

## Correlative studies on the absorption and emission characteristics of isomeric chlorobenzonitriles

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**Abstract.** Absorption, fluorescence and phosphorescence characteristics of isomeric chlorobenzonitriles have been studied and similarities and differences in these have been noted and compared with those of analogous compounds reported in the literature. The variations in absorption spectral characteristics have been explained and the correlation between the dipole moments of the molecules and the energy of the para isomers has been elucidated. Analyses of the phosphorescence data have led to the conclusion that internal heavy atom spin-orbit coupling effect is important in the chlorobenzonitriles and that the radiative and nonradiative rates from their triplet states may be reasonably rationalized on this basis.

**Keywords.** Isomeric chlorobenzonitriles; dipolemoment; charge transfercharacter; internal heavy atom effect; radiative and nonradiative rates.

### 1. Introduction

Carsey *et al* (1979) investigated from both experimental and computational points of view the variation in the absorption and emission properties of para-disubstituted benzenes with the nature of the substituents, one being an electron donor and the other an electron acceptor. Similar, but less detailed, studies in the case of *ortho*- and *meta*-disubstituted benzenes were reported by Findley *et al* (1979). On the basis of these studies they proposed that the energy,  $E(^1L_a)$ , of the  $^1L_a$  state of these molecules may serve to parametrize the charge transfer (CT) character in their  $^1L_a$  state and that, in the case of the *para*-compounds, the  $E(^1L_a)$  energy is a useful and convenient gauge of their molecular polarity in their ground and excited singlet and triplet states.

According to Carsey *et al* (1979) the general trends of variation in the luminescence characteristics, as systematized by them, are in good agreement with the experimental results of Lui and McGlynn (1975a, b and c, 1978). Recently such studies in isomeric tolunitriles, which are weak polar compounds, have been reported by Maiti *et al* (1984) and the present investigation is an extension of this to isomeric chlorobenzonitriles. The purpose of this study is, firstly, to test the validity of the conclusions of Carsey *et al* (1979) for these weakly polar substituted benzonitriles as regards the correlation between the energy of the  $^1L_a$  state and the solvent shift of the  $^1L_a$  absorption band, and their dependence on the dipole moments in the ground and excited electronic states; secondly, to find out how the radiative and nonradiative properties of the phosphor-

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escence emitting triplet state of the chlorobenzonitriles are modified relative to those of the fluoro substituted analogues.

With these objects in mind, detailed investigations on the absorption, fluorescence and phosphorescence properties of the isomeric chlorobenzonitriles in the vapour phase, in polar and nonpolar solvents, and at different temperatures have been carried out. The results obtained and their discussion form the subject of the present paper.

## 2. Experimental

Pure samples of three isomeric chlorobenzonitriles, obtained from Fluka A.G. (Switzerland), were sublimed several times under reduced pressure till no impurity was detected with GLC (Hewlett-Packard Model 5730A) using flame ionisation detector in conjunction with the column ucw 982, twenty inches in length. Solvents ethanol and methylcyclohexane were of spectrograde quality from E. Merck (W. Germany) and they were distilled under reduced pressure before use each time. De-oxygenated solutions of the chlorobenzonitriles of  $\approx 10^{-4}$  M concentration were prepared by the usual freeze and thaw-cycles. Details of the experimental methods for recording absorption, fluorescence and phosphorescence spectra and the procedure for the determination of fluorescence and phosphorescence quantum yields are the same as described in our previous paper (Maiti *et al* 1984). The accuracy of measurement is also the same as given there.

