

Spectroscopic studies on 9H-carbazole-9-(4-phenyl) boronic acid pinacol ester by DFT method

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ABSTRACT

9H-Carbazole-9-(4-phenyl) boronic acid pinacol ester (9-CPBAPE) molecule was investigated by FT-IR, Raman, UV–vis, ¹H and ¹³C NMR spectra. FT-IR, FT-Raman and dispersive Raman spectra were recorded in the solid phase. ¹H, ¹³C NMR and UV–vis spectra were recorded in dimethyl sulfoxide (DMSO) solution. The results of theoretical calculations for the spectra of the title molecule were compared with the experimental spectra. The highest occupied molecular orbital (HOMO) the lowest unoccupied molecular orbital (LUMO) and molecular electrostatic potential (MEP) analyses were performed. The theoretical calculations for the molecular structure and spectroscopic studies were performed with DFT (B3LYP) and 6-311G (d,p) basis set calculations using the Gaussian 09 program. The total (TDOS), partial (PDOS) density of state and overlap population density of state (OPDOS) diagrams analyses were performed using GaussSum 2.2 program.

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1. Introduction

Great advances have been made in the development of materials high-efficiency organic light emitting diodes (OLEDs) due to their potential for solid-state lighting OLEDs [1–6]. Multilayer OLEDs are known as one of the potential technologies for next-generation flat-panel display devices [7,8]. A typical organic light-emitting device has a structure including a substrate, an anode, organic layers and a cathode, which are sequentially stacked on the substrate, where in the organic layers include a hole transport layer (“HTL”), an emission layer (“EML”) and an electron transport layer (“ETL”) [9]. In later studies, phosphorescent organic light-emitting diodes (PHOLEDs) have attracted much attention because of their high quantum efficiency as compared to conventional fluorescent OLEDs through utilizing both singlet and triplet excitons for emission [10–14].

In a typical organic electroluminescence (EL) device, the most

suitable device design has been made depending on fluorescent emission mechanism or phosphorescent emission mechanism. Phosphorescent organic electroluminescence (EL) device, a carbazole derivative that exhibits a high triplet energy and is typically known as a hole transporting material has been used as a useful phosphorescent host material [15].

Studies conducted in recent years, the 9H-Carbazole-9-(4-phenyl) boronic acid pinacol ester molecule is used as intermediate product in the OLEDs and PHOLEDs [9,16–18]. In this work, the spectroscopic attitude, geometric structure, electronic properties and thermodynamic properties of 9H-Carbazole-9-(4-phenyl) boronic acid pinacol ester molecule were investigated with DFT/B3LYP method and 6-311G(d,p) basis set. Infrared and Raman spectra were calculated and vibrational assignments were based upon potential energy distributions (PED). ¹H, ¹³C NMR spectra were recorded in DMSO and compared with theoretically obtained spectra. Additionally, HOMO-LUMO and natural bond orbital (NBO) analyses were also carried out for 9-CPBAPE. Besides, to obtain total density of states (TDOS or DOS) the partial density of states (PDOS) and overlap population density of states (OPDOS) spectra of molecule were used GaussSum 2.2 [19].

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2. Experimental

9-CPBAPE molecule in solid form were prepared using a KBr disc technique for the infrared measurements. The spectra were recorded at room temperature using a Bruker IFS 66/S spectrometer in the range of 4000–400 cm^{-1} range. The spectrum was recorded, with a scanning speed of 10 cm min^{-1} and the spectral resolution of 4.0 cm^{-1} . The Raman spectra of the compound were recorded between 4000 and 100 cm^{-1} with a Thermo Fisher Scientific model DXR dispersive Raman instrument using 532 nm laser excitation. Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser was used and recorded between 4000 and 400 cm^{-1} . NMR experiments were performed in Varian 400 MHz spectrometer at 300 K. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra in DMSO. NMR spectra were obtained at the base frequency of 400 MHz for ^{13}C and ^1H nuclei. The ultraviolet absorption spectra of sample solved in DMSO and ethanol was examined between 200 nm and 1100 nm with resolution of 1 nm by using HITACHI U-4100/1J0-0016 with two monochromators, UV–vis recording spectrometer. The sample spectrum was taken inside a quartz tube with DMSO.

2.1. Computational details

The geometry optimization of the title molecule were carried out by DFT/B3LYP/6-311G(d,p) method and calculated geometric parameter values were tabulated with X-ray data of 9-(4-Ethynylphenyl)-9h-carbazole molecule [20]. Vibrational wavenumbers were calculated with the same method and they were presented with the scale factors. By using the following relationship, the Raman activities (S_{Ra}) were converted to relative Raman intensities (I_{Ra}) and derived from the intensity theory of

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(-\frac{h\nu_i}{kT}\right) \right]} \quad (1)$$

where ν_0 is the wavenumber of the exciting laser ($\nu_0 = 9398.5 \text{ cm}^{-1}$), ν_i is the vibrational wavenumber of the i th normal mode and S_i is the Raman scattering activity of the normal mode ν_i . f is a constant and equal to 10^{-12} . h , k , c and T are Plank and Boltzmann constant, the speed of light and the temperature in kelvin, respectively. In Eq. (1) $[1 - \exp(-h\nu_i/kT)]$ is called Boltzmann distribution and it is a temperature factor which accounts for the intensity contribution of excited vibrational states. The presented theoretical Raman intensities have been computed assuming $[1 - \exp(-h\nu_i/kT)]$ equal 1. The vibration modes are assigned on the basis of potential energy distribution (PED) computed by using VEDA 4 program [21].

^1H and ^{13}C NMR chemical shift values of the title molecule were computed in DMSO, water and gas phase using B3LYP/IEF-PCM/6-311G(d,p) basis set by the GIAO method. Experimental chemical shifts obtained from DMSO solution. UV spectra, HOMO and LUMO energies were calculated with TD-DFT methods in DMSO, water and gas phase. Experimental UV spectra recorded in DMSO and ethanol solutions. The natural bonding orbitals (NBO) [9], thermodynamics and non-linear optic properties were done using the DFT/B3LYP 6-311G(d,p) method. Furthermore, GaussSum 2.2 program were used to obtain density of states (TDOS or DOS), the partial density of states (PDOS) and overlap population density of states (OPDOS) spectra [19]. The PDOS and OPDOS spectra were generated by convoluting the molecular orbital information with Gaussian curves of unit height and a FWHM (Full Width at Half

Maximum) of 0.3 eV. Geometry optimization, vibrational wavenumbers, ^1H and ^{13}C NMR chemical shift values, UV spectra, NBO values, HOMO and LUMO energies of the title molecule were made on the personal computer using Gaussian 09 program package [22].

3. Result and discussion

3.1. Molecular geometry

Possible conformers of 9-CPBAPE depend on the rotation of C29–B32 bond, linked to pinacol group and benzene ring. This bond is responsible for the flexibility and conformational stability of 9-CPBAPE. Thus, C27–C29–B32–O33 dihedral angle is a coordinate related to conformational flexibility. The potential energy surface (PES) of the dihedral angle C27–C29–B32–O33, calculated at the B3LYP level of theory, is displayed in Fig. S1. The internal rotational profile of C29–B32 bond was obtained at B3LYP level of theory by allowing the torsional coordinate to vary in steps of 10° from 0° to 360° . This rotation bond yielded the energetically three minima at 0° , 180° and 360° , with $E = -1159.49487468$ Hartree, $E = -1159.49487475$ Hartree and $E = -1159.49487469$ Hartree, respectively. For the C27–C29–B32–O33 rotation, the maximum energy ($E = -1159.49487475$ Hartree) was obtained at 180° in the potential energy curve.

Molecular structure of 9H-Carbazole-9-(4-phenyl) boronic acid pinacol ester molecule optimized with DFT/B3LYP/6-311G(d,p) method and given with the number of atoms in Fig. 1. The some geometric parameters of molecule are tabulated in Table 1 with X-ray data of 9-(4-Ethynylphenyl)-9h-carbazole molecule and whole data are given Table S1 [20].

The molecular structure of the title compound is formed the benzene ring including boronic acid pinacol ester and the carbazole rings. Bond angles attached to nitrogen are C3–N11–C22 and C12–N11–C22 are 125.8° and bond angle of C3–N11–C12 is 108.4° for 9-CPBAPE. Bond angles C–N–C of 9-(4-Ethynylphenyl)-9h-carbazole molecule were observed as 124.9° , 126.1° and 108.3° , respectively [29]. The bond angles in similar molecule were calculated as 125.6° , 125.8° and 108.6° and observed as 126.0° , 126.9° and 106.8° [23].

Bond lengths of the C–C bond in phenyl ring systems were observed in the range of 1.375–1.389 Å for 9-(4-Ethynylphenyl)-9h-

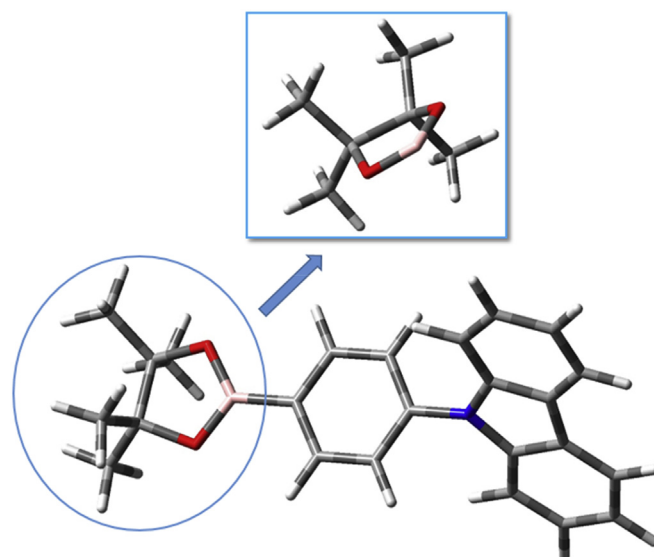


Fig. 1. Theoretical optimized geometric structure of the 9-CPBAPE.

Table 1

The some geometrical parameters optimized in 9-CPBAPE [bond length (Å) and bond angle (°)].

