

Microscopic Parameters in the Excited State of Toluene and Some of Its Haloderavatives

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Abstract

The Ultraviolet-visible (UV) spectra of toluene, ortho-bromo and para-bromo toluene in different solvents have been studied. The electric dipole moments and polarizabilities in the molecular excited electronic states were determined. It was found that the electric dipole moments for the excited states (μ^*) and the ground states (μ) of these compounds are equal, and the change in dipole moment is zero. This implies, in part, little or no change in potential energy surfaces of the ground and the excited states. The negative values obtained for the change in polarizabilities ($\Delta\alpha$) for the Lb state in various transitions indicate contraction in the excited state relative to the ground state, because the polarizability is proportional to the molecular volume.

Keywords: Microscopic; Dipole moment; Polarizability; Toluene; Haloderivatives

Introduction

Extensive studies on the electronic absorption spectra of different compounds have been reported [1-3], however, few works were reported specifically on benzene and its various derivatives [4-5]. Perturbation of electronic spectra of benzene and some of its derivatives have been previously investigated by a number of workers both experimentally and theoretically by electronic absorption spectroscopy and molecular orbital calculations [6-8]. It was well established that the electronic transition 1Lb is symmetry forbidden but appears at longer wavelength on substitution at various positions on the benzene ring [7,9]. Recently, the electronic and vibrational spectra of benzene and some of its derivatives have been reported, [10] and of all the systems of benzene and its derivatives, the 1B_{2u} ← 1A_{1g} electronic system (lying around $\lambda = 2600$ nm) has been studied in great detail. In

view of the limited studies, particularly in the second system (groups that can resonate with benzene π electrons through the process of hyper – conjugation) it was felt that an extension of the studies to the infrared and electronic absorption spectra of some more di substituted benzenes would be worthwhile as this would enable one to have more insight into the structure of the molecules in their ground and excited states. Therefore we have particularly chosen some molecules of the type toluene and its halo derivatives and studied their infrared and electronic absorption spectra. The results are reported in this work.

Materials and Methods

Experimental

*Materials

(a) Reagents; (i) Organic compounds used; benzene,

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toluene, ortho-bromo and para-bromo toluene compounds; (ii) Solvents used; Polar: -methanol, dichloro methane, propan -1-ol, propan -2-ol; Nonpolar: n-hexane, n-pentane, cyclohexane and 2,2,4-trimethyl pentane ; (b) Equipments;(i) Distillation Kits; (ii) Hilger and Watts Abbe refractometer M46; (iii) Perkin-Elmer, Lambda 3B double beam Spectrophotometer;

*Method

The solvents used are the products of British Drug Houses Ltd and were redistilled several times. The refractive indices of all liquids were determined with the Hilger and Watts Abbe refractometer M46 with accuracy of 0.0002. The magnitudes of the measured refractive indices showed conformity with the literature values [4,11-12] for pure grade types. Dichloromethane, 2,2,4-trimethyl pentane and cyclohexane were products of Tokyo Kasei (Japan) and are of spectroscopic grade. The absorption spectra of dilute solutions of all these compounds are in the concentration range of 10⁻⁵ – 10⁻⁴ mol dm⁻³ were determined with the Perkin-Elmer, Lambda 3B double beam spectrophotometer in the wavelength range of 190-300 nm. A pair of matched cuvettes of 1cm optical path-length and thermostated at 20°C contained separately the solution and the solvent as reference. Spectral runs were made with the instrumental band width set at 1.0 nm and a scan speed of 1 nm s⁻¹ and absorbance of 0.5 that corresponds to the recorder chart full scale. In spectra that showed vibrational fine structures, typical of all runs except for p-bromo toluene in the solvents, the position of the first intense vibrational component of a vibronic band was chosen as the transition frequency in harmony with the reported 0-0 bands of vapour phase spectra.

At least 11 solvents including polar and nonpolar were used in the study of electronic spectrum of each compound.