## 3. Results

### 3.1 Absorption spectra

Like all other substituted benzonitriles belonging to the D-Ph-A system, where D and A are respectively electron donor and electron acceptor substituents and Ph is the

**Table 1.** Absorption spectral data of chlorobenzonitriles in the vapour phase and in solution at room temperature.

Molecule	Phase	$^1L_a$ band system		$^1L_b$ band system		$E(^1L_a) - E(^1L_b)$ ( $\text{cm}^{-1}$ )
		$\nu_{0,0}$ ( $\text{cm}^{-1}$ )	$f$	$\nu_{0,0}$ ( $\text{cm}^{-1}$ )	$f$	
<i>o</i> -Chlorobenzonitrile	Vapour	43 497		35 026		8471
	MCH	42 181	0.166	34 712	0.021	
	EtOH	42 813	0.216	34 772	0.024	
<i>m</i> -Chlorobenzonitrile	Vapour	44 209		35 149		9060
	MCH	42 813	0.134	34 772	0.030	
	EtOH	42 813	0.127	34 480	0.025	
		(42 920)		(34 780)		
<i>p</i> -Chlorobenzonitrile	Vapour	42 409		36 166		6243
	MCH	41 653	0.254	35 451	0.013	
	EtOH	41 653	0.290	35 514	0.015	
		(42 640)		(35 710)		

Values in parentheses are from Carsey *et al* (1979) (in ethanol). In this and subsequent tables MCH and EtOH denote methyl cyclohexane and ethanol media, respectively.  $\nu_{0,0}$  indicates band origin.

phenyl ring, the isomeric chlorobenzonitriles exhibit, in the vapour phase and in solutions, two systems of absorption bands in the near UV region designated, respectively,  ${}^1L_a \leftarrow {}^1A$  and  ${}^1L_b \leftarrow {}^1A$  under Platt notation. Symmetrywise, for the *ortho*- and *meta*-isomers ( $C_s$ -point group) both these transitions are  ${}^1A' \leftarrow {}^1A'$ , while for the *para* isomer ( $C_{2v}$  point group) the former transition is  ${}^1A_1 \leftarrow {}^1A_1$  and the latter  ${}^1B_2 \leftarrow {}^1A_1$ . In subsequent descriptions  ${}^1A$ ,  ${}^1L_b$  and  ${}^1L_a$  denote respectively ground and first and second excited states in the singlet manifold of these molecules. The relevant data on the absorption spectral characteristics of the three isomers are presented in table 1, while vibrational assignments of their spectra in ethanol glass at 77 K are given in table 2.

In all cases, the spectra due to the *ortho*- and *meta*-isomers are similar but different

**Table 2.** Vibrational analysis of the absorption and fluorescence spectra of chlorobenzonitriles in ethanol at 77 K.

Absorption			Fluorescence		
$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment
<i>o</i> -Chlorobenzonitrile					
(34 250)					
34 712 (s)	0	0,0	34 622 (w)	0	0,0
35 101	389	0+389	34 320 (w)	302	0-302
35 768 (s)	1056	0+1056	33 533 (w)	1089	0-1089
36 889 (ms)	2177	0+2 × 1056	32 432 (w)	2190	0-2 × 1089
37 689 (w)	2977	0+3 × 1056			
38 326 (w)	3614	0+389+3 × 1056			
38 975	4263	0+4 × 1056			
39 336	4624	0+389+4 × 1056			
Ground state vibration frequencies <sup>a</sup> ; 391, 1031, 1132 $\text{cm}^{-1}$					
<i>m</i> -Chlorobenzonitrile					
(34 480)					
34 783 (s)	0	0,0	34 745 (w)	0	0,0
35 111 (s)	328	0+328	34 431 (ms)	314	0-314
35 842	1059	0+1059	33 745 (ms)	1000	0-1000
36 900 (w)	2117	0+2 × 1059	33 385	1360	0-314-1000
37 951	3168	0+3 × 1059	32 670 (w)	2042	0-2 × 1000
Ground state vibration frequencies <sup>a</sup> ; 302, 995, 1076, 1192 $\text{cm}^{-1}$					
<i>p</i> -Chlorobenzonitrile					
(34 250)					
35 640 (s)	0	0,0	35 736 (ms)	0	0,0
36 386 (ms)	746	0+746	35 437	299	0-299
36 686 (ms)	1046	0+1046	34 622 (s)	1114	0-1114
37 164 (s)	1524	0+1524	33 488 (w)	2288	0-2 × 1114
37 477	1837	0+746+1046			
37 867	2227	0+746+1524			
38 230 (w)	2590	0+1046+1524			
34 748	3108	0+2 × 1524			
Ground state vibration frequencies <sup>a</sup> ; 302, 780, 1086, 1177, 1198, 1596 $\text{cm}^{-1}$					

s—strong, m—medium, w—weak; <sup>a</sup> Green and Harrison (1976); Values in parentheses are from Carsey *et al* (1979) (in EPA).

