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Synthesis, experimental and theoretical investigation of molecular structure, IR, Raman spectra and ¹H NMR analyses of 4,4′-dihydroxydiphenyl ether and 4,4′-oxybis(1-methoxybenzene)

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HIGHLIGHTS

- ► Theoretical geometrical parameters match with the X-ray analysis data.
- ► Calculated IR and Raman spectra may reproduce the experimental results.
- ▶ Description of the largest vibrational contributed to the normal modes are given.
- ► Calculated ¹H NMR chemical shifts mainly agree with the experimental values.
- ▶ Theoretical B3LYP/6-311G(d,p) calculations are valid for the structural-similar compounds.

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ABSTRACT

4,4'-Dihydroxydiphenyl ether and 4,4'-oxybis(1-methoxybenzene) are synthesized. Experimental and theoretical studies on molecular structure, infrared spectra (IR), Raman spectra and nuclear magnetic resonance (¹H NMR) chemical shifts of the two synthesized compounds have been worked out. All the theoretical results, which are obtained with B3LYP/6-311G(d,p) method by using the Gaussian 09 program, have been applied to simulate molecular structure, infrared, Raman and NMR spectra of the compounds. The compared results reveal that the calculated geometric parameters match well with experimental values; the scaled theoretical vibrational frequencies are in good accordance with observed spectra; and computational chemical shifts are consistent with the experimental values in most part, except for some minor deviations. These great coincidences prove that the computational method B3LYP/6-311G(d,p) can be used to predict the properties of other similar materials where it is difficult to arrive at experimental results.

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1. Introduction

4,4'-Dihydroxydiphenyl ether has been produced at low cost with a high yield by simple methods and can be used as intermediate in the manufacture of agrochemicals and pharmaceuticals [1]. Koga et al. [2] developed a method to prepare pure product of 4,4'-dihydroxydiphenyl ether with 87% yield. It is one of surface bound products in heterogeneous light-induced ozone process [3]. The most extensive application of 4,4'-dihydroxydiphenyl ether is taking part in some polymer synthesis reactions, such as the preparation of six different ionomers having various aromatic polymer backbones with pendant 2-sulfobenzoyl side chains [4], the composition of polytriazole resins [5], the modification of 4,4'-bismaleimidodiphenylmethane [6], the synthesis of 4,4'-bis(4-nitro-2-trifluoromethylphenoxy) diphenyl ether (p-6FNPE) [7], and so on. It is reported that polysulfonates gained by interfacial polycondensation from 4,4'-dihydroxydiphenyl ether and disulfoxides have good characteristics in chemical resistance to oils, acids and alkali, and are resistant to hydrolysis and aminolysis [8]. Compared with 4,4'-dihydroxydiphenyl ether, 4,4'-oxybis(1-methoxybenzene) draws less attention, on which the relevant studies are inadequate. Generally, it is regarded as the intermediate in synthetizing 4,4'-dihydroxydiphenyl ether. Recently, many studies indicate that methoxylated polybrominated diphenyl ethers (MeO-PBDEs) can be demethoxylated to hydroxylated polybrominated diphenyl ethers (OH-PBDEs) in vitro [9,10]. Moreover, the structures of 4,4'-dihydroxydiphenyl ether and 4,4'-oxybis(1-methoxybenzene) are similar to 4,4'-dibromodiphenyl ether (BDE-15) and 4,4'-dichlorodiphenyl ethers (CDE-15), which have been detected

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extensively in environment. The extensive application and the typical structure of 4,4'-dihydroxydiphenyl ether urge us to explore its environmental behavior and potential environmental risk.

Vibrational spectroscopy and nuclear magnetic resonance (NMR) techniques are widely used in the research of molecular systems. Study on vibrational spectroscopy of compounds may provide a convenient way to understand molecular properties of theirs analogues and the degradation nature involving bond cleavage [11]. Arguably NMR is one of the most sensitive and versatile analytical probes of molecular structure and dynamics of complex organic compounds [12]. Hence, experimental and theoretical studies on the vibrational spectra and NMR chemical shifts would be of significance for understanding their environmental behavior and assessing their potential environmental risk [13]. Furthermore, the density functional theory (DFT) method has been one of the most frequently used calculated methods in exploring molecular vibrational spectra in computational physics. chemistry, and material science [14-16]. Some studies have revealed that the DFT computations, combining the hybrid exchange-correlation functional Becke-3-Lee-Yang-Parr (B3LYP) with the standard 6-311G(d,p) basis set, yield good and consistent results in molecular analyses [17-20]. The combination of DFT calculations of chemical shifts and harmonic vibrational frequencies with experimental NMR and IR parameters has become an accepted technique to gather insight into the molecular structures [21].

Thus, in the present study, we give experimental and computational descriptions and characteristics of 4,4'-oxybis(1-methoxybenzene) and 4,4'-dihydroxydiphenyl ether on geometrical parameters, vibrational properties and hydrogen chemical shifts. The structural parameters, vibrational frequencies and chemical shifts are calculated using the DFT/B3LYP method with the 6-311G(d,p) basis set. The aim is to check whether the B3LYP/6-311G(d,p) method is reliable to forecast the characteristics of other structural-similar compounds by comparing the agreement between experimental and calculated results.

2. Synthesis and experimental methods

The two researched compounds were synthesized by ourselves. The general synthetic route is shown in Fig. 1.

2.1. Materials

4-Methoxyphenol (AR), cuprous iodide (CuI, AR), and tetramethylethylenediamine (TEMED, >98.0%) were purchased from Sinopharm Group Co. Ltd. 4-Iodoanisole (99.5%) and cesium carbonate (Cs_2CO_3 , 99.9%) were bought from Energy Chemistry Sa En Group. *N*,*N*-dimethylformamide (DMF, 99.5%) and hydrobromic acid (HBr, 48%) were supplied by Aladdin Chemistry Co. Ltd.

2.2. Synthetic steps

(1) 5 mmol of 4-methoxyphenol and 5 mmol of 4-iodoanisole were dissolved in 15 mL of DMF. Then, 0.5 mmol of TEMED (serves as ligand), 12 mmol of Cs₂CO₃ (serves as base), together with 0.5 mmol of CuI (as catalyst) were added into

the mixture. And the solution was heated to 150 °C for 12 h under nitrogen. After cooling to room temperature, the reaction solution was diluted with 50 mL of water and extracted four times with 20 mL of ethyl acetate. The extracted liquid was absterged with saturated sodium chloride solution and dried with anhydrous magnesium sulfate, and then filtered and concentrated. The obtained crude product was further eluted and purified by silica gel column chromatography (300-400 mesh) with petroleum ether and ethyl acetate at the ratio of 30:1–15:1. Thus, we got 4,4'-oxybis(1-methoxybenzene) product and the purity was 95%. Then, the product was recrystallized from *n*-hexane for spectroscopic studies. ¹H NMR (CDCl₃, 400 MHz) δ: 3.81 (s, 6H), 6.86 (d, *J* = 7.2 Hz, 4H), 6.93 (d, *J* = 7.2 Hz, 4H); **IR** (**KBr**) υ: 3062, 2956, 1608, 1509, 1467, 1455, 1441, 1298, 1248, 1104, 835, 762 cm⁻¹: **Raman** (**Ar**⁺) υ: 3066, 3009, 2953, 2903, 1604, 1452, 1242, 1164, 1029, 872, 837 cm⁻¹.

