

Electronic absorption spectra of 2-, 3- and 7-methyl indoles

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The ultraviolet absorption spectra of 2-, 3- and 7-methyl indoles in the vapour state and in solution have been studied. The observed fundamentals and their assignments are reported and discussed.

1. INTRODUCTION

Although a great deal of work has been done on the ultraviolet absorption spectra in the vapour state of benzene and substituted benzenes, relatively not much work has been done on the substituted indole molecules. Therefore, a study of substituted indoles has been carried out with a view to investigating the ultraviolet spectra of these in more detail and with a view to drawing some conclusions about the electronic structure of the parent molecule using the sharpness of bands. The electronic absorption spectrum of indole has been studied in great detail by different workers (Vishwanath 1954; Hollas 1963). In this paper are given the details of an investigation of the ultraviolet absorption spectra of 2-, 3- and 7-methyl indoles. Since the data on the ground state vibrational frequencies of the molecules are not available in the literature, the infrared absorption spectra are also recorded and analysed.

2. EXPERIMENTAL

The 2-, 3- and 7-methyl indoles were obtained from Fluka, Switzerland. The vapour phase spectra were recorded with 10 to 200 cm cells at temperatures from -10°C to 150°C on a Hilger Large quartz spectrograph. Ilford R-40 plates were used to photograph the spectra. The accuracy of measurements has been estimated to be $\pm 5\text{ cm}^{-1}$ for sharp bands and $\pm 10\text{ cm}^{-1}$ for broad and diffuse bands. The solution spectrum was recorded on a DK2A Beckmann recording spectrophotometer and the f values of the solution spectrum were computed. The method of computation of the values is described elsewhere (Shashidhar 1971).

The infrared absorption spectra of 2- and 3- methyl indoles were recorded using a Perkin-Elmer model 221 double beam automatic spectrophotometer equipped with NaCl optics. The samples being solid, were mixed in nujol and in hexachlorobuta-1, 3 diene and pastes of sufficient concentration were prepared. A little amount of these pastes was enclosed between the windows and its absorption spectrum recorded.

3. RESULTS AND DISCUSSION

The ultraviolet absorption spectra of these molecules lies in the region 2950A-2740A. The spectra in general are sharp.

The analysis of the infrared spectrum has been done by comparison with the parent molecule, Indole and similar other molecules (Lamberst & Lecomte, 1939). The characteristic contours have been used to identify the symmetry species. If we assume C_s symmetry for this molecule taking CH_3 as an atomic point, the studied molecules will have 51 normal modes of vibration with the distribution, $35a' + 16a''$. The infra-red frequencies together with their alignments are given in tables 1 and 2.

Table 1. Infrared frequencies of 2-methylindole

Wave number in cm^{-1} & intensity	Probable Assignment
730 vs	a' skeletal deformation, in plane
750 s	a' skeletal deformation, in-plane
785 vs	a' ring breathing
845 m	a'' C — H out of plane bending
880 m	a'' C — H out of plane bending
925 s	a'' C — H out of plane bending
975 m	a' C skeletal deformation, in-plane
995 m	a'' C — H out of plane bending
1010 m	a' C — H in-plane bending
1035 m	a' C — H in-plane bending
1055 m	a'' N — H out of plane bending
1110 ms	CH_3 rocking
1150 ms	a' C — H in-plane bending
1215 s	a' C — CH_3 stretching
1235 s	a' C — H in-plane bending
1285 vs	a' C — N stretching
1340 s	a' C — C stretching
1380 ms	CH_3 symmetric bending
1400 s	a' C — C stretching
1450 s	CH_3 asymmetric bending

Table 1 (Contd.)