from that of the *para*-isomer, the  $f$ -values of the  ${}^1L_a$  and  ${}^1L_b$  bands of the *para* isomer are higher than the corresponding values of the parent benzonitrile molecule, the energy gap  $E({}^1L_a) - E({}^1L_b)$  changes in the order  $m > o > p$  and its value is the least in the *para*-compound.

The absorption spectra of the three isomers in ethanol glass at 77 K show sufficient vibrational structures (table 2). In each of the *ortho*- and *meta*-isomers short progression involving 3 or more quanta of the excited state frequency  $1050\text{ cm}^{-1}$  is observed. In contrast, such progression is absent in the spectrum of the *para*-isomer in which combination bands are more prominent.

### 3.2 Fluorescence spectra

Though the fluorescence intensities of all the three chlorobenzonitriles in ethanol (EtOH) and methylcyclohexane (MCH) glasses at 77 K are small, some vibronic structures are observed in the spectrum of each of the compounds. The analysis of the bands in the ethanol glass spectrum is presented in table 2. It is seen from the table that in each of these molecules the position of the fluorescence band origin is very nearly coincident with that in absorption in the same medium at 77 K. From the vibrational assignment in table 2, it is also found that besides one or two other vibrational modes, two quanta of vibration involving  $1089\text{ cm}^{-1}$  in the *ortho*,  $1000\text{ cm}^{-1}$  in the *meta*- and  $1114\text{ cm}^{-1}$  in the *para*-compound are present in the respective spectra.

### 3.3 Phosphorescence emissions

Unlike fluorescence emission, the phosphorescence intensities of the compounds in both EtOH and MCH glass are moderately strong and show greater vibrational features. These data together with the assignments are presented in table 3. It is found that in all cases many ground state fundamental frequencies occur, and of these the frequency  $\approx 1600\text{ cm}^{-1}$  corresponding to  $\nu(\text{C}=\text{C})$  vibration of the phenyl ring is very prominent and occurs upto two quanta of excitation. Besides, in the spectra of each of *meta*- and *para*-isomers a strong band with frequency shift  $\sim 2300\text{ cm}^{-1}$  attributable to the  $\nu(\text{C}\equiv\text{N})$  vibration in these molecules is observed, while bands at a separation of  $\sim 1150\text{ cm}^{-1}$ , attributable to  $\nu(\text{C}-\text{CN})$  vibration, are seen in the spectra of *ortho*- and *para*-chlorobenzonitriles.

### 3.4 Other luminescence characteristics

Some of the luminescence characteristics of the isomeric chlorobenzonitriles are collected in table 4 and for comparison the data for tolunitriles (Maiti *et al* 1984) and fluorobenzonitriles (Lui and McGlynn 1975a) are included. The following trends in the variations of these characteristics between the different triads and among the members of the same triad are discernable.

The singlet-triplet ( $S_1 - T_1$ ) separation increases in the order  $p > m > o$  and is the largest for the *para*-compound. This is similar to that observed in the tolunitriles (Maiti *et al* 1984) and in fluorobenzonitriles and cyanoanisoles (Lui and McGlynn 1975a, b). The fluorescence intensity in the isomeric chlorobenzonitriles is very small and in fact, in these compounds the fluorescence quantum yield  $\Phi_F$  is smaller than that in the tolunitriles (Maiti *et al* 1984) and fluorobenzonitriles (Lui and McGlynn 1975a) by at least two orders of magnitude, so that  $\Phi_F(\text{CH}_3) > \Phi_F(\text{F}) \gg \Phi_F(\text{Cl})$ .

Table 3. Vibrational analysis of phosphorescence spectra of chlorobenzonitriles.