(2) 1 mmol of 4,4'-oxybis(1-methoxybenzene) which was synthesized according to the above method, mixed with 48% HBr, and the solution was heated to reflux for 16 h at 160 °C. After cooling to room temperature, the reaction liquid was evaporated to nearly dry in the rotary evaporator and then extracted with dichloromethane. The obtained crude product was further eluted and purified by silica gel column chromatography (300–400 mesh) with petroleum ether and ethyl acetate at the ratio of 15:1–10:1. Hence, we gained the solid product, 4,4'-dihydroxydiphenyl ether, with 99% purity level. ¹H NMR (CDCl₃, 400 MHz) δ : 6.70 (d, *J* = 7.2 Hz, 4H), 6.75 (d, *J* = 7.2 Hz, 4H), 9.17 (s, 2H); **IR** (**KBr**) v: 3602, 3035, 1601, 1502, 1463, 1285, 1211, 1157, 844, 828 cm⁻¹; **Raman** (**Ar**⁺) v: 3066, 1604, 1247, 1221, 1190, 1151, 850, 819, 632 cm⁻¹.

Finally, the target products of high purity can be used for the determination of molecular structure and spectral properties.

2.3. Experiments

The crystals of 4,4'-dihydroxydiphenyl ether suitable for X-ray analyses were grown from chloroform. A crystal was put on a glass fiber. The X-ray diffraction measurements were carried on a Nonius CAD₄ single-crystal diffractometer equipped with a graphitemonochromated Mo K α radiation (k = 0.71073 Å) by using an x/2h scan mode at 293 K. The structure was solved by the direct method and refined by the full-matrix least squares procedure on F^2 using SHELXL-97 program [22]. The FT-IR spectra of the title compounds diluted in the KBr pellets were measured on a Nicolet Nexus 870 spectrophotometer in the range of 400–4000 cm⁻¹ at room temperature. The Raman spectra were recorded on Renishaw Invia Raman microscope spectrophotometer in the 100–4000 cm⁻¹ region. The excitation line at 514 nm was emitted by an Ar⁺ laser. The ¹H NMR measurements of 4,4'-dihydroxydiphenyl ether and 4,4'-oxybis(1-methoxybenzene) were carried out using a Bruker DPX-300 NMR spectrometer at room temperature with tetramethvlsilane (TMS) as an internal standard in dimethylsulfoxide- d_6 $(DMSO-d_6)$ and deuterochloroform $(CDCl_3)$ respectively.



Fig. 1. The general synthetic route of 4,4'-oxybis(1-methoxybenzene) and 4,4'-dihydroxydiphenyl ether.

Table 1

0	ptimized	parameters	of 4,4'-oxy	ybis(1-me	ethoxybenzene	e) and 4,	4'-dihydro:	kydiphen	vl ether.
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Geometrical parameters	B3LYP/6-311G(d,p)	Exp. ^a	
	4,4'-Oxybis(1-methoxybenzene)	4,4'-Dihydroxydiphenyl ether	
Bond length (Å)			
$\gamma C_1 - C_2$	1.397	1.395	1.386(4)
$\gamma C_2 - C_3$	1.401	1.397	1.359(4)
$\gamma C_3 - C_4$	1.388	1.391	1.383(4)
γ C ₄ -C ₅	1.397	1.395	1.384(4)
$\gamma C_5 - C_6$	1.389	1.391	1.380(4)
$\gamma C_1 - C_6$	1.397	1.393	1.380(4)
$\gamma C_5 - O_7$	1.395	1.395	1.395(4)
$\gamma C_2 - O_{14}$	1.373	1.378	1.382(4)
γ O ₁₄ -H ₂₄		0.966	
γ C ₁₆ -H ₂₆	1.093		
γ C ₁₆ -H ₂₇	1.094		
γ C ₁₆ -H ₂₈	1.088		
$\gamma C_{16} - O_{14}$	1.430		
Selected bond angle (°)			
A $C_1 - C_2 - C_3$	119.569	119.858	120.5(3)
A $C_2 - C_3 - C_4$	120.583	120.182	120.9(3)
A $C_3 - C_4 - C_5$	119.611	119.751	119.0(3)
A $C_4 - C_5 - C_6$	120.160	120.256	120.0(3)
A C ₅ –C ₆ –C ₁	120.359	119.998	120.5(3)
A C ₆ –C ₁ –C ₂	119.715	119.951	119.0(3)
A $C_4 - C_5 - O_7$	122.221	122.396	123.2(3)
A $C_6 - C_5 - O_7$	117.502	117.223	116.7(3)
A $C_5 - O_7 - C_8$	119.235	119.586	116.4(3)
A $C_1 - C_2 - O_{14}$	124.508	122.445	121.4(3)
A $C_3 - C_2 - O_{14}$	115.923	117.696	118.1(3)
$AC_2 - O_{14} - H_{24}$		109.619	116.0(2)
A $C_2 - O_{14} - C_{16}$	118.001		
Selected dihedral angle (°)			
D C ₄ -C ₅ -O ₇ -C ₈	-44.777	-44.531	-34.8(5)
$D C_6 - C_5 - O_7 - C_8$	139.136	144.593	149.2(3)
$D C_5 - O_7 - C_8 - C_9$	-44.708	-42.891	-73.3(5)

^a The experimental X-ray diffraction values of 4,4'-dihydroxydiphenyl ether.



Fig. 2. The molecular structure and atom numbering of 4,4'-oxybis(1-methoxybenzene) (top) and 4,4'-dihydroxydiphenyl ether (bottom).

