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Electronic and vibrational spectra of a series of substituted carbazole derivatives

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Abstract

The FTIR and FTR spectra of halogen (Cl, Br, I) substituted carbazole and their N-acetic and propionic acids have been recorded. A number of lines have been assigned on the basis of previous studies on the parent compound and by comparisons with the characteristic vibrations of their constituent structural units as well as comparing the spectra from FTIR and FTR. Some substituent-sensitive bands and characteristic bands were found. The electronic absorption spectra of these compounds in acetonitrile were also measured and are briefly discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Halogen substituted carbazole; Halogen substituted carbazole-9-carboxylic acids; FTIR; Raman spectra; Electronic spectra

1. Introduction

Carbazole and its derivatives have been the subject of numerous investigations over the past 30 years. Photophysical and photochemical properties as well as biological activities are the main starting points [1-3]. Polymers, like poly (9-vinyl-carbazole), containing carbazolyl moieties are some of the most sensitive photoconductive materials [4]. Thus photophysical properties of carbazoles have been attracting increasingly detailed investigations focused on charge transfer characteristics. The photochemical behavior of carbazole

and some derivatives in different solutions has been studied. Some thermodynamically stable products from photochemical reaction have been identified and separated with discussion of reaction pathway and mechanism [5]. On the other hand, carbazole derivatives exhibit significant biological activity, such as anticonvulsant [6], antimicrobial [7], antiviral [8], antiinflammatory [9], and analgesic [10].

In this regard, a considerable number of carbazole derivatives have been prepared and probed for the nature of electronic states, excimer formation and energy transfer of the monomeric chromophore units of carbazoles by spectroscopic studies as well as testing the biological activity of carbazoles [11,12]. The spectroscopic properties of carbazoles have been studied in solution and solid

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state [13,14]. Bree and Zwarich made fairly complete vibrational and electronic spectral assignments of carbazole [15]. Chakravorty and Ganguly researched polarized absorption spectra of carbazole single crystals [16]. Benali and Kadiri studied the modification of UV absorption spectra of carbazole in different solutions [17]. A number of theoretical investigations of its electronic properties have also been undertaken [18-20]. After consulting the literature, we found that few absorption data for aromatic ring and nitrogen substituted carbazole are available except some interesting compounds like 3,6-dibromocarbazole and N-ethylcarbazole [1,21]. Since we used carbazole-9-acetic/propionic acid as the amino acids derivation agent for high performance liquid chromatography [22], we have synthesized a series of substituted carbazoles including some novel substituted carbazole-9-carboxylic acids. Their structures have been carefully characterized by ¹³C and ¹H nuclear magnetic resonance spectroscopy and mass spectroscopy.

For the tentative assignments of a series of derivatives of carbazole, having only the results of formal normal coordinate analysis of carbazole is not enough. On examination of a series of closely-related compounds, correlations between spectra are evident that can be ascribed either to common structural functional groups or to specific functional groups. It is often possible to make reasonable assignments of spectral features or specific features to vibrational motions on a semi-empirical basis. This is often an effective way to make tenable band assignments, especially where the structures under study are complex [23]. In this paper we seek to assign the infrared and Raman spectra of a series of substituted carbazoles in

such a manner, identifying the features characteristic of known functional groups. Combining these two data sets, which are complementary to each other, should permit the unambiguous assignment of some given compounds. We also compare their electronic spectra to find the changes induced by different substitutions. The structure and numbering of these compounds are shown in Scheme 1 and Table 1.

2. Experimental

2.1. Synthesis

The compounds (1b-1h) were prepared by the methods described in the literature [24-26]. The various carbazole-9-carboxylic acids were synthesized by microwave-assisted reaction. The general procedure (2a-2i) is as follows. A mixture of the carbazole (1a-1e) (0.012 mol), sodium hydroxide (0.072 mol), and the bromo-ester (0.015 mol) in DMF was heated in a domestic microwave oven in an open round-bottomed flask for an appropriate time. Then water was poured into the flask. The filtrate was acidified by adding hydrochloric acid until the precipitate separated entirely. The precipitate was filtered, washed with water, and dried in a vacuum. The crude product was purified by recrystallization from chloroform/alcohol (90:10) to give the desired product, yield 45-85% (Scheme 1).

