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A study of estimation of excited state dipole moments of di(4-bromophenyl)carbazone and its Cu(II), Zn(II), Cd(II) complexes from the solvent effect on their electronic spectra

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Abstract

The solvent effect on the electronic spectra of di(4-bromophenyl)carbazone and its Cu(II), Zn(II), Cd(II) complexes have been studied by synthesizing and characterizing them by magnetic moment, IR, EPR and ^{1}H NMR spectral measurements. The electric dipole moments of these compounds in the first electronically excited state have been determined. The results indicate that the observed band systems in these compounds may be attributed to $\pi^* \leftarrow \pi$ transition.

Keywords: Solvent effects; Dielectric constants and dipole moment

1. Introduction

Literature survey reveals that diphenylcarbazone (DPC) is widely used as a spectrophotometric reagent for the determination of chromium in ore [1], sea water [2], animal tissue digests [3] etc.; there seems to be no reports on its electronic spectral studies and dielectric measurements. No studies have been reported on di(4-bromophenyl)carbazone, nor on its Cu(II), Zn(II) and Cd(II) complexes. Dipole moment is an important parameter [4,5] which gives an idea of the electronic structure of the molecule and is of prime importance in understanding the molecular interactions. The present studies have been undertaken keeping these views in mind. From the study of the solvent effect on the electronic spectrum of the above compounds, it is possible to determine its electric dipole moment in its electronically excited states. This parameter so determined gives, some insight into electron distribution, reactivity, photochemical reactions etc., of the solute molecule in its electronically excited states. Apart from obtaining the permanent dipole moment in the excited states, it is also possible from these studies to determine the shape parameters, which is another important parameter that gives knowledge about the shape of the cavity in which solute molecule is supposed to lie.

2. Experimental

2.1. Apparatus

Electronic spectra were recorded on Hitachi 150-20 UV-Vis spectrophotometer. Elemental analysis was carried out on Perkin-Elmer 240 CHN analyser. IR and ^{1}H NMR spectra were recorded on Nicolet-170 FT IR spectrometer and VXR 300 S Varian spectrometer, respectively. EPR spectra of Cu(II) complex was recorded on a EPR-E-4 spectrometer, operating in the X-band region with TCNE as the reference material at liquid nitrogen temperature. The magnetic moment of Cu(II) complex was found out by Gouy method. The metal estimation was done by EDTA titration method [6]. The dielectric measurements were recorded with the help of Forbes Tinsley (FT) 6421 LCR data bridge at 10 kHz frequency. The refractive indices of various dilute solutions for sodium D line were determined, using Abbe's refractometer.

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2.2. Reagents

Carbontetrachloride, isopropyl alcohol, dimethylformamide, butanol-1, chloroform, 1,4-dioxane, *n*-propyl alcohol used were of Fisher AR grade. Benzene (Fluka) used was of spectroscopic grade. Copper chloride, zinc chloride and cadmium chloride used were of Fisher AR grade.

2.3. Preparation of the ligand

It was synthesized by a method described earlier [7,8]. Di(4-bromophenyl)carbazide was prepared by heating a mixture of 4-bromophenylhydrazine and urea (2:1) at 155–160 °C for about 3 h. The crude carbazide so obtained was crystallized from ethyl alcohol. About 1 g of the carbazide was dissolved in a mixture of 60 ml glacial acetic acid, 20 ml of 1N sulfuric acid and 2–3 drops of 10% ferric alum and oxidized by adding 20 ml of 0.06 M potassium persulfate ($K_2S_2O_8$) dropwise with vigorous stirring for about 30 min. The resulting carbazone (D4BrPC) was extracted with ether, washed several times with water, dried and purified by column chromatography using silica gel (60–120 mesh) column. A mixture of Me_2CO:$CHCI_3$ (1:4) is used as an eluent.

Yield 60%, mp, 108 °C.