Wave number in cm^{-1} & intensity	Probable Assignment
1465 sh	a' C — C stretching
1485 ms	a' C — C stretching
1545 s	a' C — C stretching
1580 s	a' C — C stretching
1615 s	a' N — H in plane bending
2850 s	CH ₃ asymmetric stretching
2945 s	CH ₃ asymmetric stretching
2985 ms	CH ₃ asymmetric stretching
3030 m	a' C — H stretching
3050 ms	a C — H stretching
3070 m	a' C — H stretching
3085 w	a' C — H stretching

Table 2. Infrared frequencies of 3-methylindole

Wave number in cm^{-1} & intensity	Probable Assignment
735 vs	a' skeletal deformation, in-plane
755 s	a' skeletal deformation, in-plane
800 s	a' C — C stretching
845 m	a'' C — H out of plane bending
870 ms	a'' C — H out of plane bending
925 s	a'' C — H out of plane bending
970 ms	a' skeletal deformation, in-plane
995 sh	a'' C — out of plane bending
1005 s	a' C — H in-plane bending
1055 sh	a' C — H in-plane bending
1070 s	a'' N — H out of plane bending
1085 s	CH ₃ rocking
1145 m	a' C — H in-plane bending
1225 ms	a' C — CH ₃ stretching
1245 ms	a' C — H in-plane bending
1300 s	a' C — N stretching
1335 s	a' C — C stretching
1380 s	CH ₃ symmetric bending

Table 2 (Contd.)

Wave number in cm^{-1} & intensity	Probably Assignment
1420 m	a' C — C stretching
1435 s	CH_3 asymmetric bending
1460 s	a' C — C stretching
1480 s	a' C — C stretching
1550 m	a' C — C stretching
1585 ms	a' C — C stretching
1610 s	a' N — H in plane bending
2860 s	CH_3 symmetric stretching
2925 s	CH_3 asymmetric stretching
2970 s	CH_3 asymmetric stretching
2990 m	a' C — H stretching
3020 m	a' C — H stretching
3035 m	a' C — H stretching
3055 ms	a' C — H stretching
3080 m	a' C — H stretching

In the molecules investigated, the 0,0 band is the strongest band in this electronic system. The ratio of the intensity of the 0,0 band to that of the next most intense band has been measured approximately for both the molecules and this together with the fact that no progressions with more than two members have been observed show that there is no change of shape and very little change of size of the molecules accompanying the excitation of the electron. The intensity of the 0,0 band confirms the transitions as allowed and as π - π^* transitions; they must be $A'-A'$ with only a' , totally symmetric vibrations active, apart from those in sequences

Vibrational structure extends to about 2500 cm^{-1} to the violet of the 0,0 band in both the spectra with a gradual increase in diffuseness of the bands with increasing frequency. A few hot bands to the red of the 0,0 band group are observed. The strongest band at 35164 , 34876 and 35212 cm^{-1} in 2-, 3- and 7-methyl indoles has been chosen as the 0,0 band of the system. The bands with separations 379 , 433 , 622 , 780 , 904 , 1033 and 1125 cm^{-1} in 2-methyl indole, bands with separations 366 , 418 , 596 , 761 , 957 cm^{-1} in 3-methyl indole and bands with separations 372 , 403 , 627 , 739 , 772 , 964 cm^{-1} in 7-methyl indole from 0,0 towards the long wavelength side are assigned as the ground state fundamentals, while the bands with shifts 329 , 371 , 529 , 728 , 753 , 901 , 931 , 969 , 1130 , 1319 and 1428 cm^{-1} in 2-methyl indole, 346 , 362 , 546 , 717 , 742 , 925 , 954 , 972 , 1129 and 1308 cm^{-1} in 3-methyl indole

