

Infrared and ultraviolet absorption spectra of some tri-substituted benzenes and their dipole moments in the first excited electronic states

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Received 11 July 1989, accepted 28 August 1989

The near ultraviolet and the vibrational spectra of aniline, benzonitrile, their mono and di derivatives have been studied in detail by different investigators (Green 1961, Green and Harrison 1979, Goel *et al* 1978, 1979, Goel and Agarwal 1982, Ginsberg *et al* 1946, Ginsberg and Matson 1947, Varsanyi 1974, Huded *et al* 1987, Shashidhar and Suryanarayana Rao 1966 and Evans 1960). As a part of our research programme and in continuation of our work on some aspects of the spectra of benzene derivatives, the present communication reports the study on the vibrational analyses of the infrared and UV absorption spectra of 3,4- and 3,5-difluoroanilines, 3-chloro-4-methyl benzonitrile and 3,5-difluorobenzonitrile (hereafter referred to as compounds I, II, III and IV). The solvatochromic shift of the $\pi^* \leftarrow \pi$ system of the compounds in different solvents have been utilised to calculate the electric dipole moments in the upper electronic states.

Compounds I and II are liquids while compounds III and IV are solids. They were obtained from Aldrich Chemical Co., USA and used to record the absorption spectra. The experimental methods adopted to record the i.r. and uv spectra and the accuracies in the measurement of band positions are the same as that given in our earlier work (Shashidhar 1971).

Compounds I and III may be considered as belonging to the point group C_2 , while compounds II and IV may be considered as belonging to C_{2v} point group if we consider the substituents to behave as a single mass point and coplanar with the ring.

The 36 and 42 normal modes of vibration for compounds I and III will have the distribution $25a' + 11a''$ and $29a' + 13a''$, all of these being active in i.r. spectrum. Under C_{2v} symmetry of compounds II and IV, the 36 and 33 normal modes of vibration will have the distribution $13a_1 + 3a_2 + 12b_1 + 8b_2$

Table I. Correlation of the fundamental frequencies (cm^{-1}) of compounds I, II, III and IV.

	Compound I			Compound II			Compound III			Compound IV			Description of mode
	IR	Electronic GS	ES	IR	Electronic GS	ES	IR	Electronic GS	ES	IR	Electronic GS	ES	
220 w				220 mw	225 ms	88 s	220 w			225 m			X sensitive
240 w							240 mw			—			$\gamma_{\text{C-H}}$
270 w				260 mw			260 w			260 mw			X sensitive
310 w							390 w			—			X sensitive
390 s	—	263 ms		420 m	—	375 s	280 s	282 w	223 m	450 m	—	307 s	X sensitive
405 ms	405 mw	311 s		505 s	505 m	462 s	460 s	467 w	421 m	460 s	453 m	397 vs	X sensitive
450 vs	445 mw	364 m		330 s	330 m	232 s	425 s	425 w	301 m	330 w	326 m	223 ms	X sensitive
470 w	465 mw	412 ms		370 w	366 mw	270 s	360 s	—	—	420 s	414 m	359 s	X sensitiv
520 m				530 m			605 w			510 w			$\gamma_{\text{C-C}}$
605 s	600 w	452 s		610 m			605 vs			600 ms			$\delta_{\text{C-C}}$
715 s				730 ms			700 s			725 m			$\gamma_{\text{C-C}}$
735 vs				806 s			835 s			870 vs			$\gamma_{\text{C-C}}$
770 vs				617 m	670 s	552 s	730 s			551 ms	670 vs	510 s	X sensitive
860 s				756 s	1010 s		726 ms	820 vs	738 m	985 s	741 ms		X sensitive

Table I. (Contd.)

IR	Compound I		Compound II		Compound III		Compound IV		Description of mode
	Electronic	IR	Electronic	IR	Electronic	IR	Electronic	IR	
	GS	ES	GS	ES	GS	ES	GS	ES	
940 s		805 s		900 m					γ C-H
975 ms		975 s		920 m		940 s			γ C-H
1130 ms		914 m	1120 s	834 ms	1040 m	943 ms	1050 m	968 s	β C-H
1170 ms		1067 s	1170 s	1043 m	1150 w	1023 ms	1140 s	1012 ms	β C-H
1205 w		1166 ms	1245 m	1128 m	1210 m	1143 ms	1260 s	1231 ms	X sensitive
1245 vs		1191 ms	1220 m	1193 m	680 m	591 ms	1230 s	1177 m	X sensitive
1285 m		1270 m		1305 w		1290 m			δ C-H
1315 vs		1247 m	1300 ms	1235 m	1190 s	1125 ms	1160 m	1113 ms	X sensitive
1340 w		1330 ms		1270 mw		1325 ms			ν C-C
1430 vs		1460 s		1420 sh		1420 s			ν C-C
1480 vs		1380 s		1480 sh		1375 s			ν C-C
1570 m		1570 m		1590 m		1590 vs			ν C-C
1600 m		1605 s		1540 m		1610 m			ν C-C
3010 mw		3080 w		3020 sh		3060 m			ν C-H

Table I. (Contd.)

