

Electronic absorption spectra of 1-Br-3,4- and 1-Br-3,5-difluorobenzenes

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In continuation of the work on the electronic absorption spectra of trisubstituted benzenes (Rekha Rao *et al* 1989a, b Aralakkanavar *et al* 1989), the present note reports the electronic absorption spectra of 1-Br-3,4- and 1-Br-3,5-DFB (Difluorobenzene) in the vapour phase and the results are discussed.

The samples of 1-Br-3,4- and 1-Br-3,5-DFB used in this work, were obtained from Aldrich Chemical Co., USA and were further purified before use (Shashidhar 1971). 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 20 C to 75 C for different pathlengths ranging from 5 cm to 50 cm. The accuracy of the band positions is a little better than $\pm 5 \text{ cm}^{-1}$ for sharp bands and $\pm 10 \text{ cm}^{-1}$ for broad and diffuse bands.

The infrared absorption spectra of the molecules have also been recorded and analysed by considering 1-Br-3,4-DFB belonging to C_2 point group and 1-Br-3,5-DFB to C_{2v} point group. The data are with the authors.

The electronic absorption spectra of 1-Br-3,4- and 1-Br-3,5-DFB lie approximately in the region λ 2780 Å λ 2500 Å and the bands are degraded to the red. The observed band system in 1-Br-3,4- and 1-Br-3,5-DFB has been identified as corresponding to the forbidden electronic transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ of benzene.

The effect of temperature on the band system has facilitated the choice of the band at 36440 cm^{-1} and 37332 cm^{-1} as the 0,0 band in 1-Br-3,4-DFB and 1-Br-3,5-DFB respectively. The identification of the fundamentals chosen has been mainly done on the basis of the intensities of the bands and the available literature on the analysis of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of other trisubstituted benzenes (Rekha Rao *et al* 1989a, b, Goel *et al* 1979, Sinha and Chatterjee 1976). So chosen fundamentals are listed in Table 1 along with their probable assignments and their corresponding infrared data. The longer wavelength side bands with spacing 29, 86 cm^{-1} in 1-Br-3,4-DFB and 22, 87 cm^{-1} in 1-Br-3,5-DFB from

Table I. Correlation of fundamental frequencies (cm⁻¹) of 1-Br-3,4- and 1-Br-3,5-difluorobenzenes.

IR	1-Br-3,4-DFB		IR	1-Br-3,5-DFB		Assignment
	Ground state	Excited state		Ground state	Excited state	
220 mw	223 m	185 m	240 mw	238 m	164 m	β_C Br
320 w	317 w	256 ms	380 m	382 mw	273 ms	β_C F
450 m	440 w	424 m	470 m	460 w	412 m	β_C F
480 ms	483 w	441 ms	520 s	526 w	427 s	β_C C
575 ms	580 w	477 m	585 ms		475 s	ν_C Br
630 ms		553 s				β_C C
770 s		737 s	620 s	615 w	516 s	β_C C
1025 s		808 s	995 s		874 ss	ν_C C
1060 s		981 s	1075 s		960 s	β_C H
1110 s		1035 ms	1115 s		1034 m	β_C H
1200 s		1163 m	1240 s		1204 m	ν_C F
1275 s		1251 ms	1280 s		1248 ms	ν_C F

DFB difluorobenzene; β in-plane-bending; ν stretch, w weak; mw medium weak, m medium; ms medium strong; s strong.

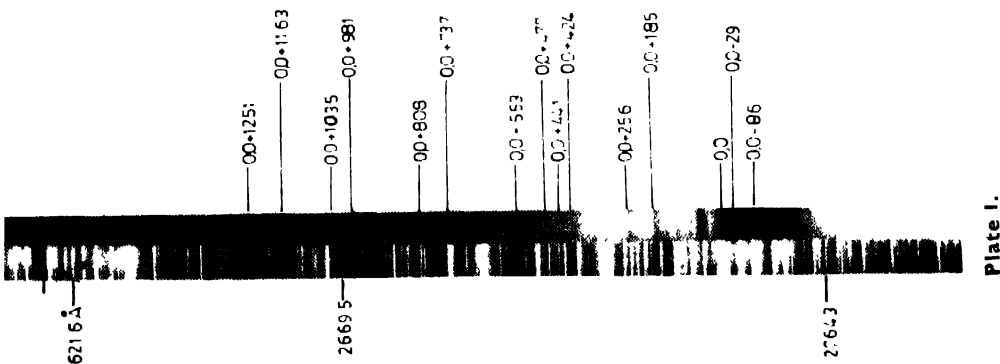
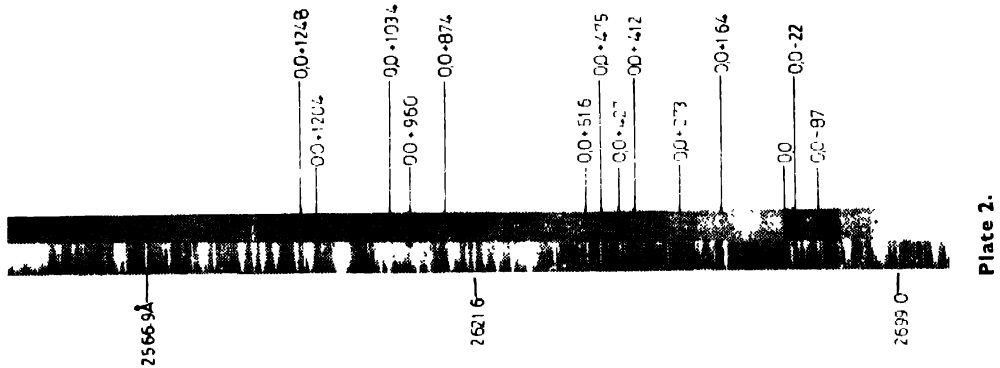


Plate 1. Ultraviolet absorption spectra (1B_u , 1A_g) of 1-Br-3,4-Difluorobenzene. **Plate 2.** 1-Br-3, 5-Difluorobenzene.

their respective 0,0 band have been identified as sequence intervals. It was found that most of the bands in the respective spectra could be accounted for in terms of the identified fundamentals and sequence intervals as combinations and overtones. Plates 1 and 2 give enlarged reproductions of ultraviolet spectra of 1-Br-3,4- and 1-Br-3,5-DFB wherein only the fundamentals are marked.

The analyses of the electronic spectra of the molecules show a red shift in the order of 1-Br-3,5- > 1-Br-3,4-DFB with respect to the 0,0 band of benzene. Such a trend was also reported in the literature (Padhye and Varadarajan 1963).

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