	9-CPBAPE	X-ray [29]
Bond length		
C1–C2	1.40	1.39
C1–C6	1.39	1.37
C1–H7	1.08	0.96
C2–C3	1.42	1.40
C2–C13	1.45	1.44
C3–C4	1.40	1.38
C3–N11	1.40	1.40
C4–C5	1.39	1.38
C4–H8	1.08	0.97
C5–C6	1.40	1.38
C5–H9	1.08	0.96
C6–H10	1.08	0.99
N11–C12	1.40	1.40
N11–C22	1.42	1.42
C12–C13	1.42	1.40
Bond angle		
C2–C1–C6	119.2	119.1
C2–C1–H7	120.4	119.7
C6–C1–H7	120.4	121.2
C1–C2–C3	119.5	119.8
C1–C2–C13	133.6	133.1
C3–C2–C13	106.9	107.1
C2–C3–C4	121.5	121.1
C2–C3–N11	108.9	108.9
C4–C3–N11	129.5	130.0
C3–C4–C5	117.8	117.6
C3–C4–H8	121.3	122.1
C5–C4–H8	120.9	120.3
C4–C5–C6	121.5	121.9
C4–C5–H9	119.1	116.7
C6–C5–H9	119.5	121.4
C1–C6–C5	120.5	120.5
C1–C6–H10	119.9	121.9
C5–C6–H10	119.6	117.6
C3–N11–C12	108.4	108.3
C3–N11–C22	125.8	126.1
C12–N11–C22	125.8	124.9
N11–C12–C13	108.9	108.6
N11–C12–C14	129.5	129.7
C29–B32–O34	123.5	
O33–B32–O34	113.0	
B32–O33–C35	107.7	
B32–O34–C36	107.7	
C36–C35–C37	115.3	
C36–C35–C45	113.4	
C37–C35–C45	110.2	
O34–C36–C35	102.1	
O34–C36–C49	106.6	
C36–C49–H50	111.3	
C36–C49–H51	111.7	
C36–C49–H52	108.8	
H50–C49–H51	108.6	
H50–C49–H52	108.0	
H51–C49–H52	108.4	

carbazole [20]. Same bond lengths were calculated in the range of 1.392–1.400 Å and observed 1.356–1.399 Å for 9-p-tolyl-9H-carbazole-3-carbaldehyde [23]. For 2-amino-3-((E)-(9-p-tolyl-9H-carbazol-3-yl) methyleneamino) maleonitrile the C–C bond lengths were observed from 1.371 Å to 1.392 Å and calculated from 1.392 Å to 1.395 Å [24]. In this study, the bond lengths of the C–C were calculated in the range of 1.390–1.403 Å. Bond lengths of N–C in the molecule N11–C3 and N1–C12 were calculated as 1.399 Å and bond length of N11–C22 was calculated as 1.421 Å. The same bond lengths were observed as 1.396, 1.397 and 1.422 Å for 9-(4-Ethynylphenyl)-9H-carbazole, respectively [20]. These bond lengths were calculated and observed as similar with 9-p-tolyl-9H-carbazole-3-carbaldehyde [23] and 2-amino-3-((E)-(9-p-tolyl-9H-

carbazol-3-yl) methyleneamino) maleonitrile [24].

3.2. Vibrational spectral analysis

The molecule has C_1 symmetry and 150 fundamental vibrational modes. The experimental and calculated IR and Raman spectra of molecule are given in Fig. 2. The vibrational frequencies were computed with the B3LYP/6-311G(d,p) basis set and scaling factor for 6-311G(d,p) was taken as 0.967 [25]. The calculated and experimental vibrational frequencies are listed in Table 2.

The correlation graphics of the experimental and calculated wavenumbers for the title molecule were also plotted and were given in Fig. 3. Also to see the correlations of infrared and Raman were graphed one by one as Fig. S2. As can be seen from these graphics, between experimental and calculated wavenumbers are usually linear and described for total and one by one as infrared and Raman.

3.3. C–H vibrations

In carbazole ring, as an band observed at 3055 cm^{-1} in FT-IR, at 3060 cm^{-1} in FT-Raman and dispersive Raman is assigned to CH asymmetric stretching vibration, the B3LYP/6-311G(d,p) calculated values are in the range of 3059–3082 cm^{-1} , PED analysis found that this mode is almost pure CH (PED, 90–98%) stretching vibration. CH asymmetric stretching vibration in phenyl ring calculated in the range of 3069–3070 cm^{-1} and at 3086 cm^{-1} . CH symmetric stretching vibration calculated at 3093 cm^{-1} and at 3088 in carbazole ring and phenyl ring, respectively. The C–H in-plane bending vibration appears in the range of 1000–1300 cm^{-1} in the literature [26,27]. The C–H in-plane bending vibrations were calculated at 1299–1277, 1168–1143, 1135, 1104, 1014–1007 cm^{-1} and at 1303–1277, 1096, 1087 cm^{-1} in carbazole ring and phenyl ring, respectively. These vibrations observed at 1138 cm^{-1} in FT-IR, at 1010, 1310 cm^{-1} in dispersive Raman spectrum and at 1015, 1311 in FT-Raman for 9-CPBAPE. The C–H out-of-plane bending vibration is shown in the range of 800–950 cm^{-1} for aromatic compounds in the literature [26,27]. The C–H out-of-plane bending vibrations were computed in the range 841–836, 830–829 cm^{-1} in phenyl ring and in the range 957–944, 910–909, 841–836, 830–829, 762, 741–716 cm^{-1} in carbazole ring were observed at 848 cm^{-1} in FT-IR, at 717 cm^{-1} in dispersive Raman and at 719 in FT-Raman spectrum. In the present work, both in-plane and out-of plane C–H bending vibrations were observed in the region mentioned.

3.4. CH₃ vibrations

CH₃ asymmetric stretching vibration observed at 2988 cm^{-1} in FT-IR and at 2976 cm^{-1} in FT-Raman spectrum and calculated in range of 2998–3027 cm^{-1} for 9-CPBAPE. CH symmetric stretching vibration was observed at 2941 and 2933 cm^{-1} in FT-Raman and dispersive Raman, respectively. The same vibration calculated in the range of 2935–2945 cm^{-1} , show more than 92% of PED contribution suggesting that it is a pure stretching mode. FT-IR band at 1452, 1358 cm^{-1} , FT-Raman band at 1453, 1366 cm^{-1} and dispersive Raman band at 1450, 1370 cm^{-1} are assigned to CH₃ scissoring vibration and are in excellent agreement with the theoretically calculated value by the B3LYP/6-311G(d,p) method in the range 1476, 1459, 1457–1438, 1379–1355 cm^{-1} .

3.5. Ring vibrations

C–C and C=C stretching vibrations usually occur in range of 1430–1625 cm^{-1} in the ring [28–30]. These bands by Varsanyi et al.

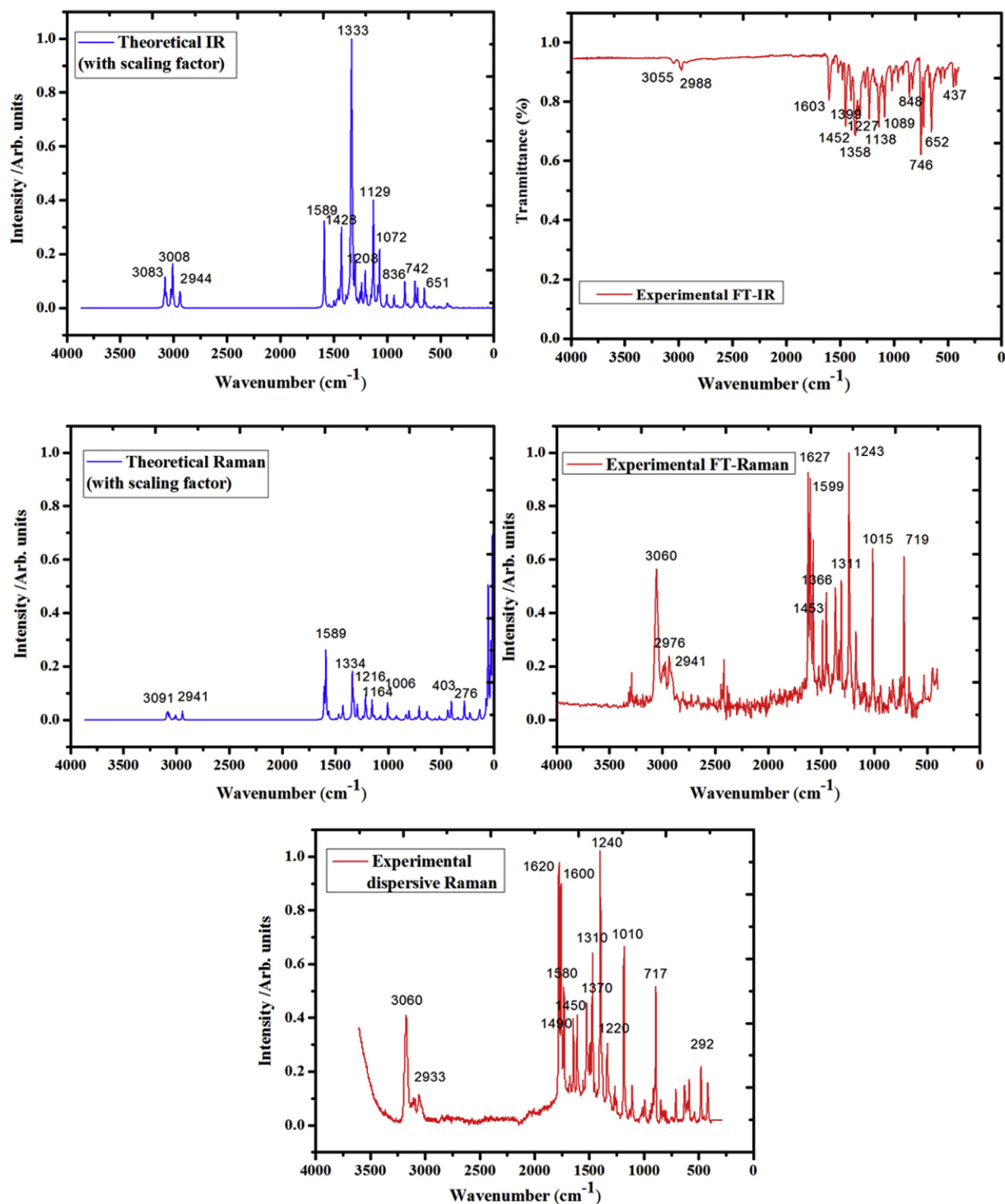


Fig. 2. The experimental and calculated (with the scale factor) FT-IR, FT-Raman and dispersive Raman spectra of the 9-CPBAPE.

are observed in the ranges 1625–1590, 1575–1590, 1470–1540, 1430–1465 and 1280–1380 cm^{-1} [31]. C–C stretching vibrations of 9-CPBAPE molecule were calculated at 1606–1590, 1543, 1387, 1333, 1328, 1303, 1299, 1255 cm^{-1} in phenyl ring and at 1606–1562, 1459, 1436, 1429, 1340, 1328–1325, 1299, 1215 cm^{-1} in carbazole ring by using B3LYP/6-311G(d,p) method and observed at 1603, 1399 cm^{-1} , at 1627, 1599, 1311 cm^{-1} and at 1620, 1600, 1580, 1310 cm^{-1} in FT-IR, FT-Raman and dispersive Raman, respectively. The biggest C–C stretching vibration in phenyl ring is calculated at

1543 cm^{-1} with the PED contribution 71%. Also the PEDs of these modes are not pure modes as in Table 1.

3.6. C–N and C–B

The C–N stretching vibration of aromatic amines was assigned in the region 1382–1266 cm^{-1} [32–34]. The same stretching vibration for 2-amino-3-((E)-(9-p-tolyl-9H-carbazol-3-yl) methyl-eneamino) maleonitrile was calculated as 1191 cm^{-1} [24]. For the

Table 2

Comparison of the calculated and experimental vibrational spectra and proposal assignments of 9-CPBAPE molecule.