MCH-glass at 77 K			EtOH glass at 77 K		
$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Assignment
<i>o</i> -Chlorobenzonitrile (25 970) [26 378]					
26 291 ( <i>ms</i> )	0	0,0	26 317 ( <i>s</i> )	0	0,0
26 059 ( <i>ms</i> )	232	0-232	26 084 ( <i>s</i> )	233	0-233
25 775 ( <i>ms</i> )	516	0-516	25 807	510	0-510
25 150 ( <i>w</i> )	1141	0-1141	25 121 ( <i>w</i> )	1196	0-1196
24 691 ( <i>s</i> )	1600	0-1600	24 730 ( <i>vs</i> )	1587	0-1587
24 155 ( <i>w</i> )	2136	0-516-1600	24 555 ( <i>ms</i> )	1762	0-233-1587
23 630 ( <i>uw</i> )	2661	0-2 × 516-1600	24 220 ( <i>m</i> )	2097	0-510-1587
Ground state vibration frequencies <sup>a</sup> : 207, 505, 1132, 1197, 1584 $\text{cm}^{-1}$					
<i>m</i> -Chlorobenzonitrile (26 320) [26 041]					
26 291 ( <i>ms</i> )	0	0,0	26 395 ( <i>ms</i> )	0	0,0
26 079	212	0-212	26 188 ( <i>ms</i> )	207	0-207
25 658 ( <i>s</i> )	633	0-633	25 763 ( <i>s</i> )	632	0-632
25 286 ( <i>w</i> )	1005	0-1005	25 418 ( <i>w</i> )	977	0-977
24 741 ( <i>ms</i> )	1550	0-1550	24 829 ( <i>s</i> )	1566	0-1566
23 981 ( <i>vs</i> )	2310	0-2310	24 600	1795	0-207-1566
23 767 ( <i>s</i> )	2524	0-212-2310	24 024 ( <i>vs</i> )	2371	0-2371
23 392 ( <i>ms</i> )	2899	0-633-2310	23 392 ( <i>ms</i> )	3003	0-2 × 1566
		0-2 × 1550			0-632-2371
22 637 ( <i>m</i> )	3654	0-633-2 × 1550			
Ground state vibrational frequencies <sup>a</sup> : 197, 677, 995, 1587, 2233 $\text{cm}^{-1}$					
<i>p</i> -Chlorobenzonitrile (25 840) [26 229]					
26 009 ( <i>ms</i> )	0	0,0	26 136 ( <i>w</i> )	0	0,0
25 783	226	0-226	25 832 ( <i>ms</i> )	304	0-304
25 634 ( <i>ms</i> )	375	0-375	25 324	812	0-812
25 197	812	0-812	25 009 ( <i>s</i> )	1127	0-1127
24 899 ( <i>s</i> )	1110	0-1110	24 600 ( <i>vs</i> )	1536	0-1536
24 442 ( <i>vs</i> )	1567	0-1567	24 199 ( <i>ms</i> )	1937	0-304-1536
24 089 ( <i>ms</i> )	1920	0-812-1110	23 789 ( <i>s</i> )	2347	0-2346
					0-812-1536
23 661 ( <i>s</i> )	2348	0-2348	23 474 ( <i>m</i> )	2662	0-1127-1536
23 330 ( <i>ms</i> )	2679	0-1110-1567	23 048	3088	0-2 × 1536
22 890 ( <i>m</i> )	3119	0-2 × 1567			
Ground state vibration frequencies <sup>a</sup> : 248, 302, 350, 780, 1090, 1171, 1596, 2236 $\text{cm}^{-1}$					

*s*—strong, *m*—medium, *w*—weak, *v*—very; <sup>a</sup>Green and Harrison (1976); Values in parentheses are from Carsey *et al* (1979) (in EPA) and in square brackets are from Asahi and Hirota (1982).

The phosphorescence quantum yield ( $\Phi_p$ ) also decreases in the same order but the variation between the different triads is not as large as for  $\Phi_f$ . In the fluorobenzonitriles (Maiti *et al* 1984) and tolunitriles (Lui and McGlynn 1975a) the values of  $\Phi_p$  and as well as of  $\Phi_p/\Phi_f$  are the largest for the *para*-isomer whereas in the chlorobenzonitriles this occurs in the case of the *meta*-compound. On the other hand, though phosphorescence lifetime  $\tau_p$  varies as  $\tau_p(\text{CH}_3) > \tau_p(\text{F}) > \tau_p(\text{Cl})$ , its value is the highest for the *meta*-isomer in all cases.