Table 3. Assignments of the absorption bands of 2- 3- 7-methyl indole

2-methyl indole		3-methyl indole		7-methyl indole	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
34039 w	0,0 - 1125	33919 w	0,0 - 957	34248 w	0,0 - 964
34131 w	0,0 - 1033	33998 w	0,0 - 761 - 3 × 48	34389 w	0,0 - 772 - 48
34260 w	0,0 - 904	34046 w	0,0 - 761 - 2 × 48	34440 m	0,0 - 772
34333 w	0,0 - 780 - 48	34115 m	0,0 - 761	34473 m	0,0 - 739
34384 m	0,0 - 780	34208 w	0,0 - 595 - 48	34494 w	0,0 - 627 - 2 × 48
34542 m	0,0 - 622	34280 s	0,0 - 596	34546 w	0,0 - 627 - 48
34645 w	0,0 - 2 × 208 - 2 × 48	34411 w	0,0 - 418 - 48	34585 s	0,0 - 627
34704 w	0,0 - 433 - 2 × 13	34458 m	0,0 - 418	34665 w	0,0 - 403 - 3 × 48
34731 m	0,0 - 433	34510 w	0,0 - 366	34709 w	0,0 - 403 - 2 × 48
34795 w	0,0 - 379	34535 w	0,0 - 7 × 48	34757 w	0,0 - 403 - 48
34863 w	0,0 - 208 - 2 × 48	34562 w	0,0 - 6 × 48 - 22	34809 m	0,0 - 403
34956 m	0,0 - 208	34585 w	0,0 - 6 × 48	34840 m	0,0 - 372
34968 m	0,0 - 4 × 48	34616 w	0,0 - 5 × 48 - 22	34910 w	0,0 - 207 - 2 × 48
35006 w	0,0 - 3 × 48 - 13	34635 w	0,0 - 5 × 48	34951 m	0,0 - 207 - 48
35022 m	0,0 - 3 × 48	34663 w	0,0 - 4 × 48 - 22	34972 w	0,0 - 5 × 48
35065 w	0,0 - 2 × 48 - 13	34690 m	0,0 - 4 × 48	34991 w	0,0 - 207 - 14

Table 3. Assignments of the absorption bands of 2- 3- 7-methyl indole—Contd.

2-methyl indole		3-methyl indole		7-methyl indole	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
35078 m	0,0 - 2 × 48	34728 m	0,0 - 3 × 48	35005 m	0,0 - 207
35097 m	0,0 - 48 - 13	34754 m	0,0 - 2 × 48 - 22	35023 m	0,0 - 4 × 48
35116 s	0,0 - 48	34778 s	0,0 - 2 × 48	35031 w	0,0 - 3 × 48 - 3 × 14
35133 m	0,0 - 3 × 13	34804 s	0,0 - 48	35043 w	0,0 - 3 × 48 - 2 × 14
35140 m	0,0 - 2 × 13	34854 s	0,0 - 22	35057 w	0,0 - 3 × 48 - 14
35151 s	0,0 - 13	34876 vs	0,0	35064 m	0,0 - 3 × 48
35164 vs	0,0	35082 w	0,0 + 346 - 3 × 48	35074 w	0,0 - 2 × 48 - 3 × 14
35265 w	0,0 + 529 - 433	35122 w	0,0 + 346 - 2 × 48	35083 w	0,0 - 2 × 48 - 2 × 14
35349 w	0,0 + 329 - 3 × 48	35167 w	0,0 + 346 - 48	35104 w	0,0 - 2 × 48 - 14
35404 w	0,0 + 329 - 2 × 48	35222 m	0,0 + 346	35112 m	0,0 - 2 × 48
35462 w	0,0 + 329 - 48	35238 m	0,0 + 362	35120 w	0,0 - 48 - 3 × 14
35493 m	0,0 + 329	35279 w	0,0 + 546 - 3 × 48	35132 w	0,0 - 48 - 2 × 14
35535 m	0,0 + 371	35326 w	0,0 + 546 - 2 × 48	35145 m	0,0 - 48 - 14
35582 w	0,0 + 529 - 2 × 48	35371 w	0,0 + 546 - 48	35156 m	0,0 - 4 × 14
35660 w	0,0 + 529 - 48	35422 s	0,0 + 546	35164 s	0,0 - 48
35693 s	0,0 + 529	35455 w	0,0 + 717 - 3 × 48	35171 m	0,0 - 3 × 14

