Vibrational, NMR spectrum and orbital analysis of 3,3',5,5'-tetrabromobisphenol A: A combined experimental and computational study

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HIGHLIGHTS

- The calculated structure and vibration correspond well with the experimental data.
- The calculated NMR showed good agreement with the experimental data ($r^2 = 0.999$).
- The p- π conjugation between O and benzene leads to the red shift of C-Br vibration.
- The lower $E^{(2)}$ (LP(3)Br $\rightarrow \pi^*$ (C-C)) leads to the preferential tendency of C-Br breakage.
- The main excitation by TDDFT exhibit π - π^* character localized on the benzene rings.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 21 May 2012

Received in revised form 30 November 2012

Accepted 3 December 2012

Available online 12 December 2012

Keywords:

3,3',5,5'-Tetrabromobisphenol A

Density functional theory

Vibrational spectrum

NMR

NBO

Orbital

ABSTRACT

In the present work, the experimental and theoretical studies on the structure, vibrations, NMR and HOMO–LUMO analysis of 3,3',5,5'-tetrabromobisphenol A (TBBPA) are presented. The FT-IR (400–4000 cm^{-1}) and FT-Raman (100–4000 cm^{-1}) spectra of TBBPA were recorded. The molecular geometry, vibrational frequencies were calculated by using density functional theory (DFT) method with the 6-31G(d) basis set. The optimized geometric properties, scaled vibrational wavenumbers, IR intensities, Raman activities show good agreement with the experimental data. The assigned vibrational modes of the IR and Raman spectra were compared with the corresponding properties of the polybrominated diphenyl ethers (PBDEs). Comparative analysis indicated that the red shift of C-Br vibration could probably be ascribed to the further electronic density equalization due to the p- π conjugation between O atom and the benzene. The natural bonding orbital (NBO) analysis demonstrated that the intermolecular hyperconjugative interactions are mainly formed by the orbital overlap between σ (O-H), σ^* (C-C), π (C-C), π^* (C-C) bond orbitals. Compared to the higher $E^{(2)}$ value (33.65–34.82 kcal/mol) originated from LP(2)O to π^* (C-C), the one ($E^{(2)}$: 8.23–9.73 kcal/mol) from LP(3)Br and π^* (C-C) contributes to the preferential tendency of C-Br breakage to the C-O breakage in the transformation. The calculated NMR results obtained on the 6-31G(d) level proves good agreement with the experimental data ($r^2 = 0.999$). Analysis of isosurface of the related orbital shows that all the main excitation exhibit π - π^* character localized on the benzene rings.

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Introduction

Brominated flame retardants (BFRs) have attracted worldwide concern because of their wide dispersion, high lipophilicity and

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persistence [1]. 3,3',5,5'-tetrabromobisphenol A (TBBPA), one of the most widely used BFRs around the world [2], has been detected in various environmental matrices such as air, dust, wastewater, sediments and aquatic biota [3]. In November 2010, TBBPA has been restricted and banned on the use of in plastic infant feeding bottle by European Commission (EC) due to the potential endocrine disrupting effect [4]. To the best of our knowledge, current studies on TBBPA include the experimental work on the exposure concentration, toxicity and elimination [5–7]. However, theoretical understanding towards the properties of TBBPA is still lacking except thermodynamic property [1] and the establishment of QSAR models [8].

Theoretical and experimental understanding of the structure and vibration is urgently necessary especially for the pure chemicals of limited availability. Previous studies from our laboratory have shown that the number and position of the bromine substituent of typical polyhalogenated compounds such as polybrominated diphenyl ethers (PBDEs) have great influence on their electronic structures [9,10]. Chemical structure of TBBPA resembles that of the PBDEs. However, the metabolism mechanisms of the two in environment are quite different. The main objective of this paper is to elucidate difference between TBBPA and PBDEs. To investigate the electronic structure and spectroscopic properties with density functional theory (DFT) method, we identified the effect of the C–O–C bond or phenolic hydroxyl on the molecular properties. In addition to this, the molecular orbital analysis based on the natural bonding orbital (NBO) analysis was employed to understand the nature of the degradation processes of TBBPA.