3. Computational details

Gaussian 09 software [23] was used in the calculations of geometrical parameters, vibrational frequencies and chemical shifts. Qiu et al. [24] reported that DFT/B3LYP method was better than Hartree–Fock (HF) method in the calculation on structural geometry of BDE-15. Thus, all the calculations were performed by using DFT/B3LYP method with 6-311G(d,p) basis set in this study. There are no imaginary frequencies in the results of vibrational analyses, indicating that all the computations were converged on a true energy minimum. NMR chemical shifts were calculated with the gauge including atomic orbital (GIAO) approach. Absolute isotropic magnetic shielding constants were transformed into chemical shifts ($\delta_i = \sigma_{TMS} - \sigma_i$) by referring to one of the standard compounds, TMS [12,25,26]. The value of $\sigma_{\rm TMS}$ is 31.88 ppm for $^{1}{\rm H}$ NMR spectra [17]. Detailed assignments of the signals for each spectrum were made by employing the animate vibration function of the Gaussview program [27]. The calculated vibrational wavenumbers were scaled with the scale factors, as will be explained in more detail in Section 4, yielding a good agreement between calculated assignments and experimental data. The calculations of potential energy distribution (PED) were done by Gaussian 09 software package with the key word: freq = intmodes. The Raman intensities were calculated using Eq. (1), which is derived from the basic theory of Raman scattering [28,29]:

$$I_{i} = \frac{f(v_{0} - v_{i})^{4} s_{i}}{v_{i} [1 - \exp(-hc v_{i}/kT)]}$$
(1)

where v_0 is the laser exciting wavenumber in cm⁻¹ (in this work, the excitation wavenumber v_0 is 19455.3 cm⁻¹, which corresponds to the wavelength of 514 nm of a Ar⁺ laser), v_i is the vibrational wavenumber of the *i*th normal mode (cm⁻¹); while S_i is the Raman scattering activity of the normal mode v_i ; f (a constant equal to 10^{-12}) is a suitably chosen common normalization factor for all peak intensities; h, k, c and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.



Fig. 3. Calculated and experimental IR spectra of 4,4'-oxybis(1-methoxybenzene) and 4,4'-dihydroxydiphenyl ether. (A) 4,4'-oxybis(1-methoxybenzene) (Cal.); (B) 4,4'-oxybis(1-methoxybenzene) (Exp.); (C) 4,4'-dihydroxydiphenyl ether (Cal.); (D) 4,4'-dihydroxydiphenyl ether (Exp.).

4. Results and discussion

4.1. Optimized structures

The optimized structural parameters of the two compounds, which are calculated at the B3LYP/6-311G(d,p) level, are summarized in Table 1, and shown in Fig. 2, using a consistent atom numbering scheme. The experimental X-ray diffraction values of 4,4'-dihydroxydiphenyl ether are also listed in Table 1 for comparisons.



Fig. 4. Calculated and experimental Raman spectra of 4,4'-oxybis(1-methoxybenzene) and 4,4'-dihydroxydiphenyl ether. (A) 4,4'-oxybis(1-methoxybenzene) (Cal.); (B) 4,4'-oxybis(1-methoxybenzene) (Exp.); (C) 4,4'-dihydroxydiphenyl ether (Cal.); (D) 4,4'-dihydroxydiphenyl ether (Exp.).

As shown in Table 1, most of the calculated bond lengths and bond angles are slightly larger than the corresponding experimental values. Differences between the calculated results and experimental data are reasonable based on a fact that the theoretical results are based on the gas phase, while the experimental data are obtained in the solid phase. The ranges of C–C bond lengths of 4,4'-dihydroxydiphenyl ether and 4,4'-oxybis(1-methoxybenzene) are 1.388–1.401 Å and 1.391–1.397 Å respectively. The ether

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Table 2	
Comparison of the observed and calculated vibrational spectra of 4,4'-oxybis(1-methoxybenzene).	