No	Experimental wavenumbers			Theoretical wavenumber				PED (>10%)
	FT-IR	FT-Raman	Dis-Raman	Scaled	I _{IR}	S _{Ra}	I _{Ra}	Assignments ^a
150				3093	1.47	420.75	0.63	vCH (91)sm
149				3093	18.15	4.32	0.01	vCH (83)sm
148				3088	2.43	129.1	0.19	vCH (86)sm
147				3086	6.51	2.05	0	vCH (93)asm
146				3082	47.52	363.8	0.55	vCH (94)asm
145				3081	25.39	140.91	0.21	vCH (96)asm
144				3070	4.29	97.39	0.15	vCH (98)asm
143				3069	16.83	43.86	0.07	vCH (92)asm
142				3069	2.12	260.45	0.4	vCH (92)asm
141				3067	11.74	0.59	0	vCH (90)asm
140		3060	3060	3059	0.29	5.29	0.01	vCH (97)asm
139	3055			3059	0.18	73.54	0.11	vCH (95)asm
138				3027	31.67	1.4	0	vCH (91)asm
137				3026	10.5	107.99	0.17	vCH (91)asm
136				3011	56.3	3.58	0.01	vCH (91)asm
135				3010	33.5	241.01	0.39	vCH (93)asm
134				3008	32.48	38.39	0.06	vCH (92)asm
133				3006	1.36	60.4	0.1	vCH (96)asm
132				2999	11.43	8.4	0.01	vCH (91)asm
131	2988	2976		2998	0.02	28.39	0.05	vCH (94)asm
130				2945	31.85	551.58	0.95	vCH (97)sm
129		2941		2940	8.45	4.59	0.01	vCH (96)sm
128				2938	22.02	4.67	0.01	vCH (92)sm
127			2933	2935	1.54	6.89	0.01	vCH (96)sm
126	1603	1627	1620	1606	0.24	344.35	2.31	vCC (62) + δ CCH(14)
125		1599	1600	1590	220.66	749.72	5.13	vCC (66) + δ CCH(12)
124			1580	1583	23.51	39.5	0.27	vCC (50)
123				1563	0.79	15.61	0.11	vCC (61)
122				1562	0.02	60.09	0.42	vCC (57)
121				1543	7.95	0.46	0	vCC (71) + δ CCH(11)
120			1490	1499	16.83	13.2	0.1	δ CCH(45)
119				1476	11.09	0.75	0.01	ρ CH(δ CHH(89))
118				1470	12.78	51.16	0.4	δ CCC(21) + δ CCH(27)
117				1459	5.16	6.54	0.05	ρ CH(δ CHH(89))
116				1459	27.5	0.14	0	vCC (33) + δ CCH(26)
115				1457	6.38	6.78	0.05	ρ CH(δ CHH(85))
114	1452	1453	1450	1455	4.9	4.75	0.04	ρ CH(δ CHH(89))
113				1439	6.79	14.02	0.11	ρ CH(δ CHH(87))
112				1438	0.57	10.78	0.09	ρ CH(δ CHH(84))
111				1436	35.84	0.28	0	vCC (22) + δ CCH(54)
110				1434	2.94	13.2	0.11	δ CCH(96)
109				1429	199.06	117.39	0.97	vCC (30) + δ CCH(35)
108				1424	0.02	5.69	0.05	δ CCH(87)
107	1399			1387	24.25	0.12	0	vCC (51) + δ CCH(23)
106				1379	5.76	1.47	0.01	ρ CH(δ CHH(91))
105		1366	1370	1369	16.55	1.54	0.01	ρ CH(δ CHH(89))
104	1358			1358	26.58	1.21	0.01	ρ CH(δ CHH(86))
103				1355	0.01	1.42	0.01	ρ CH(δ CHH(85))
102				1340	340.62	339.99	3.13	vCC (54)
101				1333	581.96	130.03	1.21	vCB (59) + δ CCH(19)
100				1328	1.73	2.91	0.03	vCC (68)
99				1325	172.27	99.82	0.94	vCC (69) + δ CCH(10)
98		1311	1310	1303	108.1	0.54	0.01	vCC (46) + δ CCH(56) + δ CCB(11)
97				1299	23.2	4.97	0.05	vCC (11) + δ CCH(47)
96				1294	2.01	105.88	1.03	δ CCC(12) + δ CCH(53)
95				1277	15.6	2.94	0.03	δ CCH(66)
94				1255	34.36	0.14	0	vCC (74)
93		1243	1240	1240	58.73	21.01	0.22	vCC (22) + δ CCH(28)
92	1227		1220	1221	0.45	4.8	0.05	vCC(33) + δ CCH(16) + δ CHH(10) + τ CCOC(27)
91				1215	11.56	155.4	1.68	vCC (50)
90				1206	90.99	45.84	0.5	vCN (53) + δ CCH(14)
89				1192	25.23	1.53	0.02	vCC (24) + δ CCH(34) + δ COB(12)
88				1168	0.11	1.76	0.02	vCC(11) + δ CCH(50)
87				1154	23.74	117.2	1.38	vCC(11) + δ CCH(46)
86				1143	0.01	1.82	0.02	δ CCH(76)
85				1141	25.83	1.72	0.02	vCC(37) + δ CCH(32)
84	1138			1135	6.27	10.93	0.13	δ CCH(66)
83				1130	274.3	17.07	0.21	δ CCH(46)
82				1104	7.61	0.01	0	vCC(30) + δ CCH(41)
81				1096	3.44	0.32	0	δ CCH(65)
80	1089			1088	28.5	9.8	0.13	δ CCC(29) + δ CHH(10)
79				1087	18.34	0.85	0.01	vCC(21) + δ CCH(56)
78				1072	148.9	22.2	0.29	vCC(62)

Table 2 (continued)

No	Experimental wavenumbers			Theoretical wavenumber				PED (>10%)
	FT-IR	FT-Raman	Dis-Raman	Scaled	I _{IR}	S _{Ra}	I _{Ra}	Assignments ^a
77		1015	1010	1014	7.5	0.89	0.01	$\nu_{\text{CC}}(53) + \delta_{\text{CCH}}(26)$
76				1007	1.42	73.19	1.06	$\nu_{\text{CC}}(50) + \delta_{\text{CCH}}(18)$
75				1003	33.61	9.94	0.15	$\delta_{\text{CCC}}(86)$
74				987	0.08	3.47	0.05	$\delta_{\text{CHH}}(10) + \tau_{\text{CCCH}}(66)$
73				986	6.36	8.21	0.12	$\nu_{\text{CC}}(36) + \delta_{\text{CC}}(43)$
72				978	0.03	1.59	0.02	$\delta_{\text{CCH}}(81)$
71				965	0.58	0.05	0	$\tau_{\text{CCNH}}(84) + \tau_{\text{CCCN}}(10)$
70				957	0.02	0.33	0.01	$\tau_{\text{CHCH}}(90)$
69				945	0	0.08	0	$\tau_{\text{CCCC}}(12) + \tau_{\text{CHCH}}(70)$
68				944	0.14	0.08	0	$\tau_{\text{CHCH}}(93)$
67				937	32.12	7.89	0.13	$\nu_{\text{CC}}(44) + \delta_{\text{CCH}}(39)$
66				927	2.25	3.63	0.06	$\nu_{\text{CC}}(32) + \delta_{\text{CCH}}(44)$
65				923	1.61	14.84	0.25	$\nu_{\text{CC}}(28) + \delta_{\text{CCC}}(24)$
64				910	1.3	0.37	0.01	$\tau_{\text{CCCH}}(85)$
63				909	0.03	0.07	0	$\tau_{\text{CCCH}}(94)$
62				906	0	3.9	0.07	$\nu_{\text{CC}}(24) + \delta_{\text{CCH}}(58)$
61				903	6.07	0.9	0.02	$\nu_{\text{CC}}(12) + \delta_{\text{CCC}}(26)$
60				901	0.19	2.79	0.05	$\nu_{\text{CC}}(44) + \delta_{\text{CCH}}(39)$
59	848			841	0.65	3.17	0.06	$\tau_{\text{CCCH}}(80) + \tau_{\text{CCCN}}(11)$
58				836	2.02	1.48	0.03	$\tau_{\text{CCCH}}(85)$
57				835	62.68	11.07	0.21	$\nu_{\text{CC}}(59) + \delta_{\text{CHH}}(14)$
56				830	1.91	12.11	0.23	$\tau_{\text{CCCH}}(86)$
55				829	10.29	0.04	0	$\tau_{\text{CCCH}}(65)$
54				813	4.42	0.07	0	$\nu_{\text{CC}}(68)$
53				804	9.08	28.81	0.58	$\nu_{\text{CC}}(30) + \delta_{\text{COB}}(42)$
52				762	2.14	1.18	0.03	$\tau_{\text{CCCH}}(12) + \tau_{\text{CCCN}}(63)$
51	746			748	0.26	6.4	0.14	$\delta_{\text{CCC}}(58)$
50				741	45.15	0.45	0.01	$\tau_{\text{CCCH}}(16) + \tau_{\text{CCCN}}(64)$
49				739	30.2	0.3	0.01	$\tau_{\text{CCCH}}(19) + \tau_{\text{CCCN}}(51)$
48				727	1.44	6.39	0.15	$\tau_{\text{CCCH}}(89)$
47		719	717	716	51.36	0.79	0.02	$\tau_{\text{CCCH}}(51) + \tau_{\text{CCCN}}(22)$
46				709	1.08	35.18	0.86	$\nu_{\text{CC}}(27) + \delta_{\text{CCB}}(47)$
45				653	0	3.96	0.11	$\nu_{\text{CC}}(19) + \delta_{\text{CCC}}(52)$
44	652			652	51.53	0.45	0.01	$\tau_{\text{CCCB}}(67)$
43				636	9.56	16.19	0.46	$\nu_{\text{CC}}(60) + \delta_{\text{CCC}}(13)$
42				632	1.55	4.32	0.12	$\nu_{\text{CC}}(10) + \delta_{\text{CCC}}(72)$
41				616	1.42	2.99	0.09	$\delta_{\text{CCC}}(60)$
40				608	1.67	2.03	0.06	$\delta_{\text{CCC}}(79)$
39				565	0.33	0.66	0.02	$\tau_{\text{CCCC}}(88)$
38				562	3.39	0.11	0	$\tau_{\text{CCCC}}(58) + \tau_{\text{CCCH}}(15)$
37				559	3.77	2.63	0.09	$\nu_{\text{CC}}(22) + \delta_{\text{COB}}(53)$
36				519	3.96	6.39	0.24	$\nu_{\text{CC}}(10) + \delta_{\text{CCC}}(61)$
35				504	0.16	0.21	0.01	$\delta_{\text{CCB}}(52) + \tau_{\text{CCCN}}(10)$
34				502	3.6	1.21	0.05	$\nu_{\text{CC}}(26) + \tau_{\text{CCCO}}(50)$
33				495	0.68	0.12	0	$\delta_{\text{CCB}}(14) + \tau_{\text{CCCN}}(36)$
32	437			438	9.39	11.38	0.56	$\delta_{\text{CCC}}(12) + \tau_{\text{CCCC}}(60)$
31				433	3.93	4.89	0.24	$\delta_{\text{CCC}}(26) + \tau_{\text{CCCC}}(22)$
30				430	6.18	0.87	0.04	$\delta_{\text{CCO}}(49)$
29				419	4.35	0.09	0	$\tau_{\text{CCCC}}(74)$
28				408	0.06	3.75	0.2	$\nu_{\text{CC}}(10) + \delta_{\text{COB}}(41)$
27				406	0.63	0.21	0.01	$\delta_{\text{CCN}}(38)$
26				404	4.05	20.6	1.14	$\tau_{\text{CCCN}}(84) + \tau_{\text{CCNH}}(12)$
25				361	0.1	0.8	0.05	$\tau_{\text{CCCO}}(57)$
24				351	1.67	1.11	0.08	$\delta_{\text{CCB}}(61)$
23				342	1.37	2.28	0.16	$\delta_{\text{CCO}}(51)$
22				313	0.04	0.04	0	$\delta_{\text{CCB}}(28) + \tau_{\text{CCCH}}(18) + \tau_{\text{CCCB}}(23)$
21			292	289	0.06	0.03	0	$\tau_{\text{CCCH}}(56) + \tau_{\text{CCCB}}(16)$
20				286	0.01	0.5	0.05	$\delta_{\text{CCO}}(36) + \tau_{\text{CCCH}}(29) + \tau_{\text{CCOH}}(10)$
19				282	1.58	13.26	1.28	$\tau_{\text{CCCC}}(92)$
18				281	0.01	1.22	0.12	$\tau_{\text{CCCH}}(13) + \tau_{\text{CCCB}}(48)$
17				277	0	0.48	0.05	$\delta_{\text{CCO}}(25) + \tau_{\text{CCCH}}(58)$
16				261	0.55	0.94	0.1	$\tau_{\text{CCCB}}(14) + \tau_{\text{CCCO}}(44) + \tau_{\text{CCOH}}(11)$
15				231	0.87	2.9	0.39	$\delta_{\text{CCB}}(14) + \delta_{\text{CCN}}(11) + \tau_{\text{CCOH}}(32)$
14				227	0.82	2.38	0.33	$\delta_{\text{CCC}}(51) + \tau_{\text{CCOH}}(15)$
13				218	0.15	0.57	0.08	$\delta_{\text{CCO}}(10) + \tau_{\text{CCOH}}(49)$
12				216	0.24	0.24	0.04	$\delta_{\text{CCO}}(13) + \tau_{\text{CCOH}}(63)$
11				146	0.8	1.23	0.36	$\tau_{\text{CCCC}}(85)$
10				138	0.32	2	0.64	$\delta_{\text{CCB}}(13) + \tau_{\text{CCCB}}(59)$
9				134	0.01	2.26	0.76	$\nu_{\text{CC}}(11) + \delta_{\text{COB}}(10) + \delta_{\text{CCC}}(26) + \delta_{\text{CCB}}(12)$
8				107	1.03	0.17	0.09	$\tau_{\text{CCCN}}(86)$
7				90	0.02	0.6	0.41	$\tau_{\text{CCBO}}(71)$
6				77	0.19	3.17	2.96	$\delta_{\text{CCB}}(60)$
5				57	0.35	2.91	4.74	$\delta_{\text{CCB}}(20) + \tau_{\text{CCCN}}(36) + \tau_{\text{CCCB}}(11)$