Experiments

The solid TBBPA was purchased from Sigma–Aldrich Company with a stated purity of 97% and used as such without further purification for the spectral measurements. The FT-IR spectrum of the sample was recorded in the region 400–4000 cm^{−1} on Nicolet Nexus 870 Spectrophotometer at room temperature. The Raman spectrum of the sample was measured using 514 nm excitation line of Ar⁺ laser in the frequency region 100–4000 cm^{−1} on Renishaw in-via Raman microscope spectrophotometer. The ¹³C and ¹H NMR spectra were tested in MeOH-d₄ on Bruker DPX-300 with tetramethylsilane (TMS) as in internal standard at room temperature.

Computational details

Evidence accumulated in literature and our previous work on PBDEs [9,10] have proved that the theoretical calculations with DFT method have good performance in the prediction of the structural and vibrational properties of the polyhalogenated compounds.

With the consideration of calculation at the higher level making no significant improvement in the accuracy of the geometrical structure of polyhalogenated compounds [9,10], the method of DFT/B3LYP at the basis level of 6-31G(d) was adopted to calculate the geometrical parameters and other properties of the title molecule TBBPA in the present work. Actually, the vibrational results calculated on the level of 6-311++G(d,p) by our laboratory also showed that the basis of 6-31G(d) is sufficient. (The comparison results are presented in Figs. 1 and 2 in Supplementary.) All the calculations were performed using Gaussian 03W program package [11] with the default convergence criteria without any constraint in the potential energy surface.

Detailed assignments of the signals for each vibrational spectrum were made with a high degree of confidence by the results of the Gaussview program [12]. The NBO calculations were performed using NBO 3.1 program as implemented in the Gaussian

03W [11] package. The time-dependant density functional theory (TDDFT) was taken to calculate the vertical excitation energies and oscillator strengths to identify which functional group would preferentially get excited.

NMR Chemical shifts were calculated with the GIAO approach [9]. Absolute isotropic magnetic shielding constants were transformed into chemical shifts ($\delta_i = \sigma_{TMS} - \sigma_i$) by referring to the standard compound TMS.

Results and discussion

Geometrical structure

The structure of TBBPA optimized on the basis of B3LYP/6-31G(d) and the atomic numbering scheme are shown in Fig. 3 in Supplementary. The optimized geometrical parameters are presented in Table 1 and compared with the values in literature [13]. Both rings of TBBPA are planar in the range of 1.387–1.405 Å (C–C). The substitution of H with Br at C–H bond results a considerable increase of the bond length. As shown in Table 1, the C–Br bond length of TBBPA fall in range 1.904–1.920 Å, similar to those observed in BDE-47 and BDE-15 in our precious studies [9,10]. The bond length between the carbon and the oxygen lies at 1.350 Å, while the C–O ether bond in BDE-47 and BDE-45 are 1.370 Å [9,10]. This may be due to the intra-molecular interaction between O and benzene rings. X-ray data [13] exhibit minor stabilization of the structure owing to the intermolecular O...O contacts, which contributes the shorter distance 0.820 Å of O–H than the calculated value 0.975 Å in this work.

The two benzene rings are joined with C10 atom and the dihedral angle (AC₄–C₁₀–C₁₃–C₁₁, 118.2°) shows the atoms of C4, C10, C11, C12, C13 constitute the typical tetrahedral structure. Another calculated dihedral angle (AC₁₄–C₁₂–C₁₀–C₄, 52.9°) is in great agreement with the experimental value (54.9°) [13].

Clearly, the optimized structure with the B3LYP/6-31G(d) method could well reproduce the experimental values. The discrepancy between the calculated and the X-ray data from reference may be due to the fact that molecular packing in crystal structure was excluded in present calculations.

Vibrational spectra

Comparison of the unscaled calculated frequencies with experimental values reveals the overestimation of the former due to the

Table 1
Calculated geometric parameters of TBBPA by DFT/B3LYP/6-31G(d).