Table 4. Fluorescence and phosphorescence quantum yields, lifetimes, intersystem crossing, radiative and nonradiative phosphorescence rates and other parameters of substituted benzonitriles.

Molecule (at 77 K)	Solvent	$\Phi_F$	$\Phi_p$	$\phi_f/\phi_F$	$\tau_p$ sec	$S_1 - T_1$ cm <sup>-1</sup>	$K_{ISC} \times 10^{-6}$ (sec <sup>-1</sup> )	$K_p$ (sec <sup>-1</sup> )	$K_p^r$ (sec <sup>-1</sup> )	$\frac{K_p(Cl)}{K_p(F)}$
o-Chlorobenzonitrile	MCH	0.004	0.054	13.8		8037				
	EtOH	0.003	0.088	31.4		8331				
m-Chlorobenzonitrile	EPA <sup>a</sup>			10.6	0.38		68.3	0.232	2.40	3.01
	MCH	0.005	0.120	35.3		8421				
	EtOH	0.003	0.236	47.2		8421				
p-Chlorobenzonitrile	EPA <sup>a</sup>			18.7	0.47		24.2	0.505	1.66	7.29
	MCH	0.004	0.101	26.6		9600				
	EtOH	0.003	0.107	34.5		9642				
o-Tolunitrile	EPA <sup>a</sup>			16.8	0.15		42.2	0.725	5.96	4.80
	EtOH <sup>b</sup>	0.36	0.24	0.67	3.40	8506	0.40	0.18		
m-Tolunitrile	EtOH <sup>b</sup>	0.51	0.23	0.45	4.60	8795	0.14	0.10		
	EtOH <sup>b</sup>	0.36	0.33	0.92	3.80	9332	0.20	0.14		
o-Fluorobenzonitrile	EtOH <sup>c</sup>	0.51	0.093	0.18	2.43	8700	0.19	0.077	0.33	
	EtOH <sup>c</sup>	0.54	0.082	0.15	2.60	8900	0.19	0.068	0.31	
p-Fluorobenzonitrile	EtOH <sup>c</sup>	0.24	0.23	0.96	2.05	9300	0.24	0.15	0.33	

<sup>a</sup>Carsey *et al* (1979); <sup>b</sup>Maiti *et al* (1984); <sup>c</sup>Lui and McGlynn (1975a).

## 3.5 Dipole moment and solvent effect

The dipole moments of the isomeric chlorobenzonitriles in the  ${}^1L_a$  and  ${}^1L_b$  states have been calculated from the solvent shift data in MCH solution at room temperature in the same way as in tolunitriles (Maiti *et al* 1984). The ground state dipole moments are taken from published literature (Wesson 1948) and the volume of the molecule ( $a^3$ ) has been taken to be  $25A^3$  in all cases. The relevant data for the chlorobenzonitriles together with those for some other benzonitriles are given in tables 5 and 6. The solvatochromic shifts in the position of the  ${}^1L_a$ -band of these molecules in ethanol are shown in table 6 and the computed values of  $\mu^2({}^1L_a) - \mu^2({}^1A)$  are included therein.

Table 5. Solvent shifts and dipole moments of substituted benzonitriles.