(continued on next page)

Table 2 (continued)

No	Experimental wavenumbers			Theoretical wavenumber				PED (>10%)
	FT-IR	FT-Raman	Dis-Raman	Scaled	I _{IR}	S _{Ra}	I _{Ra}	Assignments ^a
4				57	2.26	15.31	25	τ CCCN(92)
3				33	0.18	5.32	24.2	δ CCN(10) + δ CCB(26) + τ CCCN(33)
2				19	0.24	2.35	30.64	τ CCCB(71)
1				16	0.12	5.23	100	τ CCCN(88)

^a n; stretching, d; bending (d; in plane bending g; out of plane bending), t; torsion, sm; symmetric, asm; asymmetric

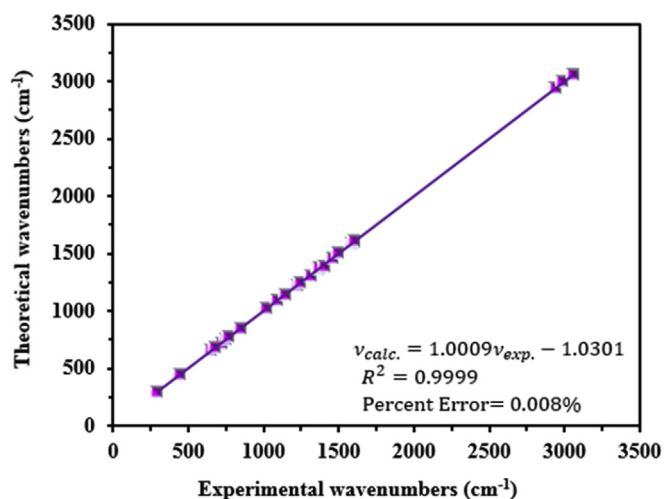


Fig. 3. Correlation graphic of calculated and experimental frequencies for 9-CPBAPE.

title molecule, these vibrations were obtained at 1206 cm⁻¹ by DFT calculations. This band is a mixed band with CCH bending vibration

as it is evident from PED calculations.

The C–B stretching modes are calculated at 1333 cm⁻¹ by using B3LYP/6-311G(d,p) with the PED contribution 59% in this work. The calculated C–B stretching modes were computed at 1345, 899, 635 cm⁻¹ for 2,3 difluorophenylboronic acid, observed at 1352 and 1351 cm⁻¹ as the bands in FT-IR and FT-Raman, respectively [35]. C–B stretching modes determined at 1339 cm⁻¹ (1346 cm⁻¹ in FT-IR), for 3BrPBA [36].

3.7. NBO analysis

In quantum chemistry, natural bond orbital (NBO) analysis is an important technique for studying hybridization and covalent effects. We used in computational chemistry to calculate the distribution of electron density in atoms and in bonds between atoms. Weak occupancies of the valence anti-bonds signal irreducible departures from an idealized localized Lewis structure, which means true “delocalization effects” [37]. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor–acceptor interaction. The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis

Table 3

Second order perturbation theory analysis of Fock matrix in NBO basis for 9-CPBAPE.

Donor (i)	Type	ED/e	Acceptor(j)	Type	ED/e	E ⁽²⁾ ^a (KJ mol ⁻¹)	E(j)–E(i) ^b (a.u)	F(i,j) ^c (a.u)
C1–C2	σ	1.973	C2–C3	σ^*	0.029	4.58	1.23	0.067
C1–C6	σ	1.977	C2–C13	σ^*	0.031	4.96	1.22	0.069
C1–C6	π	1.707	C2	LP(1)	1.052	43.21	0.15	0.091
			C4–C5	π^*	0.337	21	0.28	0.069
C12–C13	σ	1.959	C13–C15	σ^*	0.024	3.89	1.24	0.062
C12–C14	σ	1.974	C12–C13	σ^*	0.029	5.06	1.25	0.071
			C14–C16	σ^*	0.015	3.38	1.29	0.059
C12–C14	π	1.638	C13–C15	π^*	0.414	17.16	0.3	0.064
			C16–C18	π^*	0.390	22.23	0.29	0.072
C13–C15	π	1.631	C12–C14	π^*	0.418	21.37	0.27	0.069
			C16–C18	π^*	0.390	20.07	0.28	0.067
C22–C24	σ	1.972	C22–C23	σ^*	0.028	4.55	1.26	0.068
			C24–C27	σ^*	0.016	3.46	1.29	0.06
C22–C24	π	1.653	C23–C25	π^*	0.304	18.01	0.29	0.066
			C27–C29	π^*	0.351	21.35	0.3	0.071
C23–C25	σ	1.976	C22–C23	σ^*	0.028	3.64	1.26	0.061
			C25–C29	σ^*	0.023	3.46	1.27	0.059
C23–C25	π	1.660	C22–C24	π^*	0.374	22.65	0.28	0.071
			C27–C29	π^*	0.351	18.21	0.29	0.065
C27–C29	π	1.627	C22–C24	π^*	0.374	21.01	0.27	0.067
			C23–C25	π^*	0.304	21.76	0.28	0.07
C12–C14	π^*	0.418	C13–C15	π^*	0.414	320.52	0.01	0.079
C22–C24	π^*	0.374	C27–C29	π^*	0.351	234.49	0.01	0.084
C2	LP(1)	1.052	C1–C6	π^*	0.322	72.79	0.14	0.108
			C13–C15	π^*	0.414	62.25	0.14	0.097
C3	LP*(1)	1.010	C4–C5	π^*	0.337	62.81	0.15	0.105
B32	LP*(1)	0.393	C27–C29	π^*	0.351	100.53	0.03	0.078

^a E(2) means energy of hyper conjugative interaction (stabilization energy).

^b Energy difference between donor and acceptor *i* and *j* NBO orbitals.

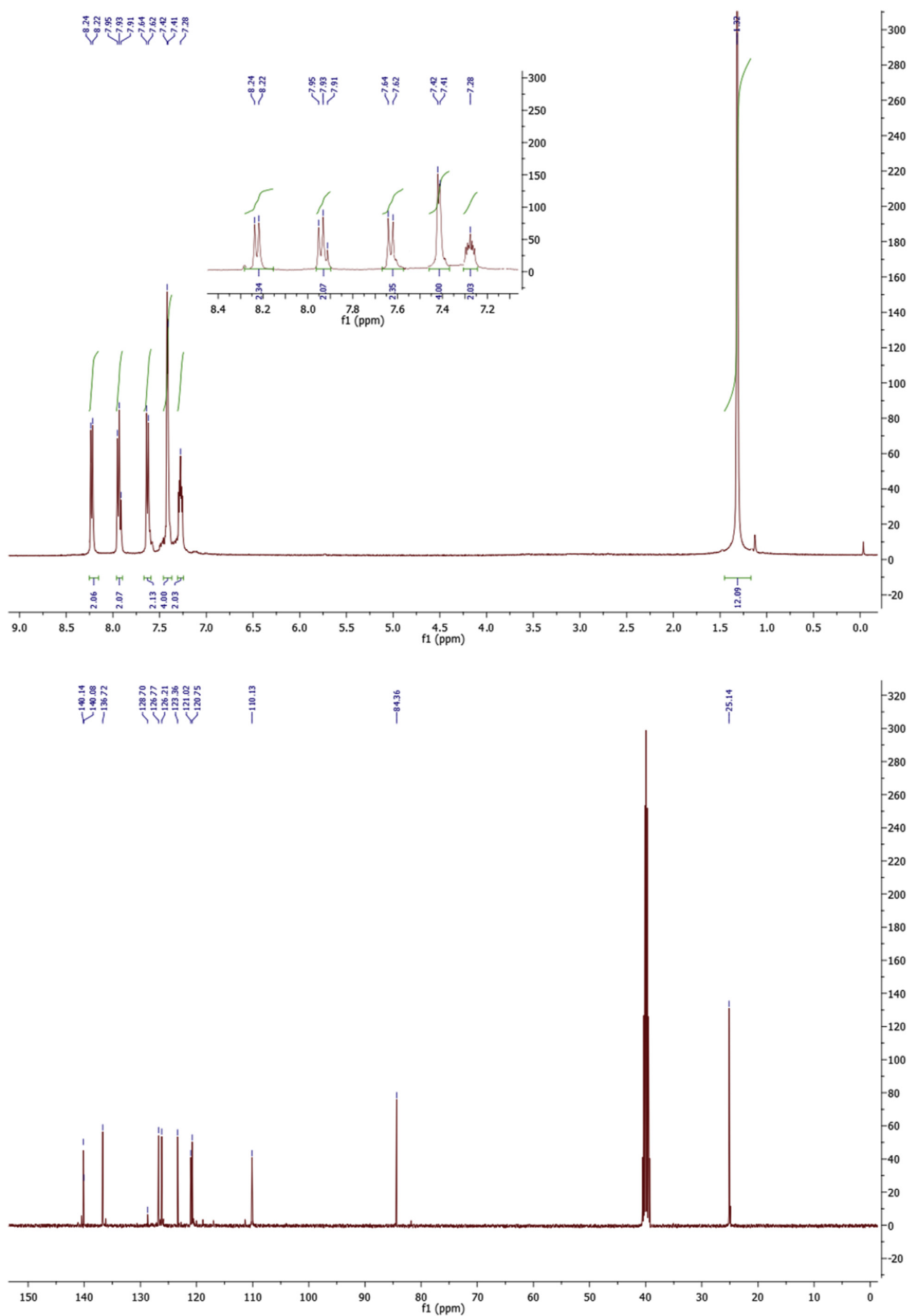


Fig. 4. ¹H and ¹³C NMR spectra of the 9-CPBAPE in DMSO solution.