IR	Compound I		Compound II		Compound III		Compound IV		Description of mode
	IR	Electronic GS ES	IR	Electronic GS ES	IR	Electronic GS ES	IR	Electronic GS ES	
3040 sh			3100 w		3080 m		3040 w		ν C-H
3080 ms			3120 w		3120 sh		3080 s		ν C-H
					570 m		545 ms		β C=N
					2230 ms		2230 s		ν C=N
Internal vibrations of NH ₂ group									
635 ms		620 m		γ N-H sym.			870 s		CH ₂ rock
1070 sh		1050 w		β N-H asym.			1060 s		CH ₂ rock
1620 m		1630 s		β N-H			1380 s		C-H sym. def. in CH ₂ group
3375 s		3360 ms		ν N-H sym.			1440 vs		C-H asym. def. in CH ₂ group
3440 s		3430 s		ν N-H asym.			1460 vs		C-H asym. def. in CH ₂ group
							2845 ms		C-H sym. stretch in CH ₂ group
							2920 s		C-H asym. stretch in CH ₂ group
							2960 ms		
Internal vibrations of CH ₃ group									

Letters in front of wavenumbers indicate the visual intensities of band observed.

mw = medium weak ; w = weak ; s = strong ; ms = medium strong ; vs = very strong ; m = medium ;

sh = shoulder ; X = NH₂ in compounds I and II, CH₂ in Compound III and F in compound IV.

γ = out-of-plane bend ; β = in-plane bend ; ν = stretch ; sym = symmetric ; asym = asymmetric ; def = deformation.

Table 2. Static dielectric constant (*D*), refractive index (*n*) and spectral data (ν_{\max} in cm^{-1}) for the solute molecules in different solvents used.

Solvents used	Refractive index (<i>n</i>)	Dielectric constant (<i>D</i>)	ν_{\max} (in cm^{-1})			
			Compound I	Compound II	Compound III	Compound IV
Cyclohexane	1.4260	2.0240	34190	36432	34906	35703
Hexane	1.3749	1.8836	34307	36486	—	—
<i>n</i> -Heptane	1.3870	1.9203	—	36480	35004	—
Chloroform	1.4460	4.8100	—	36221	34772	—
Decalin	1.4742	2.1530	—	—	34809	—
Methanol	1.3290	5.7210	—	—	35028	35262
Iso-propylalcohol	1.3770	20.3170	34050	—	34869	35450
<i>n</i> -Propylalcohol	1.3837	21.2400	340061	35909	34857	35387
Carbon tetrachloride	1.4595	2.2368	34096	36379	34809	35603
Methylacetate	1.3610	6.7210	—	—	35004	—
Ethanol	1.3600	3.4710	34260	—	34809	—
Dichloromethane	1.4240	9.0800	—	36169	—	35450
Dimethylformamide	1.4280	36.7100	—	—	—	35450
<i>n</i> -Pentane	1.3580	1.8371	34331	36512	—	—

and $12a_1 + 3a_2 + 11b_1 + 7b_2$ with all species active in i.r. spectra except a_2 . The infrared absorption spectra of the compounds studied were analysed keeping in view the symmetry of the molecules, the analysed i.r. spectra of similar molecules. The fundamental vibrational frequencies along with their assignments are given in Table 1.

The electronic absorption spectra of the compounds lie approximately in the region λ 3090 to λ 2550 Å and the bands are degraded to the red. The bands observed in this region corresponds to the forbidden electronic transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ of benzene. Under the reduced symmetry of C_s or C_{2v} of the compounds the above forbidden transitions become ${}^1A' \leftarrow {}^1A'$ in C_s and ${}^1B_2 \leftarrow {}^1A_1$ in C_{2v} and they are allowed.

