

Absorption and emission spectra of isomeric tolunitriles

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Abstract. Absorption and emission characteristics of *o*-, *m*- and *p*-tolunitriles in polar and non-polar solvents under different conditions have been investigated in detail. Solvatochromic shifts of band origin of these molecules in non-polar solvents show that their dipole moments in the first excited singlet state are almost the same while its value in the second excited singlet is larger in the meta- than in the para-isomer. Vibronic analyses of the low temperatures absorption, fluorescence and phosphorescence spectra of all the three molecules have provided evidence that these molecules are slightly distorted in the first excited singlet state while such distortion in the phosphorescence emitting triplet state is larger. The data on fluorescence and phosphorescence quantum yield and phosphorescence lifetime of the tolunitriles are reasonably interpreted as showing that in these molecules, particularly *m*- and *p*- tolunitriles, the internal conversion rate from the first excited singlet to the ground state is probably small and that the charge transfer character of the triplet state in the *p*-isomer is larger than that in the meta.

Keywords. Isomeric tolunitriles; dipole moment; molecular geometry; CT-character; radiative and non-radiative rates.

1. Introduction

Benzonitrile which belongs to C_{2v} -point group exhibits two systems of absorption bands of π, π^* character in the near UV region designated as ${}^1A_1 \rightarrow {}^1A_1$ and ${}^1B_2 \rightarrow {}^1A_1$ and correspond to ${}^1L_a \rightarrow {}^1A$ and ${}^1L_b \rightarrow {}^1A$ transitions respectively under Platt notation. Vapour phase absorption measurements (Hirt and Howe 1948) have led to the conclusion that the first excited singlet π, π^* state of the molecule possesses both intramolecular charge-transfer ($\sigma\tau$) and local excitation character. According to Brand and Knight (1970) the phenyl nucleus acts as an electron donor in the $\sigma\tau$ -process. Furthermore, LeBel and Laposa (1972) have shown that the phosphorescence emitting state of benzonitrile is a 3A_1 (π, π^*) level and the molecule in the first excited singlet state is a nearly regular but slightly expanded hexagon, while in the first excited triplet the molecule is planar but a non-regular hexagon. In connection with the EPR study of the triplet states of fluorobenzonitriles Wagner and May (1976) observed that the first excited triplet state of benzonitrile is a 1,4-diradical, often referred to as the 'quinodal' form of the triplet.

Among the substituted benzonitriles, the phosphorescence of three isomeric tolunitriles were studied by Takei and Kanda (1962) who concluded that the emission characteristics of the three molecules should be attributed to the electronic transition

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based on resonance between the nitrile group and the phenyl ring. Later, Lui and McGlynn (1975a, b) investigated the absorption and emission characteristics of three isomeric cyanoanisoles and fluorbenzonitriles and observed certain similarities in the variations of spectral characteristics among the corresponding members of the two triads. For example, in each triad, the *p*- isomer has the smallest ${}^1L_a \rightarrow {}^1L_b$ energy gap, highest ${}^1L_b \leftarrow {}^1A$ transition energy with the smallest *f*-value and the lowest ${}^1L_a \leftarrow {}^1A$ transition frequency having the largest *f*-value. These authors, on the basis of their experimental results, concluded that in all the substituted benzonitriles, the phosphorescence emitting triplet states have varying amount of π -character. However, they made no attempt to find out if the geometrics of these molecules are affected in the excited singlet and triplet states.

It is known that the methyl group is a weaker electron donor than either the fluorine atom or the methoxy group and therefore, it would be interesting to investigate if the spectral characteristics of the three isomeric tolunitriles show similar variations as found in the two above mentioned triads. It would also be in order to find out, at least qualitatively, if the excited states of these molecules possess any π -character, whether the geometrics of these molecules in the excited states are altered and how these excited state properties are related to the phosphorescence characteristics of the molecules. With these objectives, the absorption, fluorescence and phosphorescence of the three isomeric tolunitriles in polar and non-polar solvents have been investigated. The results obtained and discussion of these results form the subject matter of the present communication.