Geometrical parameter	B3LYP/6-31G(d)	Exp ^a
<i>Bond length (Å)</i>		
r _{C6–Br1}	1.920	1.877(7)
r _{C8–Br2}	1.904	1.862(7)
r _{C10–C4}	1.543	1.532(9)
r _{C10–C11}	1.548	1.533(9)
r _{C7–O3}	1.350	–
r _{O3–H23}	0.975	–
<i>Bond angle (°)</i>		
AC ₉ –C ₄ –C ₅	117.6	115.8(7)
AC ₁₄ –C ₁₂ –C ₁₀	119.4	123.6(6)
AC ₄ –C ₁₀ –C ₁₁	112.2	107.9(5)
AC ₄ –C ₉ –C ₁₀	122.9	120.5(6)
AO ₃ –C ₇ –C ₆	123.8	121.1(8)
AO ₃ –C ₇ –C ₈	119.7	119.6(8)
<i>Dihedral angle (°)</i>		
AC ₁₀ –C ₁₂ –C ₁₄ –C ₁₆	177.2	178.9(7)
AC ₄ –C ₁₀ –C ₁₃ –C ₁₁	118.2	–
AC ₁₄ –C ₁₂ –C ₁₀ –C ₄	52.9	54.9(9)

^a The experimental data taken from Ref. [14].

neglect of the anharmonicity effect in model compound. In order to improve the agreement with the experiment, it is customary to scale down the calculated harmonic frequencies. Consequently, the frequencies of C–H and O–H stretching vibrations in this study were scaled down by multiplying a factor of 0.958 [14,15] while other frequencies were scaled down by factors of 0.9613 [16]. The experimental and the scaled stimulated FT-IR and Raman spectra are presented in Figs. 1 and 2. The frequencies for main modes of vibrations are listed in Table 2. It is evident that the scaled frequencies lead to excellent agreement with the observed spectral patterns. No imaginary frequency has been observed at the optimized structure, proving that a true minimum on the potential.

C–H and C–C vibrations

Aromatic structure commonly shows multiple weak bands in the region 3000–3100 cm^{-1} , which is the characteristic region for the identification of C–H stretching vibrations [17]. The bands in this range are not affected appreciably by the nature of substituents [18]. In the FT-IR spectrum, the frequency 3070 cm^{-1} was assigned to the C–H vibration of benzene. It should be noted that the calculated bands around 2995 cm^{-1} were ascribed to the C–H stretching modes of the methyl groups of TBBPA.

In the substituted benzenes, the C–H in-plane and out-of-plane bending vibrations are often coupled and appear in the frequency range 1000–1300 cm^{-1} [19] and 667–900 cm^{-1} [20], respectively. In this work, the peaks at 1180 cm^{-1} , 1240 cm^{-1} , 1320 cm^{-1} in IR were assigned to C–H in-plane bending vibrations. The FT-IR bands at 779 cm^{-1} and Raman bands at 854 cm^{-1} confirms the C–H out-of-plane bending vibrations. As the vibration frequencies owing to para- and ortho-substitution are strongly mixed [18], we were unable to distinguish the modes clearly. The calculated intensities and frequencies due to C–H stretching, in-plane and out-of-plane bending vibrations are coinciding very well with the observed frequencies.

Generally, the ring C–C stretching vibrations of benzene derivative occur in the region 1400–1650 cm^{-1} [19]. Present work has

shown that the typical bands of this vibration are of variable intensity and observed at 1240 cm^{-1} , 1270 cm^{-1} , 1320 cm^{-1} , 1400 cm^{-1} , 1470 cm^{-1} in IR spectrum. It should be mentioned here that the IR signal of this vibration mode in TBBPA is similar to the ones of BDE-15 and BDE-47 [9,10]. Nevertheless, only one peak at 1599 cm^{-1} in Raman with intensive activity was observed and we speculated that the phenol hydroxyl substitution and the higher signal base line lead to the prominent decrease of other relative peaks in recorded spectra. In this work, the IR spectrum assignments for another ring are in good agreement with literature values [9,10,19].

C–O and O–H vibrations

Phenols always show characteristic O–H stretching band in the region 3200–3650 cm^{-1} [19]. The prominent IR intensity (101.6) and Raman activity (101.6) of the calculation show good agreement with the experimental observations.