Theoretical Consideration and Data Analysis

Equation (1) derived by ABE [11] relates the transition energy in solution ($h\nu_s$) to that of the vapour phase ($h\nu_v$) and to the Van der Waals' interaction energies because the energy of the electronic transition in the isolated molecules ($\langle h\nu_a \rangle$) needed to be modified by the solvation energies of the initial and final states of the molecule.

$$h\nu_s = h\nu_v \left\{ \frac{2(\mu_a^{*2} - \mu_a^2)}{3} \frac{1}{dkT} + \alpha_a^* - \alpha_a \right\} \frac{\mu_b^2}{dr_{ab}^6} - \left\{ \frac{(\mu_a^{*2} - \mu_a^2)}{d} + \frac{3}{2} \left(\frac{\alpha_a^* I_b}{1 + \frac{I_b}{I_a}} - \frac{\alpha_a I_b}{1 + \frac{I_b}{I_a}} \right) \right\} \frac{\alpha_b}{r_{ab}^6} \quad (1)$$

In this equation, h is planck's constant and ν the transition frequency; μ , α , and I are the electronic dipole moment, polarizability and the ionization potential, respectively, of the solute or solvent in the ground electronic state while the corresponding starred symbols are those of the excited state, subscript a and b denote the solute and solvent molecules, while s and v identify the solution and vapour phases respectively;

$r_{ab}^{-6} = \sum_{i=1}^m r_{abi}^{-6}$ where r_{ab} is the internuclear distance

between the solute and the i -th solvent molecule, m being the number of solvent molecules interacting with the solute molecule; r_{ab}^{-6} is computed using the following equation [11,13],

$$r_{ab}^{-6} = \frac{\pi}{r_v^2(r_u + r_v)^4} + \frac{\pi}{r_v^2(r_u + 3r_v)^4} \quad (2)$$

$$\text{in which } r = \left\{ \frac{(0.75)V_m}{N\pi} \right\}^{1/3}$$

V_m is the molar volume obtained from Van der Waals volume [14,15], r represents the molecular radius of the solute (r_u) or solvent (r_v) derived from molar volume. In the present analysis the molecular radius of a solute or solvent was determined from mass and density or its Van der Waals' volume: $d=4\pi\epsilon_0$ in the S.I units (ϵ_0 being the permittivity of free space) and in the c.g.s units; k and T are Boltzmann constant and temperature of the solution respectively. For our present purpose we rearrange equation (1) into the following convenient linear regression forms;

$$Y = \frac{(\mu_a^{*2} - \mu_a^2)}{d} X_1 + \alpha_a^* X_2 \quad (3)$$

$$\frac{Y}{X_2} = \alpha_a^* + \frac{(\mu_a^{*2} - \mu_a^2)}{d} \frac{X_1}{X_2} \quad (4)$$

$$\frac{Y}{X_1} = \frac{(\mu_a^{*2} - \mu_a^2)}{d} + \alpha_a^* \frac{X_2}{X_1} \quad (5)$$

The dependent variables are Y , Y/X_2 and Y/X_1 in equations (3) – (5) respectively, and the independent variables are X_1 and X_2 in equation (3), X_1/X_2 in equation (4) and X_2/X_1 in equation (5).

The following definitions hold in eqns. (3) – (5):

$$Y = (h\nu_s - h\nu_v) + \alpha_a X_3 \quad (6)$$

$$X_1 = \left(\frac{2}{3} \frac{\mu_b^2}{dkT} + \alpha_b \right) r_{ab}^{-6} \quad (7)$$

$$X_2 = \left(\frac{\mu_b^2}{d} + \frac{3}{2} \frac{\alpha_b I_b}{\left(1 + \frac{I_b}{I_a^*}\right)} \right) r_{ab}^{-6} \quad (8)$$

$$X_3 = \left\{ \frac{\mu_b^2}{d} + \frac{3}{2} \frac{\alpha_a I_b}{\left(1 + \frac{I_b}{I_a}\right)} \right\} r_{ab}^{-6} \quad (9)$$

$$I_a^* = I_a - h\nu_v \quad (10)$$

In the application of LINDER'S variant of Equation (1), $Y = 2(h\nu_v - h\nu_s + \alpha_a X_3)$ in Equations (3) – (5) satisfy the statistical criterion for regression or graphical analysis, that is, the error in the dependent variable is far greater than that of the independent variable.

Tables 1 to 3 show the behaviour of toluene, o-bromo and p-bromo toluene in polar and nonpolar solvents. Table 4 shows the molecular data used for the generation of Y, X1 and X2 for the least square and graphical analyses of data while Table 5 shows the summary of excited state electric dipole moment, polarizability and ionization potentials for all the compounds, as calculated.