2. Experimental

Highly pure samples of *m*- and *p*-tolunitriles were obtained from Koch-Light laboratories (England) and *o*-tolunitrile was procured from Fluka (Switzerland). The samples were distilled several times till no impurity could be detected by the GLC-method. The solvents ethanol, *n*-hexane and methylcyclohexane (MCH) were of spectrograde quality from E. Merck (W. Germany) and they were carefully distilled under reduced pressure before being used in the investigation. De-oxygenated solutions of the tolunitriles of *ca.* 10^{-4} M concentration were prepared by the usual freeze and thaw technique and their fluorescence and phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter equipped with a compensated spectral unit. The phosphorescence life-time (τ_p) was measured following the decay of phosphorescence signal on the chart recorder having a response of 0.3 sec. The fluorescence and phosphorescence quantum yields (Φ_F and Φ_p respectively) in ethanol glass (EtOH) were determined by the standard method using benzonitrile as reference. In the case of MCH glass the ratio of the yields (Φ_p/Φ_F) was computed from the ratio of the areas under phosphorescence and fluorescence spectra respectively. The errors in lifetime measurements are $\pm 5\%$ while those in Φ_p and Φ_F are $\pm 10\%$.

Absorption spectra of the tolunitriles under different conditions were recorded on a Shimadzu UV-Vis spectrophotometer model 210-A. The accuracy in the measured positions of the bands in the absorption and emission spectra is $\pm 15 \text{ cm}^{-1}$ for moderately sharp bands while for broad bands the errors are $\pm 30 \text{ cm}^{-1}$.

3. Results

3.1 Absorption spectra

Like benzonitrile, all the tolunitriles show two systems of absorption bands in the near UV region. The first system of bands at the lower energy has a low f -value and corresponds to ${}^1L_b \leftarrow {}^1A$ transition while the second system with higher energy and moderately large f -value is attributed to ${}^1L_a \leftarrow {}^1A$ transition. If the CH_3 -group is treated as a single mass point, then in the reduced symmetry C_s of *o*- and *m*-tolunitriles both these transitions are ${}^1A' \leftarrow {}^1A'$ while in *p*-tolunitrile (C_{2v} -point group) the designations of the transitions are the same as in benzonitrile. For each isomer the vapour phase absorption spectra undergo bathochromic shifts in solutions and these shifts for the 1L_a -band are larger than those for the 1L_b -band. The absorption spectra of the compounds recorded in rigid EtOH and MCH glasses at 77 K show slight shifts with respect to those recorded at room temperature but the vibrational structures in the former are more pronounced. The relevant data on the absorption of the tolunitriles are presented in table 1 while their vibrational assignments are shown in tables 3a, b and c. For comparison the vibrational frequencies as determined by Padhye and Varadarajan (1962) from vapour phase absorption measurements on the tolunitriles are included in the relevant tables.

Analysis presented in these tables shows that in the absorption spectra of each of the isomeric tolunitrile molecules in EtOH and MCH glasses, at 77 K there are, besides a few fundamental excited state frequencies, progressions involving the frequencies 730 and 757 cm^{-1} in *o*-tolunitrile, 958 and 996 cm^{-1} in *m*-tolunitrile and 778 and 789 cm^{-1} in *p*-tolunitrile. These frequencies most probably correspond to the ground state ring vibration frequencies 715, 995 and 815 cm^{-1} in *o*-, *m*- and *p*-tolunitriles respectively.

Table 1. Absorption spectral data of benzonitrile and isomeric tolunitriles at room temperature.