Mode	de Exp. ^a Freq.		Inte. (IR)	Assignments, PED ^c (>10%)			
	IR	Raman	Unscaled	Scaled ^b			
1			3209	3074	31	573.8	$\nu_{\rm cu}(79.6)$ $\beta_{\rm cu}(10.1)$
2	3076w		3208	3073	12.1	151.4	$\nu_{C-H}(79.9), \beta_{ring}(10.1)$
3	56761	3066vs	3200	3066	2.0	163.5	$v_{C-H}(82.4)$
4	3062w		3199	3065	4.7	512.5	$\upsilon_{C-H}(82.7)$
5			3190	3056	2.5	347.8	υ _{C-H} (79)
6			3189	3055	5.6	253.5	υ _{C-H} (82.3)
7			3185	3055	4.8	145.0	υ _{C-H} (83.3)
8			3185	3055	19.7	103.6	υ _{C-H} (77.7)
9		3009m	3131	2999	18.5	174.2	υ _{asCH3} (91.1)
10	2956m	2953m	3131	2999	35.7	252.7	υ _{asCH3} (91.8)
11	2913m		3053	2925	46.6	148.4	$\upsilon_{asCH3}(98.9)$
12		2002	3052	2924	43.8	1/5.1	$v_{asCH3}(98.8)$
15	2838m	29055	2997	2901	7.0 123.0	27.0	$U_{sCH3}(91.4)$
15	1608w	1604m	1662	1609	125.0	351 5	$v_{scH3}(31.2)$
16	1575w	100 111	1653	1600	2.6	91.3	$V_{ring}(52), \rho_{C} = (37.2)$
17			1629	1577	3.9	114.6	$v_{ring}(62.8), \rho_{C-H}(29.0)$
18	1509vs		1619	1568	14.9	15.2	$v_{ring}(63.2), \rho_{C-H}(26.7)$
19			1543	1494	43.4	6.8	$\rho_{C-H}(49.4), \omega_{CH3}(12.2), \beta_{ring}(28.8)$
20	1466m		1532	1483	565.8	1.9	ρ _{C-H} (45.3), ω _{CH3} (13.8), β _{ring} (25.6)
21		1452s	1507	1457	7.4	25.1	σ _{CH3} (81.9)
22	1441m		1505	1444	147.5	15.4	σ _{CH3} (74.8), ρ _{C-H} (10.6)
23			1491	1443	7.7	40.9	$\sigma_{CH3}(96.1)$
24			1490	1442	8.0	21.9	$\sigma_{CH3}(91.3)$
25	1.110		1478	1430	6.6	9.8	$\omega_{CH3}(63.9), \rho_{C-H}(17.6)$
26	1419w		14//	1408	55.2	29.4	$\omega_{CH3}(61.5), \rho_{C-H}(21.2)$
27	1208m		1454	1401	0.7	1.5	$p_{C-H}(42.1), \omega_{CH3}(12.0), p_{ring}(34.9)$
28	1298111	1295s	13447	1287	0.2	15.6	$U_{\text{ring}}(33.8), P_{\text{C-H}}(43.0)$
30		12555	1329	1287	72.2	43	$\mathcal{D}_{ring}(43.0), p_{C-H}(17.0), \mathcal{D}_{ring}(14.0), p_{C-0}(17.1)$
31			1324	1278	0.0	5.3	$\rho_{c} = (65.5), \rho_{c} = (12.3)$
32	1248vs		1320	1249	2.3	4.3	$\upsilon_{ring}(11.7), \rho_{C-H}(57.5), \rho_{C-O}(21.8)$
33		1242m	1290	1234	0.6	25.4	$v_{asC-O}(29.1), v_{ring}(32.2), \rho_{C-H}(21.0), \omega_{CH3}(12.9)$
34	1195s		1275	1203	28.5	130.6	υ _{asC-0} (20.7), υ _{ring} (28.9), ρ _{C-H} (22.0), ω _{CH3} (22.1)
35	1180s		1243	1180	1111.1	1.9	$ υ_{asC-O}(26.7), υ_{ring}(24.3), ρ_{C-H}(26.1), ω_{CH3}(17.6) $
36		1164s	1219	1167	7.4	74.8	υ _{sC-0} (21.0), υ _{ring} (33.3), ρ _{C-H} (31.4)
37	1155m		1205	1165	0.6	79.5	$ρ_{C-H}(13.0)$, $ω_{CH3}(62.5)$, $β_{ring}(13.9)$
38			1203	1142	55.3	14.3	$ρ_{C-H}(14.9), ω_{CH3}(60.4), β_{ring}(13.8)$
39			1180	1139	4.3	4.4	$\beta_{\text{ring}}(20.1), \rho_{\text{C-H}}(64.9)$
40			1176	1134	0.4	9.1	$\beta_{\text{ring}}(26.3), \rho_{\text{C-H}}(60.0)$
41	1104s		1171	1091	0.7	2.5	$\rho_{CH3}(75.8), \omega_{C=0}(12.0)$
43	11043		1170	1089	15.6	16	$\beta_{\text{H3}}(12,2), \alpha_{\text{H3}}(13,1), \alpha_{\text{H3}}(13,1), \beta_{\text{H3}}(13,1), \beta_{\text$
44	1032vs		1125	1031	13.1	1.1	$\beta_{ring}(25.8), \ \rho_{CH}(59.0)$
45		1029w	1065	1030	149.5	0.6	$\upsilon_{C-O}(36.9), \beta_{ring}(30.2), \rho_{C-H}(16.2)$
46	1007m		1064	990	4.5	32.9	$υ_{C-O}(38.3), β_{ring}(31.6), ρ_{C-H}(15.1)$
47			1023	990	4.6	0.1	ρ _{C-H} (33.6), τ _{ring} (54.6)
48			1022	932	0.5	1.1	ρ _{C-H} (34.9), τ _{ring} (56.7)
49			963	929	0.1	0.3	$\omega_{C-H}(82.7), \tau_{ring}(10.8)$
50			959	908	0.3	0.0	$\omega_{C-H}(82.2), \tau_{ring}(10.4)$
51	070	072	938	906	0.5	1.7	$\omega_{C-H}(73.3), \tau_{ring}(17.7)$
52	878m	872VS	936	801	0.2	0.1	$\omega_{C-H}(73.7), \tau_{ring}(16.0)$
54	034VS 81/c	057VS 815vs	850	052 818	39.5 33.7	22.5	$U_{as} = C_0(10.4), p_{ring}(44.5), p_{C-H}(50.1)$
55	0143	01503	845	807	81.2	03	$\gamma_{ring}(17.2), \omega_{C-H}(01.3), \mu_{C-O}(13.0)$
56			833	790	11.5	168.9	$\beta_{\text{ring}}(25.7), \ \Theta_{\text{C}}(48.3), \ \Omega_{\text{C}}(15.0)$
57			816	787	2.8	0.4	$\omega_{C-H}(88.2)$
58	762s		813	752	1.9	3.4	$\omega_{C-H}(90.5)$
59			777	723	49.5	7.7	$\beta_{ring}(30.8), \rho_{C-H}(21.4), \rho_{C-O}(33.1)$
60	698w	693w	747	693	1.4	14.6	$\tau_{ring}(32.7), \omega_{C-H}(38.8), \rho_{C-O}(21.7)$
61			716	674	5.4	3.3	$τ_{ring}$ (35.8), $ω_{C-H}$ (42.3), $ω_{C-O}$ (17.7)
62			696	632	9.2	3.0	$\tau_{ring}(36.1), \omega_{C-H}(28.8), \rho_{C-O}(25.8)$
63		627w	653	628	2.6	31.6	$\beta_{\text{ring}}(49.7), \rho_{\text{C-H}}(26.2), \rho_{\text{C-O}}(18.5)$
64 65	FD 4-		649	628	0.3	11.6	$\beta_{\text{ring}}(79.2), \rho_{\text{C-H}}(27.2)$
65 66	524S		649 540	525	8.1 12.1	3.5 5 7	$\gamma_{\text{ring}}(24.9), \omega_{\text{C-H}}(39.2), \rho_{\text{C-O}}(30.1)$
00 67	504m	5011	542 525	508	12.1	5./ 0.6	$\gamma_{ring}(2\delta,\delta), \omega_{C-H}(22.1), \rho_{C-O}(32.3)$
68	JU4111	301W	525 521	304 449	29.1 71	3.0	$\gamma_{\text{ring}}(32.6), \text{ wc}_{\text{H}}(33.6)$ $\gamma_{\text{ring}}(32.1), \text{ wc}_{\text{H}}(33.6), \text{ wc}_{\text{H}}(31.8)$
69			464	445	2.4	1.1	$\beta_{\text{ring}}(21.7), \ \Theta_{C=H}(31.6), \ \Theta_{C=O}(51.6)$
70			460	421	0.5	13.7	$\tau_{ring}(17.0), \ \omega_{c=H}(21.9), \ \omega_{c=0}(30.9)$
71			435	417	0.0	3.6	$\gamma_{ring}(65.2), \omega_{C-H}(28.4)$
72			431	379	1.2	0.1	$\gamma_{\rm ring}(64.1), \omega_{\rm C-H}(25.2)$
73			391	349	3.7	7.6	$\gamma_{ring}(19.4)$, $\omega_{C-0}60.1$, $\rho_{CH3}(11.8)$

(continued on next page)