Results and Discussion

Figures 1 - 4 shows the plots of the data on solvent frequency perturbation of 1L_b band of benzene, toluene, p-bromo and o-bromo toluene according to equations (4) and (5) respectively. Tables 1-3 summarize the maximum absorption frequencies ($\bar{\nu}_{\max}$) and the corresponding molar absorptivities (ϵ_{\max}) for the transitions in each compound. Although three bands are expected to show the different transition levels, however, these varies based on solvents used and the compound caged [10]. For example in table 1 toluene has 2 major bands both in some of the polar and nonpolar solvents used though at different wavelength-shift except in cyclohexane and 2,2,4 trimethyl pentane where the third band appear as a shoulder at higher wavelength. This could be attributed to their transparency to the compound caged. However, dichloro methane and methyl acetate have only one band.

These transition bands are been refer to as 1L_b for the first band because the transition is from S_0 to S_1 energy levels; 1L_a for the second band as the transition is from the S_0 to S_2 energy level and the third band has transition from S_0 to S_3 (1B_b) where the S_0 stands for the ground state.

Tables 4 and 5 give the summary of the values of the vapour phase transition frequency, equivalent hard

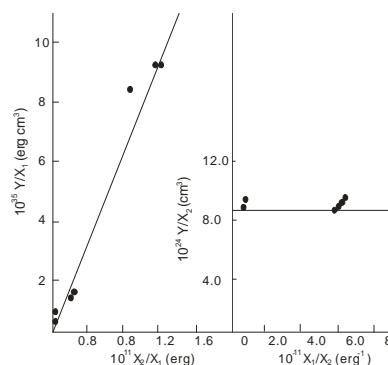


Figure 1. Benzene.

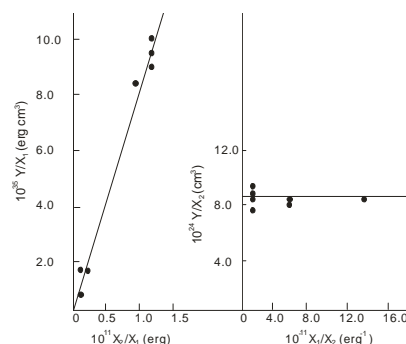


Figure 2. Toluene.

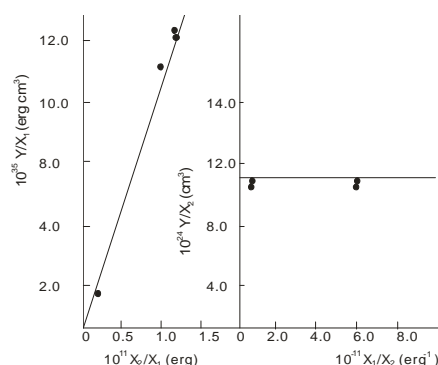


Figure 3. P-bromo toluene.

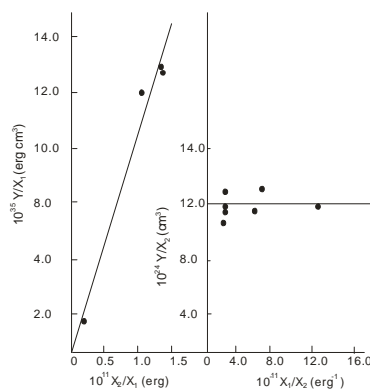


Figure 4. O-bromo toluene.

Table 1. The transition frequencies (cm^{-1}) and molar absorptivity ($\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) of toluene in different cavities

Solvent	Band 1		Band 2		Band 3	
	$S_0 \rightarrow S_1 (^1L_b)$		$S_0 \rightarrow S_2 (^1L_a)$		$S_0 \rightarrow S_3 (^1B_b)$	
	ν_{\max}	ϵ_{\max}	ν_{\max}	ϵ_{\max}	ν_{\max}	ϵ_{\max}
Pentane	38222	291	48217	7194	-	-
Cyclohexane	38529	259	48217	7803	51932	19,775
2,2,4-trimethylpentane	38259	223	48336	6507	51359	4502
Dichloromethane	38158	265	-	-	-	-
Methyl acetate	38265	272	-	-	-	-
Propan-1-ol	38222	203	48039	6337	-	-
Propan-2-ol	38222	228	47514	6564	-	-
Methanol	38222	237	48098	6215	-	-
Butyl acetate	38222	246	48098	6205	-	-
Ethyl acetate	38222	256	48298	6110	-	-

