

NOTE

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Infrared and ultraviolet absorption spectra of 3,4- and 3,5-difluorobenzonitriles

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Extensive studies on the ultraviolet, infrared and Raman spectra of benzonitrile and their derivatives have been reported (Green 1961, Lebas 1962, Bak and Nielsen 1960, Jacobsen 1965, Shurvel *et al* 1968, Green and Harrison 1979, Varsanyi 1974, Sinha and Chatterjee 1976, Singh 1969, Goel *et al* 1979, Chatterjee *et al* 1978, Goel and Agarwal 1980, Huded *et al* 1986). Of all the systems of benzene, the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ electronic system lying around λ 2600 Å has been studied in great detail and so also the corresponding system in substituted benzenes. In substituted benzenes, the ${}^3B_{1u} \leftarrow {}^1A_{1g}$ (λ 2100 Å) transition is not much studied in vapour phase. In view of the limited studies on the second system it was felt that a continuation of the studies of electronic and infrared absorption spectra of some more trisubstituted benzenes would be worthwhile, as this would give some insight into the structure of the molecules in their ground and excited states. As a part of our research programme, the present note reports the vibrational analysis of the infrared and electronic absorption spectra of 3,4- and 3,5- DFB.

The experimental techniques used to record the vapour absorption UV spectra and IR spectra and accuracy in the position of the bands reported, are the same as given in our earlier work (Shashidhar 1971).

3,4- and 3,5-DFB may be considered as belonging to the point group C_s and C_{2v} respectively if we consider -CN group to behave as a single mass point and co-planar with the benzene ring. The total number of 33 normal modes of vibration will have the distribution $23a' + 10a''$ in C_s and $12a_1 + 10b_2 + 8b_1 + 3a_2$ in C_{2v} symmetry. The choice of the fundamentals from the observed bands in the infrared spectra of 3,4- and 3,5-DFB has been done keeping in view the symmetry of the molecules and the infrared spectra of benzonitrile and substituted benzonitriles. It must however, be emphasized that many modes are most likely considerably mixed precluding in fact the use of terms such as stretching or deformation. It might be that a ring stretch also implies a certain amount of

Table 1. Fundamental infrared and ultraviolet absorption frequencies (cm^{-1}) of 3,4- and 3,5-difluorobenzonitrile.

IR	Wavenumber (cm^{-1}) and intensity				C ₁ /C ₄ symmetry species	Description of mode [†]
	3,4-DFB (C ₁)		3,5-DFB (C _{3v})			
	Ground state	Excited state	Ground state	Excited state		
220 w	—	—	220 w	—	α''/b_1 ν_1	$\gamma_{\text{C}\equiv\text{N}}$
240 w	—	—	—	—	α''/a_2 ν_2	X-sensitive
250 mw	—	—	260 mw	—	α''/b_1 ν_2	X-sensitive
290 mw	294 w	235 mw	335 ms	326 mw	α'/a_1 ν_4	X-sensitive
330 m	333 w	314 m	220 s	414 w	α'/a_1 ν_6	X-sensitive
410 m	—	—	—	—	α''/a_2 ν_6	$\gamma_{\text{C}=\text{C}}$
440 m	446 w	405 m } (419 m)}	440 sh	—	α'/a_1 ν_7	X-sensitive
470 ms	477 w	376 m } (378 m)}	460 s	453 ms	α'/b_1 ν_9	X-sensitive
500 ms	—	—	510 s	—	α'/b_2 ν_9	$\beta_{\text{C}\equiv\text{N}}$
540 m	—	—	550 s	—	α'/b_1 ν_{10}	$\beta_{\text{C}=\text{N}}$
625 s	—	514 m	600 ms	—	α'/b_2 ν_{11}	$\beta_{\text{C}=\text{C}}$
705 ms	—	—	730 m	—	α''/b_1 ν_{12}	$\gamma_{\text{C}=\text{C}}$

Table 1. (Contd)

