotometer in the range λ 3000 Å to λ 2400 Å.

The infrared absorption spectrum of compound II was analysed by considering it as belonging to the point group C_6 and the fundamental vibrational frequencies along with their assignments are given in Table 1.

The electronic absorption spectra of compounds I and II show two $\pi^* \leftarrow \pi$ band systems, one consisting of well defined bands around λ 2800 Å (system I) and the other shows some diffuse bands around λ 2200 Å in compound I and an intense maxima at λ 2139 Å in compound II. System II in the vapour phase was recorded on a U-3200 Hitachi spectrophotometer. The first and second systems observed in the compounds studied have been identified as corresponding to the forbidden electronic transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ and ${}^1B_{1u} \leftarrow {}^1A_{1g}$ of benzene respectively.

The effect of temperature on the band system has facilitated the choice of the band at 36452 and 35650 cm^{-1} as the o,o band in compound I and II respectively. The identification of the fundamentals has been mainly done on the basis of the intensities of the bands and the available literature of other trisubstituted benzenes. So chosen fundamentals for compounds I and II are given in Table 2 along with their probable assignments. The strong bands on the longer wavelength side with spacing 34, 47 cm^{-1} in compound I and 32 cm^{-1} in compound II have been identified as sequence intervals. The analyses of the electronic spectra of the molecules show a red shift in the order of 1,3-dichloro-4 > 1,3-dichloro-2-fluorobenzene. Such a trend is also reported in the literature (Padhye and Varadrajana 1963).

In the second system lying in the region λ 2400 Å- λ 2000 Å, the band observed towards the longer wavelength side at 45153 cm^{-1} in compound I has

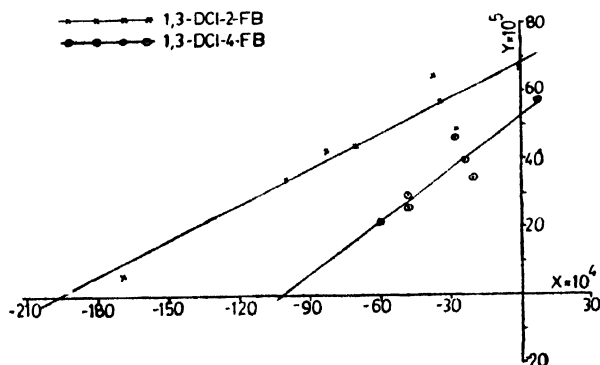


Figure 1. X vs Y plots for 1,3-dichloro-2- and 1,3-dichloro-4-fluorobenzenes,

been identified as the o,o band. The identified excited state fundamentals of this system are listed in Table 2 and they are correlated to the fundamentals of λ 2600 Å system.

The electric dipole moments of these compounds in the first excited electronic state have been calculated using a method suggested from our laboratory (Ayachit

et al 1986) from the solvent effect on their electronic spectra. Using the solvents of spectroscopic grade, purity, namely, cyclo-hexane, *n*-heptane, carbon-tetra-chloride, iso-propanol, *n*-propanol, ethanol, methanol, butanol, dichloromethane and diethylether. The ν_{\max} values (The data are with the authors may be obtained on request) observed for ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of benzene are used to calculate μ_e and θ , the direction of μ_e with respect to μ_g . The electric dipole moments in the ground state were determined as given in our earlier work (Aralakkanavar and Shashidhar 1989) and they are 2.56 and 1.59 D respectively for compounds I and II. The molecular radius has been calculated using the method of atomic increments (Edward 1956) and is found to be 3.058 Å for compounds I and II.

The relevant plots obtained for the observed system of the compounds are given in Figure 1. The values of μ_e , θ obtained are 3.88 D, 46° and 3.65 D, 58° respectively for compounds I and II. It is expected that the value of μ_e should be greater for the upper state (Jaffe and Orchin 1962). In the present work this expected behaviour is observed.

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