2.4. Preparation of the complexes

About 1 g of copper chloride was dissolved in an acetate buffer (pH 4.5) and added to an alcoholic solution of D4BrPC dropwise at room temperature. The mixture was stirred for about 30 min and the resulting precipitate was collected under suction and washed several times with water. The complex was dried over P_2O_5 under vacuum at room temperature and purified by Soxhlet method [9].

The zinc and cadmium complexes were similarly prepared by using the acetate buffer of pH 6.2.

2.5. Measurements of dielectric constant

The dielectric constants of the dilute solutions were measured in a suitably fabricated cell of usually of small capacitance where the accurate determination of small changes in capacitance would be possible. This small capacitance can be measured with the help of Forbes Tinsley (FT) 6421 LCR Data Bridge at 10 kHz frequency. The necessary dielectric sample holder should consist of two concentric brass cylinders kept in position with small strips (to achieve electric isolation) and their leads are coated with gold. This assembly is kept in a glass beaker so that dilute solution can be filled into the cell. The capacitance of the empty cell (air) would be of the order of pico- Faraday.

3. Results and discussion

3.1. Characterization of ligand and the complexes

The elemental analyses of the ligand and the complexes along with the magnetic data are reported in Table 1. The C, H, N and metal analyses confirm that the stoichiometry of the complex is 1:2 for metal to ligand. The magnetic moment for the copper complex is 1.58 BM, which can be interpreted in terms of weak Cu–Cu interaction [10]. The Cu–Cu interaction is also confirmed by EPR spectrum analysis.

3.2. IR spectra

The IR spectra of the ligand and the complexes were recorded in 4000–400 cm^{-1} range. The ligand showed bands at 3312, 3090 which may be attributed to –NH vibrations. The band at 1712 cm^{-1} is assigned to (>C=O) stretching. The disappearance of (>C=O) stretching band around 1700 cm^{-1} in the spectra of the complexes indicated that oxygen atom of the ligand is involved in the coordination with the metal through the enolic form. This was further confirmed by the appearance of a band around 1600 cm^{-1} due to –C=N stretching in the spectra of the complexes. The IR peaks of the ligand and the complexes are given in the Table 2.

3.3. ^1H NMR spectra

The ^1H NMR spectrum of the ligand was recorded using $CDCl_3$ as solvent and the TMS as an internal reference. The broad signals at δ 5.9 and 6.40 are due to aniline –NH and amide –NH groups, respectively. The multiplets observed in the region δ 6.5–7.8 may be attributed to aromatic hydrogen atoms. It is observed for the diamagnetic Zn(II) and Cd(II) complexes that the broad signal of amide –NH has disappeared indicating that the azo nitrogen atom is involved in the coordination to the central metal atom through deprotonation. The data is given in Table 2.

Table 1
Analytical, magnetic moment data of the compounds

Compound	Found/(calculated) (%)				Molecular formula	μ_{eff} (BM)
	C	H	N	M		
D4BrPC	39.17 (39.22)	2.59 (2.54)	14.13 (14.08)	–	$C_{13}H_{10}N_4OBr_2$	–
$Cu(D4BrPC)_2$	36.61 (36.41)	2.05 (2.12)	13.18 (13.07)	7.31 (7.40)	$C_{26}H_{18}N_8O_2Br_4Cu$	1.58
$Zn(D4BrPC)_2$	36.43 (36.33)	2.19 (2.12)	13.21 (13.04)	7.73 (7.61)	$C_{26}H_{18}N_8O_2Br_4Zn$	–
$Cd(D4BrPC)_2$	34.71 (34.45)	2.11 (2.01)	12.43 (12.36)	12.51 (12.40)	$C_{26}H_{18}N_8O_2Br_4Cd$	–