Molecule	Phase	1L_a band system		1L_b band system		$\nu({}^1L_a) - \nu({}^1L_b)$ (cm^{-1})
		$\nu_{00}(\text{cm}^{-1})$	f	$\nu_{00}(\text{cm}^{-1})$	f	
Benzonitrile	vapour	44740	—	36500	—	8240
	<i>n</i> -hex	43465	0.22	36221	0.012	
	MCH	43277	0.22	36090	0.012	
	EtOH	43277	0.22	36090	0.012	
<i>o</i> -tolunitrile*	vapour	43855	—	35770	—	8085
	<i>n</i> -hex	44234	0.22	35388	0.019	
	MCH	43655	0.24	35263	0.018	
	EtOH	42540	0.25	35139	0.030	
<i>m</i> -tolunitrile	vapour	44430	—	35806	—	8624
	<i>n</i> -hex	43183	0.24	35451	0.021	
	MCH	43090	0.22	35356	0.018	
	EtOH	42722	0.27	35263	0.025	
<i>p</i> -tolunitrile	vapour	43185	—	36204	—	7981
	<i>n</i> -hex	42181	0.30	35961	0.010	
	MCH	42181	0.30	35864	0.008	
	EtOH	42004	0.31	35894	0.013	

* 1L_a band position of *o*-tolunitrile in solution refers to the maximum of band intensity.

Table 2. Solvent-shift* data for band-origins, rotor-volume (a^3) and dipole moments (μ) of benzonitrile and isomeric tolunitriles.

Molecule	Solvent	1L_a -band system	1L_b -band system	a^3 in (AU ³)	Dipole moment D		
		$\Delta\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$		Ground state	1L_b	1L_a
Benzonitrile	<i>n</i> -hex	1275	279	20	4.10	4.81	5.83
	MCH	1463	410				
	EtOH	1463	410				
$\mu_e^2 - \mu_g^2$ average		1.40a ³ – 10.80	0.35a ³ – 0.71				
<i>o</i> -tolunitrile	<i>n</i> -hex		382	25	3.95	5.07	
	MCH		507				
	EtOH		631				
$\mu_e^2 - \mu_g^2$ average			0.45a ³ – 1.12				
<i>m</i> -tolunitrile	<i>n</i> -hex	1247	355	25	4.25	5.21	6.31
	MCH	1343	450				
	EtOH	1708	543				
$\mu_e^2 - \mu_g^2$ average		1.32a ³ – 11.35	0.41a ³ – 1.18				
<i>p</i> -tolunitrile	<i>n</i> -hex	1004	243	25	4.40	5.23	5.43
	MCH	1004	340				
	EtOH	1181	310				
$\mu_e^2 - \mu_g^2$ average		1.03a ³ – 15.65	0.30a ³ – 0.53				

*Solvent shift $\Delta\nu = \nu_{00}(\text{gas}) - \nu_{00}(\text{solution}) \text{ cm}^{-1}$.

The frequencies 1214 and 1222 cm^{-1} in *o*-tolunitrile, 1263 and 1289 cm^{-1} in the *m*- and 1176 and 1198 cm^{-1} in the *p*-isomer are believed to represent the valance $\nu(\text{C}-\text{CN})$ vibration frequencies in the excited state of these molecules. It should be noted that Padhye and Varadarajan (1962) observed this frequency at 1199, 1251 and 1175 cm^{-1} in the vapour phase absorption spectra of the *o*-, *m*- and *p*-tolunitriles respectively. In the above the two entries for each compound refer to data from the spectra in the two solvents.

3.2 Fluorescence emission spectra

The tolunitrile molecules exhibit well-defined band origin and structured fluorescence in the rigid MCH and EtOH glasses at 77 K. Since all of them are very similar, the spectra of only one, *viz o*-tolunitrile are reproduced in figure 1. For comparison the corresponding $^1L_b \leftarrow ^1A$ absorption spectra recorded at the same temperature are also shown in the same figure and the fair mirror image symmetry between them is evident. Accordingly, the fluorescence is attributed to the reverse $^1L_b \rightarrow ^1A$ transition. From the vibrational analyses of these spectra (only one is presented in table 4) it is found that, as in absorption a few ground state frequencies in addition to a short progression involving ring vibration is observed in each of the tolunitriles. These frequencies are 760 and 775 cm^{-1} in the ortho-, 997 and 1002 cm^{-1} in the meta and 850 cm^{-1} in the para-compounds. The ground state $\nu(\text{C}-\text{CN})$ frequencies are found at 1175 and 1209 cm^{-1} ,

Table 3. Vibrational analysis of the absorption spectra at 77K.