Table 4
Experimental and calculated chemical shifts (ppm) of 9-CPBAPE.

Atom	Calculated			Experimental
	DMSO	Ethanol	Gas	DMSO
C22	146.66	146.67	147.08	140.19
C3	145.55	145.56	145.55	140.11
C12	145.55	145.56	145.55	140.11
C25	140.65	140.66	140.91	136.72
C27	140.65	140.66	140.91	136.72
C29	132.59	132.59	132.10	128.70
C24	130.50	130.48	129.97	126.79
C23	130.50	130.48	129.97	126.79
C16	129.72	129.69	129.14	126.24
C5	129.72	129.69	129.14	126.24
C2	127.32	127.35	127.98	123.38
C13	127.32	127.35	127.98	123.38
C1	123.82	123.80	123.44	121.02
C15	123.82	123.80	123.44	121.02
C6	123.66	123.64	123.44	120.76
C18	123.66	123.64	123.44	120.76
C14	112.20	112.18	111.65	110.14
C4	112.20	112.18	111.65	110.14
C36	89.70	89.67	88.91	84.33
C35	89.70	89.67	88.91	84.33
C49	25.99	25.99	26.13	25.15
C45	25.99	25.99	26.13	25.15
C37	22.96	22.97	23.36	25.15
C41	22.96	22.97	23.36	25.15
H7	8.40	8.39	8.20	8.25
H19	8.40	8.39	8.20	8.25
H31	8.21	8.21	8.17	7.95
H30	8.21	8.21	8.17	7.95
H28	7.68	7.68	7.56	7.65
H26	7.68	7.68	7.56	7.65
H9	7.59	7.58	7.41	7.43
H20	7.59	7.58	7.41	7.43
H17	7.52	7.52	7.38	7.43
H8	7.52	7.52	7.38	7.43
H10	7.48	7.48	7.32	7.31
H21	7.48	7.48	7.32	7.31
H40	1.55	1.55	1.55	1.34
H44	1.55	1.55	1.55	1.34
H46	1.49	1.49	1.49	1.34
H50	1.49	1.49	1.49	1.34
H38	1.45	1.45	1.46	1.34
H42	1.45	1.45	1.46	1.34
H48	1.26	1.26	1.28	1.34
H52	1.26	1.26	1.28	1.34
H47	1.22	1.22	1.03	1.34
H51	1.22	1.22	1.03	1.34
H39	1.20	1.19	0.97	1.34
H43	1.20	1.19	0.97	1.34

orbital. The intramolecular interactions were observed an increase in electron density (ED) in (C–C) anti-bonding orbital that weakens the respective bonds. The electron density of conjugated bonds of aromatic ring (1.97e) clearly demonstrates strong delocalization for 9-CPBAPE molecule. The occupancy of π bonds is less than that of σ bonds leads to more delocalization.

The intramolecular hyperconjugative interaction of the σ (C12–C14) distributed to σ^* (C13–C15), (C16–C18) leads to less stabilization of 5.06, 3.38 kJ/mol for 9-CPBAPE. These have enhanced further to conjugate with antibonding orbital of π^* (C13–C15), (C16–C18) which leads to strong delocalization of 17.16, 22.23 kJ/mol. This enhanced π^* (C12–C14) NBO further conjugates with π^* (C13–C15), resulting in an enormous stabilization energy of 320.52 kJ/mol, as shown in Table 3.

3.8. NMR analysis

^{13}C and ^1H NMR chemical shifts calculations of molecule were carried out in DMSO, ethanol and gas phase by using B3LYP functional with 6-311G(d,p) basis set with the GIAO method [38,39].

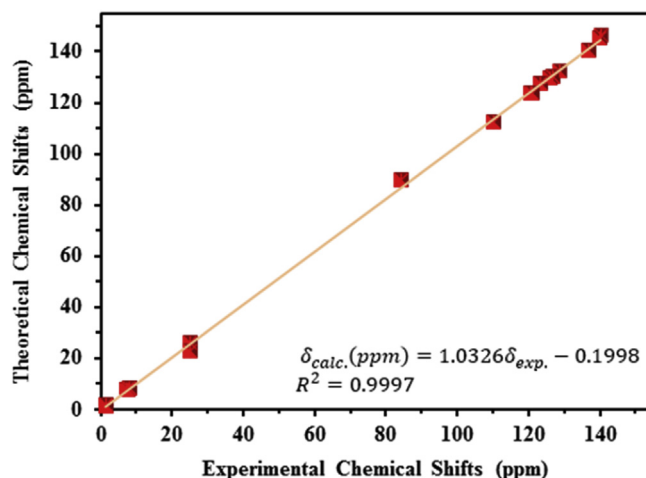


Fig. 5. Correlation graphic of calculated and experimental (total) chemical shifts of the 9-CPBAPE.

Table 5

The experimental and computed (TD-B3LYP/6-311(d,p)) absorption wavelength λ (nm), excitation energies E (eV), absorbance and oscillator strengths (f) of 9-CPBAPE molecule.

DMSO			Theoretical Gas			Ethanol			Experimental (DMSO)		Experimental (Ethanol)	
λ (nm)	E (eV)	f	λ (nm)	E (eV)	f	λ (nm)	E (eV)	f	λ (nm)	E (eV)	λ (nm)	E (eV)
322.66 (98 $\rightarrow$ 99) $\pi \rightarrow \pi^*$	3.8426	0.2381	328.69 (98 $\rightarrow$ 99) $\pi \rightarrow \pi^*$	3.7720	0.1879	322.64 (98 $\rightarrow$ 99) $\pi \rightarrow \pi^*$	3.84288	0.2320	324	3.8310	324	3.8310
314.41 (98 $\rightarrow$ 100) $\pi \rightarrow \pi^*$	3.9433	0.0756	312.52 (98 $\rightarrow$ 100) $\pi \rightarrow \pi^*$	3.9673	0.0579	314.28 (98 $\rightarrow$ 100) $\pi \rightarrow \pi^*$	3.9450	0.0752	294	4.2219	292	4.4254
286.65 (97 $\rightarrow$ 99) $\pi \rightarrow \pi^*$	4.3253	0.0032	295.06 (97 $\rightarrow$ 99) $\pi \rightarrow \pi^*$	4.2021	0.0004	286.83 (97 $\rightarrow$ 99) $\pi \rightarrow \pi^*$	4.3226	0.0029	—	—	—	—

Fig. 4 shows ^{13}C and ^1H NMR spectra of the molecule and the spectrum values are given in Table 4. ^1H NMR chemical shift signal of carbazole ring in molecule was calculated (with respect to TMS) in the range of 7.48–8.40 ppm and was observed in the range of 7.31–8.25 ppm in DMSO. Chemical shifts aromatic protons of the title compound were calculated in the ranges 7.68–8.21 ppm and experimental shifts of the solution prepared in DMSO are observed in the range of 7.65–7.95 ppm. The calculated proton NMR chemical shifts are coherent with experimental values. Chemical shifts of aromatic carbons give signals in overlapped areas of the spectrum in the range of 100–150 ppm [40,41]. In this study, the chemical shift values of phenyl ring carbons were calculated in the range of 146.66–130.50 ppm and were observed in the range of 140.19–126.79 ppm in DMSO. The proton chemical shift values of

the carbazole ring are in agreement with experimental data.

Correlation graphics between the experimental and theoretical chemical shifts were drawn in Fig. 5. Also the correlation graphics of ^1H and ^{13}C NMR were given in Fig. S3. The relations between experimental chemical shifts (δ_{exp}) and the calculated chemical shifts described.

4. Electronic properties

4.1. UV–vis analysis

Electronic absorption spectra of the compound were computed with TD-DFT-B3LYP/6-311G(d,p) basis set in DMSO, ethanol and gas phase. The calculated and experimental absorption wavelengths,