2.2. Spectral measurements

FTIR spectra were recorded in the solid state as KBr pellets on a Bruker IFS 120HR instrument



Scheme 1. Synthesis procedure and conditions.

Table 1

The nomenclature used in describing the carbazole series derivatives

Nomenclature
$R_1 = R_2 = R_3 = R_4 = H$
$R_1 = R_3 = R_4 = H; R_2 = Cl$
$R_1 = R_4 = H; R_2 = R_3 = Cl$
$R_1 = R_3 = R_4 = H; R_2 = Br$
$R_1 = R_4 = H; R_2 = R_3 = Br$
$R_4 = H; R_1 = R_2 = R_3 = Br$
$R_1 = R_2 = R_3 = R_4 = Br$
$R_1 = R_3 = R_4 = H; R_2 = I$
$R_1 = R_3 = R_4 = H; R_2 = Cl;$
$R_5 = CH_2$
$R_1 = R_4 = H; R_2 = R_3 = Cl;$
$R_5 = CH_2$
$\mathbf{R}_1 = \mathbf{R}_3 = \mathbf{R}_4 = \mathbf{H}; \ \mathbf{R}_2 = \mathbf{B}\mathbf{r};$
$R_5 = CH_2$
$R_1 = R_3 = R_4 = H; R_2 = Br;$
$\mathbf{K}_5 = \mathbf{C}\mathbf{H}_2\mathbf{C}\mathbf{H}_2$
$R_1 = R_4 = H; R_2 = R_3 = Br;$
$R_5 = CH_2$
$\mathbf{R}_1 = \mathbf{R}_4 = \mathbf{H}; \ \mathbf{R}_2 = \mathbf{R}_3 = \mathbf{B}\mathbf{\Gamma};$
$\mathbf{K}_5 = \mathbf{C}\mathbf{H}_2\mathbf{C}\mathbf{H}_2$
$R_4 = H; R_1 = R_2 = R_3 = Br;$
$R_5 = CH_2$
$R_4 = H; R_1 = R_2 = R_3 = Br;$
$\mathbf{K}_5 = \mathbf{C}\mathbf{H}_2\mathbf{C}\mathbf{H}_2$
$\kappa_1 = \kappa_2 = \kappa_3 = \kappa_4 = Br; \ \kappa_5 = CH_2$
$\kappa_1 = \kappa_3 = \kappa_4 = H; \ \kappa_2 = I;$
$K_5 = CH_2$

between 4000 and 400 cm⁻¹. The resolution obtained for the FTIR spectra is 2 cm⁻¹. FT Raman spectra were recorded between 3400 and 100 cm⁻¹ shift on a Nicolet Raman 910 instrument equipped with a Nd:YOV₄ laser source ($\lambda = 1064$ nm). Samples were mounted as powders in commercially supplied sample holders. The spectral acquisition conditions were 4 cm⁻¹ resolution, 100 scans, and laser power in a range of 50–200 mW varying with different samples. Electronic spectra were recorded in MeCN on a Hitachi 330 spectrophotometer, using 10-mm quartz cells.

2.3. Molecular model

The optimal conformation of the molecule was derived by the molecular mechanism method using a MM2 force field on a personal computer.

3. Results and discussion

3.1. Structure characteristics

The site symmetry of carbazole in a crystal lattice is C_s , being bent about the z axis to the extent that the angle between the planes of the two benzene rings is 178.4° [15]. Assuming a planar molecule, the carbazole molecule symmetry can be represented by the C_{2v} group. The aromatic ring 3,6 and 1,3,6,8 positions in substituted carbazoles are also kept in the C_{2v} group. The molecular symmetry of aromatic ring monosubstituted carbazoles becomes C_s group. The N-substituted carbazole by carboxylic group could still be treated as a planar molecule. The 3,6-disubstituted carbazole-9-actec acids and 1,3,6,8-tetrasubstituted carbazole-9-actec acids molecules are represented by the C_s group, while other substituted carbazole-9-carboxylic acid molecule symmetry are represented by the C_1 group. Scheme 2 shows the stereo view of the optimal conformation of 2c.