Molecule	Solvatochromic shift* $\Delta\nu(\text{cm}^{-1})$ in ethanol at room temperature		Dipole moment (Debye)		
			Ground state ( ${}^1A$ )	First excited state ( ${}^1L_b$ )	Second excited state ( ${}^1L_a$ )
	${}^1L_a$ band	${}^1L_b$ band			
<i>o</i> -Chlorobenzonitrile	684	254	4.73	5.37	6.80
<i>m</i> -Chlorobenzonitrile	1396	409	3.38	4.34	6.25
<i>p</i> -Chlorobenzonitrile	756	652	2.50	4.79	3.43
<i>o</i> -Fluorobenzonitrile <sup>a</sup>	1170	310			
<i>m</i> -Fluorobenzonitrile <sup>a</sup>	1170	380			
<i>p</i> -Fluorobenzonitrile <sup>a</sup>	800	60	2.64		
<i>o</i> -Tolunitrile <sup>b</sup>		631	3.95	5.07	
<i>m</i> -Tolunitrile <sup>b</sup>	1708	543	4.25	5.21	6.31
<i>p</i> -Tolunitrile <sup>b</sup>	1181	310	4.40	5.23	5.43
Benzonitrile <sup>b</sup>	1463	410	4.10	4.81	5.83

\*  $\Delta\nu = \nu_{00}(\text{gas}) - \nu_{00}(\text{solution}) \text{ cm}^{-1}$ ; <sup>a</sup>Lui and McGlynn (1975a); <sup>b</sup>Maiti *et al* (1984).

Table 6. Comparative data on some parameters of  ${}^1L_a$  state of *para*-substituted benzonitriles.

Molecule parameters	Benzonitrile <sup>a</sup>	Paratolu- nitrile <sup>a</sup>	Parafuoro- benzonitrile <sup>b</sup>	Parachloro- benzonitrile
$\mu({}^1A)$ Debye	4.10	4.40	2.64	2.50
$\mu({}^1L_b)$ "	4.81	5.23		4.79
$\mu({}^1L_a)$ "	5.83	5.43		3.43
$E({}^1L_a) \text{ cm}^{-1}$	44740	43185	44100	42409
$E({}^1L_a) - E({}^1L_b) \text{ cm}^{-1}$	8240	7981	7500	6243
Solvatochromic shift in ethanol $\text{cm}^{-1}$	1463	1181	800	756
$\mu^2({}^1L_a) - \mu^2({}^1A)$	17.17	10.30		5.51

<sup>a</sup> Maiti *et al* (1984); <sup>b</sup> Lui and McGlynn (1975a).

## 4. Discussion

### 4.1 Energies and oscillator strengths

Similarities in the absorption characteristics of the *ortho*- and *meta*-isomers and their differences from those of the *para*-substituted benzonitriles have already been noted in §3. To provide a qualitative rationalization for these observations, the methods of linear combination of configuration wave functions (Suzuki 1967) for the description of the  $\pi$  electronic states of the D-Ph-A system are considered. These states are expressed in terms of linear combinations of the locally excited (LE) configurations, corresponding to  $\alpha$ ,  $p$ ,  $\beta$  and  $\beta'$  bands of the phenyl ring and the symmetric and antisymmetric  $\pi$  configurations arising from the entities  $D^+-Ph^-A$ ,  $D-Ph^+A^-$  and  $D^+-Ph-A^-$ . The degree of mixing of the configurations is governed by the energies of the configurations, corrected for the inductive effects of the substituents, and the Hamiltonian matrix elements between pairs of these configurations. It may be noted that in the  $C_{2v}$ -symmetry (benzonitrile and the *para* compounds) the lower energy state ( $^1B_2$ ) will be composed of linear combinations of the LE ( $\alpha$ ), LE( $\beta'$ ) and antisymmetric  $\pi$  configurations while the upper excited state ( $^1A_1$ ) will comprise LE( $p$ ), LE( $\beta$ ) and the symmetric  $\pi$  configurations. In the  $C_s$ -symmetry (*ortho* and *meta*) both the lower and upper excited states will be linear combinations of all the configurations. Though no definite statements may be made as to the energies of the excited states and the proportion of each configuration in them without actual calculations, it is apparent that because of the mixing of fewer number of configurations, the energy of the lower excited state ( $^1B_2$ ) of benzonitrile and its *para*-derivatives is expected to be higher than that of the *ortho*- and *meta*-isomers. Also the mixing of all the configurations in the excited states in the *ortho*- and *meta*-isomers provides qualitative explanation for the similarities in their absorption characteristics.