Table 2
IR frequencies and ^{1}H NMR data of the compounds

Compound	IR frequencies (cm^{-1})						^{1}H NMR
	$\nu_{(-\mathrm{NH})}$	$\nu_{(\mathrm{C=O})}$	$\nu_{(\mathrm{C=N})}$	$\nu^{\mathrm{ar}}_{\mathrm{C=O}}$	$\nu_{(\mathrm{C-O})}$	$\nu_{(\mathrm{N-H})}$ Bend	
D4BrPC	3312, 3090	1712	–	1486	–	771	5.9 br (–NH phenyl) 6.4 br (–NH amide) 6.5–7.8 m (–H aromatic)
Cu(4BrPC)$_2$	3123	–	1603	1463	1131, 1250	758	–
Zn(D4BrPC)$_2$	3171	–	1612	1453	1150, 1212	763	5.83 br (–NH phenyl) 6.7–8.1 m (–H aromatic)
Cd(D4BrPC)$_2$	3132	–	1597	1471	1171, 1241	769	5.75 br (–NH phenyl) 6.3–7.8 m (–H aromatic)

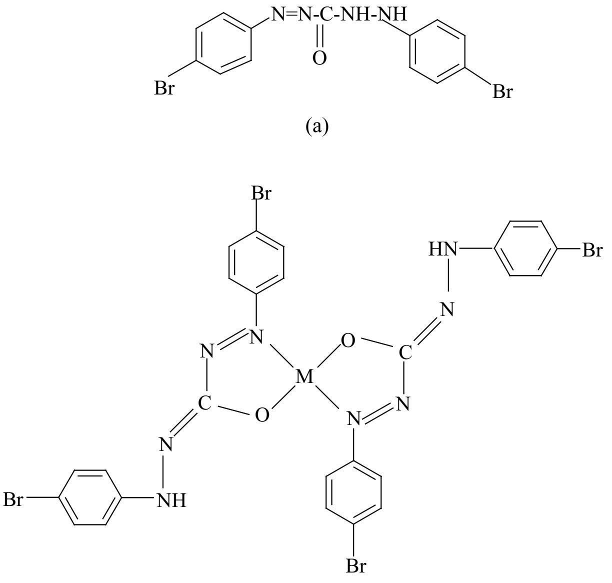
ar = Aromatic.

3.4. EPR spectra

In the EPR spectra, from the observed of value of Cu(II) complex at liquid nitrogen temperature ($g_{\|} = 2.20$, $g_{\perp} = 2.07$), it is evident that the unpaired electron is predominantly in d$x^2 - y^2$ orbital with the possibility of some dz^2 with it because of low symmetry. The $g_{\|}$ value ($g_{\|} = 2.20 < 2.3$) indicates a larger percentage of covalency. The G value, which is, less than four confirms a weak interaction between copper centres. The relation $g_{\|}/A_{\|} = 119\,\mathrm{cm}^{-1}$ suggests the square planar geometry. Based on the analytical and spectral data, the structure of the ligand and the complexes are assigned as shown in Fig. 1(a and b), respectively.

3.5. Evaluation of ground state and excited state dipole moment

The UV absorption spectra (for S$_1$ band) of a single particular weight fraction (concentration) of each of the pure samples D4BrPC and its Cu(II), Zn(II), Cd(II) complexes are recorded on a Hitachi 150–20 UV-Vis spectrophotometer with a cell path length of 1 cm, in various polar and non-polar solvents (concentration 0.01–0.03 gm l^{-1}). The data is represented in Tables 3 and 4. The permanent dipole moments in the excited states ($\vec{\mu}_e$) and the radius of the cavity in which the solute molecule supposed to lie are obtained by using the method reported in the literature as follows:



(a)

(b)

Fig. 1. (a) Structure of the ligand; (b) suggested structure of the complexes (M = Cu(II), Zn(II) or Cd(II)).