3.2. The infrared spectra

The infrared spectral stack-plots for the whole series 1a-1h and 2a-2j between 1800 and 500 cm⁻¹ are given in Figs. 1 and 2, respectively. The substituted carbazole series 1a-1h are assigned firstly before their N-substituted carboxylic acids.

The N–H stretching modes of unsubstituted carbazole and halogen substituted carbazole 1a-1h appear at 3417-3403 cm⁻¹ with strong intensity. But the halogen substituent shifts this band to a lower wavenumber in the 14- to 11-nm range.



Scheme 2. Stereo view of 2c.

The effect of conjugation of the halogen atom increases the density of electrons around the nitrogen, and results in the enhancement of the acidity of the molecule as well as weakening of the N–H bond. So, the stronger NH…N and NH… π

type hydrogen bonding of the halogen substituent exhibits N-H stretching frequencies with lower values [27].

The lines present in the $1400-1650 \text{ cm}^{-1}$ spectral range are the ring stretching vibration modes



Fig. 1. IR spectra (1800-500 nm) of 1a-1h.



Fig. 2. IR spectra (1800-500 nm) of 2a-2j.

mixed with the N–H bending mode. The wavenumber and intensity of these bands are distinctly variable with different substituents. The wavenumber of bands around 1490 cm⁻¹ for 3-halocarbazole are 3–5 cm⁻¹ lower than carba-

zole, and their intensity also becomes weaker. This band in 3,6-dibromocarbazole (1e) and 3,6dichrolcarbazole (1c) has almost disappeared and a new band appears at a higher wavenumber. This new band becomes wider and medium in intensity when the ring is substituted by three (1f) and four bromine atoms (1g). Meanwhile, the other ring vibration bands at 1560-1625 and 1400-1480 cm⁻¹ also vary with different substituents. When the aromatic ring has one and two halogen atoms present, a weak band is seen at 1560-1570 cm⁻¹ that becomes weaker with increasing bromine atoms on the ring, while the bands at 1400-1480 cm⁻¹, strongly mixed with in-plane C-H bending, are split into two strong bands. The higher frequency band shifts to a higher wavenumber for maximum 21 cm $^{-1}$, whereas the lower frequency band shifts to a lower wavenumber 10 cm^{-1} . The variations in this region are due to halogen substitution and its conjugation as well as the heavier mass effect [28].

The bands at 1320 cm⁻¹ being a shoulder band of 1336 cm^{-1} that is an aromatic ring stretch mode are assigned to asymmetric C-N stretching mode, and symmetric C-N stretching mode in the 910 cm⁻¹ region which is mixed with the substituted phenyl ring to some extent [29]. Both bands become weaker to non-existent with addition of the halogen atoms. In the 1300-1000 cm⁻¹ region, many interactions occur between ring and substituent modes. The in-plane C-H bending blending with ring stretching are the main attributes of these bands [30]. The band at 1270-1286 cm^{-1} , strong in intensity, and induced by the aromatic ring substituent is the substituentsensitive band of carbazole. The C-halogen characteristic band located at 1043-1068 cm⁻¹ is easy to distinguish by comparing the spectra. The frequency of this band is affected by the mass of the halogen atom and progressively shifts to lower wavenumber from 1068 cm⁻¹ (1c) to 1043 cm⁻¹ (1h). The bands near 1000 cm⁻¹ are the ring breathing mode and in-plane ring bending by sextants of the carbazole phenyl ring [30]. When two or more substituents link on the aromatic ring, they combine into one band, and intensity becomes medium.