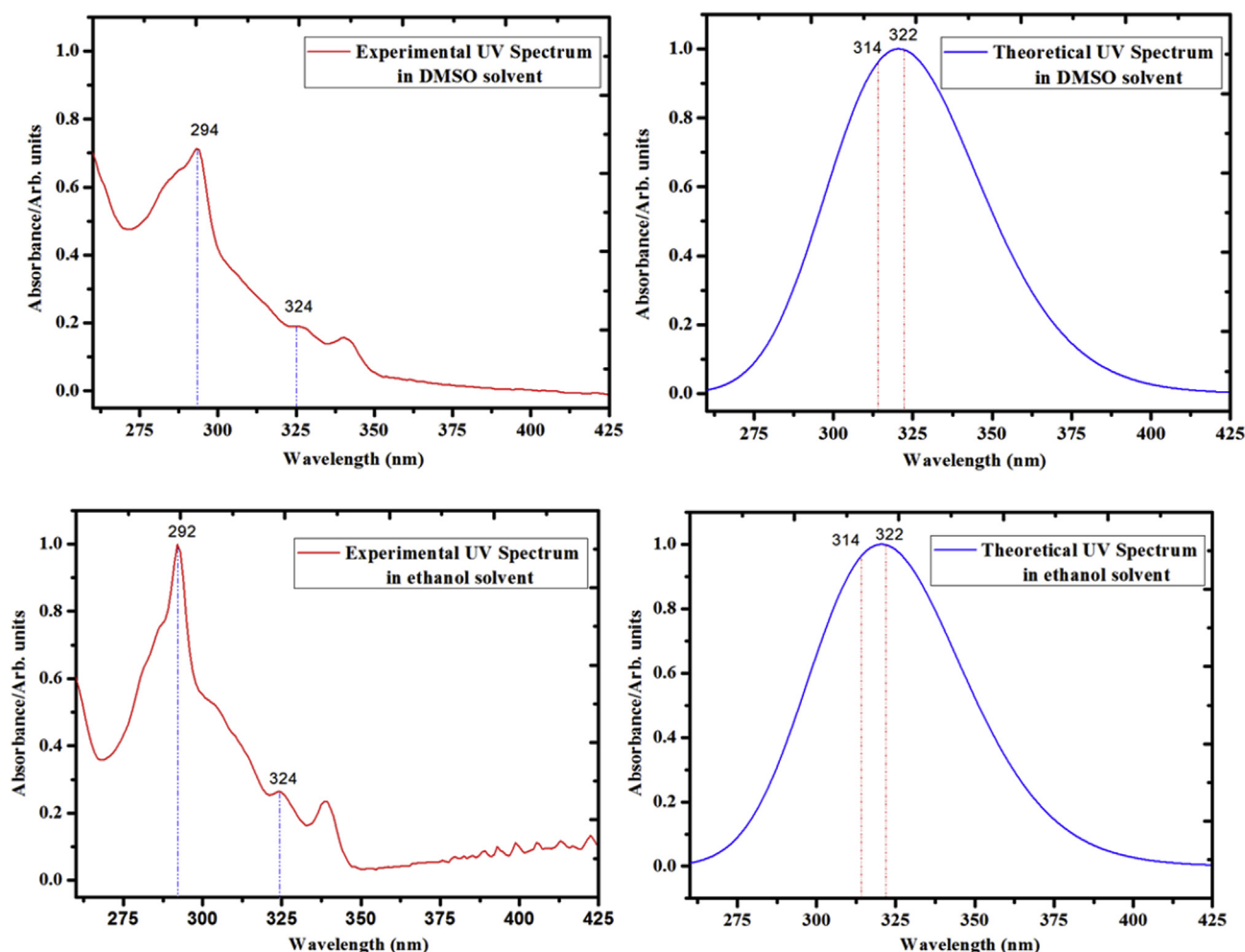


Fig. 6. The theoretical and experimental UV–vis spectrum (DMSO and ethanol) of the 9-CPBAPE.

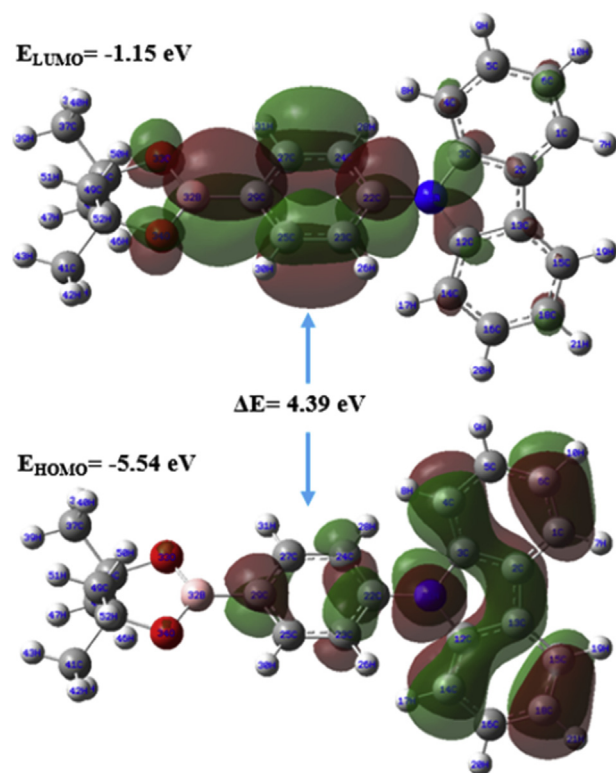


Fig. 7. The frontier molecular orbitals of the 9-CPBAPE for gas phase.

excitation energies and electronic values of molecule are given in Table 5. Absorption wavelengths for 9-CPBAPE were calculated at 322.66, 314.41 and 286.65 nm in DMSO and at 322.64, 314.28 and 286.83 nm in ethanol. The experimental and theoretical electronic absorption spectra appear in DMSO and ethanol for the title compound and are given in Fig. 6. As it can be seen from Fig. 6, experimental electronic absorption spectra showed two bands at 294, 324 nm in DMSO and at 292, 324 nm in ethanol.

4.2. Frontier molecular orbitals analysis

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMO). While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. The total energy, energy gap and dipole moment affect the stability of a molecule. The HOMO and LUMO energy levels were calculated with TD-DFT/B3LYP/6-311G(d,p)

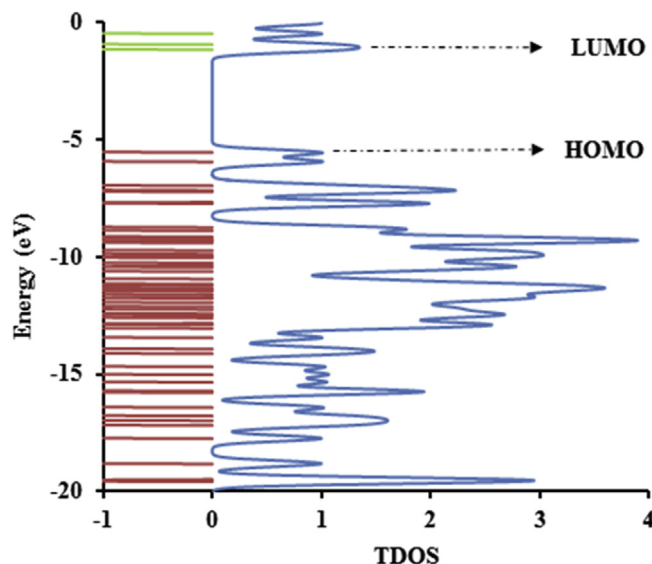


Fig. 8. The total electronic density of states (TDOS) diagram of the 9-CPBAPE.

method in DMSO, ethanol and gas phase. The calculated energy values are given in Table 5. This is also used by the frontier electron density for predicting the most reactive position in p-electron systems and also explains several types of reaction in conjugated system [42].

Four important MOs were examined: the second highest and the highest occupied, the lowest and the second lowest unoccupied MOs are denoted as HOMO–1, HOMO, LUMO and LUMO+1, respectively. The plots of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are shown in Fig. 7 for gas phase. It is clear from the figure, while HOMO orbitals are localized on the carbazole rings, LUMO orbitals are localized on the phenyl ring and boronic group of 9-CPBAPE. The energy gap is a critical parameter in determining molecular electrical transport properties. The energy difference between HOMO and LUMO levels are 4.48 eV in DMSO and ethanol solution, but it is 4.39 eV in gas phase for 9-CPBAPE. Besides, chemical hardness, electronegativity, chemical potential and electrophilicity index values were calculated for the molecule and are given Table 6.

4.3. Total, partial and population density of states (TDOS, PDOS and OPDOS) spectra analysis

The TDOS, PDOS, and OPDOS or COOP (Crystal Orbital Overlap Population) [43–45] were calculated and created by convoluting

Table 6

The calculated energies values of 9-CPBAPE using by the TD-DFT/B3LYP method using 6-311G(d,p) basis set.

C_2 symmetry	Gas	DMSO	Ethanol
E_{total} (Hartree)	–1159.49487461	–1159.50421014	–1159.50387578
E_{total} (eV)	31551.01503	31551.26926	31551.25996
E_{HOMO} (eV)	–5.54	–5.79	–5.78
E_{LUMO} (eV)	–1.15	–1.31	–1.30
$E_{\text{HOMO}-1}$ (eV)	–5.92	–6.20	–6.19
$E_{\text{LUMO}+1}$ (eV)	–0.92	–1.19	–1.18
$E_{\text{HOMO}-1}-\text{LUMO}+1$ gap (eV)	5.00	5.01	5.01
$E_{\text{HOMO}}-\text{LUMO}$ gap (eV)	4.39	4.48	4.48
Chemical hardness (h)	2.20	2.24	2.24
Electro negativity (χ)	–3.35	–3.55	–3.54
Chemical potential (μ)	3.35	3.55	3.54
Electrophilicity index (ω)	2.55	2.81	2.80

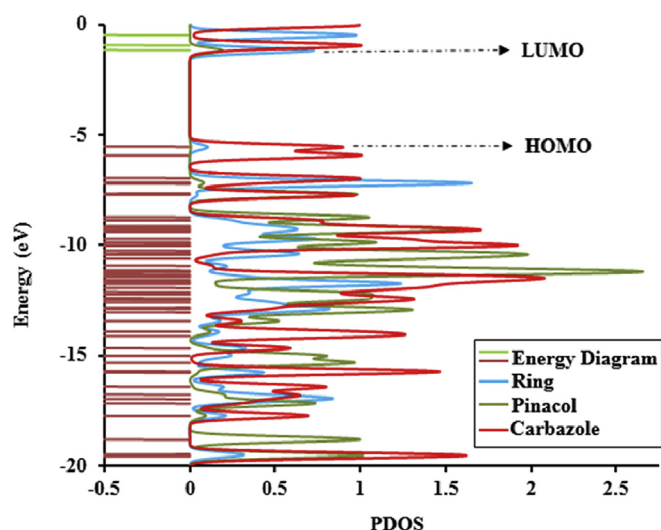


Fig. 9. The partial electronic density of states (PDOS) diagram of the 9-CPBAPE.

the molecular orbital information with Gaussian curves of unit height and FWHM of 0.3 eV by using the GaussSum 2.2 program [19] for in the border region, neighboring orbitals were investigated degenerate energy levels, given Figs. 8–10, respectively. The OPDOS shows the bonding, anti-bonding and nonbonding nature of the interaction of the two orbitals, atoms or groups. Positive value of the OPDOS shows a bonding interaction (because of the positive overlap population), negative value shows anti-bonding interaction (because of negative overlap population) and zero value shows nonbonding interactions [46]. The OPDOS diagram is shown in Fig. 10, and some of the orbitals of energy values of interaction between selected groups which are shown from figures easily, phenyl ring ↔ pinacol groups (red line) system are positive, that is bonding interaction. However, phenyl ring ↔ carbazole ring (blue line) system is negative, that is anti-bonding character.

4.4. Molecular electrostatic potential surface

The molecular electrostatic potential is interested with electronegativity and the partial charges on the different atoms of the molecule. The color scheme for the MEP surface is as follows: red

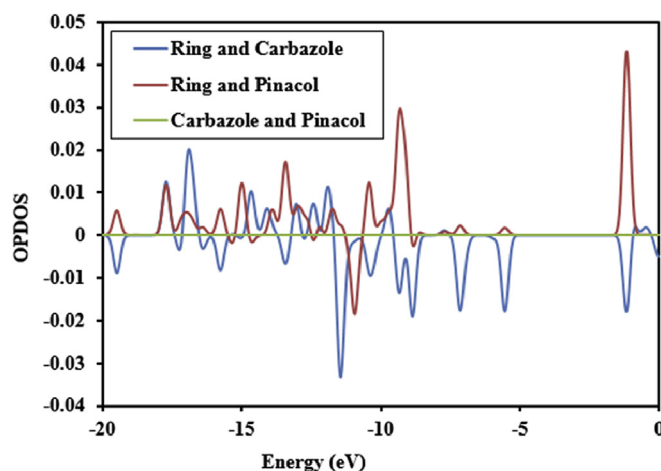


Fig. 10. The overlap population electronic density of states (OPDOS) diagram of the 9-CPBAPE.

for electron rich, partially negative charge; blue for electron lacking, partially positive charge; light blue for slightly electron deficient region; yellow for slightly electron rich region; green for neutral, respectively [47,48]. In the study, the color code maps is in the range between -0.2980 (dark red) and 0.2980 a.u. (dark blue) in compound. 3D plots and 2D contour of molecular electrostatic potential (MEP) map which is a plot of electrostatic potential mapped onto the constant electron density surface of 9-CPBAPE, are illustrated in Fig. 11 and Fig. S4. As seen from the MEPs map, while regions having the positive potential are near CH groups, the regions having the negative potential are over the oxygen atoms for 9-CPBAPE. From these results, we can say that the H atoms indicate the strongest attraction and O33 and O34 atoms indicate the strongest repulsion.

