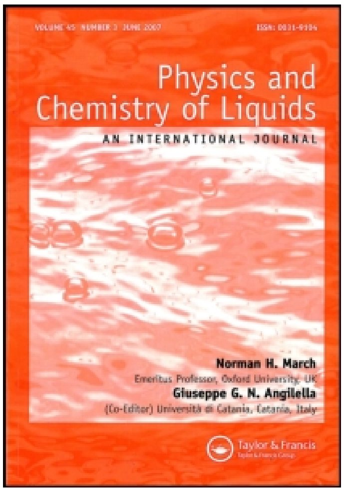

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Vibrational analysis of *p*-*tert*-butyl-calix[4]arene conformers by *ab initio* calculations

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Band frequencies and intensities in the IR spectra of calix[4]arene have been calculated. *Ab initio* calculations at HF/6-311G (d, p) level gave vibrational frequencies and infrared intensities for four conformers: cone, partial cone, 1,2- and 1,3-alternate. The geometry optimization has been performed in the basis of C2 symmetry frame of *p*-*tert*-butyl-calix[4]arene as a calculation input because it contains no imaginary vibrational frequencies. Additionally the experimental IR spectra of the *p*-*tert*-butyl-calix[4]arene were measured and related to the theoretical geometric parameters and force constants. The bands characteristic for each conformation and its reference with respect to specially the OH stretching were defined. Finally we discuss the possibility of hydrogen bonding stability of conformers were discussed.

Keywords: Calixarenes; Conformations; Normal vibrations; IR spectra

1. Introduction

Calix[4]arenes are macrocyclic molecules which are receiving increasing attention in the fields of supramolecular chemistry [1]. They belong to a class of the macrocycles in organic compounds [1] with cavities of sufficient size and hydroxyl groups capable to form intramolecular and intermolecular hydrogen bonds [1]. Normal calixarene molecules have a vase form, and therefore they are capable to contain in their cavity a wide row of organic ions and molecules [1,2]. Hydroxyl groups of calixarenes can be simply modified. That enables one to supply high selectivity of guests, because of the optimal locality of functional groups on the calixarene molecule; this maybe successfully used as a platform for complexes during extraction processes [2,3].

p-*tert*-butyl-calix[4]arenes are produced by condensation of *p*-*tert*-butyl-phenol with formaldehyde and many derivatives of calixarenes are synthesized based upon the calix parent compounds [1–3].

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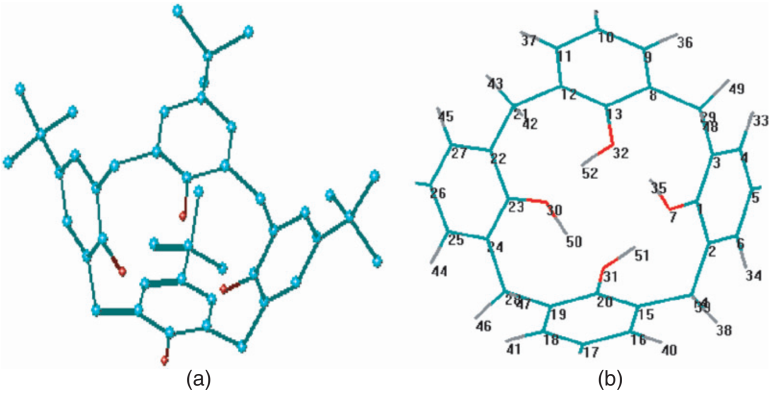

Figure 1. (a) The structure *p-tert*-butyl-calix[4]arene, the hydrogen atoms deleted for clarity, (b) numbering of the atoms in the steric structure (carbon: green, oxygen: red, hydrogen: gray), the *tert*-butyl groups are eliminated for clearness (colour version available online).

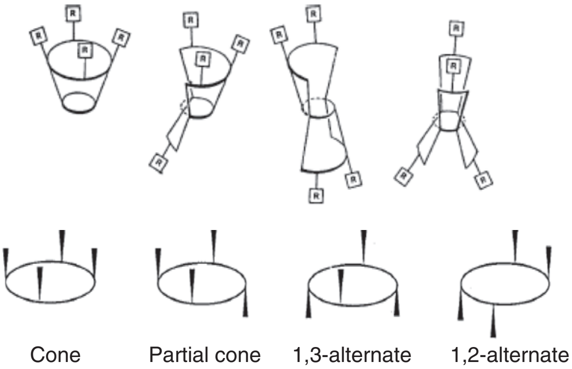

Figure 2. The four main conformers of calix[4]arenes.