The distinct information below 1000 cm^{-1} is the different types of adjacent CH out-of-plane wag vibrations. The four and two adjacent CH and one lone CH are at 740–760, 805–815 and 845–880 cm⁻¹, respectively [28]. The substituentsensitive band among them is the two adjacent CH bands whose frequency shifts to a lower wavenumber with the augmentation of the substituent mass and number. Furthermore, this band is mixed with the ring deformation mode and appears as a multi-peak complex in the spectra of 3,6-disubstitution. In the $600-700 \text{ cm}^{-1}$ region, the halogen substituent gives distinct medium to strong intensity bands that are two weak shoulder peaks in carbazole spectrum. The band at about 680 cm^{-1} is probably the out-of-plane bending of N–H, which disappears in the spectra of their N-carboxylic acid analogue. Other bands in this region arise from phenyl deformation modes and it is difficult to interpret the chemical structure features.

Based on the assignment of halogen substituted carbazole, the special bands of their N-carboxylic acid analogue are identified with ease. On account of forming carboxylic acid dimer by hydrogen bonding, the OH stretch band superimposed on the CH stretch vibrations are in a wide region around 3000 cm⁻¹. The C=O stretch band of the dimer is around 1710 cm $^{-1}$ with strong intensity. Two wide bands at 1408-1430 and 1245 cm⁻¹ are medium and strong in intensity both involving the coupled vibration of C-O stretch and C-O-H in-plane bending, mixing the intrinsic ring vibrations. The out-of-plane OH…O wag band is of medium intensity and a rather wide band at around 900 cm⁻¹ is coupled with the C-N bending vibration. The C-halogen band is little affected by the substituted carboxylic group. But below the two adjacent CH bands, a strong band can be seen at about 790 cm⁻¹ in the spectra of mono-, di- and trisubstituted carbazole rings (2a-2h, 2j). In view of the comparison of 1g and 2i, which do not have this band with the addition of the carboxylic group on nitrogen, it could be that this band is not the CH vibration of the carboxylic group, and perhaps is the vibration of the carbazole ring. In the 620-670 cm⁻¹ region, there is one more new band brought by carboxylic group substitution. The O-C=O in-plane bending vibration and carbazole ring deformation modes are mingled in these bands. This is verified by the comparison of the three monosubstituted halogen carbazole-9-acetic acids (2a, 2c, 2j) of which these bands are shifted to lower frequency with the

sequence from chlorine, to bromine and to iodine [28].

3.3. The Raman spectra

The FT Raman spectral stack-plot between 1800 and 200 cm^{-1} shift for the whole series



Fig. 3. Raman spectra (1800-200 nm) of 1a-1h.



Fig. 4. Raman spectra (1800-200 nm) of 2a-2f, 2i and 2j.

1a-1h and 2a-2j (except 2f and 2g which both did not give clear spectra) are given in Figs. 3 and 4, respectively. The substituted carbazole series 1a-1h are also assigned firstly before their N substituted carboxylic acids.

Compared with the IR spectra, several bands of IR and Raman appear in the same region, making

unambiguous assignment not too difficult. The bands at high shifts above 3000 cm⁻¹ only observed at around 3050 cm⁻¹ are the CH stretching of the aromatic ring, strong in intensity, while the N–H stretching is not found due to it is very weak nature or because it is out of the range of observation [30]. Between 1400 and 1630 cm⁻¹ shift the bands, medium-to-strong in intensity, are obviously associated with aromatic ring stretching modes [31]. The halogen substitution results in the band at 1450 cm⁻¹ shift of carbazole moving to the lower shift direction, and becoming strong in intensity. The other ring stretching bands at around 1626, and 1573 cm⁻¹ are disturbed by the substituent moving to low wavenumber maximum 5 and 19 cm⁻¹, respectively. The strongest band of the Raman spectra locate around 1290 cm⁻¹ shift, and this band is IR inactive. When the carboxylic group replaced the hydrogen on nitrogen, this band disappeared entirely in mono-substituted carbazole, and became weaker in the other halogen substituted carbazole. So, this band is transparently associated with the $C_2 > N-H$ bonds. In addition, this band is obviously weaker in 1,3,6-trisubstituted carbazole than in the other substituted one, and this fact implies that the substituent at the 1 or 8 position of carbazole directly affects this band intensity. Thereby we assigned this band as the stretching vibration of C-C bridge bond of two phenyl rings [32]. The C-N stretch modes being a shoulder peak in IR are observed at around 1315 cm⁻¹ shift as a medium to strong peak. The band at 1336 cm⁻¹ is attributed to the aromatic ring stretch mode and their varying trend agrees with IR spectra. In this region, the substituent-sensitive band of carbazole found in IR, is much more versatile in Raman spectra and appears in mono- and trisubstituted carbazole but does not show in di- and tetrasubstituted carbazole.