4.5. Mulliken atomic charges

Mulliken populations yield is one of the simplest pictures of charge distribution. In this work, charge distributions of 9-CPBAPE molecule were computed with B3LYP/6311G(d,p) method and shown in Fig. 12. The calculated values were presented in Table 7. The N11 atom of the carbazole ring has the highest negative charge, C3 and C12 atoms have the highest positive charge when compared to other carbon atoms of carbazole ring. The C22 atom of the phenyl ring has the highest positive charge. While B32 atom of 9-CPBAPE has high positive charge (0.516e), O33 and O34 atoms have high negative charge ($-0.335e$). This may be due to B–O intermolecular interactions.

4.6. Thermodynamic properties

The temperature dependence of the thermodynamic properties heat capacity at constant pressure (C), entropy (S) and enthalpy (H) for 9-CPBAPE were calculated with B3LYP/6-311G(d, p) method and were tabulated in Table 8. Thermodynamic functions are increasing with temperature ranging from 100 to 700 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy and enthalpy with temperatures were filled by quadratic formulas and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9992, 0.9999 and 0.9998, respectively. The corresponding fitting equations are as follows and the correlation graphs are shown in Fig. 13. It can be observed that these thermodynamic functions are increasing with temperature. The calculations performed at room temperature (298.15 K) for molecule also were listed in Table 9.

$$C = -6.4447 + 0.3973T - 2 \times 10^{-4}T^2 \quad R^2 = 0.9992$$

$$S = 63.01 + 0.3618T - 5 \times 10^{-5}T^2 \quad R^2 = 0.9999$$

$$\Delta H = -1.0599 + 0.0151T - 1 \times 10^{-4}T^2 \quad R^2 = 0.9998$$

4.7. Nonlinear optical properties and dipole moment

Nonlinear optical properties (NLO) viz, molecular polarizability (α), anisotropy of polarizability ($\Delta\alpha$), molecular first hyperpolarizability (β) and electronic dipole moment (μ) for the study compound were evaluated. These values can be obtained by a frequency job output file of Gaussian. However, α and β values of Gaussian output are in atomic units (a.u.) so they have been converted into electronic units (esu) (α ; 1 a.u. = 0.1482×10^{-24} esu, β ; 1

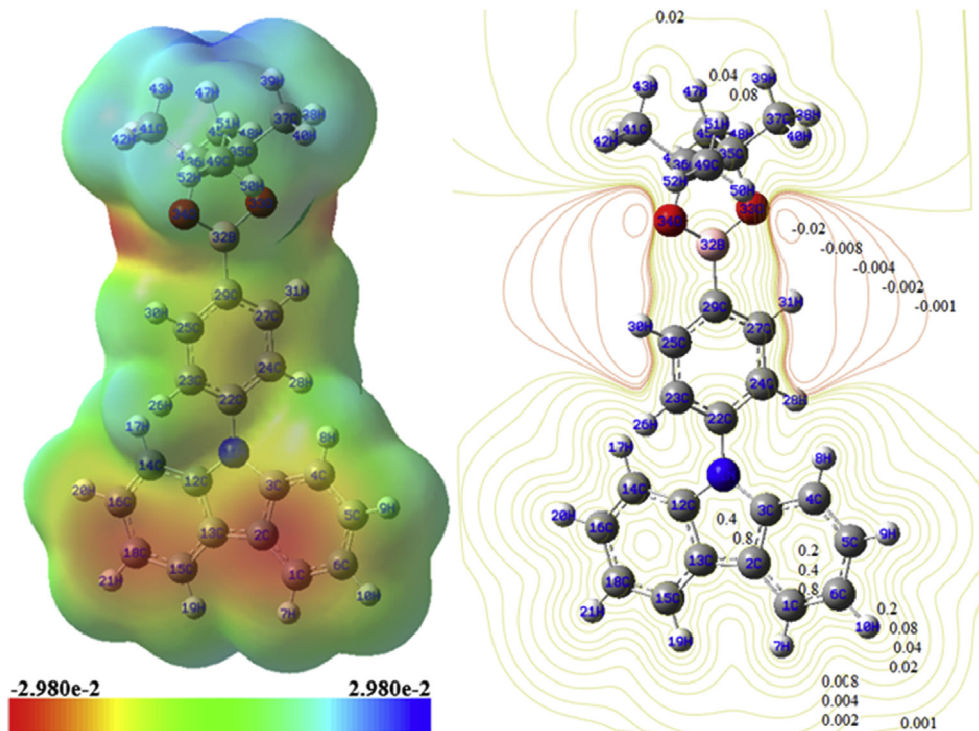


Fig. 11. Molecular electrostatic potential (MEPs) 3D and 2D contour map for 9-CPBAPE.

a.u. = 8.6393×10^{-33} esu). The calculated parameters and electronic dipole moment for 9-CPBAPE are tabulated in Table 10. It is well known that the higher values of dipole moment, molecular polarizability, and hyperpolarizability are important for more active NLO properties. 9-CPBAPE has relatively homogeneous charge distribution and it does not have large dipole moment. The calculated value of dipole moment was found to be 3.8634 Debye. The highest value of dipole moment is observed for component μ_x . In this direction, this value is equal to -3.8634 D and μ_y is the smallest one. The calculated polarizability and anisotropy of the polarizability of 9-CPBAPE are 45.0968×10^{-24} and

110.2499×10^{-24} esu, respectively. The magnitude of the molecular hyperpolarizability β , is one of important key factors in a NLO system. The B3LYP/6-311G(d,p) calculated first hyperpolarizability value (β) of NA is equal to $23593.0001 \times 10^{-33}$ esu. If we compare the common values of urea; the first hyperpolarizability, polarizability, anisotropy of the polarizability and dipole moment values of 9-CPBAPE are larger than those of urea.

5. Conclusion

9H-Carbazole-9-(4-phenyl) boronic acid pinacol ester molecule

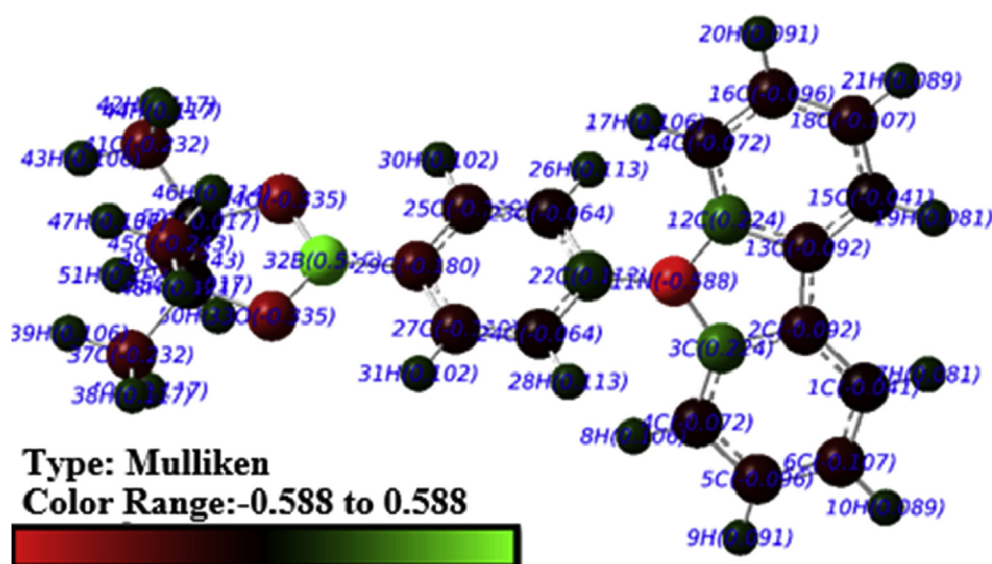


Fig. 12. The Mulliken charge distribution for 9-CPBAPE.

Table 7

Mulliken charges of 9-CPBAPE using by B3LYP/6-311G(d,p) basis set.

Atoms	Atoms	Atoms	Atoms
C1	−0.041	C14	−0.072
C2	−0.092	C15	−0.041
C3	0.224	C16	−0.096
C4	−0.072	H17	0.106
C5	−0.096	C18	−0.107
C6	−0.107	H19	0.081
H7	0.081	H20	0.091
H8	0.106	H21	0.089
H9	0.091	C22	0.112
H10	0.089	C23	−0.064
N11	−0.588	C24	−0.064
C12	0.224	C25	−0.119
C13	−0.093	H26	0.113
C27	−0.119	H28	0.113
C29	−0.179	H30	0.102
H31	0.102	B32	0.516
O33	−0.335	O34	−0.335
C35	−0.017	C36	−0.017
C37	−0.232	H38	0.117
H39	0.106	H40	0.117
C41	−0.232	H42	0.117
H43	0.106	H44	0.117
C45	−0.243	H46	0.114
H47	0.107	H48	0.121
C49	−0.243	H50	0.114
H51	0.107	H52	0.121

Table 8

Thermodynamic properties at different temperatures at the B3LYP/6311G(d,p) level for 9-CPBAPE.