Table 2. The transition frequencies (cm^{-1}) and molar absorptivity ($\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) of p-bromo toluene in different cavities

Solvent	Band 1		Band 2		Band 3	
	$S_0 \rightarrow S_1 (^1L_b)$		$S_0 \rightarrow S_2 (^1L_a)$		$S_0 \rightarrow S_3 (^1B_b)$	
	ν_{\max}	ϵ_{\max}	ν_{\max}	ϵ_{\max}	ν_{\max}	ϵ_{\max}
Pentane	37062	397	45416	9459	49688	8849
Cyclohexane	37062	457	45310	9622	50719	36415
2,2,4-trimethylpentane	37062	418	45521	10581	50917	34984
Dichloromethane	37097	359	43690	4055	-	-
Methyl acetate	37097	465	44250	4369	-	-
Propan-1-ol	37097	350	45416	8931	49187	5685
Propan-2-ol	36104	362	45575	8850	49625	6906
Methanol	36104	646	45521	8513	49688	8786
Butyl acetate	36104	725	45527	10651	49688	10521
Ethyl acetate	36104	629	45617	8260	50421	9625

Table 3. The transition frequencies (cm^{-1}) and molar absorptivity ($\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$) of o-bromo toluene in different cavities

Solvent	Band 1		Band 2		Band 3	
	$S_0 \rightarrow S_1 (^1L_b)$		$S_0 \rightarrow S_2 (^1L_a)$		$S_0 \rightarrow S_3 (^1B_b)$	
	ν_{\max}	ϵ_{\max}	ν_{\max}	ϵ_{\max}	ν_{\max}	ϵ_{\max}
Pentane	37619	312	-	-	49436	10787
Cyclohexane	37611	387	-	-	50785	39791
2,2,4-trimethylpentane	37619	295	-	-	50851	34535
Dichloromethane	37561	320	43788	1982	-	-
Methyl acetate	37561	281	43785	2008	-	-
Propan-1-ol	37611	161	-	-	49126	7349
Propan-2-ol	37852	300	-	-	49312	9077
Methanol	36508	291	-	-	49374	10860
Butyl acetate	36508	493	-	-	49526	10042
Ethyl acetate	36508	356	-	-	49132	9274

sphere radius, ground state and excited state electric dipole moments, polarizabilities and ionization potentials of all the compounds according to equations 3 -5

and 10.

The bands 1, 2, and 3 are denoted by $S_0 \rightarrow S_1$ ($1L_b$), $S_0 \rightarrow S_2$ ($1L_a$) and $S_0 \rightarrow S_3$ ($1B_b$) in order of

increasing energy respectively. The 1Lb, band is well separated from the other two bands in all the compounds. The magnitude of bathochromic and hypsochromic effects depends on how polar or nonpolar the solvent is relative to methanol and pentane, respectively.

Toluene

Benzene is the parent compound upon which different substitution were made and tested in different solvents. In Tables 5 and 6, benzene has the highest vapor phase frequency, the least hard sphere radius, electric polarizabilities and highest ionization potential in ground state from the literature [16] compared to all of its derivatives used in this study. Since polarizability (α) is directly proportional to the cube of radius (r^3), the change in polarizabilities, that is, $\Delta\alpha = -2.953\text{\AA}^3$, shows that it exhibits lowest contraction in its transition to 1Lb excited state compared to its other derivatives.

For toluene the $S_0 \rightarrow S_1$ (1Lb) band appear slightly shifted towards the red in non polar solvents. This transition is quantum mechanically and overlap forbidden which make it symmetry forbidden.

The 1Lb and 1Bb bands appeared together and overlap more in polar compared to nonpolar solvent where they are fairly resolved. The intensity of $S_0 \rightarrow S_2$ band in different solvents decreases as polarity of the solvent decreases. The most intense band is $S_0 \rightarrow S_2$ while the least is $S_0 \rightarrow S_1$, i.e. 1La band is quantum mechanically forbidden but overlap allowed (partially symmetry allowed). The magnitude of $\Delta\alpha$ is more negative in toluene than it is in benzene, i.e., contractions of the benzene ring in toluene's excited state are larger, which could be attributed to resonance of methyl group of toluene with the π electrons of benzene through the process of hyper-conjugation [17]