Table 3. Assignments of the absorption bands of 2-3-7-methyl indole—*Contd.*

2-methyl indole		3-methyl indole		7-methyl indole	
ν (cm^{-1}) and intensity	Assignment	ν (cm^{-1}) and intensity	Assignment	ν (cm^{-1}) and intensity	Assignment
35723 w	0,0 + 763 - 208	35501 w	0,0 + 717 - 2 × 48	35185 m	0,0 - 2 × 14
35763 w	0,0 + 728 - 3 × 48	35537 w	0,0 + 717 - 48	35198 s	0,0 - 14
35781 w	0,0 + 728 - 2 × 48	35568 w	0,0 + 742 - 48	35212 vs	0,0
35812 w	0,0 + 753 - 3 × 48	35593 s	0,0 + 717	35303 w	0,0 + 342 - 207 - 48
35830 w	0,0 + 753 - 2 × 48	35618 m	0,0 + 742	35346 w	0,0 + 342 - 207
35852 m	0,0 + 728 - 48	35683 m	0,0 + 954 - 3 × 48	35411 w	0,0 + 342 - 3 × 48
35875 m	0,0 + 753 - 48	35710 w	0,0 + 954 - 2 × 48 - 22	35457 w	0,0 + 342 - 2 × 48
35892 s	0,0 + 728	35743 w	0,0 + 954 - 2 × 48	35512 w	0,0 + 342 - 48
35917 m	0,0 + 753	35781 w	0,0 + 954 - 48	35554 m	0,0 + 342
35974 w	0,0 + 901 - 2 × 48	35802 s	0,0 + 925	35609 m	0,0 + 397
36023 w	0,0 + 901 - 48	35830 m	0,0 + 954	35640 w	0,0 + 721 - 207 - 2 × 48
36065 s	0,0 + 901	35848 m	0,0 + 972	35668 w	0,0 + 603 - 3 × 48
36101 m	0,0 + 937	35954 w	0,0 + 1129 - 48	35687 w	0,0 + 721 - 207 - 48
36133 m	0,0 + 969	36005 w	0,0 + 1129	35713 w	0,0 + 603 - 2 × 48
36247 w	0,0 + 1130 - 48	36050 w	0,0 + 1308 - 3 × 48	35729 w	0,0 + 721 - 207
36294 w	0,0 + 1130	36093 w	0,0 + 1308 - 2 × 48	35745 w	0,0 + 742 - 207

Table 3. Assignments of the absorption bands of 2- 3- 7-methyl indole—Contd.

2-methyl indole		3-methyl indole		7-methyl indole	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
36349 w	0,0 + 1319 — 3 × 48	36184 m	0,0 + 1308	35772 w	0,0 + 603 — 48
36391 w	0,0 + 1319 — 2 × 48	36216 w	0,0 ± 972 ± 362	35796 w	0,0 + 603 — 14
36426 w	0,0 + 728 + 529	36354 w	0,0 + 925 ± 546	35815 s	0,0 ± 603
36448 w	0,0 + 1319 — 48			35839 w	0,0 + 721 — 48
35483 m	0,0 + 1319			35888 w	0,0 + 721 — 48
36537 w	0,0 + 1428 — 48			35935 s	0,0 ± 721
36592 m	0,0 + 1428			35954 m	0,0 + 742
36643 w	0,0 + 753 + 728			36014 w	0,0 + 925 — 2 × 48 — 2 × 13
36793 w	0,0 ± 901 ± 728			36053 w	0,0 + 925 — 2 × 48
36855 w	0,0 + 969 + 728			36093 w	0,0 + 925 — 48
37008 w	0,0 — 901 + 937			36137 s	0,0 + 925
37113 w	0,0 + 2 × 969			36159 m	0,0 + 947
37190 w	0,0 + 1130 + 901			36183 m	0,0 ± 971