The tetra hydroxyl calix[4]arene (figure 1) has been widely investigated and its derivatives are used as sensing components in ionic sensors [1–3] or for extraction [4,5], both due to their complex forming properties [6–8].

They have also been studied as artificial ion channels [9,10]. Therefore, it is reasonable to study the structure of the basic compound for the understanding of the properties and reaction mechanism.

p-tert-butyl calix[4]arene (figure 1) reveals four different conformer, namely cone, partial cone, 1,2-alternate or 1,3-alternate (figure 2).

In this work our aim is to combine experimental results with *ab initio* quantum chemical calculations, to interpret IR spectra of *p-tert*-butyl-calix[4]arene and to evaluate its conformational structure.

The absorption curves for four main conformations of: cone, partial cone (paco), 1,2-alternate, and 1,3-alternate (1,2-alt and 1,3-alt) were calculated and compared with experimental IR spectra over a large frequency range.

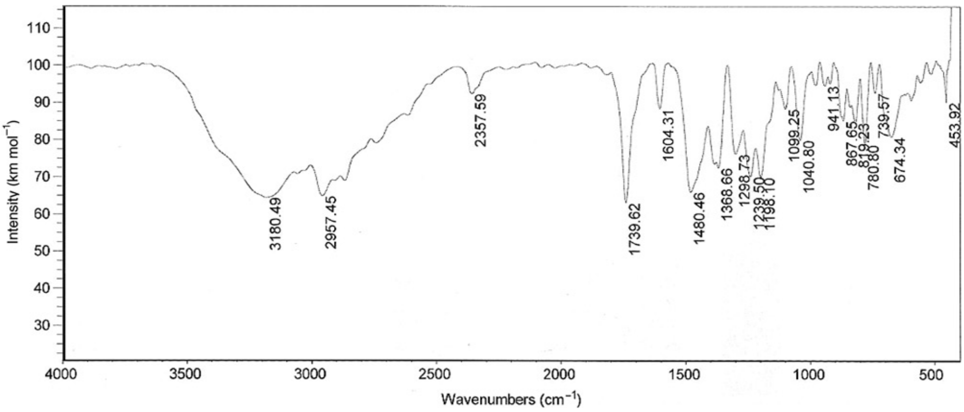

Figure 3. Experimental IR spectra of crystalline *p*-*tert*-butyl-calix-[4]arene.

IR spectroscopy is used generally for characterization of host–guest interactions [11–13] in calixarenes [14]. For a reliable explanation of IR spectra an analysis of normal vibrations must be platformed. However, the full interpretation of IR spectra, based on a normal coordinate analysis, has been reported only for the calix[4]arene [13,15]. This research study deals with the interpretation of the vibrational spectra of *p*-*tert*-butyl-calix[4]arene, to provide the properties of this compound.

2. Experimental

Spectra were recorded in the medium infrared region on a Perkin-Elmer 2000 type spectrometer, using the diffuse reflectance (DRIFT) technique (dried KBr powder was mixed simply with 4% w/w) between 4000 and 500 cm^{-1}, with 1 cm^{-1} resolution and the accumulation of 512 scans (figure 3).

3. Computational procedure

Quantum chemical calculations were used by means of the GAUSSIAN 98 program package [16].

The method and basis set were chosen on the basis of the size and the number of orbitals in the molecule. As a result the HF method with 6-311G (d, p) basis set learned out to be appropriate for the calculations in accordance with the size of the molecule and the essential computing time. IR spectra studied in conjunction with normal mode calculations by quantum chemical methods provide details of conformational studies. IR band intensities reveal their high sensibility to the conformation of the calixarene molecule. The first step of the calculations consisted in the geometry optimization of the calix[4]arene molecules. The initial structures of *p*-*tert*-butyl-calix[4]arene conformers were constructed after 900 hours CPU time with Hyper Chem 6.3 software [17] on Pentium (IV) by using the Gaussian 98 Molecular-modeling package [18,19].