The effect of temperature on the band system has facilitated the choice of the bands at 33258, 35624, 35334 and 35745 as the 0,0 band in compounds I, II, III and IV respectively. The identification of the fundamentals chosen in the compounds has been mainly done on the basis of the intensities of the bands and the available literature of other trisubstituted benzenes. The fundamentals so chosen are also listed in Table 1. The strong bands on the longer wavelength side with spacing 24 cm^{-1} in compound I, 26 cm^{-1} in compound II, 30 cm^{-1} in compound III and 45 cm^{-1} in compound IV have been identified as sequence intervals.

Table 3. Values of electric dipole moments.

Molecule	Ground state electric dipole moment μ_g in Debye units	Excited state electric dipole moment μ_e in Debye units	θ in degrees
Compound I	4.05	5.87	53°
Compound II	2.83	4.07	66°
Compound III	3.75	6.18	58°
Compound IV	2.54	5.35	78°

The electric dipole moment of compounds I, II, III and IV in the first excited electronic state has been calculated using a new method given by Ayachit et al (1986) from the solvent effect on their electronic spectra. The ν_{\max} values observed for ${}^1A' \leftarrow {}^1A'$, ${}^1B_2 \leftarrow {}^1A_1$ transition which are given in Table 2 are used to calculate μ_e and θ , the direction of μ_e . The values of refractive index (n) and dielectric constant (D) of solvents used are taken from literature (Weast 1973-74) and are also given in Table 2. The dipole moment in the ground state (μ_g) has been calculated using the method of vectorial addition of group moments (Smallwood and Herzfeld 1930) and are given in Table 3. The molecular radius has been calculated using the method of atomic increments (Edward 1956).

The relevant plots obtained for the observed system of the compounds are given in Figures 1a, b, c and d. The values of μ_e and θ determined are given in

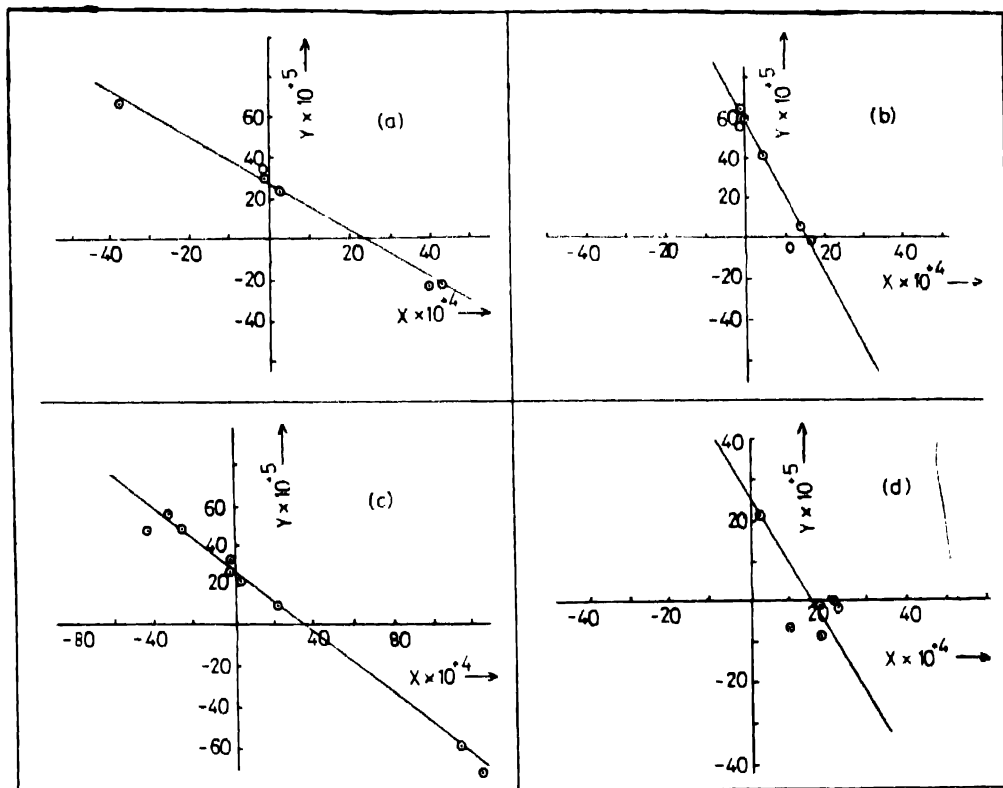


Figure 1. X vs Y plot for (a) compound I, (b) compound II, (c) compound III and (d) compound IV.

Table 3. It is expected that the values of μ_e should be greater for the upper state (Jaffe and Orchin 1962). In the present work this expected behaviour is observed.

Acknowledgment

The authors (KSR and MAS) gratefully acknowledge with thanks the financial support by CSIR, New Delhi in the form of a research scheme.

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