P-bromo toluene

Conjugation between the methyl and the bromine atom in the 1, 4 position is larger relative to the 1, 2 position which causes the $S_0 \rightarrow S_1$ band of p-bromo to occur at lower energy and higher intensity relative to o-bromo. The high ϵ_{\max} could be attributed to the lack of steric effect between CH methyl hydrogen atom and the bromine also due to 1, 4 positions. This is reverse in the case of o-bromo toluene based on the juxtaposition of the CH methyl group and bromine atom. The reduced transition energy is due to the reduction of energy separation between the LUMO and HOMO energy levels. All these accounted for its having the highest contraction in the excited state ($\Delta\alpha = -3.966\text{\AA}^3$) compared to all other compounds used.

O-bromo toluene

In table 3 the $S_0 \rightarrow S_1$ (1Lb) transition appears red shifted in nonpolar solvents relative to polar solvents. The band is symmetry forbidden. Relative to toluene, a red shift is observed and molar absorptivity is low as expected from a forbidden transition. $S_0 \rightarrow S_2$ (1La) band occurs separately with a small shoulder in the high frequency region. The band has high (ϵ_{\max}) relative to p-bromo, due to intensity borrowing from $S_0 \rightarrow S_3$ band as well as larger mesomeric effect of bromine relative to chlorine which allows delocalization of lone pair electrons into the benzenoid ring. $S_0 \rightarrow S_3$ occurs only in near UV region in transparent solvents like 2, 2, 4 trimethyl pentane and is red shifted relative to p-bromo toluene. Considering the $\Delta\alpha$ value (-3.389) it shows that excited state contraction is lower than that of para derivative but higher than that of benzene, that is, the value of $\frac{dE}{dr}$ in its excited state is almost negligible compared to that of benzene.

Solvent and substituent perturbations of the electronic spectral properties as well as excited state electric dipole moment and polarizability of toluene, o-bromo, and p-bromo toluene have been determined. The introduction of methyl group to benzene ring affects its symmetry (lowers it) and it is found that

Table 4. calculated Ionization potentials, dipole moments, polarizabilities, approximate (spherical) radii and wavenumber of the 0-0 electronic transitions of selected bands of the compounds

Parameter (Unit)	Benzene	Toluene	p-bromo toluene	O-bromo toluene
$10^{11}I(\text{erg})$	1.41296	1.41296	1.38413	1.37721
$\bar{\nu}_v$ (cm^{-1})	38089	37484	36263	36174
$10^8 r_v(\text{\AA})$	2.86789	2.86789	3.05749	3.05744
$10^{24}\alpha(\text{cm}^3)$	10.546	12.174	15.231	15.231
$\mu(D)$	0.0	0.0	0.0	0.0

Table 5. Excited state electric dipole moment, polarizability and ionization potentials of the compounds

Compounds	Change in dipole $\Delta\mu(D)$	Polarizability $\alpha^*(\text{\AA}^3)$	Change in polarizability $\Delta\alpha^*(\text{\AA}^3)$	Ionization potentials $10^{12}(\text{ergmol}^{-1})$
Benzene	0.0	7.593	-2.953	7.23115
Toluene	0.0	8.888	-3.286	6.62676
4-bromotoluene	0.0	9.090	-3.966	6.62676
2-bromotoluene	0.0	11.842	-3.389	6.58673

further introduction of halide substitutes to this (toluene) causes red shift in the frequency of transition. As the substitute changes from the C4 to C2 position, there is a band shift towards shorter wavelength (blue-shift). All these observations accounted for in terms of Fermo theory, as discussed by Creswell [18] and Keefe [7]. The solvent perturbation allows the assignment of the transition to be $\pi \rightarrow \pi^*$, [19] the differentiation between allowed and forbidden transition, and comparison of the relative charge densities of the structures of the compound in ground and excited states. Following the work done by Iweibo [4], an extension of the solvent frequency shift theory of ABE [11] and Linder's work [20], we were able to determine a relatively precise value of the excited state electric dipole moments and polarizabilities of all the compounds. It is found that the electric dipole moment of excited state and ground state are equal since $\Delta\mu$ is zero. Considering the change in the electric dipole polarizabilities of these compounds during a transition, it was found that they increase in the order benzene < toluene < o - bromo toluene < p - bromo toluene. The negative obtained for $\Delta\alpha$ values show that all these compounds contract in their excited state in the order listed above.

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