

Electronic absorption spectrum of 4-bromoisoquinoline

M. A. SHASHIDHAR AND K. SURYANARAYANA RAO

Department of Physics, Karnatak University, Dharwar 3, Karnataka

1 INTRODUCTION

In continuation of our work on the ultraviolet absorption spectra of some substituted quinolines (Shashidhar & Rao, 1967, 1970, 1973) and isoquinolines (Shashidhar, 1973, 1974), the electronic absorption spectrum of 4-bromoisoquinoline in the vapour phase has been recorded in the range 3260Å-2600Å and analysed. The spectrum has also been recorded in methylcyclohexane solution and the f values determined. Since data on ground state vibrational frequencies of the molecule are not available in the literature, its infrared absorption spectrum has also been recorded and analysed.

2. EXPERIMENTAL

The vapour phase spectrum was recorded on a Hilger Large quartz spectrograph with 10 to 150 cm long cells at 0°C to 150°C. Ilford R-40 plates were used to record the spectrum. The accuracy of measurements is estimated to be $\pm 5 \text{ cm}^{-1}$ for sharp bands and $\pm 10 \text{ cm}^{-1}$ for broad or diffuse bands.

The solution spectrum was recorded with a DK2A Beckmann recording spectrophotometer at room temperature and the f values of the solution spectrum were computed. The method of computation of f values is described elsewhere (Shashidhar 1971).

The infrared absorption spectrum was recorded using Perkin-Elmer model 221 double beam automatic spectrophotometer equipped with NaCl optics. As 4-bromoquinoline is a solid it was mixed in nujol and in tetrachloroethylene and a paste of sufficient concentration was prepared. A small amount of this paste was enclosed between the windows and its absorption spectrum, recorded.

3. RESULTS AND DISCUSSION

The ultraviolet absorption spectrum of this molecule lies in the region 2360Å-2600Å. Two band systems have been recorded for this molecule; one in the region 3260Å-2870Å (System I) which occurred with a cell of 150 cm and with the bulb containing the compound at about 50°C. With a cell of

75 cm and the bulb at about 30°C a few diffuse bands have been further found to develop in the region 2690Å-2600Å (System II).

Table 1. Fundamental vibrational frequencies (in cm^{-1}) of 4-bromoisoquinoline

Wave number & intensity	Probable Assignment
3075 m	a' C - H stretching
3050 m	a' C - H stretching
3020 m	a' C - H stretching
3005 w	a' C - H stretching
2985 m	a' C - H stretching
1620 s	a' C - C stretching
1590 m	a' C - C stretching
1565 s	a' C - C stretching
1485 s	a' C - C stretching
1470 m	a' C - C stretching
1405 m	a' C - C stretching
1370 s	a' C - C stretching
1345 ms	a' C - C stretching
1310 s	a'' C - N stretching
1255 s	a' C - H stretching
1225 s	a' C - H in-plane bending
1150 s	a' C - H in-plane bending
1090 m	a' C - H in-plane bending
1050 m	a' C - H in-plane bending
1015 m	a' C - H in-plane bending
955 s	a'' C - H out-of-plane bending
940 s	a'' skeletal deformation, in-plane
920 m	a'' C - H out-of-plane bending
890 m	a'' C - H out-of-plane bending
865 m	a'' C - H out-of-plane bending
840 m	a'' C - H out-of-plane bending
785 m	a' C - H out-of-plane bending
765 s	a' ring breathing
740 s	a' skeletal deformation, in-plane
655 m	a' skeletal deformation, in-plane

The infrared frequencies are given in table 1. The analysis of the infrared spectrum has been made by comparing it with the infrared spectra of the parent molecule isoquinoline and quinoline (Wait & McNerney, 1970), 3-methylisoquinoline (Shashidhar, 1974). The characteristic contours have been used to identify the fundamentals. The assignments have been made by assuming O_h symmetry for the molecule. Out of the 45 normal modes of vibration 31 are of a' type and 14 are of a'' type