$\nu(\text{cm}^{-1})$	MCH-glass		$\nu(\text{cm}^{-1})$	EtOH-glass	
	$\Delta\nu(\text{cm}^{-1})$	assignment		$\Delta\nu(\text{cm}^{-1})$	assignment
(a) Orthotolunitrile					
35263	0	0,0	35139	0	0,0
35767	504	0 + 504	35576	437	0 + 437
35993	730	0 + 730	35896	757	0 + 757
36485	1222	0 + 1222	36353	1214	0 + 1214
36760	1497	0 + 2 × 730	36700	1561	0 + 2 × 757
37298	2035	0 + 730 + 1222	37133	1994	0 + 757 + 1214
37442	2179	0 + 3 × 730	37539	2400	0 + 3 × 757
38083	2820	0 + 4 × 730	38156	3017	0 + 4 × 757
38376	3113	5 × 730	38748	3609	0 + 5 × 757
(b) Metatolunitrile					
35356	0	0,0	35263	0	0,0
35800	444	0 + 444	35640	377	0 + 377
36090	734	0 + 734	36221	958	0 + 958
36352	996	0 + 996	36552	1289	0 + 1289
36619	1263	0 + 1263	37232	1969	0 + 2 × 958
36991	1635	0 + 734 + 996	38193	2930	0 + 3 × 958
37302	1946	0 + 2 × 996			
37582	2226	0 + 996 + 1263			
38266	2910	0 + 3 × 996			
(c) Paratolunitrile					
35864	0	0,0	35894	0	0,0
36485	621	0 + 621	36419	523	0 + 523
36653	789	0 + 789	36684	778	0 + 778
37040	1176	0 + 1176	37094	1198	0 + 1198
37407	1543	0 + 2 × 789	37442	1548	0 + 2 × 778
37796	1932	0 + 789 + 1176	37864	1970	0 + 778 + 1198
38229	2365	0 + 3 × 789	38229	2335	0 + 3 × 778
38598	2734	0 + 2 × 789 + 1176	38598	2704	0 + 2 × 778 + 1198
38957	3111	0 + 4 × 789	38974	3080	0 + 4 × 778
39749	3885	0 + 5 × 789	39749	3855	0 + 5 × 778

Vapour phase absorption ν_{00} for a. 35770 cm^{-1} b. 35806 cm^{-1} and c. 36204 cm^{-1} . The excited state frequencies for a. 669, 961 and 1199 cm^{-1} . b. 672, 970 and 1251 cm^{-1} c. 507, 761 and 1175 cm^{-1} (Padhye and Varadarajan).

1171 and 1178 cm^{-1} and 1216 cm^{-1} in the *o*-, *m*- and *p*-tolunitrile respectively. These frequencies in the Raman spectra as reported by Takei and Kanda (1962) are respectively at 1209, 1245 and 1194 cm^{-1} for *o*-, *m*- and *p*-tolunitriles. The two entries have the same connotation as given in the preceding paragraph.

3.3 Phosphorescence emission

Like fluorescence the phosphorescence spectra of the tolunitriles in MCH and EtOH glasses show vibrational structures. These spectra, one of which is shown in figure 2, are similar to those observed by Takei and Kanda (1962) and the vibrational analyses of these bands are almost identical with those of the two authors. It is found that in all cases the spectra are dominated by a long progression and combination involving the frequencies corresponding to $\nu(\text{C}=\text{C})$ vibration, characteristic of the benzene ring.