Table 3. Assignments of the absorption bands of 2-3-7-methyl indole—*Concld.*

2-methyl indole		3-methyl indole		7-methyl indole	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
37358 w	0,0 + 1428 + 769			36203 m	0,0 + 1129 - 3 × 48
37418 w	0,0 + 2 × 1130			36244 m	0,0 + 1129 - 2 × 48
37562 w	0,0 + 1428 + 969			36289 w	0,0 + 1129 - 48
				36341 w	0,0 + 1129
				36384 w	0,0 + 1310 - 3 × 48
				36421 w	0,0 + 1310 - 2 × 48
				36473 w	0,0 + 1310 - 48
				36522 m	0,0 + 1310
				36547 w	0,0 + 721 + 603
				36578 w	0,0 + 1406 - 48
				36618 m	0,0 + 1406
				36630 m	0,0 + 2 × 721
				36686 w	0,0 + 721 + 742
				36708 m	0,0 + 2 × 742
				36758 w	0,0 + 947 + 603
				36800 w	0,0 + 971 + 603

Table 4. Ultraviolet absorption bands of 2- 3- and 7-methyl indole in methycyclohexane (concentration 0.01 gm/lt, $\pi \rightarrow \pi^*$ transition)

2-methyl indole		3-methyl indole		7-methyl indole	
ν (cm ⁻¹) and intensity	Assignment	ν (cm ⁻¹) and intensity	Assignment	ν (cm ⁻¹) and intensity	Assignment
34748 s	0.0	34532 s	0.0	34803 s	0.0
35678 s	0.0 + 930	35450 s	0.0 + 918	35716 s	0.0 + 913
36195 s	0.0 + 1447	35961 s	0.0 + 1429	36221 s	0.0 + 1418
37115 m	0.0 + 930 + 1447	35869 m	0.0 + 918 + 1429	37143 m	0.0 + 1418 + 913
37622 w	0.0 + 2 × 1447	37372 m	0.0 + 2 × 1429	37653 m	0.0 + 2 × 1418
		38328 w	0.0 + 2 × 1429 + 918	38083 w	0.0 + 2 × 913 + 1418
				38583 w	0.0 + 2 × 1418 + 913
	$f_{\lambda} = 0.0339 \pm 0.002$		$f_{\lambda} = 0.0428 \pm 0.002$		$f_{\lambda} = 0.03952 \pm 0.002$

and 342, 397, 603, 721, 742, 925, 947, 971, 1129, 1310 and 1406 cm^{-1} in 7-methyl indole from the 0,0 band towards the shorter wavelength side are identified as the excited state fundamental frequencies. The observed sequence intervals in 2-methyl indole are 13, 48 and 208 cm^{-1} and in 3-methyl indole they are 22 and 48 cm^{-1} while in 7-methyl indole they are 14, 48 and 207 cm^{-1} .

The principal bands in the band groups are easily picked out from the spectra. Their positions and assignments with visual estimates of relative intensities are given in table 3. All the bands in the spectra apart from the principal bands are sequence members as in the case of indole. The low frequency vibrations which give rise to sequences are most likely non-totally symmetric (a'') and not active in this system in single quanta.

As in the case of indole, in these spectra of these molecules it is possible to select some vibrations which are changed very little in frequency and intensity. The vibration which has a frequency 753, 742 and 742 cm^{-1} in 2-, 3- and 7-methyl indoles is active and its frequency changes only by a few wavenumbers indicating that it is a vibration involving substituent and probably a vibration of the benzene ring. Another frequency which changes very little is 901, 954 and 947 cm^{-1} in 2-, 3- and 7-methyl indoles respectively.

In the absorption spectra of 2-, 3- and 7-methyl indoles in the solution of methylcyclohexane the strong band at 34748, 34532 and 34803 cm^{-1} has been chosen as the 0,0 band respectively. It is interesting to note that the absorption spectra of these molecules in solution retain some of the vibrational structure observed in the corresponding vapour spectrum. Table 4 gives the spectral data of these molecules in solution.

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