In all these cases the  $f$ -value of  $^1L_b \leftarrow ^1A$  transition mainly depends on the weight of LE( $\beta$ ) and LE( $\beta'$ ) configurations in the linear representation of the first excited state, because transition to these states in the phenyl ring has the highest  $f$ -value, while those to the LE( $\alpha$ ) and LE( $p$ ) states are nil. The contributions to  $f$ -value from the  $\pi$  configurations are negligible for the donors considered in the present investigation. Since in the *para*-compounds only the LE( $\beta'$ ) contributes, their  $f$ -values are smaller than that in the other two isomers. Findley *et al* (1979) presented explanations for the above mentioned observed features in a similar manner. However, according to them, the increase in the  $f$ -value of the two transitions in the *ortho*- and *meta*-compounds are due to such  $\pi$  configurations for which  $^1\pi$  dipole transition moments are considerable.

### 4.2 Polarities of the ground, $^1L_b$ and $^1L_a$ excited states of *para*-substituted benzonitriles and their correlation with the energy of $^1L_a$ state

According to Carsey *et al* (1979) the energy of the  $^1L_a \leftarrow ^1A$  band of *para*-D-Ph-A compounds is a useful gauge of the polarity of the molecules in the ground and excited singlet and triplet states. They also proposed a correlation between  $E(^1L_a)$  and the magnitude of solvatochromism of the  $^1L_a$  band in polar solvents and contended that this shift should be proportional to  $\mu(^1L_a) - \mu(^1A)$ . From the relevant data for the *para*-compounds including benzonitrile, collected in table 6, it is seen that there is no regular relationship between the  $^1L_a \rightarrow ^1A$  transition energy of the individual molecule and its dipole moment values in the  $^1L_a$  and  $^1L_b$ , and the ground states. This observation is not

in agreement with the conclusions of Carsey *et al* (1979) and might be due to the fact that these authors used computed dipole moment values instead of the values derived from experimental data. As regards their other observation that for a fixed acceptor (nitrile) group the values of  $E(^1L_a)$  and the energy gap  $E(^1L_a) - E(^1L_b)$  decrease with increasing donor capability, the data in table 6 show clearly that  $E(^1L_a) - E(^1L_b)$  rather than  $E(^1L_a)$  decreases smoothly as the donor capability of the substituent increases. From the same table it is seen that the solvatochromic shift follows the same trend as the band gap value, and there is a rough proportionality between the two. Furthermore, the shift decreases with decrease in the value of  $\mu^2(^1L_a) - \mu^2(^1A)$ . This is partly in agreement with the conclusion of Carsey *et al* (1979).

#### 4.3 Character of the excited states of chlorobenzonitrile molecules

It has already been noted in §3.2 that in each of these molecules the position of the fluorescence band origin is almost coincident with that in absorption implying a mirror image symmetry. Since fluorescence is the reverse process of absorption, the fluorescence emitting state is the same as the first excited  $\pi, \pi^*$  state in the singlet manifold, and hence is a  $^1L_b$  state. As regards the character of the phosphorescence emitting triplet state, it is noted that the phosphorescence lifetimes of the chlorobenzonitrile molecules are about 0.5 sec (Carsey *et al* 1979) and that the phosphorescence spectra comprise mainly of ring vibrational modes. From these facts it is reasonably concluded that the emitting triplet state in each of these molecules is of the  $\pi, \pi^*$  type. From theoretical considerations Carsey *et al* (1979) and Findley *et al* (1979) concluded that this state may be designated as  $^3L_a$ .

#### 4.4 Phosphorescence lifetime of chlorobenzonitriles and nonradiative rates

From table 4 it is seen that the measured phosphorescence lifetime ( $\tau_p$ ) of the chlorobenzonitriles (Carsey *et al* 1979) is about an order smaller than that of the tolunitriles (Maiti *et al* 1984) and fluorobenzonitriles (Lui and McGlynn 1975a). The smallness of the  $\tau_p$  values clearly points to the well known internal heavy atom spin-orbit coupling effect on the phosphorescence lifetime. A theoretical explanation of this effect has been given by McGlynn *et al* (1969), who from simplified considerations showed that in a system of analogous planar aromatic molecules with different halogen atoms as substituents, like the 1-halonaphthalenes, the ratio of the phosphorescence radiative lifetime ( $\tau_p^0$ ) for the chlorine substituted member to that of the member with a fluorine substituent is given by