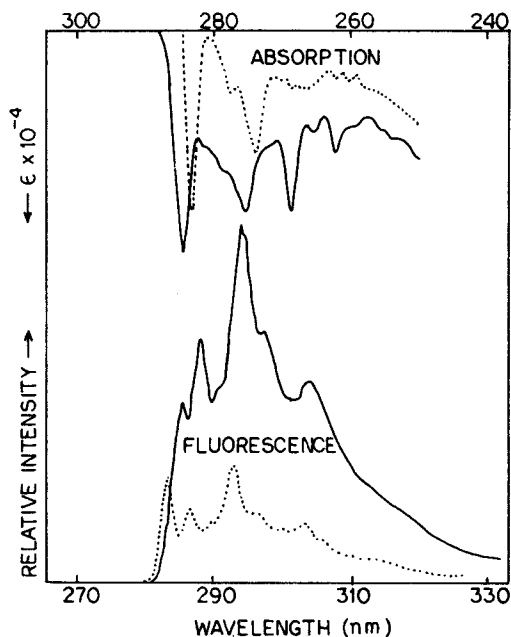


Figure 1. Fluorescence and absorption spectra for *o*-tolunitrile in EtOH (—), and MCH (.....) at 77 K.

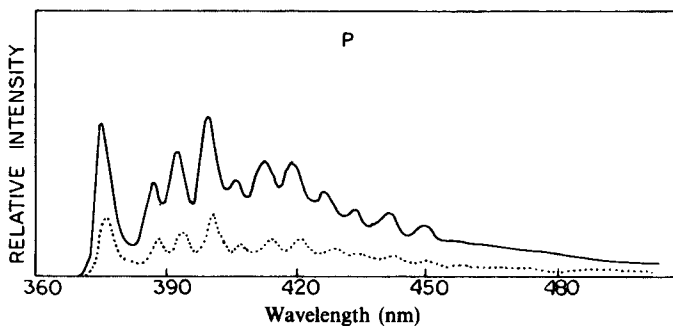


Figure 2. Phosphorescence emission spectra (*P*) of *p*-tolunitrile in EtOH (—) and MCH (.....) at 77 K.

Table 4. Vibrational analysis of fluorescence spectra at 77 K.

$\nu(\text{cm}^{-1})$	EtOH-glass		MCH-glass		
	$\Delta\nu(\text{cm}^{-1})$	assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment
Orthotolunitrile					
35170	0	0,0	35263	0	0,0
34757	413	0-413	34848	415	0-415
34410	760	0-760	34488	775	0-775
33961	1209	0-1209	34090	1173	0-1173
33618	1552	0-2 × 760	33703	1560	0-2 × 775
32872	2298	0-3 × 760	33323	1940	0-775-1173
			32993	2270	0-3 × 775

Table 5. Fluorescence and phosphorescence quantum yields, lifetime, intersystem crossing and radiative rates and singlet-triplet separation of substituted benzonitriles.

Molecule (medium 77 K)	$K_s \equiv O$								
	ϕ_F	ϕ_p	ϕ_p/ϕ_F	τ_p (sec)	$K_{ISC} \times 10^{-7}$ (sec ⁻¹)	K_p (sec ⁻¹)	$K_{ISC} \times 10^{-7}$ (sec ⁻¹)	K_p (sec ⁻¹)	$S_1 - T_1$ (cm ⁻¹)
<i>o</i> -Tolunitrile									
EtOH	0.36	0.24	0.67	3.40	4.0	0.18	0.24	0.29	8505
MCH			0.51	3.90					8736
<i>m</i> -tolunitrile									
EtOH	0.51	0.23	0.45	4.60	1.4	0.10	0.086	0.22	8795
MCH			0.80	4.40					8961
<i>p</i> -tolunitrile									
EtOH	0.36	0.33	0.92	3.80	2.0	0.14	0.099	0.26	9332
MCH			1.10	3.40					9344
<i>d</i> -fluorobenzonitrile									
EtOH	0.51	0.093	0.18	2.43	1.9	0.077	0.36	0.41	8700
<i>m</i> -fluorobenzonitrile									
EtOH	0.54	0.082	0.15	2.60	1.9	0.068	0.35	0.38	8900
<i>p</i> -fluorobenzonitrile									
EtOH	0.24	0.23	0.96	2.05	2.4	0.15	0.71	0.49	9300
<i>o</i> -cyanoanisole									
EtOH	0.26	0.11	0.42	1.40	14.0	0.11	2.20	0.71	7310
<i>m</i> -cyanoanisole									
EtOH	0.21	0.094	0.45	1.80	15.0	0.066	1.90	0.86	8070
<i>p</i> -cyanoanisole									
EtOH	0.22	0.24	1.00	1.60	10.0	0.18	3.10	0.63	9040