Following Suppan and Tsiamis [11], the change in the permanent dipole moment for a series of solvents of different static dielectric constants (ε) but similar refractive indices (n) is related to the observed energy shift $\Delta\nu_{a\text{–}b}$ between solvents a and b by

$$-\Delta\nu_{a-b} = \frac{\vec{\mu}_g \cdot \Delta\vec{\mu}_{g-e}}{hca_g^3}\{\Delta[f(\varepsilon) - f(n^2)]_{a-b}\} + \frac{\mu_e^2 - \mu_g^2}{hca_g^3}\,\Delta f(n^2)_{a-b} \qquad (1)$$

where $\vec{\mu}_g$ is the permanent dipole moment in the ground state, h the Planck's constant, c the velocity of light and, a_g the radius of the of the cavity in which the solute molecule is supposed to lie and $f(\varepsilon)$, $f(n^2)$ are the polarity polarizability functions defined by

$$f(\varepsilon) = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)}, \quad f(n^2) = \frac{2(n^2 - 1)}{(2n^2 - 1)}, \text{ respectively.}$$

Recently a method is proposed by Ayachit et al. [12] to determine $\vec{\mu}_e$ by expressing Eq. (1) in the form

$$\frac{X}{C_1} + \frac{Y}{C_2} = 1 \qquad (2)$$

which is an equation of a straight line with intercepts on either axes. By plotting the graph between $X(= \Delta[f(\varepsilon) - f(n^2)]_{a-b}/-\Delta\nu_{a-b})$ and $Y(= \Delta f(n^2)_{a-b}/-\Delta\nu_{a-b})$ the intercepts $C_1[= hca_g^3/\vec{\mu}_g \cdot \Delta\vec{\mu}_{g-e}]$ and $C_2[= hca_g^3/(\mu_e^2 - \mu_g^2)]$ on the X and Y axes, respectively, are determined and the magnitude and direction of them are obtained. The required data are obtained by measuring static permitivities of solvents and various dilute solutions (in benzene only for this purpose) at 10 kHz with the help of Forbes Tinsley (FT) 6421 LCR data bridge. The estimated values of $\vec{\mu}_g$ using Guggenheim's modified equation [13] are estimated to be

Table 3
Dielectric constants and refractive indices of the compounds in benzene at 25 ± 1 °C $d_1 = 0.874$, $\varepsilon_1 = 2.278$, $n_1 = 1.5010$

Compound	Molecular weight (M_2)	Weight fraction (W_2)	Dielectric constant (ε_{12})	$\varepsilon_{12} - \varepsilon_1/W_2$	Refractive index (n_{12})	$n_{12}^2 - n_1^2/W_2$	Intercepts			Calculated μ_g (D)	
							Δ'	Δ''	Δ	Eq. (3)	Eq. (4)
D4BrPC	398.08	0.5112×10^{-3}	2.3812	201.88	1.5043	19.4024	212.50	19.50	193.30	26.54	27.41
		1.1230×10^{-3}	2.4512	154.23	1.5060	13.3891					
		1.6171×10^{-3}	2.4932	128.79	1.5065	10.2296					
		2.1130×10^{-3}	2.5122	110.84	1.5073	8.9698					
		2.7621×10^{-3}	2.5468	97.32	1.5080	7.6261					
$Cu(D4BrPC)_2$	857.57	0.5231×10^{-3}	2.3711	177.98	1.5048	21.8372	201.92	22.42	179.5	37.54	39.22
		1.1133×10^{-3}	2.4351	141.11	1.5063	14.3175					
		1.4967×10^{-3}	2.4756	132.00	1.5067	11.4551					
		2.2231×10^{-3}	2.4973	98.65	1.5075	8.7968					
		2.5312×10^{-3}	2.5021	88.54	1.5080	8.3217					
$Zn(D4BrPC)_2$	859.51	0.6121×10^{-3}	2.4112	217.60	1.5040	14.7296	240.22	16.11	224.11	42.00	42.83
		1.0231×10^{-3}	2.4421	160.39	1.5050	11.7535					
		1.5102×10^{-3}	2.4763	131.31	1.5057	9.3580					
		2.0131×10^{-3}	2.4982	109.38	1.5063	7.9180					
		2.6131×10^{-3}	2.5131	89.97	1.5075	7.4839					
$Cd(D4BrPC)_2$	906.53	0.7215×10^{-3}	2.3912	156.90	1.5053	17.9184	172.92	19.00	153.92	35.75	37.31
		1.1532×10^{-3}	2.4131	117.15	1.5060	13.0385					
		1.6053×10^{-3}	2.4532	109.14	1.5070	11.2434					
		2.1562×10^{-3}	2.4912	98.88	1.5075	9.0698					
		2.5138×10^{-3}	2.5039	89.86	1.5080	8.3793					

