

Letter to the Editors

On the electronic spectra of some trisubstituted benzenes

M. A. SHASHIDHAR

Department of Physics, Karnatak University, Dharwar-580003

(Received 7 April 1977, revised 27 June 1977)

In further continuation of our work on the ultra-violet absorption spectra of some substituted benzenes the electronic spectra of 2, 4-dichloroaniline, 3-Amino-4-chlorotoluene, 3-chloro-6-aminotoluene, and 3-Amino-2-chlorotoluene have been recorded in the vapour phase and analysed. The spectra of all the above molecules were also recorded in methylecyclohexane solution and the f values have been obtained. In this paper the results of an investigation of these spectra are reported and discussed.

The vapour phase spectra of all the molecules studied were recorded on a Hilger-Littrow spectrograph with 10 to 150 cm cells at temperatures ranging from 0°C to 150°C. The solution spectra were recorded with a DK2A Beckmann recording spectrophotometer. The accuracy of measurements has been estimated to be ± 5 cm⁻¹ for sharp bands and ± 10 cm⁻¹ for broad or diffuse bands. The f values of the solution spectrum were computed for all the molecules studied and have been reported elsewhere (Shashidhar 1971).

The electronic absorption bands of the molecules studied occur approximately in the region 2840 to 3165 Å and the bands are rather sharp and are degraded to the red and this corresponds to the $A_{1g}-B_{2u}$ transition of benzene. The spectra have been analysed with the help of the analyses of the corresponding spectra of some trisubstituted benzenes (Singh & Singh 1966, 1969; Mehrotra 1968). Tables 1 to 4 give the data and their assignments for all the molecules investigated in the vapour and in solution phase.

In all the molecules studied two excited state frequencies between 600-700 cm⁻¹ and 950-1000 cm⁻¹ have been observed and is found to combine strongly with other frequencies to give rise to combination bands. These two frequencies may correspond to the two totally symmetric carbon vibrations corresponding to the mode A_1 and $12a(A_1)$ of benzene respectively. In most of the trisubstituted benzenes these two frequencies have been attributed to this mode.

Probable correlation of some of the excited state frequencies are given in table 5.

Table 1. Spectral data of 2,4-dichloroaniline

a) In vapour phase.		b) In methylecyclohexane solution.	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
31616 w	0, 0-613	31940 s	0, 0
31819 w	0, 0-410	32353 ms	0, 0+413
31933 m	0, 0-296	33280 m	0, 0+2×677
32014 w	0, 0-215	33698 m	0, 0+2×677+413
32503 m	0, 0+274		
32583 m	0, 0+354		$f_s = 0.027 + 0.002$
32724 m	0, 0+495		
32908 s	0, 0+679		
33072 m	0, 0+495+354		
32225 m	0, 0+995		
33402 w	0, 0+1173		
33584 w	0, 0+2×679		
33903 w	0, 0+995+679		
34086 w	0, 0+1173+679		

Table 2. Spectral data of 3-Amino-4-chlorotoluene

a) In vapour phase.		b) In methylecyclohexane solution.	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
32927 w	0, 0-430	33268 s	0, 0
33130 w	0, 0-227	33831 m	0, 0+363
33173 w	0, 0-184	34295 ms	0, 0+927
33357 s	0, 0	34412 m	0, 0+1144
33510 w	0, 0+153	35127 m	0, 0+2×927
33632 m	0, 0+275		
33742 m	0, 0+385		$f_s = 0.031 \pm 0.002$
33782 m	0, 0+425		
34040 m	0, 0+673		
34145 w	0, 0+425+385		
34218 w	0, 0+2×425		
34351 m	0, 0+968		
34462 w	0, 0+673+425		
34497 w	0, 0+1140		
34740 w	0, 0+968+425		
35160 w	0, 0+1140+673		

Table 3. Spectral data of 3-chloro-6-aminotoluene

a) In vapour phase		b) In methyleyclohexane solution	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
32723 w	0, 0-236	32724 s	0, 0
32959 s	0, 0	33935 m	0, 0+711
33154 w	0, 0+195	33707 m	0, 0+983
33260 m	0, 0+301	34672 m	0, 0+2×983
33321 m	0, 0+362	35388 m	0, 0+2×983+711
33385 ms	0, 0+426		
33645 ms	0, 0+686		$f_s = 0.015+0.002$
33741 w	0, 0+426+362		
33807 w	0, 0+2×426		
33930 m	0, 0+975		
34063 w	0, 0+686+426		
34103 w	0, 0+1144		
34341 w	0, 0+2×686		
34633 w	0, 0+975+686		

Table 4. Spectral data of 3-Amino-2-chlorotoluene

a) In vapour phase		b) In methyleyclohexane solution	
$\nu(\text{cm}^{-1})$ and intensity	Assignment	$\nu(\text{cm}^{-1})$ and intensity	Assignment
33278 w	0, 0-219	34178 s	0, 0
33497 s	0, 0	34532 m	0, 0+354
33666 w	0, 0+169	35896 ms	0, 0+718
33790 m	0, 0+293	35139 ms	0, 0+961
33845 m	0, 0+348	35831 m	0, 0+961+718
33932 m	0, 0+435	36090 m	0, 0+2×961
34147 m	0, 0+650		
34386 w	0, 0+2×435		$f_s = 0.019+0.002$
34469 m	0, 0+972		
34572 w	0, 0+650+435		
34642 w	0, 0+1145		
34890 w	0, 0+972+435		

Table 5. Probable correlation between the ground and excited state fundamentals (cm^{-1})

2, 4-dichloro-aniline		3-Amino-4-chlorotoluene		3-chloro-6-aminotoluene		3-Amino-2-chlorotoluene		Probable nature of the mode
Ground state	Excited state	Ground state	Excited state	Ground state	Excited state	Ground state	Excited state	
215	--	227	153	236	195	219	169	
296	274		275		301	--	293	γ_{C-C}
410	354	430	385	—	362	—	348	β_{C-C}
613	495		425	--	426	—	435	β_{C-C}
-	679		673	-	686	--	650	ν_{C-C}
	995		968	-	975	--	972	β_{C-C}
	1173		1140		1144		1145	β_{C-H}

REFERENCES

- Mehrotra V. K. 1968 *Ind. J. Pure and Appl. Phys.* **6**, 137
 Shashidhar M. A. 1971 *Spectrochimica Acta* **27A**, 2363.
 Singh S. N. & Singh N. L. 1969 *Ind. J. Pure and Appl. Phys.* **7**, 250.
 Singh S. N. & Singh N. L. 1966 *Current Sci.* **35**, 62.