The vibrational assignment of the phosphorescence bands and the second-order magnitude of the phosphorescence lifetime indicate the π, π^* nature of the phosphorescence emitting state in these molecules. Following LeBel and Laposa's (1972) assignment of the phosphorescence emitting state in benzonitrile, which is $^3A_1 (\pi, \pi^*)$, the corresponding state in each of *o*- and *m*-tolunitriles may be designated $^3A' (\pi, \pi^*)$. The data on fluorescence and phosphorescence characteristics are collected in table 5 and for comparison those for cyanoanisoles and fluorobenzonitriles (Lui and McGlynn 1975a, b), are included in this table.

4. Discussion

From the data on the absorption spectra of the three tolunitriles (table 1), it is seen that the *p*-isomer shows spectral features which are different from those of the other two. For example, the 1L_b -band in *p*-tolunitrile has the highest frequency and the lowest *f*-value while the energy of the 1L_a -band is the lowest but its *f*-value is the largest. Moreover, the 1L_a - 1L_b energy gap is smallest for this molecule. These features are similar to those observed in the isomeric cyanoanisoles and fluorobenzonitriles by Lui and McGlynn (1975a, b). Following Suzuki (1967) the higher energy of the $^1L_b \leftarrow ^1A$ transition in *p*-tolunitrile as compared to that of the *o*-isomer may be understood in terms of the difference in the energy of the CT-configuration arising from difference in the electrostatic interaction between the methyl and nitrile O groups in the two molecules.

Since the two groups in the *o*-isomer is closer than in the *p*-isomer, the energy of the CT state in the *o*-compound will be lower than in the para. Consequently, the interaction of the CT-state with the locally excited states of benzene will lower the energy of the first transition of the *o*-molecule more than that of the *p*-isomer.

4.1 Estimate of CT-character in the excited singlet states

To estimate the relative CT-character in the first and second excited π, π^* singlet states, denoted respectively by S_1 and S_2 , of the isomeric tolunitriles, the data on the solvatochromic shifts of band origin, summarized from table 1, are presented in table 2 and analysed. The solvent-shift data in the non-polar *n*-hexane and MCH solvents only are considered and those in EtOH solvent are excluded because of the known complications arising with the hydrogen bonding ethanol. The shift of the positions of the origin of 1L_a - and 1L_b -band systems in going from vapour phase to the non-polar solvents may be represented by the equation,

$$\Delta\nu = \nu_{00}^{\text{gas}} - \nu_{00}^{\text{Solution}} = \left[10.71 \times \frac{10^9 f}{\nu a^3} + \frac{5031}{a^3} (\mu_e^2 - \mu_g^2) \right] \frac{n^2 - 1}{2n^2 + 1}$$

where the first term on the right side expression is the dispersion term of Bayliss (1950) and the second term represents the difference in the electrostatic energies of the excited and ground state dipolemoments embedded in a continuum of dielectric constant n^2 (Mataga and Kubota 1970). In this equation, ν and $\Delta\nu$ are in cm^{-1} , a is the cavity radius in AU, μ_e and μ_g are the dipolemoments (in Debye unit) of the excited and ground states respectively, n is the refractive index of the solvent and f -represents the oscillator strength of the transition considered. From the data on the 1L_b -band of benzonitrile presented in table 2, the $\mu_e^2 - \mu_g^2$ values calculated from the above relation are $0.30 a^3 - 0.71$ in *n*-hexane and $0.40 a^3 - 0.71$ in MCH with a mean value given by $\mu_e^2 - \mu_g^2 = 0.35 a^3 - 0.71$. Similarly for the 1L_a -band, $\mu_e^2 - \mu_g^2 = 1.36 a^3 - 10.78$ in *n*-hexane and $1.43 a^3 - 10.83$ in MCH with the average $1.40 a^3 - 10.81$. In both the cases the $\mu_e^2 - \mu_g^2$ value computed for *n*-hexane and MCH solvents are about 15% of which, taking into account the uncertainties in the solvent-shift values, may be considered fairly satisfactory. The value of the dipole moment of benzonitrile in the ground state (S_0) is 4.1D (Brown 1959) and if a value of $20 A^3$ is assumed for a^3 , which may not be unreasonable, the dipole moments μ_e in the $^1L_b(S_1)$ and $^1L_a(S_2)$ states work out as 4.81 and 5.83D respectively. The former may be compared with 4.45D in the first excited singlet (S_1) state estimated by Hirst and Howe (1948). These dipole moment values show that the CT-character in the S_1 state is small and is moderate in the S_2 -state. It is noted that though the actual μ_e value is dependent on the assumed a^3 value nonetheless, for reasonable a^3 values μ_e in the S_2 -state is always greater than that in the S_1 -state.