IR	Wavenumber (cm ⁻¹) and intensity				C _j /C ₁₈ symmetry species	Description of mode ^a
	3,4-DFB (C ₄)		3,5-DFB (C _{3r})			
	Electronic Ground state	Electronic Excited state	Electronic Ground state	Electronic Excited state		
795 vs	—	671 ms } 661 ms }	670 vs	—	α'/a ₁ ν ₁₃	X-sensitive
770 m	—	—	940 s	—	α''/b ₁ ν ₁₄	γ _{C-H}
840 vs	—	742 vs } (722 m)}	980 s	—	α'/a ₁ ν ₁₅	X-sensitive
910 vs	—	—	870 vs	—	α''/b ₁ ν ₁₆	γ _{C-H}
965 s	—	—	—	—	α''/a ₂ ν ₁₇	γ _{C-H}
1040 m	—	896 ms	1050 m	—	α'/a ₁ ν ₁₈	β _{C-H}
1130 s	—	970 m } (968 m w)}	1140 s	—	α'/b ₂ ν ₁₉	β _{C-H}
1150 ms	—	1116 s	1160 m	—	α'/a ₁ ν ₂₀	X-sensitive
1235 s	—	1229 ms	1230 s	—	α'/a ₁ ν ₂₁	X-sensitive
1280 ms	—	1962 s } (1258 m)}	1260 s	—	α'/b ₂ ν ₂₂	X-sensitive
1315 vs	—	—	1290 s	—	α'/b ₂ ν ₂₃	β _{C-H}
1330 sh	—	—	1337 s	—	α'/b ₂ ν ₂₄	ν _{C=C}

Table 1. (Contd.)

IR	Wavenumber (cm ⁻¹) and intensity				C ₁ /C ₃₂ symmetry species	Description of mode ⁺
	3,4-DFB (C ₁)		3,5-DFB (C _{3v})			
	Ground state	Excited state	Ground state	Excited state		
1390 s	—	—	1375 s	—	a'/a ₁ ν ₃₅	ν ₁ C=C
1430 s	—	(1342 ms)}	1420 s	—	a'/b ₂ ν ₃₄	ν ₂ C=C
1520	—	—	1590 vs	—	a'/a ₁ ν ₃₇	ν ₃ C=C
1620 s	—	(1552 m)}	1620 s	—	a'/b ₂ ν ₃₆	ν ₄ C=C
2240 s	—	—	2235 ms	—	a'/a ₁ ν ₃₉	ν ₅ C≡N
3050 w	—	—	3040 w	—	a'/a ₁ ν ₃₀	ν ₆ C=C
3100 ms	—	—	3080 m	—	a'/a ₁ ν ₃₁	ν ₇ C-H
3150 m	—	—	3100 s	—	a'/b ₂ ν ₃₂	ν ₈ C-H

+ γ = out-of-plane bending; β = in-plane bending; ν = stretch; X = substituents; vs = very strong; s = strong; ms = medium strong; m = medium, mw = medium weak; w = weak; sh = shoulder.

DFB = Difluorobenzonitrile.

() — the value in the parenthesis corresponds to ¹B_{1u} ← ¹A_{1g} system (System II).

C-H deformation and vice-versa. Thus with some assignments a certain vibration turns out to be predominantly a stretch or a deformation whereas in others this might not be the case. The fundamental vibrational frequencies so chosen are listed in Table 1, along with their assignments.

The electronic absorption spectra of 3,4- and 3,5-DFB show two $\pi \rightarrow \pi^*$ systems, one consisting of well defined bands around λ 2700 Å (System I) and the other having some weak bands around λ 2300 Å (System II). Even under the widely varied experimental conditions with the spectrographs used it was not possible to improve the System II. So this system was also recorded on a U-3200 UV/VIS Hitachi Spectrophotometer in vapour phase and in this record, some bands were observed in the region λ 2300 to λ 2100 Å. The System I has been identified as corresponding to the forbidden electronic transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ and the System II to the transition ${}^1B_{1u} \leftarrow {}^1A_{1g}$ of benzene.

UV spectra of System I of the molecules lie approximately in the region λ 2900 Å and they show well-defined vibrational structure. The effect of temperature on the band system has facilitated the choice of the band at 36430 cm^{-1} and 35750 cm^{-1} as the O,O band in 3,4- and 3,5-DFB respectively. The identification of the fundamentals chosen in the compounds has been done mainly on the basis of the intensities of the bands and the available literature on the analyses of other trisubstituted benzenes. So chosen fundamentals are also listed in Table 1 along with their assignments. The strong bands on the longer wavelength side with spacing 35 cm^{-1} and 45 cm^{-1} in 3,4- and 3,5-DFB have been identified as sequence intervals. The band data are with the authors.

In System II, bands observed towards the longer wavelength side at 44410 cm^{-1} and 44609 cm^{-1} in 3,4- and 3,5-DFB have been identified as O,O bands. The identified excited state fundamentals are also listed in Table 1 and they are correlated to the fundamentals of System I. The existence of such System II has been reported in literature (Nair *et al* 1969, Goel and Agarwal 1980, Amma *et al* 1969).

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