Table 1. Energy difference (in kcal mol^{-1}) between the calix[4]arene conformers partial-cone (PC), l,2-alternate (l,2-alt) and l,3-alternate (l,3-alt) and the cone (C).

Method		PC–C (kcal mol^{-1})	1,2-alt–C (kcal mol^{-1})	1,3-alt–C (kcal mol^{-1})
Semi empirical	AM1	16.2	19.8	30.2
Ab initio	HF/6-31G	11.2	19.2	21.7
	HF/3-21G (d, p)	15.5	25.6	26.4
	HF/6-31G (d, p)	8.4	15.4	14.3

The duration of the calculation shows that application of the stronger quantum chemical method with the larger basis set is impractical.

4. Results and discussion

The absorption curves for four main conformations of: *p-tert*-butyl-calix[4]arene cone, partial cone (paco), 1,2- and 1,3-alternate were calculated and compared with experimental IR spectra over a wide frequency range. The bands characteristic for each conformation are defined and assigned. The data obtained enables one to interpret IR spectra of *p-tert*-butyl-calix[4]arene.

The calculated geometric parameters of calix[4]arene are in good accordance with X-ray experiments [14]. Computation reveals that the cone conformer is observed for isolated calix[4]arene molecules (table 1). Our data are in agreement with X-ray experiments and *ab initio* calculations [20–22]. It was shown that the cone is predominant conformer of calix[4]arene; its stability is ensured by cooperative effect of cyclic H-bonds in lower rim (figure 2). The next stable conformer is the partial cone conformation, in which two H-bonds form the chain. From our results it follows that the 1,2-alt conformer is more stable then the 1,3-alt conformer, but the energy difference between 1,2-alternate and 1,3-alternate conformations in our and other calculations is about 1 kcal mol^{-1} [21,22]. The cone conformation of calix[4]arene molecules belongs to the C_{4v} point group symmetry. In the conformation 1,3-alternate the C2 point group is observed.

Thus, structural analysis of the calixarene molecule yields the following order of molecular stability for the four possible conformers: cone > paco (partial cone) > 1,2-alternate > 1,3-alternate [23]. Of course it is important to mention that the most stable conformer stability completely depends to the chemical environment [21]. Quantum chemical calculations have shown that the most stable conformers the cone conformer.

The geometry optimizations have been carried out with the HF/6-31G, HF/6-31G (d, p), HF/3-21G (d, p) and HF/6-31lG(d, p) and also Am1 semi empirical method [24]. The result is comparable with Lee, Yang and Parr correlation functional (LYP) [25], the second order Møller–Plesset perturbation theory [26], MP2/6-31G(d, p), single-point energy B3LYP/6-31G (d, p) density functional calculations and also with the experimental data [27] and CHARMM simulation methods [28].

In table 1, the calculated energies are presented and also according to optimized calix[4]arene macromolecule the calculated geometric parameters are listed in table 2.

Table 2. Some geometric parameters of optimized *p*-*tert*-butyl-calix[4]arene.