The expressions for $\mu_e^2 - \mu_g^2$ relating to the $^1L_a(S_2)$ and $^1L_b(S_1)$ states of the three isomeric tolunitriles derived in the same way as in benzonitrile are shown in table 2 which also contain the μ_e -values for the two states. For *p*-tolunitrile the reported value of $\mu_g = 4.4$ D (Brown 1959) is used and for the other two molecules, for which experimental data are not available in the published literature, the respective μ_g -value has been derived by the vector-composition method. The computed values are 3.95 and 4.25 D for the *o*- and *m*-tolunitrile respectively. The μ_e -values in table 2 have been calculated with $a^3 = 25 A^3$ which is a little larger than that used with benzonitrile. These values indicate that while the CT-character of the S_1 state of the tolunitriles may

be slightly greater than that of benzonitrile in the same state, this is not probably true for all the molecules in the S_2 -state. In the S_2 -state the *m*-tolunitrile molecule has more π -character than the *p*-isomer which in turn seems to possess nearly the same π -character as benzonitrile. The μ_e -value of *o*-tolunitrile in the S_2 -state could not be calculated because it has not been possible to determine the position of band origin owing to the broadness of its 1L_a -band even in the non-polar solvents.

4.2 Excited state molecular geometries

From the vibronic analysis of the absorption data in EtOH and MCH glasses for the three isomeric tolunitriles presented in table 3a, b and c it is seen that in all cases moderately long progressions of ring vibration frequencies are present. In *p*-tolunitrile vibronic band with five quantum of excitation of ring frequency is observed while in the *o*- and *m*-compounds respectively four and three quantum of excitations of this vibrational mode are evident. Moreover, the $\nu(\text{C-CN})$ vibrational frequency and its combination with the ring vibration frequency are also found. Similarly in the fluorescence spectra of these compounds (table 4) the ring vibration frequency seems to form the more prominent progression. These two observations are complimentary and they point to the fact that in the fluorescent S_1 -singlet state each of the tolunitrile molecules suffers small ring distortions in comparison with its geometry in the ground state (S_0). These observations and the conclusion derived therefrom is broadly the same as those made by LeBel and Laposa (1972) from the analyses of the fluorescence spectra of benzonitrile and its various deuterated derivatives. The coupling of $\nu(\text{C-CN})$ frequency probably indicates that the C-CN bond is also slightly affected in the S_1 -excited state.

The characteristics of the phosphorescence emissions of the isomeric tolunitriles in EtOH and MCH glasses have been presented in a previous section. From the vibronic data derived from these spectra, it is found that the phosphorescence spectrum of each of these molecules shows progression of a vibrational frequency (*ca.* 1600 cm^{-1}) corresponding to the $\nu(\text{C=C})$ of benzene and combinations of this frequency with ring vibration and valence $\nu(\text{C-CN})$ frequencies. These results are again similar to that reported by LeBel and Laposa (1972) from the analyses of the phosphorescence spectra of benzonitrile and the different deuterio substituted benzonitriles. Hence, their conclusion that the benzonitriles in the phosphorescence triplet state (T_1) are non-regular planar hexagons is also applicable to the tolunitriles. However, no definite suggestion about the shape of the molecules in the triplet state (T_1) could be made.