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Table	2	(continued)
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Mode	Exp. ^a		Freq.		Inte. (IR)	Acti. (Raman)	Assignments, PED ^c (>10%)
	IR	Raman	Unscaled	Scaled ^b			
74			360	328	2.1	15.7	γ _{ring} (12.3), ω _{C-H} (10.0), ω _{C-O} (51.9), ρ _{CH3} (18.2)
75			339	314	1.5	1.4	$\gamma_{ring}(14.9), \omega_{C-H}(10.0), \omega_{C-O}(48.9), \rho_{CH3}(19.2)$
76			324	300	0.1	2.3	$\beta_{ring}(21.4), \omega_{C-H}(14.8), \rho_{C-O}(42.9), \omega_{CH3}(15.1)$
77			248	240	2.3	1.1	$\rho_{CH3}(53.1), \rho_{C-0}(27.8)$
78			245	237	0.1	4.0	$\gamma_{ring}(16.8), \omega_{C-H}(10.4), \rho_{CH3}(62.9)$
79			227	220	3.8	0.9	$\rho_{CH3}(34.0), \rho_{C-0}(41.7)$
80			196	190	0.6	4.8	$\beta_{ring}(35.1), \rho_{C-0}(57.3)$
81			160	155	1.8	2.7	$\gamma_{ring}(34.9), \omega_{C-O}(33.3), \omega_{C-H}(26.4)$
82			147	142	3.1	0.4	$\omega_{ring}(28.6), \tau_{C-0}(66.2)$
83			86	83	1.3	0.6	ω _{CH3} (34.0), τ _{C-0} (52.8)
84			79	76	4.2	0.4	$\omega_{CH3}(25.2), \omega_{ring}(10.0), \tau_{C-0}(59.9)$
85			56	54	0.0	34.4	$\beta_{C-O}(60.0), \beta_{CH3}(10.7), \omega_{ring}(20.4)$
86			31	30	1.2	10.4	$\beta_{C-O}(81.1)$
87			7	7	1.2	5.8	β _{C-0} (88.4)

^a vs, Very strong; s, strong; w, weak; m, medium.

^b With the scale factor of 0.958 for calculated wave numbers greater than 3000 cm⁻¹ and the scale factor of 0.9682 for other lower wavenumbers.

^c υ, Stretching; υ_s, sym. stretching; υ_{as}, asym. stretching; β, in-plane-bending; γ, out-of-plane bending; τ, torsion; ρ, wagging; ω, rocking; σ, scissoring.

bonds C₅–O₇, C₂–O₁₄ and C₁₆–O₁₄ are 1.395 Å, 1.373 Å and 1.430 Å. The range of C–H bond lengths of methyl is 1.088–1.094 Å. For both compounds, the calculated values of the C-C-C angles in the aromatic rings are around the typical hexagonal angle of 120°. The calculated values of the dihedral angles of C_4 - C_5 - O_7 - C_8 (-44.777°/ 139.136° for 4,4′-oxybis(1-methoxybenzene), and -44.531°/ 144.593° for 4,4'-dihydroxydiphenyl ether), which are a critical geometry parameter for conformers in the ground state, are closer to the experiment results $(-34.8(5)^{\circ}/149.2(3)^{\circ})$. The phenomenon demonstrates the non-planar nature of the two aromatic rings in the two compounds, which is attributed to the steric interaction. The calculation can be supported by the stereochemic study of Kurt Mislow [30-32]. Qu et al. [13] reported that the sum of two dihedral angles $(C'_1-S-C_1-C_6, C_1-S-C'_1-C'_6)$ for four types of TCDPSs (2,2',3,3'-TCDPS, 2,2',3,4'-TCDPS, 2,2',3,5'-TCDPS, and 2,2',3,6'-TCDPS) is about equal to $\pm 90^{\circ}$, indicating that the plane of the two benzene rings are almost vertical to each other. In the present work, the same conclusion is reached based on the calculated results. Dihedral angle C₄-C₅-O₇-C₈ and C₅-O₇-C₈-C₉ of 4,4'-oxybis(1-methoxybenzene) is -44.777° and -44.708° separately, and the corresponding value for 4,4'-dihydroxydiphenyl ether is -44.531° and -42.891° . The sum of the two angles is -89.485° and -87.422° , close to -90° . However, the sum of the two experimental data is $-108.1(10)^\circ$, deviated from -90° . The existence of extended hydrogen bonding in 4,4'-dihydroxydiphenyl ether and the stacking interaction may explain such results. For the two dihedral angles, there are some slight deviations between the two compounds and DPS $(-50.1^{\circ}/-49.5^{\circ})$ (Cal.) and $-49.6^{\circ}/$ -49.6° (Exp.)) [33], confirming that the steric effect of the substituted functional groups on the dihedral angles of $C_4-C_5-O_7-C_8$ and C₅-O₇-C₈-C₉.

4.2. Vibrational assignments

Calculated and experimental IR and Raman spectra of the two compounds are shown in Figs. 3 and 4, respectively. It is easy to discover that the main absorption peaks of the calculated spectra are mainly in accordance with those of the experimental spectra, demonstrating that the calculated results are dependable. However, as to 4,4'-dihydroxydiphenyl ether, there are some differences between the simulated spectra and the observed one, because the fluorescence effect reduces the quality of the experimental Raman spectra. 4,4'-oxybis(1-methoxybenzene) has 31 atoms and 87 normal vibrational modes and 4,4'-dihydroxydiphenyl ether has 25 atoms and 69 normal vibrational modes. Theoretical (unscaled and scaled) and experimental vibrational frequencies (cm⁻¹), peak intensities (km mol⁻¹) and the corresponding assignments for the vibrational modes are gathered in Tables 2 and 3. The tables also give PED values and the description of the largest vibrational contributions to the normal modes. It is a fact that the DFT method systematically overestimates the vibrational wavenumbers because of the neglect of anharmonicity effects in the real system [34]. So, we use generic frequency scale factors to fit the theoretical results with experimental ones. Moreover, previous studies have revealed increasing frequency overestimation of DFT in the high frequency regions (>3000 cm^{-1}) [35]. As a result, the frequencies larger than 3000 cm^{-1} are scaled down by multiplying a factor of 0.958 [36], while other frequencies are scaled down by a factor of 0.9682 [13, 37]. In addition, we use linear regression method to analyze the consistency between calculated and experimental frequencies. The results are given in Table 4. The squared correlation coefficients R^2 are all greater than 0.99, showing that good linearity exist between theoretical frequencies and experimental values for the two compounds. In other words, the calculated results with Gaussian package can be used to predict vibrational frequencies.

4.2.1. Ring vibrations

The C–H and C–C related vibrations can help to determine the existence of aromatic rings in a structure. The C–H stretching vibrations of aromatic structures often occur in the range of $3000-3100 \text{ cm}^{-1}$. The nature of substituents has little influence on the band in this region [38,39]. The C–H in-plane bending vibrations often appear in the region $1000-1300 \text{ cm}^{-1}$. And $750-1000 \text{ cm}^{-1}$ is the C–H out-of-plane bending vibrational region. It is reported that the bands of the phenyl C–C stretching vibrations generally appear at 1450 cm^{-1} , 1500 cm^{-1} , 1580 cm^{-1} , and 1600 cm^{-1} in IR spectra with variable intensities [40].