The C–O stretching vibration of phenol normally lies in the region of 1200–1300 cm^{-1} while the O–H in-plane bending vibration is often observed near 1260–1420 cm^{-1} . However, as suggested by Balachandran et al. [19], these two vibration modes are usually not independent because they are always coupled with the vibrations of adjacent groups. For TBBPA, the frequencies at 1270 cm^{-1} (IR) and 1280 cm^{-1} (Raman) demonstrated interaction between the C–O and the C–C stretching vibration. The O–H in-plane bending and the ring skeleton vibration jointly produced bands near 1240 cm^{-1} and 1400 cm^{-1} with moderate intensity in IR spectrum.

C–Br vibrations

As Balachandran et al. reported [19], the C–X stretching mode has red shift relative to the one in the C–H bond. The reason is because of the decreased force constant and increased the reduced mass arising from the inductive effect of the halogen atom. Mooney et al. assigned vibrations of C–X (X = Cl, Br, I) in the wide frequency range of 480–1129 cm^{-1} [21,22]. Compared to the C–Br vibrational modes for BDE-47 (348 cm^{-1} , 313 cm^{-1} , and 275 cm^{-1})

Fig. 1. Comparison of the calculated and the experimental IR spectra of TBBPA: (a) and (b) present the observed spectra and the scaled spectra by B3LYP/6-31G(d), respectively.

Fig. 2. Comparison of the calculated and the experimental Raman spectra of TBBPA: (a) and (b) present the observed spectra and the scaled spectra by B3LYP/6-31G(d), respectively.

Table 2

Comparison of the main calculated vibrational frequencies and experimental (FT-IR and Raman) spectra of TBBPA.

No.	Approximate assignments ^a	Experimental freq. ^b		Calculated freq. ^c			
		IR	Raman	Unscaled	Scaled	I(IR)	S(R)
1	ν O–H	3510 m	3483 m	3657	3503	101.6	82.7
2	ν C–H	3070 sh	3079 vs	3222	3087	0.5	41.9
3	ν C–H	2990 m	2993 m	3125	2994	49.5	101.1
4	ν C–H	–	2957 m	3057	2928	18.3	213.3
5	ν C–C	–	1599 ms	1647	1583	0.8	68.6
6	γ C–C, ν C–H	1470 vs	–	1515	1456	111.1	11.1
7	ν C–C, β O–H	1400 m	–	1442	1386	28.2	0.5
8	ν C–C, β C–H	1320 s	–	1384	1330	85.1	3.9
9	ν C–C, β C–H, β O–H	1240 vs	–	1300	1250	104.0	6.0
10	ν C–C, ν C–O	1270 s	1280 s	1324	1273	48.5	21.2
11	β O–H, β O–H, ν C–H	1180 m	–	1213	1166	79.4	1.6
12	ν C–C, β O–H	1130 ms	1125 s	1207	1160	136.1	1.9
13	ν C–C, γ C–H	–	1066 s	1082	1040	2.4	10.0
14	ν_{as} C–O, γ C–H	–	854 m	869	836	1.7	45.7
15	γ C–H, γ C–H	779 w	–	795	764	41.5	2.6
16	τ C–H	706 w	–	739	710	51.2	0.6
17	ν C–Br, τ -ring, γ O–H	648 m	652 ms	672	646	5.7	8.3
18	β C–H	480 vs	485 m	501	481	3.2	11.5
19	ν C–Br, β ring	–	401 m	408	392	0.9	2.7
20	β C–Br	–	261 m	271	261	0.9	6.4
21	γ C–Br, γ C–C, γ ring	–	205 m	208	200	0.4	2.5
22	τ ring	–	185 ms	180	173	0.1	4.6
23	δ C–Br, δ -ring	–	118 w	123	118	0.0	1.9
24	δ C–Br, δ -ring	–	111 w	119	114	0.0	0.9

^a ν -stretching; ν_{as} -asym. stretching; β -in-plane-bending; γ -out-of-plane bending; τ -torsion; δ -deformation.

^b vs, very strong; s, strong; w, weak; sh, shoulder; ms, medium strong; m, medium.

^c With the scale factor of 0.958 for calculated wavenumbers upper than 3000 cm^{-1} [15,16] and the scale factor of 0.9613 for lower wavenumbers [17].