In the range of $1250-1000 \text{ cm}^{-1}$ shift, many interactions between ring and substituent modes occur, and the halogen substitution of phenyl ring induces many changes. But the C-halogen characteristic band located at $1030-1080 \text{ cm}^{-1}$ shift, weak in intensity, is easily found. A group of weak bands at $1250-1100 \text{ cm}^{-1}$ shift are mainly due to the in-plane CH bending modes. The strong and narrow band at approximately 1000 cm^{-1} shift of carbazole is the characteristic of the phenyl group 'ring-breathing' mode which moves to a lower value with the mono-substitution of halogen. The net changes of this band (6, 8, 9 cm^{-1} of Cl, Br, I, respectively) are associated with the mass of the halogen, and this band becomes very weak when more halogen atoms connect to the phenyl ring. As a result, the assignment of this band is confirmed unambiguously, and the mass effect is expressed distinctly here [15,31].

In Raman spectra, the bands at around 900 cm^{-1} shift showed that there are few vibration modes combined at this region including symmetric C-N stretching mode and ring vibration [28]. A reversed change of trend of this band is observed here relative to the IR spectra. It is due to the fact that the conjugate effect of the halogen substituent makes the density of electrons of the carbazole ring more intense and results in the symmetric C–N stretching mode becoming stronger in Raman spectra with the amount increasing with the halogen substituent. The one lone CH out-of-plane wag vibration of the halogen substituted carbazole at 871-848 cm⁻¹ shift is not visible except in 1g, and the other CH out-of-plane wag vibrations could not be found. At the 800-600 cm⁻¹ shift range, the phenyl deformation modes are located, and these are distinctly different between the mono-, di-, and tri-, tetra-substituent so that these bands almost disappear in the latter two.

The bands of carbazole below 600 cm⁻¹ shift are mainly deformation modes of the phenyl group although the C–N bending are also involved in this region. However, by comparing the 1a–1h series, the tentative assignment of certain bands may be made. The band at around 430 cm⁻¹ shift is probably due to the C–N bending vibration, which changes to weak band with halogen substitution. The lines of 1b–1h within 300– 400 cm⁻¹ shift arise from the halogen substitution, and probably are associated with the out-of-plane bending of the C–X bond (X = Cl, Br, I). The remaining bands are difficult to assign to a specific structural feature.

The OH stretching and the line of C=O are not observed in the Raman spectra of halogen substituted carbazole carboxylic acids dimer [28]. In the high wavenumber shift region, asymmetric and symmetric CH₂ stretching appears at about 2900 cm^{-1} in a pattern of combination below the CH stretching mode of the phenyl ring. The CH₂ scissoring mode and the OH in-plane deformation overlap with the ring vibration in the range of 1400-1500 cm⁻¹ shift, which gives rise to difficulty in making out the mode with certainty. The strong line at about 1225 cm^{-1} that is a characteristic band of the substituted carbazole carboxylic acid is assigned to the C-O stretch mode of the carboxylic acid dimer. But this line of the 2i is weak in intensity; and it is affected by the two bromine atoms attached on position 1 and 8 of carbazole. The out-of-plane bending of the OH of the dimer appears at 870-895 cm⁻¹ as a weak band. The weak line at 821 cm⁻¹ is assigned to the CH_2 rocking mode [28]. Comparing the lines



Fig. 5. UV absorption spectra of 2c, 2e, 2g and 2i.

of the halogen substituted carbazole acetic and propionic acids, between 690 and 760 cm⁻¹ there was a distinct difference. The two medium bands disappear and the weak band at about 720 cm⁻¹ becomes a strong band in the propionic acid. We assigned this band to carbazole ring deformation. The band at about 235 cm⁻¹ is the C–C torsion of the carboxylic group.