For 4,4'-oxybis(1-methoxybenzene), the aromatic C–H stretching vibrations appear at 3076 and 3062 cm⁻¹ in the IR spectrum with weak peaks, while with very strong intensity at 3066 cm⁻¹ in Raman spectrum. Scaled theoretical C–H stretching modes are found to be at 3073 and 3065 cm⁻¹. In IR spectrum, the frequencies 1298, 1248 and 1032 cm⁻¹ are assigned to the C–H in-plane bending vibrations, and two intensive bands at 814 cm⁻¹ and 762 cm⁻¹ are expected to be the C–H out-of-plane bending vibrations. The wavenumbers at 698 cm⁻¹ in IR and 501 cm⁻¹ in Raman spectra are ascribed to the C–H out-of-plane deformation. As shown in Table 2, the IR wavenumbers 1466 cm⁻¹, 1509 cm⁻¹, 1575 cm⁻¹ and 1608 cm⁻¹, in agreement with the calculated data, are

Table 3
Comparison of the observed and calculated vibrational spectra of 4,4'-dihydroxydiphenyl ether.

Mode	Exp. ^a		Freq.		Inte. (IR) Acti. (Raman)		Assignments, PED ^c (>10%)	
	IR	Raman	Unscaled	Scaled ^b				
1			3781	3622	139.8	267.2	(91.4)	
2	3602s		3779	3620	152.3	249.6	$v_{0-H}(91.4)$	
3	50025		3208	3074	47	367.4	$v_{c,u}(754)$	
4		3066vs	3206	3071	46	453.2	$u_{c,u}(75.6)$	
5			3202	3067	10.0	309.9	$\nu_{\rm CH}(59.0)$	
6			3201	3066	7.7	355.4	$\nu_{C-H}(59.1)$	
7	3035w		3191	3057	14.9	191.0	$v_{C-H}(74.5)$	
8			3191	3057	15.7	168.6	$v_{C-H}(74.4)$	
9			3179	3046	17.0	248.9	$v_{C-H}(64.3)$	
10			3179	3045	19.2	232.2	υ _{C-H} (64.2)	
11	1873w	1604m	1659	1607	0.0	185.4	$\upsilon_{ring}(53.6), \beta_{C-H}(39.3)$	
12	1601w		1651	1598	0.5	70.6	$v_{\rm ring}(54.7), \beta_{\rm C-H}(37.6)$	
13		1594m	1643	1591	8.1	151.4	υ _{ring} (54.1), β _{C-H} (29.4), β _{COH} (12.8)	
14			1637	1585	13.1	29.5	υ _{ring} (30), β _{C-H} (41.6), β _{COH} (14.6)	
15	1502vs		1540	1491	101.3	4.8	υ _{ring} (54.6), β _{C-H} (55.2)	
16	1463vs		1528	1479	732.3	1.3	υ _{ring} (34.8), β _{C-H} (55.4)	
17			1479	1432	55.8	0.5	υ _{ring} (35.2), β _{C-H} (41.6), β _{COH} (14)	
18	1383s		1470	1423	117.4	0.1	υ _{ring} (31.6), β _{C-H} (43.2), β _{COH} (13.8)	
19	1362m		1384	1340	82.4	6.0	υ _{ring} (38), β _{C-H} (37.6), β _{COH} (17.1)	
20			1380	1336	115.5	7.5	υ _{ring} (32.4), β _{C-H} (44.4), β _{COH} (18.6)	
21	1285w		1332	1290	1.8	2.1	υ _{ring} (23.8), ρ _{C-H} (56.6), β _{C-O} (11.4)	
22			1314	1272	8.4	1.5	υ _{ring} (26.6), ρ _{C-H} (51.6), β _{C-O} (12.2)	
23	1249s	1247m	1289	1248	233.9	35.6	v_{asC-O} (17.6), v_{ring} (31.2), $ρ_{C-H}$ (24.6), $β_{COH}$ (17.3)	
24		1221w	1264	1224	2.0	59.6	$v_{ring}(40.4), \rho_{C-H}(35.4), v_{COH}(16.3)$	
25	1211vs	1100	1254	1214	252.7	3.8	$\upsilon_{asC-O}(21.6), \upsilon_{ring}(25.4), \rho_{C-H}(35.4)$	
26		1190w	1224	1185	54.3	65.5	$\upsilon_{sC-O}(18.5), \upsilon_{ring}(33.3), \beta_{C-H}(33.0)$	
27	1157-	11515	1206	1167	280.7	142.8	$\beta_{\text{COH}}(30.8), \psi_{\text{ring}}(26.2), \beta_{\text{C-H}}(30.2)$	
28	11575		1202	1103	838.1	19.2	$\beta_{COH}(31.0), 0_{ring}(29.2), \beta_{C-H}(28.0)$	
29		1142m	1170	1142	0.0	11.1	$\beta_{C-H}(73.4), U_{ring}(12.8)$	
21		1142111	1170	1027	3.2 20.2	50.0	$\rho_{C-H}(00.4), \ 0_{ring}(10.0)$	
22	1007.00		1123	1087	29.2	1.1	$p_{C-H}(00.7), p_{ring}(20.5)$	
32	109775		1027	1085	44.9	1.1	$p_{C-H}(35.0), p_{ring}(24.0)$	
34	1005111		1025	993	10.0	1.5	(84.2) $\beta_{CH}(34.4)$	
35			957	927	0.2	02	$\omega_{c,u}(831) \gamma_{min}(111)$	
36			949	919	0.4	0.2	$\omega_{C-H}(0.5.1), \gamma_{Hing}(11.1)$	
37			940	910	2.3	1.1	$\Theta_{C,H}(73.0), \gamma_{ring}(17.2)$	
38			932	903	1.0	0.6	$\omega_{C-H}(75.3), \gamma_{ring}(17.4)$	
39	874w		892	864	30.2	25.7	$\upsilon_{asC-O}(13.8), \beta_{ring}(49.9), \beta_{C-H}(34.6)$	
40	844m	850s	860	833	45.9	76.8	$\gamma_{C-H}(53.6), \upsilon_{asC-O}(18.5), \upsilon_{COH}(17.7), \beta_{ring}(25.0)$	
41		819s	844	817	94.8	97.4	γ _{C-H} (59.1), β _{C-O} (17.9), υ _{COH} (21.0), β _{ring} (14.5)	
42	828vs		841	814	126.9	41.1	$\omega_{C-H}(78.2), \gamma_{ring}(20.9)$	
43			816	790	3.8	2.0	ω _{C-H} (85.8)	
44			811	785	2.9	2.3	γ _{C-H} (47.4), υ _{COH} (15.7), β _{C-O} (10.7), β _{ring} (18.5)	
45	791s		798	773	165.7	6.5	ω _{C-H} (80.3)	
46			755	731	6.1	7.1	$τ_{ring}(32.2), ω_{C-H}(37.1), β_{C-O}(17.7)$	
47			716	693	5.0	2.0	$\tau_{\rm ring}(38.6), \omega_{\rm C-H}(32.8), \beta_{\rm C-O}(11.0)$	
48			706	683	14.7	4.9	$\tau_{ring}(37.4), \omega_{C-H}(33.7), \gamma_{COH}(10.6), \upsilon_{sC-O}(12.4)$	
49		C 22	654	633	4.6	13.7	$\beta_{\rm ring}(53), \beta_{\rm C-H}(28.2)$	
50	F 0 7 m	632W	652	531	1.0	25.7	$\beta_{ring}(47.9), \beta_{C-H}(24.3)$	
51	507m	364W	509	570	13.2	0.2	$\gamma_{C-H}(41.5), p_{C-O}(17.9), p_{ring}(50.7)$	
53	507111	492147	508	J07 492	13.8	6.5	$\gamma_{ring}(51.6), \gamma_{C-H}(47.3), \gamma_{COH}(14.6)$	
54	490m	49200	505	492	17.0	3.7	$p_{ring}(0.5.2), \omega_{C-H}(28.5)$ $\omega_{e,u}(41.8), \gamma_{e,v}(34.4), \gamma_{eev}(17.0)$	
55	150111		451	437	3.5	3.5	$v_{c,o}(38.7)$ $\beta_{cov}(20.6)$	
56			432	418	0.4	21	$T_{\rm ring}(40) \oplus (23.2)$	
57			429	415	1.0	0.2	$\tau_{ring}(39.6), \omega_{C} = (24.2)$	
58			425	411	7.0	4.3	$\gamma_{COH}(33.2), \omega_{C-O}(19.9)$	
59			408	395	213.8	2.5	$\tau_{C-0}(29.8), \gamma_{COH}(28.4)$	
60			396	383	222.3	3.6	$\tau_{C-O}(25.8), \gamma_{COH}(35.4)$	
61			377	365	39.0	5.6	γ _{сон} (69.2)	
62		357w	349	338	3.8	15.3	γ _{сон} (76.6)	
63			316	306	11.2	1.4	γ _{C-O} (28.6), γ _{COH} (38.0)	
64		278w	272	264	1.3	8.2	$\beta_{ring}(29.4), \tau_{COC}(31.9)$	
65			165	160	0.3	1.0	γ _{ring} (21.6), γ _{COH} (27.8), β _{C-O} (18.2)	
66			145	140	0.9	0.4	γ _{C-O} (37.9), γ _{COH} (35.2), γ _{ring} (37.6)	
67			63	61	0.1	24.1	$\tau_{C-O}(42.5)$	
68			47	46	1.9	27.6	$\tau_{C-O}(77.5)$	
69			21	20	2.2	9.2	$\tau_{C-O}(88.4)$	