Distance (Å)		Distance (Å)		Angle (°)		Angle (°)	
r (1, 2)	1.517	r (14, 39)	1.092	φ (2, 1, 24)	119.9	φ (16, 15, 28)	118.2
r (1, 24)	1.394	r (14, 40)	1.091	φ (2, 1, 25)	121.8	φ (15, 16, 17)	120.7
r (1, 25)	1.398	r (15, 16)	1.378	φ (24, 1, 25)	118.3	φ (15, 16, 41)	119.3
r (2, 3)	1.519	r (15, 28)	1.389	φ (1, 2, 3)	113	φ (17, 16, 41)	120
r (2, 29)	1.094	r (16, 17)	1.378	φ (1, 2, 29)	110	φ (16, 17, 18)	119.9
r (2, 30)	1.091	r (16, 41)	1.07	φ (1, 2, 30)	108.2	φ (16, 17, 42)	120.1
r (3, 4)	1.461	r (17, 18)	1.376	φ (3, 2, 29)	110.6	φ (18, 17, 42)	120
r (3, 26)	1.411	r (17, 42)	1.069	φ (3, 2, 30)	108.8	φ (17, 18, 19)	121.3
r (4, 31)	1.081	r (18, 19)	1.379	φ (29, 2, 30)	106	φ (17, 18, 43)	119.6
r (4, 5)	1.44	r (18, 43)	1.073	φ (4, 3, 26)	118.2	φ (19, 18, 43)	119.1
r (5, 6)	1.45	r (19, 28)	1.392	φ (2, 3, 26)	121.6	φ (18, 19, 20)	120.1
r (5, 32)	1.057	r (19, 20)	1.583	φ (3, 4, 5)	120.7	φ (18, 19, 28)	117.6
r (6, 7)	1.393	r (20, 21)	1.524	φ (5, 4, 31)	120	φ (20, 19, 28)	122.3
r (6, 33)	1.068	r (20, 44)	1.083	φ (3, 4, 31)	119.3	φ (20, 21, 22)	121.5
r (7, 8)	1.496	r (20, 45)	1.079	φ (4, 5, 6)	119.9	φ (20, 21, 25)	119.7
r (7, 26)	1.358	r (21, 22)	1.379	φ (4, 5, 32)	120.1	φ (22, 21, 25)	118.8
r (8, 9)	1.522	r (21, 25)	1.396	φ (6, 5, 32)	120	φ (21, 22, 23)	121.3
r (8, 34)	1.081	r (22, 23)	1.376	φ (5, 6, 7)	121.3	φ (21, 22, 46)	119.1
r (8, 35)	1.089	r (22, 46)	1.073	φ (5, 6, 33)	119.6	φ (23, 22, 46)	119.6
r (9, 10)	1.376	r (23, 24)	1.364	φ (7, 6, 33)	119.1	φ (22, 23, 24)	119.1
r (9, 27)	1.395	r (23, 47)	1.068	φ (6, 7, 26)	117.6	φ (22, 23, 47)	120.5
r (10, 11)	1.383	r (24, 48)	1.066	φ (8, 7, 26)	122.3	φ (24, 23, 47)	120.4
r (10, 36)	1.076	r (25, 49)	1.353	φ (6, 7, 8)	120.1	φ (1, 24, 23)	121.6
r (11, 12)	1.382	r (26, 51)	1.374	φ (8, 9, 10)	121.5	φ (1, 24, 48)	118.8
r (11, 37)	1.067	r (27, 53)	1.342	φ (8, 9, 27)	119.7	φ (23, 24, 48)	119.5
r (12, 13)	1.393	r (28, 55)	1.397	φ (10, 9, 27)	118.8	φ (1, 25, 21)	121
r (12, 38)	1.074	r (49, 50)	0.954	φ (9, 10, 11)	121.3	φ (1, 25, 49)	123.6
r (13, 14)	1.531	r (51, 52)	0.953	φ (11, 10, 36)	119.6	φ (21, 25, 49)	115.4
r (13, 27)	1.389	r (53, 54)	0.949	φ (10, 11, 12)	119.1	φ (3, 26, 7)	122.3
r (14, 15)	1.531	r (55, 56)	0.951	φ (10, 11, 37)	120.5	φ (3, 26, 51)	118.6

IR spectroscopy is used mainly for characterization of hydrogen bonding [29–31] and host–guest interactions in calixarenes for the reliable interpretation of IR spectra and analysis of normal vibration must be performed.

After the optimization of the calix[4]arene conformers, the molecular energy was differentiated with perfect to the Cartesian coordinates. The final result of this calculation is the Cartesian vibrational force constants, the vibrational frequencies, the infrared intensities and the depolarization factors of the normal modes.

In the frame work of normal mode analysis, we performed the calculation of IR spectra form the results of *ab initio* calculations made by HF methods with 6–311G (d, p).

The obtained spectra–structure correlation can be used for the characteristic of calix[4]arenes conformation. It shows that sufficiently satisfactory results may be obtained in the frame of relatively simple model with a considerable gain of computer time and resources.

Investigating the symmetry of the cone conformer of *p*-*tert*-butyl-calix[4]arene (figure 1) at first glance one may suppose the C_{4v} symmetry of the molecule (cone conformer), because the symmetry elements are one tetragir, four digirs parallel with the tetragir and four symmetry planes, each of them containing one of the digirs and the tetragir, but it is noticeable that the conformers of *p*-*tert*-butyl-calix[4]arene may have different geometries, whether the OH group attached to each aromatic ring points

Table 3. The digit displaying of *p-tert*-butyl-calix[4]arene conformers verity in the basis of the OH group attached to each aromatic ring points outwards (A) or inwards (B).