System I:—This consists of narrow bands degraded to the red. The structure of the bands observed here is different from that of the broad and diffuse bands of system II and these bands seem to correspond to $n \rightarrow \pi^*$ (${}^1W \rightarrow {}^1A$, ${}^1B_2 \rightarrow {}^1A_1$) system of isoquinoline. The spectrum has been analysed with the help of the infrared data and also with the help of the analyses of the corresponding spectra of isoquinoline and 3-methylisoquinoline. The study of temperature effect on band system has facilitated the choice of the band at 31396 cm^{-1} as the 0,0 band. Most of the bands could be accounted for in terms of five ground state fundamentals 277, 353, 478, 540 and 755 cm^{-1} and nine upper state fundamentals 249, 309, 441, 523, 729, 1007, 1225, 1345 and 1436 cm^{-1} . Four medium intensity bands with separations of 249, 309, 441 and 523 cm^{-1} from the 0,0 band on the violet side may be considered as the excited state skeletal deformation frequencies corresponding to 277, 353, 478 and 540 cm^{-1} respectively in the ground state, the corresponding ground and excited state frequencies in isoquinoline being 287, 382, 450, 520 cm^{-1} and 230, 345, 421, 509 cm^{-1} respectively. The first three frequencies may correspond to the out of plane and the last one to the skeletal deformation modes. There is a strong band with a separation of 729 cm^{-1} from the 0,0 band on the violet side corresponding to the ground state frequency 755 cm^{-1} , and this excited state fundamental has been found to combine, as in the case of isoquinoline, with other fundamentals and give rise to combination bands. It may correspond to the ring breathing type of vibration of frequency 765 cm^{-1} in the infrared spectrum. The excited state frequencies 1007 and 1225 cm^{-1} may correspond to C-H inplane banding vibrations 1050 and 1255 cm^{-1} in the infrared spectrum, the corresponding excited state frequencies in isoquinoline being 1009 and 1244 cm^{-1} respectively. The other frequencies in this molecule, viz. 1338 and 1436 cm^{-1} may correspond to 1323 and 1442 cm^{-1} in isoquinoline and may be correlated with C-C stretching modes of vibration of frequencies 1345 and 1485 cm^{-1} in the infrared spectrum. In addition, difference frequencies 42 and 62 cm^{-1} have been observed as combination bands. These are probably due to ν - ν transitions of some suitable, non-totally symmetric vibrations.

In the absorption spectrum of 4-bromoisoquinoline in the solution of methylcyclohexane, the strong band at 30975 cm^{-1} has been chosen as the 0,0 band of the system. It is interesting to note that the absorption spectrum of this compound in solution retains the vibrational structure observed in the corresponding vapour spectrum. Tables 2 and 4 give the spectral data of this system in vapour and in solution phase.

System II:—The band system in this region consists of broad and diffuse bands even under the very widely different experimental conditions used and are distinctly different from the sharp bands of system I. This system may be attributed to the π - π^* transition due to its resemblance with the corresponding electronic bands of isoquinoline. As the bands are broad and diffuse,

Table 2. Ultraviolet absorption bands of 4-bromoisoquinoline in the vapour state ($n-\pi^*$ transition)

Wave number in cm^{-1} & intensity	Assignment
30641 w	0,0 - 755
30763 w	0,0 - 353 - 277
30904 w	0,0 - 540 - 42
30856 w	0,0 - 540
30875 w	0,0 - 478 - 42
30918 w	0,0 - 478
30971 w	0,0 - 353 - 62
31002 w	0,0 - 353 - 42
31043 w	0,0 - 353
31088 w	0,0 - 277 - 42
31119 w	0,0 - 277
31157 w	0,0 - 478 + 249
31198 w	0,0 - 342 - 62
31267 w	0,0 - 3 x 42
31298 m	0,0 - 2 x 42
31334 ms	0,0 - 62
31354 s	0,0 - 42
31370 m	0,0 - 277 + 249
31396 s	0,0
31427 w	0,0 + 309 - 277
31481 w	0,0 + 441 - 353
31524 w	0,0 + 5 3 - 353 - 42
31560 w	0,0 + 441 - 277
31645 m	0,0 + 249
31705 m	0,0 + 309
31774 w	0,0 + 729 - 353
31837 ms	0,0 + 441
31859 w	0,0 + 1007 - 540
31919 ms	0,0 + 523
31956 w	0,0 + 249 + 309
31991 w	0,0 + 1345 - 755
32058 w	0,0 + 1007 - 353
32125 s	0,0 + 729
32192 w	0,0 + 523 + 249
32281 w	0,0 + 2 x 441
32308 w	0,0 + 1007 - 42 - 62
32334 w	0,0 + 1007 - 62