^a vs, Very strong; s, strong; w, weak; m, medium. ^b With the scale factor of 0.958 for calculated wave numbers greater than 3000 cm⁻¹ and the scale factor of 0.9682 for other lower wavenumbers. ^c υ, Stretching; v_s , sym. stretching; $ν_{as}$, asym. stretching; β, in-plane-bending; γ, out-of-plane bending; τ, torsion; ρ, wagging; ω, rocking.

Table 4

Correlation analysis of calculated and experimental vibrational frequencies.

Molecule	Correlation equations	R^2
4,4'-Oxybis(1- methoxybenzene)	IR: $\lambda_{Exp.} = 0.9897 \lambda_{Cal.} + 15.824$	0.9995
	Raman: $\lambda_{Exp.} = 0.9983 \lambda_{Cal.} + 2.1141$	0.9999
4,4'-Dihydroxydiphenyl ether	IR: $\lambda_{Exp.} = 0.9955\lambda_{Cal.} - 0.4677$ Raman: $\lambda_{Exp.} = 0.9922\lambda_{Cal.} + 10.633$	0.9982 0.9998

assigned as the aromatic C–C semicircle stretching vibrations. The aromatic ring C–C stretching vibration in observed Raman spectrum is found at 1604 cm⁻¹. As shown in Table 2, the predicted vibrations assigned to phenyl ring vibrations are in good accordance with the experimental assignments.

For 4,4'-dihydroxydiphenyl ether, the weak band observed at 3035 cm^{-1} in IR spectrum and the strong band at 3066 cm^{-1} in Raman spectrum are assigned as the aromatic C–H stretching vibration. In IR spectrum, the C–H in-plane bending vibrations are observed at 1211 cm^{-1} and 1097 cm^{-1} , and two intensive bands at 844 cm^{-1} and 828 cm^{-1} are expected to be the C–H out-of-plane bending vibrations. The wavenumbers at 791 cm^{-1} in IR and 492 cm^{-1} in Raman spectra are ascribed to the C–H out-of-plane deformation. 1463 cm^{-1} , 1502 cm^{-1} and 1601 cm^{-1} in IR spectrum are assigned as the aromatic C–C semicircle stretching vibrations, in agreement with the calculated data shown in Table 3. 1604 cm^{-1} and 1594 cm^{-1} are assigned as the aromatic ring C–C stretching vibration in observed Raman spectrum. Comparisons demonstrate that all the experimental values match with the theoretical frequencies.

The wavenumbers appearing at 1000 cm^{-1} are usually assigned as the trigonal ring breathing vibrations [41]. For 4,4'-dihydroxydiphenyl ether, the band at 1009 cm^{-1} , which coincides with the calculated value 994 cm^{-1} , is assigned to this mode. And for 4,4'-oxybis(1-methoxybenzene), the experimental and calculated value is 1007 cm^{-1} and 990 cm^{-1} , respectively. The overtone of aromatic ring is observed at 1875 cm^{-1} in the IR spectrum of 4,4'-oxybis(1-methoxybenzene), and for 4,4'-dihydroxydiphenyl ether, the band is at 1873 cm^{-1} . However, there is no corresponding peak in the theoretical spectra. The medium peaks at 874 cm^{-1} for 4,4'-dihydroxydiphenyl ether and 834 cm^{-1} for 4,4'-oxybis (1-methoxybenzene) in experimental IR spectra are the contribution of the coupling of the skeleton vibration of the aromatic ring and the C–O asymmetric stretching.