Table 4
The electronic spectral data of the compounds in different solvents

Solvents	D4BrPC		$Cu(D4BrPC)_2$		$Zn(D4BrPC)_2$		$Cu(D4BrPC)_2$	
	ν_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})
Cyclohexane	44198	Reference	44512	Reference	44821	Reference	44971	Reference
Carbon tetrachloride	33821	10377	34410	10102	34232	10589	34380	10591
Benzene	42570	1628	36121	8391	34681	10140	34921	10050
Isopropyl alcohol	46321	2123	35496	9016	36123	8698	35820	9151
Dimethylformamide	34574	9624	35621	8891	35628	9193	37213	7758
Butanol-1	42718	1480	43113	1399	40891	3930	39923	5048
Chloroform	40892	3306	40821	3691	40813	4008	40623	4348
1,4-Dioxane	32112	12086	31689	12823	32125	12696	32231	12740
n-Propyl alcohol	47410	3212	47197	2685	47138	2317	47328	2357

Table 5
Values of *X*, *Y* intercepts and molecular radius (a_g) of the compounds

Solvents	D4BrPC		$Cu(D4BrPC)_2$		$Zn(D4BrPC)_2$		$Cd(D4BrPC)_2$	
	$X \times 10^{-5}$	$Y \times 10^{-4}$	$X \times 10^{-5}$	$Y \times 10^{-5}$	$X \times 10^{-5}$	$Y \times 10^{-5}$	$X \times 10^{-5}$	$Y \times 10^{-5}$
Carbon tetrachloride	0.2356	0.0210	0.2420	0.2154	0.2309	0.2055	0.2308	0.2055
Benzene	0.4377	0.2900	0.0849	0.5627	0.0703	0.4657	0.7091	0.4699
Isopropyl alcohol	26.1976	−0.1599	6.1688	−0.3764	6.3943	−0.3902	6.0778	−0.3709
Dimethylformamide	6.1325	0.0031	6.6381	0.0336	6.4200	0.0325	7.6075	0.0385
Butanol-1	36.0217	−0.1265	38.1063	−1.3385	13.5651	−0.4765	10.5608	−0.3710
Chloroform	9.0346	0.0397	8.0922	0.3556	7.4522	0.3275	6.8694	0.3019
1–4 Dioxane	0.3596	−0.0021	0.3390	−0.0209	0.3423	−0.0211	0.3412	−0.0210
n-Propyl alcohol	17.2615	−0.0907	20.6495	−1.0854	23.9292	−1.2577	23.5231	−1.2364
Intercepts C_1	11.4300×10^{-5}		5.6600×10^{-5}		4.8837×10^{-5}		5.0000×10^{-5}	
C_2	0.0872×10^{-4}		0.2537×10^{-5}		0.3006×10^{-5}		0.3072×10^{-5}	
Molecular radius (a_g) (Å)	3.9577		5.0405		5.0513		5.0633	

Table 6
Ground state and excited state dipole moments

Compound	Eq. no.	$\vec{\mu}_g$ (D)	$\vec{\mu}_e$ (D)	θ (°)
D4BrPC	From (3)	26.54	46.01	60.75
	From (4)	27.41	46.52	59.69
$Cu(D4BrPC)_2$	From (3)	37.54	106.97	76.24
	From (4)	39.22	107.57	75.03
$Zn(D4BrPC)_2$	From (3)	42.00	101.42	73.08
	From (4)	42.83	101.77	72.51
$Cd(D4BrPC)_2$	From (3)	35.75	98.37	77.96
	From (4)	37.31	98.95	76.27

accurate up to second decimal place. The equations used are as follows:

$$\vec{\mu}_g = 0.0128\left[\frac{3}{(\varepsilon_1+2)^2}\times\frac{M_2}{d_1\times T\times\Delta}\right]^{1/2} \tag{3}$$

where $\Delta = \Delta' - \Delta'' = [(\varepsilon_{12}-\varepsilon_1)/W_2]_{w_2\to 0} - [(n_{12}^2 - n_1^2)/W_2]_{w_2\to 0}$ also

$$\vec{\mu}_g = 0.0128 \times \left\{\frac{3}{(\varepsilon_1+2)^2}\times\frac{M_2}{d_1\times T\times 0.97}\left[\frac{(\varepsilon_{12}-\varepsilon_1)}{W_2}\right]_{w_2\to 0}\right\}^{1/2} \tag{4}$$

The quantities n, d, M, W and T involved in Eqs. (3) and (4) are the refractive index, density, molecular weight, weight fraction and absolute temperature, respectively. The suffix 1, 2 and 12 refers to the solvent, solute and solution, respectively. The data of dielectric constants, the refractive indices and hence the ground state dipole moment for the compounds are presented in Table 3. The values of X, Y intercepts are presented in Table 5.

The magnitude and orientations of the dipole moment for the first excited state together with the corresponding ground state dipole moment values are given in Table 6. It may be observed that the excited dipole moment values are fairly higher when compared to the values obtained by using Guggenheim equation for ground state ones (as entered in column three of Table 6). Such large values are reported in the literature for some polymers both in polar and non-polar solvents. The method of calculation (vector addition of group moments) has its own limitation of not accounting for the possible inductive/mesomeric/hydrogen bonding effects in these systems. Under the circumstances if it is assumed that these values would not improve much when bonding effects are also taken into account, the presently observed dipole moment values remain higher. In the light of these considerations the observed values of the dipole moments may be considered as inductive of the fact that the present ligand and complexes are associated rather with large values of dipole moments which in turn may be taken as suggestive of having their structure [14].

The dipole moment values of the excited states are expected to be greater than their ground state values. In the present investigation, the excited state dipole moment values are certainly greater than the ground state values. Based on these observations, it may be presumed that the observed transitions belong to $\pi^* \leftarrow \pi$.

References

[1] G. Chunsan, F. Yuging, Fenxi Huaxue 9 (1981) 414.
[2] S. Tsunenbu, G. Shiro, Bull. Inst. Chem. Res. Kyto Univ. 55 (1977) 429.
[3] W.C. Bryson, C.M. Goodall, Anal. Chim. Acta 124 (1981) 391.
[4] C.P. Smyth, Dielectric Constant and Molecular Structure, New York, 1931.
[5] M.L.E. Sutton, Bull. Soc. Chim., France, 1949, p. D81.
[6] H.A. Flaschka, EDTA Tritrations, Pergamon Press, London, 1959, p. 79.
[7] A.H.M. Siddalingaih, S.G. Naik, J. Mol. Struct. (Theochem) 581 (2002) 149.
[8] A.H.M. Siddalingaiah, A.F. Dodamani, S.G. Naik, Spectrochim. Acta 57A (2001) 2721.
[9] A.I. Vogel, Text Book of Practical Organic Chemistry, 3rd ed., London Press, London, 1964, p. 153.
[10] B.J. Hathway, D.E. Billing, Coord. Rev. 5 (1970) 143.
[11] P. Suppan, C. Tsiamis, Spectrochim. Acta 36A (1983) 971.
[12] N.H. Ayachit, D.K. Deshapande, M.A. Shashidhar, K. Suryanarayana Rao, Spectrochim. Acta 42A (1986) 585.
[13] E.A. Guggenheim, Trans. Farad. Soc. 45 (1949) 714; 47 (1951) 573.
[14] N.E. Hill, W.E.Voughan, A.H. Price, M. Davies, Dielectric Properties and Molecular Behaviour, the Van Nostrands Series in Physical Chemistry, Van Nostrand Reinhard, London, 1969.