4.3 Interpretation of the variation of phosphorescence quantum yields

From the results of the present investigation it is found that the isomeric tolunitriles exhibit variations in their luminescence properties similar to those observed in isomeric cyanoanisoles and fluorobenzonitriles reported earlier (Lui and McGlynn 1975a, b). A careful examination of the data on the luminescence properties of the three substituted benzonitriles presented in table 5 reveals the following trends.

(i) The Φ_p/Φ_f -value is the highest in the para compound which also has the largest Φ_p -value. (ii) The phosphorescence lifetime (τ_p) is largest for the *m*-isomer for which Φ_p is the least. (iii) In each triad the singlet-triplet ($S_1 - T_1$) energy separation increases in the order $p > m > o$ and is maximum for the *p*-isomer having the smallest $S_2 - S_1$

separation. (iv) The Φ_p - and τ_p -values for any member of the tolunitriles are larger than those of the corresponding member of the other two triads.

An attempt to rationalize the observed variations in the Φ_p -values of the isomers of the tolunitrile molecules has been made following the observations of Lui and McGlynn (1975a) in cyanoanisoles. For this purpose the values of intersystem crossing rate (K_{ISC}) and phosphorescence radiative rate (K_p) have been derived for the two extreme cases, in the first of which internal conversion rate (K_S) for the process $S_1 \rightarrow S_0$ is assumed to be zero and the second for which nonradiative rate (K_T) from the phosphorescent T_1 -state, i.e. $T_1 \rightarrow S_0$ is neglected as has been done by Lui and McGlynn (1975a, b). These are shown in table 5. From the K_{ISC} , K_p and Φ_p values shown in table 5 it is found that the variation of Φ_p among the isomers of any of these triads roughly follows the variations of their K_{ISC} and K_p -values calculated on either of these two assumptions.

Actually neither K_S nor K_T is entirely negligible and the choice of one of the extremes requires justification. It is seen from table 5 that for any of the tolunitriles its phosphorescence lifetime in EtOH or MCH medium is not much different from one another, which suggests that the surrounding environment does not have much influence on the nonradiative rate constant K_T and that it is essentially a molecular property. It has been found from the previous discussions that the tolunitrile molecules are slightly distorted in the first excited state (S_1) while such distortions are greater in the triplet state (T_1). Moreover, the $S_1 - S_0$ energy difference is much larger than the $T_1 - S_0$ separation. Consequently, the internal conversion rate K_S is expected to be small and the nonradiative rate K_T to be non-negligible. These arguments seem to favour the first choice for which K_S is assumed to be zero. However, this choice is not entirely satisfactory. For example, in *o*-tolunitrile though K_{ISC} and K_p are both larger than those of *p*-tolunitrile, the Φ_p of the former is less than that of the latter. This discrepancy is also seen in the cyanoanisoles but not in the fluorobenzonitriles. Most probably the steric hindrance between the substituent and the nitrile group in both *o*-tolunitrile and *o*-cyanoanisole produces the observed discrepancy.

It is also seen from table 5 that for the limit $K_S = 0$, the phosphorescence radiative rate K_p for the *m*-isomer is smaller than that for the *p*-compound in any of the triads. This is consistent with the lower Φ_p -value for the former than that of the latter. It has been shown that in the tolunitriles the CT-character of the S_1 -state in the *m*- and *p*-compounds is probably the same while that in the S_2 -state it is greater in *m*- than in *p*-tolunitrile. It is known that the radiative rate (K_p) from the lowest triplet state (T_1) depends on the amount of singlet character induced in it due to coupling with the various excited singlets states and the coupling is controlled by the spin orbit matrix elements between the various excited singlets and the triplet in question. Hence the higher CT-character of S_2 -state in *m*-tolunitrile would give rise to a larger spin orbit matrix in this molecule than in the para, unless the combining triplet (T_1) state in the latter has much more CT-character than in the former. This conclusion is in agreement with the suggestion by Lui and McGlynn (1975a) in explaining the phosphorescence behaviour of *p*-cyanoanisole.

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