$$\tau_p^0(\text{F})/\tau_p^0(\text{Cl}) = K_p(\text{Cl})/K_p(\text{F}) = (\xi_{\text{Cl}}/\xi_{\text{F}})^2 = 4.66,$$

where  $K_p = \tau_p^{0-1}$  is the phosphorescence radiative rate constant  $\xi$  is the atomic spin orbit coupling factor and the suffixes Cl and F refer to chlorine and fluorine atoms respectively. Asahi and Hirota (1982) discussed the applicability of the concepts derived in the case of the halonaphthalenes to the halobenzonitriles and pointed out that the decay rate constants would increase with  $\xi^2$  values in going from lighter to heavier halogen atom substitution.

In order to find out how far McGlynn's relation holds in the case of chloro- and fluoro-benzonitriles, it is necessary to obtain the radiative phosphorescent rate constants ( $K_p$ ) for the two triads from their observed  $\tau_p$  values. It is at first noted that fluorescence quantum yield ( $\Phi_f$ ) of the chlorobenzonitriles is very small and this may be

due to either a large nonradiative rate constant ( $K_S$ ) from the first singlet state to the ground state, or large intersystem crossing rate constant ( $K_{ISC}$ ). Determination of  $K_{ISC}$  values would have been most appropriate, but unfortunately this has not been possible. Instead the validity of the second alternative has been assumed, and the values of  $K_{ISC}$ ,  $K_p$  and  $K_p^m$  of chlorobenzonitriles have been computed under the assumption  $K_S = 0$  as in the case of the isomeric tolunitriles (Maiti *et al* 1984) and fluorobenzonitrile (Lui and McGlynn 1975a). The values are shown in table 4.

It is seen from these data that  $K_p(\text{Cl})/K_p(\text{F})$  has the values 3.01, 7.29 and 4.80 for the *ortho*, *meta* and *para*-isomeric pairs respectively of the chloro- and fluorobenzonitriles. The agreement appears to be very good for the *para*-isomers and tolerable for the other two pairs of molecules. Though much reliance need not be placed on the quantitative agreement, it is reasonable to assume a qualitative validity of internal heavy atom effect. This by implication indicates that the nonradiative rate constant  $K_S$  is really small and  $K_{ISC}$  is large.

A large  $K_{ISC}$  value for the chlorobenzonitriles would imply a large phosphorescence quantum yield ( $\Phi_p$ ) for them, but from table 4 it is seen that the magnitude of  $\Phi_p$  in these molecules is of the same order as that in the fluorobenzonitriles (Lui and McGlynn 1975a). This indicates that a large part of the excitation transferred to the emitting triplet state of these molecules is lost through nonradiative processes. In fact, the computed data in this table show that the phosphorescence radiative rate constant ( $K_p$ ) in the chlorobenzonitriles is about an order higher than that of fluorobenzonitriles, and so are the nonradiative rate constants ( $K_p^m$ ). Since the moment of the  $T_1 \rightarrow S_0$  radiative transition is due to mixing of the excited states of the molecule in the singlet manifold with the emitting triplet state through spin-orbit coupling, the higher value of  $K_p$  in the chloroderivative is certainly attributable to the larger spin-orbit coupling matrices in them as compared to that in the fluoroderivatives.

The reasons for the larger nonradiative loss from the triplet to the ground state in the chlorobenzonitriles are not apparent at once. In the course of investigation of the internal heavy atom effect on the  $T_1$  states Najbar *et al* (1983) found that the nonradiative losses due to chlorine atom substitution in the aromatic molecules of monochloroquinolines and naphthalenes are affected. Such changes depend on many factors, of which the most evident are the changes of the spin-orbit coupling. Though no quantitative calculations have been performed in the present case, the observations may be rationalized, at least qualitatively, mainly on the basis of difference in the spin-orbit coupling factor in the chloro- and fluorobenzonitrile molecules.

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