[10], the corresponding ones in TBBPA were assigned at 261 cm^{-1} , 205 cm^{-1} , 118 cm^{-1} and 111 cm^{-1} , respectively. We propose that the red shift of C–Br is ascribed to the further electronic density equalization due to the p - π conjugation between O atom and the benzene. Moreover, the mode near 1069 cm^{-1} in the Raman spectrum of BDE-47 [10], showing the contribution of the C–Br vibrational mode, could not be observed for TBBPA. The result is consistent with the reported assignments for 3,5-dibromosalicylic

acid [19]. The calculated frequencies of C–Br vibration presented no evident discrepancy than the ones of BDE-47 [10].

Mulliken charges

The Mulliken charges at various atoms except H of TBBPA calculated at the B3LYP/6-31G(d) level were collected in Table 3. As Sudha et al. [23] showed, the substitution of halogen atom and the

Table 3
Mulliken atomic charge of TBBPA.

Atom No.	B3LYP/6-31G(d)
Br ₁	−0.132546
Br ₂	−0.090318
O ₃	−0.621639
C ₄	0.161388
C ₅	−0.212749
C ₆	0.046144
C ₇	0.304043
C ₈	0.043391
C ₉	−0.226737
C ₁₀	−0.056571
C ₁₁	−0.460162
C ₁₂	0.159758
C ₁₃	−0.459229
C ₁₄	−0.206888
C ₁₅	−0.234101
C ₁₆	0.043822
C ₁₇	0.044590
Br ₁₈	−0.104422
C ₁₉	0.304890
Br ₂₀	−0.118513
O ₂₁	−0.623904

hydroxyl group in the aromatic ring lead to the redistribution of electron density. The shift of partial charge from C7(0.304043) and C19(0.304890) to O3(−0.621639) and O21(−0.623904) demonstrated that the conjugation effect between O and benzene ring.

The four bromine atoms have the higher negative values (−0.09 to −0.13) owing to the electron withdrawing character. Mulliken population analysis chart of TBBPA was shown in Fig. 4 in Supplementary.

NBO analysis

By showing the accurate natural Lewis structural picture of model compound, NBO analysis is a powerful tool in understanding various donor–acceptor interactions between the filled and the vacant orbitals of the subsystem [24]. The NBO analysis was

performed at B3LYP/6-31G(d) level to elucidate the intra-molecular rehybridization and delocalization of electron density on TBBPA.

For each donor (i) and acceptor (j), the stabilization energy $E(2)$ associated with the delocalization $i \rightarrow j$ is estimated as.

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

where q_i is the donor orbital occupancy, while $F(i,j)$ is the off diagonal NBO Fock matrix element, and ϵ_i and ϵ_j are diagonal elements [24]. The larger of the $E^{(2)}$ value suggests the more intensive interactions between electron-donors and electron-acceptors, and the greater the extent of conjugation of the whole system [25]. From the NBO analysis (Table 4), it was observed that the intermolecular hyperconjugative interactions are mainly formed by the orbital overlap between σ (O–H), σ^* (C–C), π (C–C), π^* (C–C) bond orbital which result in the intramolecular charge transfer causing stabilization of the whole system. The maximum energy transfer occurred from π^* (C–C) to π^* (C–C) in the both benzene rings are 115.25–244.01 kcal/mol. The lone pairs of O3 and O21 have the lower occupancy (1.852 electrons) than the ones of 4 bromine atoms (1.935–1.949 electrons) and seem to be delocalized into neighboring C17–C19 or C7–C8. Compared to the interaction between the LP(3)Br and π^* (C–C) ($E^{(2)}$: 8.23–9.73 kcal/mol), the higher $E^{(2)}$ value (33.65–34.82 kcal/mol) originated from LP(2) O to π^* (C–C) may contribute to the preferential tendency of debromination to the C–O breakage in the transformation.