3.4. Electronic spectra

The electronic absorption spectra of 2c, 2e, 2g and 2i are depicted in Fig. 5. The electronic absorption spectra for the whole series are listed in Table 2. The first band at the long wavelengths, which henceforth will be designated ${}^{1}L_{b} \leftarrow {}^{1}A$ in the Platt notation [33], show considerable vibrational structure [34]. The bands at about 290 and 260 nm are ${}^{1}L_{a} \leftarrow {}^{1}A$ and ${}^{1}B_{a} \leftarrow {}^{1}A$, respectively [14,35]. The other bands at low wavelengths should be ${}^{1}C_{a} \leftarrow {}^{1}A$ according to Platt notation [33,36]. Table 2 shows that the halogen substituent causes ¹L_b, ¹L_a, ¹B_a and ¹C_a band red shift. The more the number of the halogen atoms attached to the carbazole; the larger the red shift that is obtained. Moreover, the replacement of the > N–H hydrogen by the carboxylic group results in further red shift. In contrast to the ${}^{1}L_{a}$, ${}^{1}B_{a}$ and ${}^{1}C_{a}$ bands, the red shift of the wavelength of ${}^{1}L_{b}$ band of carbazole affected by the substituent is large. The spectra of mono- and di-substituted carbazole as well as their N-carboxylic acid, visually resemble that of carbazole, differing dramatically from that of the tri- and tetra-bromo analogues, especially ¹B_a and ¹C_a bands. This is due to change of the electronic structure of the π -orbital of the heterocyclic ring with the increasing number of bromine atoms as well as conjugating intensity of the halogen atom.

4. Discussion

Although the above tentative assignments of FTIR and FTR referred to the formal normal coordinate analysis of carbazole by Bree and Zwarich [15] and the assignments of indole and its deuterated derivatives [30]as well as comparison

Compound	$^{1}L_{b} \leftarrow ^{1}A$				$^{1}\mathrm{L}_{\mathrm{a}} \leftarrow ^{1}\mathrm{A}$		${}^{1}B_{\rm a} \leftarrow {}^{1}A$		$^{1}\mathrm{C}_{\mathrm{a}} \leftarrow ^{1}\mathrm{A}$							
	$\lambda_{\rm m}~({\rm nm})$	log <i>ɛ</i>	$\lambda_{\rm m}~({\rm nm})$	log e	$\lambda_{ m m}$ (nm)	$\log \epsilon$	$\lambda_{\rm m}$ (nm)	log <i>e</i>	$\lambda_{\rm m}~({\rm nm})$	log e	$\lambda_{\rm m}~({\rm nm})$	$\log \varepsilon$	$\lambda_{\rm m}~({\rm nm})$	log <i>ɛ</i>	$\lambda_{\rm m}$ (nm)	$\log \epsilon$
la	344	3.44	322	3.52	290	4.44	254	4.38	232	4.57						
1b	341	3.67	326	3.80	294	4.46	258	4.57	233	4.90						
1c	350	3.59	337	3.67	299	4.39	264	4.47	235	4.82	229	4.83				
1d	341	3.58	328	3.66	295	4.34	259	4.48	236	4.73						
le	349	3.46	333	3.58	297	4.32	263	4.46	237	4.73	230	4.72				
1f	352	3.67	336	3.68	298	4.35	266	4.45	254	4.67	242	4.73	235	4.71	226	4.69
1g	354	3.63	337	3.68	299	4.20	268	4.23	258	4.42	248	4.61	238	4.48		
1h	340	3.48	328	3.59	296	4.27	260	4.50	236	4.69						
2a	344	3.76	333	3.83	295	4.47	259	4.59	235	4.95						
2b	352	3.71	337	3.72	299	4.41	264	4.55	238	4.87	230	4.87				
2c	345	3.70	332	3.70	295	4.37	262	4.72	237	4.83						
2d	348	3.58	335	3.60	295	4.15	264	4.35	336	4.60	331	4.58				
2e	352	3.59	337	3.63	299	4.33	266	4.45	239	4.81	231	4.80				
2f	357	3.51	342	3.51	301	4.18	269	4.41	239	4.64	233	4.67				
2g	362	3.58	342	3.67	300	4.47	268	4.43	238	4.67	230	4.67				
2h	355	3.25			300	4.02	267	4.37	239	4.67	231	4.60				
2i	364	3.65	352	3.70	298	4.02			252	4.70	231	4.65				
2j	345	3.54	332	3.58	296	4.20	264	4.39	239	4.65						