4.2.2. C-O vibrations

The frequencies around $1270-1230 \text{ cm}^{-1}$ in IR spectrum are regarded as the C–O stretching band of the aromatic ether. 1249 cm^{-1} is assigned to C–O asymmetric stretching vibrations for 4,4'-dihydroxydiphenyl ether and 1195 cm^{-1} and 1180 cm^{-1} for 4,4'-oxybis(1-methoxybenzene). The small differences may be

explained by the different functional groups in the *para*-position. And the associated dominated vibration mode is the coupling of C–O asymmetric stretching and C–H in-plane bending vibrations. Moreover, in the experimental Raman spectrum, the C–O asymmetric stretching vibration appears at 1247 cm⁻¹, and the symmetric stretching vibration wavenumber is 1190 cm⁻¹ for 4,4'-dihydroxydiphenyl ether. For, 1242 cm⁻¹ is assigned to the asymmetric stretching vibration, and the symmetric stretching vibration are observed at 850 cm⁻¹ for 4,4'-dihydroxydiphenyl ether, and at 837 cm⁻¹ and 693 cm⁻¹ for 4,4'-oxybis(1-methoxybenzene). The experimental values match well with the theoretical data in Tables 2 and 3.

4.2.3. O-H and -CH₃ vibrations

For un-substituted phenol, the frequency of O-H stretching vibration in the gas phase is 3657 cm^{-1} [42]. Sundaraganesan et al. [43] assigned a strong band in FT-IR spectrum at 3387 cm⁻¹ and a weak band in FT-Raman at 3390 cm^{-1} to O-H stretching vibration in 5-amino-O-cresol. In the present work, the strong band observed at 3602 cm⁻¹ is assigned to O-H stretching mode, and the calculated O–H band is at 3619 cm⁻¹. There is a small deviation between the calculated and the experimental data. Although the band is not observed in the experimental Raman spectrum, it is calculated to be 3621 cm⁻¹. In addition, phenols have the in-plane bending vibrations in the band region 1152–1250 cm⁻¹ [37]. The weak band observed at 1285 cm⁻¹ and the strong band observed at 1157 cm⁻¹ in IR spectrum are assigned as O-H in-plane bending vibrations. The theoretically computed values at 1272 and 1167 cm^{-1} have fine consistency with the experimental results. The O-H out-of-plane bending vibrations for phenol lie in the 290–320 cm⁻¹ region for free O–H [41]. In the present work, the scaled values of O-H out-of-plane deformation vibration are calculated to be 338 cm⁻¹ and 365 cm⁻¹, and the corresponding Raman experimental value is 357 cm⁻¹, but not observed in the IR spectra.

The CH₃ asymmetric stretching modes are found in the region of 2956–2913 cm⁻¹ in IR and 3099–2953 cm⁻¹ in Raman spectrum. The symmetric stretching vibration of CH₃ is found at 2838 cm⁻¹ in IR and 2903 cm⁻¹ in Raman spectrum. Peaks at 1441 cm⁻¹ in IR and 1452 cm⁻¹ in Raman spectra, in accordance with predicted frequencies at 1444 and 1457 cm⁻¹, are assigned to the scissoring of CH₃. The wagging vibrations are found at 1104 and 1155 cm⁻¹ in IR spectrum, with the predicted frequencies at 1091 and 1165 cm⁻¹. In this range, the wagging vibrations of methyl group mostly occur with aromatic ring vibrations.

4.3. ¹H NMR chemical shifts

NMR is the most powerful method in analytical chemistry for the identifications of structural groups and reactive ionic species.

Fal	ole	5

Comparison of theoretical and experimental values of ¹H NMR chemical shifts.

Molecule	δ_{H}					
	Calc. (ppm)	Exp. (ppm)	Assignments			
4,4'-Oxybis(1-methoxybenzene)	7.137	6.945	H-21 (H-25)			
	6.861	6.927	H-19 (H-22)			
	6.700	6.874	H-20 (H-20)			
	6.491	6.856	H-18 (H-24)			
	3.449	3.805	H-26 (H-27, H-28, H-29, H-30, H-31)			
4,4'-Dihydroxydiphenyl ether	7.010	6.771	H-19 (H-23)			
	6.780	6.753	H-17 (H-21)			
	6.670	6.718	H-18 (H-20)			
	6.397	6.700	H-16 (H-22)			
	3.282	9.168	H-24 (H-25)			



Fig. 5. Observed ¹H NMR spectra of 4,4'-oxybis(1-methoxybenzene) (A) and 4,4'-dihydroxydiphenyl ether (B).

The experimental and calculated values together with the peak assignments of 4,4'-oxybis(1-methoxybenzene) and 4,4'-dihydroxydiphenyl ether for ¹H NMR chemical shifts analyses are shown in Table 5. The observed ¹H NMR spectra are presented in Fig. 5.

The peaks with $\delta_{\rm H}$ of 7.270 ppm in Fig. 5A and 2.500 ppm in Fig. 5B are supposed to be related with the protons of the solvent CDCl₃ and DMSO-*d*₆. The presence of other peaks suggests that there are five distinct types of protons in the two compounds. The peaks with $\delta_{\rm H}$ of 3.805 ppm in Fig. 5A and 9.168 ppm in Fig. 5B are assigned to the protons of substituents in the *para*-position, methyl and hydroxyl, respectively. Normally, the protons on phenyl ring are expected to yield NMR signals in the $\delta_{\rm H}$ region of 6–8 ppm. The substitution of functional group atoms for proton in biphenyl ether changes the chemical environment of the remaining aryl protons. For 4,4'-oxybis(1-methoxybenzene), the correlation equation is

$$\delta_{H,Exp} = 0.7316 + 0.9057 \delta_{H,Cal} (R^2 = 0.983)$$
⁽²⁾

This indicates that the calculated chemical shifts may reproduce the experimental data. However, for 4,4'-dihydroxydiphenyl ether, there is an obvious difference between the experimental and theoretical chemical shift values of H24 (25) in O–H. The possible explanation is that the formation of hydrogen bond makes $\delta_{\rm H}$ move to the lower range [44,45].

5. Conclusions

The theoretical and experimental investigation on molecular structure, IR and Raman spectra and ¹H NMR chemical shifts of 4,4'-dihydroxydiphenyl ether and 4,4'-oxybis(1-methoxybenzene) have been given. In the current study, all the computations are carried out with the Gaussian 09 program using DFT/B3LYP method with 6-311G(d,p) level. The geometric parameters of

4,4'-dihydroxydiphenyl ether, gained by X-ray diffraction, match well with the calculated data. The scaled theoretical vibration frequencies show good agreement with the experimental results. The ¹H NMR chemical shifts are found to have only minor deviations from the experimental values. All these conclusions prove that the B3LYP/6-311G(d,p) method is feasible to predict the parameters and characteristics of structural-similar compounds.

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