^1H and ^{13}C NMR analysis

Fig. 5 in Supplementary shows the measured ^{13}C NMR and ^1H NMR spectra of TBBPA. The chemical shifts of C and H atoms were calculated and compared with the corresponding experimental data, and were shown in Table 5. The correlation analysis of the calculation and experimental data was performed in order to quantify the agreement, and the result was listed in Fig. 6 in Supplementary. As shown in our previous work on BDE-15 [9],

Table 4
Second order perturbation theory analysis of Fock matrix in NBO analysis for TBBPA.

Donor (i)	Type	ED/e	Acceptor (j)	Type	ED/e	$E(2)^a$ (kcal/mol)	$E(j)-E(i)^b$ (a.u.)	$F(i,j)^c$ (a.u.)
O3–H23	σ	1.987	C7–C8	σ^*	0.039	5.74	1.28	0.077
O21–H27	σ	1.987	C16–C19	σ^*	0.039	5.74	1.27	0.077
C4–C9	π	1.668	C5–C6	π^*	0.400	22.77	0.26	0.070
			C7–C8	π^*	0.440	19.03	0.26	0.064
C5–C6	π	1.978	C4–C9	π^*	0.352	15.19	0.31	0.062
			C7–C8	π^*	0.440	21.27	0.28	0.072
C7–C8	π	1.654	C4–C9	π^*	0.352	21.07	0.30	0.072
			C5–C6	π^*	0.401	16.61	0.29	0.063
C12–C15	π	1.679	C14–C16	π^*	0.373	21.64	0.27	0.069
			C17–C19	π^*	0.442	18.86	0.26	0.064
C14–C16	π	1.720	C12–C15	π^*	0.349	16.07	0.30	0.063
			C17–C19	π^*	0.442	21.77	0.27	0.072
C17–C19	π	1.683	C12–C15	π^*	0.349	20.20	0.31	0.072
			C14–C16	π^*	0.373	14.90	0.30	0.060
Br2	LP(3)	1.936	C7–C8	π^*	0.440	9.73	0.29	0.053
Br18	LP(3)	1.935	C14–C16	π^*	0.373	9.82	0.30	0.053
Br1	LP(3)	1.948	C5–C6	π^*	0.401	8.50	0.32	0.051
Br20	LP(3)	1.949	C17–C19	π^*	0.442	8.23	0.31	0.050
O21	LP(2)	1.852				34.84	0.32	0.103
O3	LP(2)	1.852	C7–C8	π^*	0.440	33.65	0.33	0.101
C5–C6	π^*	0.400	C4–C9	π^*	0.352	158.93	0.02	0.084
C7–C8	π^*	0.440				115.25	0.03	0.079
C14–C16	π^*	0.373	C12–C15	π^*	0.349	223.52	0.01	0.084
C17–C19	π^*	0.442	C14–C16	π^*	0.373	244.01	0.01	0.081

^a $E(2)$ means energy of hyperconjugative interactions (stabilization energy).

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

^c $F(i,j)$ is the Fock matrix element between i and j NBO orbitals.

Table 5

Comparison of theoretical and experimental results of NMR chemical shifts of TBBPA.

Method	Atom type	
	δ_C (ppm)	δ_H (ppm)
Experimental	147.762, 144.610, 134.473, 127.862, 110.455, 40.570, 28.147	1.528, 7.257
Calculated by B3LYP/6-31G(d)	142.149, 135.608, 124.928, 111.489, 44.754, 30.955	1.601, 5.026, 6.847
Correlation analysis	$y^a = 0.977x^b + 1.918$ $r^2 = 0.999$	

^a δ_{cal} .^b δ_{exp} .**Table 6**Main excitation energy(*E*) and oscillator strength (*f*_{osc}) calculated at the TD-B3LYP/6-31G(d) level for TBBPA.

States	<i>E</i> (eV)	Transition	Main configuration	<i>f</i> _{osc}
S ₃	4.68	HOMO → LUMO	$\pi \rightarrow \pi^*$	0.0833
S ₂₄	6.05	HOMO–1 → LUMO+5	$\pi \rightarrow \pi^*$	0.5221
S ₂₇	6.16	HOMO–2 → LUMO+5	$\pi \rightarrow \pi^*$	0.1898

the results obtained on the 6-31G(d) level proved good agreement with the experimental data ($r^2 = 0.999$). The discrepancy is probably ascribed to the exclusion of solvent effect in the calculations.