Table 2 Electronic absorption spectra for the whole series of compounds

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of the whole series of compounds, some weak bands are not certain apart from some characteristic bands. The carbazole had a pyrrole ring, but in some cases, it was regarded as composed of biphenyl and the > N-H group. So, most vibration was assigned to the phenyl vibrations with the addition of the vibration of > N-H. In this manner, sometimes it was easy to interpret some assignments. For example, the C-N stretching mode being weak bands at 1320 and 910 cm⁻¹ in IR is identified due to this geometry structure. But in some cases, the carbazole ring must be treated as an integer. Thus moving to a lower value for the wavenumber of C=O in IR was probably due to the inductive effect of the halogen substituted carbazole ring.

The halogen substituents attached to the phenyl ring give rise to a variety of factors responsible for the observed differences of the vibrational bands. Pertinent factors include the effect of conjugation, mass effect and ring geometry. The effect of conjugation of halogen (Cl, Br, I) shifts the N-H stretching mode to a lower frequency. The progressive vibrational shift of C-X (X = Cl, Br, I) and the intensity change of 'ring-breathing' should be principally due to the mass effect of the halogen. Comparison of the spectra showed some substituent-sensitive bands of the carbazole ring. Among these bands the most sensitive is that at about 1270 cm⁻¹, which appears in both IR and Raman spectra if only a substituent is connected to the phenyl ring of carbazole. The changes of stretching vibration of the C-C bridge bond of two phenyl rings at 1290 cm⁻¹ shift and the C-O stretch mode at 1225 cm⁻¹ shift in Raman spectra illustrate the interaction of substituent on nitrogen with the carbazole ring. So, these two bands could be the characteristic bands of the substituted carbazole and its N-carboxylic acid, respectively. By the way, it could be convenient to be able to distinguish between the carbazole acetic acid and the carbazole propionic acid by simply looking for the band at 720 cm^{-1} shift in Raman spectra.

In the Platt notation system, the common order of the states is ${}^{1}L_{b}$, ${}^{1}L_{a}$, ${}^{1}B_{b}$, ${}^{1}C_{b}$, ${}^{1}B_{a}$, ${}^{1}C_{a}$ [36]. The ${}^{1}B_{b}$ band of carbazole was mixed with ${}^{1}L_{b}$ known from some theoretical studies and indeed was not observed in experimental results. But there have not been discussions on the ${}^{1}C_{b}$ band of carbazole in the literature. We just found the assignment of the band at about 260 nm as ${}^{1}B_{a}$ [14]. So the band at low wavelength was assigned to ${}^{1}C_{a}$.

5. Conclusion

In this work, we have tentatively assigned the vibrational bands of the series of carbazole derivatives by means of FTIR and FTR spectroscopy. Substituent-sensitive bands were found and the substituted effect of halogen has been observed and discussed. The combined use of FTIR and FTR was effective for a precise assignment of some observed lines, since the two techniques provide complementary and contrasting information on molecular structure. Through comparison of the whole series, this procedure enabled us to gain a valuable insight into general trends and to make deductions on a comparative basis.

We also compared the electronic spectra for the whole series and showed the spectral modifications.

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