T (K)	C (calmol ^{−1} K ^{−1})	S (calmol ^{−1} K ^{−1})	ΔH (kcalmol ^{−1})
100	34.534	98.824	2.236
150	49.550	116.457	4.435
200	65.058	133.393	7.397
250	81.154	150.073	11.150
298.15	96.872	166.062	15.532
300	97.473	166.675	15.715
350	113.410	183.213	21.090
400	128.452	199.616	27.240
450	142.303	215.792	34.114
500	154.869	231.656	41.648
550	166.184	247.146	49.778
600	176.352	262.223	58.445
650	185.501	276.865	67.595
700	193.758	291.067	77.180

was characterized with FT-IR and FT-Raman spectra. Vibrational frequencies were computed with DFT/B3LYP methods, with 6-311G(d,p) basis set. Scaling factor (0.967) was used to fit the calculated wavenumbers with experimental wavenumbers. The predicted electronic absorption spectra were calculated by TD-DFT

Table 9

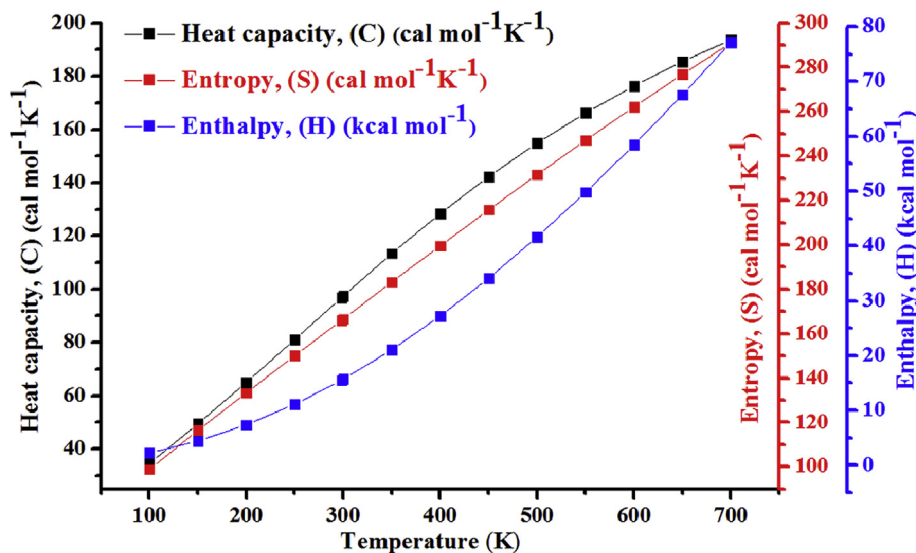
The calculated thermo dynamical parameters of 9-CPBAPE at 298.15 K for all forms in ground state at the B3LYP/6-311G(d,p) level.

Symmetry group	C2
SCF energy (a.u.)	−1159.49487461
Zero point vib.energy (kcalmol ^{−1})	268.09948
Rotational constants (GHz)	0.41045
	0.07205
	0.06501
Specific heat, Cv (calmol ^{−1} K ^{−1})	96.872
Entropy, S (calmol ^{−1} K ^{−1})	166.062

Table 10The dipole moments μ (D), the polarizability α (a.u.), the average polarizability α_0 ($\times 10^{-24}$ esu), the anisotropy of the polarizability $\Delta\alpha$ ($\times 10^{-24}$ esu), and the first hyperpolarizability β ($\times 10^{-33}$ esu) of 9-CPBAPE.

μ_x	−3.8634	β_{xxx}	20605.0543
μ_y	0.0001	β_{xyx}	−3.5489
μ_z	0.0002	β_{yzy}	3127.8268
μ_0	3.8634	β_{zyz}	1.3492
α_{xxx}	61.2206	β_{zzx}	5.5917
α_{xyx}	0.0014	β_{zzy}	40.1893
α_{yzy}	47.4627	β_{zyz}	−0.7213
α_{zzx}	−0.0084	β_{zyz}	−139.8816
α_{zyz}	−0.6470	β_{zyz}	0.0065
α_{zyz}	26.6071	β_{zyz}	0.1044
α_{total}	45.0968	β_z	23592.9995
$\Delta\alpha$	110.2499	β_y	−2.1932
		β_x	4.9747
		β	23593.0001

in gas phase and DMSO and ethanol solution. MEP, HOMO-LUMO analysis of the title compound were calculated by TD-DFT/B3LYP methods. The increase in the value of HOMO energy level of this compound can be used in optoelectronic systems such as OLED devices. ¹H and ¹³C chemical shifts were compared with experimental values recorded in DMSO solution and showing a good agreement with theoretical values. The temperature dependence of thermodynamic parameters in the range of 100–1000 K was

**Fig. 13.** The correlation graphic of heat capacity, entropy, enthalpy and temperature for 9-CPBAPE.

determined and found that all thermodynamic properties increase with the rise in temperature. The correlation equations between heat capacity, entropy and enthalpy with temperatures were found by quadratic formulas.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.molstruc.2016.03.064>.

References

- [1] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, et al., Highly efficient phosphorescent emission from organic electroluminescent devices, *Nature* 395 (1998) 151–154.
- [2] S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, et al., White organic light-emitting diodes with fluorescent tube efficiency, *Nature* 459 (2009) 234–239.
- [3] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Highly efficient organic light-emitting diodes from delayed fluorescence, *Nature* 492 (2012) 234–240.
- [4] L.X. Xiao, Z.J. Chen, B. Qu, J.X. Luo, S. Kong, Q.H. Gong, et al., Recent progresses on materials for electrophosphorescent organic light-emitting devices, *Adv. Mater.* 23 (2011) 926–952.
- [5] Y.T. Tao, C.L. Yang, J.G. Qin, Organic host materials for phosphorescent organic light-emitting diodes, *Chem. Soc. Rev.* 40 (2011) 2943–2970.
- [6] N. Toyota, H. Nakanishi, T. Ishizaka, Y.J. Pu, J. Kido, 3,3-Bicarbazole-based host materials for high-efficiency blue phosphorescent OLEDs with extremely low driving voltage, *Adv. Mater.* 24 (2012) 3212–3217.
- [7] C.W. Tang, S.A. Van Slyke, *Appl. Phys. Lett.* 51 (1987) 913–915.
- [8] C.W. Tang, S.A. Van Slyke, C.H. Chen, *J. Appl. Phys.* 65 (1989) 3610.
- [9] H. Yang, W. Joo, J. Son, H. Kang, Polymer and organic light-emitting device including the same, Patent US 2011/0156576 A1, 2011.
- [10] N.J. Lee, J.H. Jeon, I.S. In, J.H. Lee, M.C. Suh, Triphenylene containing host materials with high thermal stability for green phosphorescent organic light emitting diode, *Dyes Pigment.* 101 (2014) 221–228.
- [11] H.K. Lee, H. Ahn, C.H. Lee, Device characteristics of blue phosphorescent organic light-emitting diodes depending on the electron transport materials, *J. Inf. Disp.* 12 (2011) 219.
- [12] S.Y. Kim, J.S. Jang, J.Y. Lee, High efficiency phosphorescent organic light-emitting diodes using carbazole-type triplet exciton blocking layer, *Appl. Phys. Lett.* 90 (2007) 223505.
- [13] B.C. Krummacker, V.E. Choong, M.K. Mathai, S.A. Choulis, F. So, F. Jermann, T. Fiedler, M. Zachau, Highly efficient white organic light-emitting diode, *Appl. Phys. Lett.* 88 (2006) 113506.
- [14] K.A. King, P.J. Spellane, R.J. Watts, Excited-state properties of a triply orthometalated iridium (III) complex, *Am. Chem. Soc.* 107 (1985) 1431.
- [15] K. Nishimura, T. Inoue, Y. Mizuki, N. Yabunouchi, M. Eida, Organic electroluminescence device, Patent US 2013/0313536 A1, 2013.
- [16] J. Jeon, N. Lee, J. Lee, M. Suh, *Dyes Pigment.* 111 (2014) 116–123.
- [17] J. G. Bentsen, N. P. Goplen, Y. Li, R. R. Roberts, Electron transport agents for organic electronic devices, Patent US 2004/0214036 A1, 2004.
- [18] C. Cheng, F. Wu, Y. Tsai, Y. Chen, Triphenylene based aromatic compounds and OLEDs utilizing the same, Patent US 2011/0254436 A1, 2011.
- [19] N.M. O'Boyle, A.L. Tenderholt, K.M. Langner, *J. Comp. Chem.* 29 (2008) 839–845.
- [20] H.Y. Lin, X.B. Zhang, P. Lu, *Acta Crystallogr. A* E61 (2005) o3597–o3598.
- [21] M.H. Jamroz, *Vibrational Energy Distribution Analysis, VEDA 4 Computer Program*, Poland, 2004.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.B. Cross, Gaussian 09, Revision A, first ed., Gaussian, Inc., Wallingford, CT, 2009.
- [23] Y. Wang, Y. Zhang, H. Ni, N. Meng, K. Ma, J. Zhao, D. Zhu, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 135 (2015) 296–306.
- [24] N. Meng, Y. Zhang, Y. Wang, K. Ma, J. Zhao, G. Tang, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 121 (2014) 494–507.
- [25] <http://cccbdb.nist.gov/vibscalejust.asp>.
- [26] V. Krishnakumar, V.N. Prabavathi, *Spectrochim. Acta Part A* 71 (2008) 449.
- [27] A. Altun, K. Golcuk, M. Kumru, *J. Mol. Struct.* 637 (2003) 155.
- [28] V. Krishnakumar, R.J. Xavier, *Indian J. Pure Appl. Phys.* 41 (2003) 95–98.
- [29] K. Furic, V. Mohacek, M. Bonifacic, I. Stefanic, *J. Mol. Struct.* (1992) 267–270.
- [30] N.P. Singh, R.A. Yadav, *Indian J. Phys.* B75 (4) (2001) 347–352.
- [31] G. Varsanyi, *Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives*, vols. 1–2, Adam Hilger, 1974.
- [32] K. Pihlaja, E. Kleinpeter (Eds.), *Carbon-13 Chemical Shifts in Structural and Stereochemical Analysis*, VCH Publishers, Deerfield Beach, 1994.
- [33] M. Chen, U.V. Waghmare, C.M. Friend, E. Kaxiras, *J. Chem. Phys.* 109 (1998), 6854–6860.
- [34] J.S. Murray, K. Sen, *Molecular Electrostatic Potentials, Concepts and 399 Applications*, Elsevier, Amsterdam, 1996.
- [35] M. Karabacak, E. Kose, A. Atac, M.A. Cipiloglu, M. Kurt, *Spectrochim. Acta A* 97 (2012) 892–908.
- [36] M. Karabacak, E. Kose, A. Atac, E.B. Sas, A.M. Asiri, M. Kurt, *Spectrochim. Acta A* 1076 (2014) 358–372.
- [37] F. Weinhold, C.R. Landis, *Chem. Educ. Res. Pract. Eur.* 2 (2) (2001) 91–104.
- [38] R. Ditchfield, *J. Chem. Phys.* 56 (1972) 5688–5691.
- [39] K. Wolinski, J.F. Hinton, P. Pulay, *J. Am. Chem. Soc.* 112 (1990) 8251–8260.
- [40] H.O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR Spectroscopy*, John Wiley & Sons, Chichester, 1988.
- [41] K. Pihlaja, E. Kleinpeter (Eds.), *Carbon-13 Chemical Shifts in Structural and Stereochemical Analysis*, VCH Publishers, Deerfield Beach, 1994.
- [42] K. Fukui, T. Yonezawa, H. Shingu, *J. Chem. Phys.* 20 (1952) 722–725.
- [43] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, VCH Publishers, New York, 1988.
- [44] T. Hughbanks, R. Hoffmann, *J. Am. Chem. Soc.* 105 (1983) 3528.
- [45] J.G. Malecki, *Polyhedron* 29 (2010) 1973.
- [46] M. Chen, U.V. Waghmare, C.M. Friend, E. Kaxiras, *J. Chem. Phys.* 109 (1998) 6854.
- [47] H. Roohi, A.R. Nowroozi, E. Anjomshoa, *Comput. Theor. Chem.* 965 (2011) 211–220.
- [48] P. Munshi, T.N. Guru Row, *Acta Cryst. B* 62 (2006) 612–626, 6680.