As presented in Fig. 5 in Supplementary, the peak with δ_H of 4.905 ppm was supposed to be related with the proton of the solvent MeOH-d₄. The calculated chemical shift of 5.026 ppm was ascribed to H28–H33 atoms. The overlap signal and limited NMR spectroscopic resolution probably lead to the absence of the peak in Fig. 5 in Supplementary. Normally, the protons on phenyl ring are expected to yield NMR signals in the δ_H region of 6–8.5 ppm [26]. In the experimental spectrum, the presence of one peak with δ_H of 7.257 ppm showed that the four protons (H22, H 24, H25, H26) of the aromatic benzene are identical.

The ¹³C NMR spectrum shows 6 separate signals for all 15 carbons present in TBBPA. Normally, the aromatic and the saturated carbon in ¹³C NMR spectra usually locate in the δ_C range of 110–160 ppm and 5–55 ppm, respectively [19]. The peaks at 44.754 ppm and 30.955 ppm are assigned to C10 and C11(13). As shown in BDE-15 [9], the conjugation arising from the phenyl ring and the lone-pair electron of O21 and O3 contributes to the C7(19), generating the signal at 142.149 ppm in present work. We can expect that the interaction between the C7(19) and the adjacent bromine atoms in the real test probably contributes to the splitting of the line around 140 ppm in the observed spectrum. As for this, the average value of this signal (146.186 ppm) was chosen for linear fit. The signal at 110.455 ppm in the spectrum is assigned to the C6(8,16,17) on account of the strong electronegative property of the adjacent Br atoms. Thus, the peak at 118.2 ppm was assigned to C5(9,14,15) because of the impact of meta-Br atoms. The relative high chemical shifts at 134.473 ppm was ascribed to C4(12).

HOMO–LUMO and electronic transition adsorption analysis

The highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) represent the ability to donate or accept an electron [24,27]. The electronic transition corresponding to the transition from the ground to the excited state was listed in Table 6.

The TDDFT calculation results were listed in Fig. 7 in Supplementary. To better understand the ascription of adsorptions, isosurfaces of the main related orbitals were depicted in Fig. 8 in Supplementary. The electronic excitation coefficients indicate that the orbital excited from S₀–S₃ transition has its main contribution from transition from the HOMO to LUMO orbital with π – π^* character ($f = 0.0833$). As can be appreciated from its isosurfaces in Fig. 8

in Supplementary, the orbital excited from S₀–S₂₄ transition ($f = 0.5221$) and S₀–S₂₇ ($f = 0.1898$) are mainly described by excitation out of the HOMO–1 into the LUMO+5 orbital and HOMO–2 into the LUMO+5, respectively. Both the excitation exhibit clear π – π^* character localized on the benzene rings.

Conclusions

The optimized geometry of TPPBA was obtained by using density functional B3LYP method with the 6-31G(d) basis set. Both experimental and theoretical study on the FT-IR, Raman, ¹H NMR, and ¹³C NMR spectra of TBBPA were carried out. The calculated AC₄–C₁₀–C₁₃–C₁₁ (118.2°) clearly indicates a typical tetrahedral structure constituted by the atoms of C4, C10, C11, C12, C13. The scaled vibrational wavenumbers, IR intensities, Raman activities showed good agreement with the experimental data. Comparative analysis to corresponding vibrational properties for PBDEs showed that the red shift of C–Br vibration is probably ascribed to the further electronic density equalization due to the p– π conjugation between O atom and the benzene. The NMR calculation results demonstrated good agreement with the experimental values ($r^2 = 0.999$).

The NBO analysis result demonstrated that the intermolecular hyperconjugative interactions are mainly formed by the orbital overlap between σ (O–H), σ^* (C–C), π (C–C), π^* (C–C) bond orbital.

The lower $E^{(2)}$ value (33.65–34.82 kcal/mol) originated from LP(3)Br and π^* (C–C)($E^{(2)}$: 8.23–9.73 kcal/mol) leads to the preferential tendency of C–Br breakage in the transformation. The TDDFT computation results showed that all the main excitation exhibit π – π^* character localized on the benzene rings.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2012.12.004>.

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