Wave number in cm^{-1} Intensity	Assignment
32403 ms	0,0 + 1007
33481 w	0,0 + 1436 — 353
32559 w	0,0 + 729 + 441
32596 w	0,0 + 729 + 523—62
32621 s	0,0 + 1225
32665 m	0,0 + 729 + 523
32710 w	0,0 + 1007 + 309
32741 s	0,0 + 1315
32777 w	0,0 + 1436 — 62
32801 w	0,0 + 2 × 729 — 62
32832 s	0,0 + 1436
32860 m	0,0 + 2 × 729
32918 w	0,0 + 1007 + 523
33006 w	0,0 + 1225 + 441 — 42
33052 w	0,0 + 1225 + 441
33142 w	0,0 + 1007 + 729
33280 w	0,0 + 1345 + 523
33341 w	0,0 + 1225 + 729
33406 m	0,0 + 2 × 1007
33574 w	0,0 + 3 × 729
33614 w	0,0 + 1225 + 1007
33860 w	0,0 + 2 × 1225
33993 w	0,0 + 3 × 729 + 441
34078 w	0,0 + 2 × 1345
34157 w	0,0 + 1436 + 1345
34273 w	0,0 + 2 × 1436
34381 w	0,0 + 2 × 1345 + 309
34436 w	0,0 + 3 × 1007
34549 w	0,0 + 2 × 1345 + 441
34736 w	0,0 + 2 × 1007 + 1345
34832 w	0,0 + 3 × 729 + 1225

the exact position of the 0,0 band could not be ascertained. However, the centre of the strong band at 37085 cm^{-1} has been chosen as the 0,0 band of this system. The other bands could be analysed in terms of the excited state frequencies 267, 356, 435, 514, 719 and 980 cm^{-1} , the first four excited state

frequencies 267, 356, 435, 514 cm^{-1} may correspond to skeletal deformation modes and the other two frequencies 719, 980 cm^{-1} may correspond to the ring breathing and C-H in-plane bending modes of vibration.

Table 3. Ultraviolet absorption bands of 4-bromoisoquinoline in the vapour state $\pi \rightarrow \pi^*$ transition

Wave number in cm^{-1} & Intensity	Assignment
37085 m	0,0
37352 w	0,0 + 356
37520 w	0,0 + 435
37599 w	0,0 + 514
37712 w	0,0 + 356 + 267
37804 w	0,0 + 719
38065 w	0,0 + 980
38312 w	0,0 + 980 + 267

Table 4. Ultraviolet absorption bands of 4 bromoisoquinoline in methylecyclohexane (concentration : 0.02 gm/lt)

Wave number in cm^{-1} & Intensity	Assignment
$n \rightarrow \pi^*$ transition	
30975 s	0,0
31487 s	0,0 + 512
31686 m	0,0 + 711
31991 s	0,0 + 1016
32353 s	0,0 + 1378
32975 m	0,0 + 2 \times 1016
33717 m	0,0 + 2 \times 1378
34767 m	0,0 + 2 \times 1378 + 1016
35785 w	0,0 + 2 \times 1378 + 2 \times 1016
$f_s = 0.0159 \pm 0.002$	
$\pi \rightarrow \pi^*$ transition	
36486 s	0,0
36948 s	0,0 + 472
37183 m	0,0 + 697
37456 s	0,0 + 970
37724 m	0,0 + 1238
38136 w	0,0 + 970 + 697
$f_s = 0.048 \pm 0.002$	

The band data in vapour phase and in solution are given for this system in Table 3 and 4 respectively.

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