Conformer	Digit	Conformer	Digit
Cone	0000 $\sim$ AAAA	1,2-alt	0011 $\sim$ ABAB
	0000 $\sim$ AABA		0011 $\sim$ AAAB
	0000 $\sim$ ABAB		0011 $\sim$ ABBA
	0000 $\sim$ AABB		0011 $\sim$ AAAA
			0011 $\sim$ BBBA
Pace	0001 $\sim$ ABAA		0011 $\sim$ AABB
	0001 $\sim$ AAAA		
	0001 $\sim$ AAAB	1,3-alt	0101 $\sim$ AAAA
	0001 $\sim$ ABAB		0101 $\sim$ AABA
	0001 $\sim$ BAAA		0101 $\sim$ AABB
	0001 $\sim$ AABB		0101 $\sim$ BABA
	0001 $\sim$ BABA		0101 $\sim$ ABBB
	0001 $\sim$ BBAA		0101 $\sim$ BBBB
	0001 $\sim$ BABB		
	0001 $\sim$ ABBB		

outwards (A) or inwards (B). For example: 0001 $\sim$ AAAB is a Paco in which the OH group on the inverted aromatic ring points inwards. The digits in the names of the conformations are listed in table 3. Molecular mechanics calculations [32] found the C_{2v} symmetry for the equilibrium geometry and structure with C_{4v} symmetry as the saddle point between the two possible equivalent C_{2v} formations.

The symmetry investigation of the calixarene molecule in the cone conformation shown that at first glance it may suppose that the C_{4v} symmetry. Molecular mechanics calculations [33] represented the equilibrium symmetry is C_{2v} and C_{4v} symmetry has been found as the saddle point between the two possible equivalents C_{2v} formations. The quantum chemical was carried out with approximation and evaluation of the molecular symmetry.

The results have been shown that the number of imaginary frequencies in C_{4v} symmetry is five imaginary frequencies and this result for C_s symmetry has been shown only one imaginary frequency. So according to the computational calculation among the C_{2v}, C_{4v}, C_2, and C_s symmetries the C_2 symmetry is the most stable one, with only positive frequencies.

In table 4 some *ab initio* and experimental frequencies ν (cm^{-1}), and intensity I (km mol^{-1}) of vibrations in the IR spectra cone, partial cone, 1,3-alternate, 1,2-alternate conformers of *p-tert*-butyl-calix[4]arene are listed.

In the region 2800–3400 cm^{-1} of experimental IR spectra OH and CH stretching vibrations are observed. The band with the highest frequency at 3180 cm^{-1} corresponds to OH stretching vibrations. Certainly it is influenced to the lower rim hydrogen bond.

Ab initio computations show that the cone conformer, with the hydrogen bonds belt in lower rim, the lowest ν(OH) frequencies at 2976 and 3021 cm^{-1} with the highest intensity were computed. For the 1,2-alternate conformer, two hydrogen bonds among neighboring phenol fragments are formed and four ν(OH) bands at 3319, 3342, 3388, and 3419 cm^{-1} has been observed. The hydrogen bond formation caused rising in the intensity of ν(OH) stretching. In the 1,3-alternate conformer of, calix[4]arene, there no any hydrogen bonds and the ν(OH) band frequency is equal to 3438 cm^{-1}. Finally, for

Table 4. Some computational and experimental frequencies ν (cm^{-1}), and intensity I (km mol^{-1}) of bands in the IR spectra of *p-tert*-butyl-calix[4]arene conformers.

	Computational							
	Cone		Partial cone		1,3-alternate		1,2-alternate	
Experimental	ν	I	ν	I	ν	I	ν	I
3165	3063	4.2	3470	547.9	3469	367.5	3405	701.7
	3001	2442.7	3361	803.6	3468	820.6	3397	640
	2996	2488.8	3311	653.8	3467	865.2	3334	1306.8
	2855	17.6	3154	946.6	3456	1.3	3314	102.4
	3115	6.2	3112	8.3	3114	5.7	3111	5.8
	3114	7.2	3109	11.8	3113	6.4	3110	7
3053	3114	7.1	3109	4.6	3113	4.3	3109	4.8
	3114	6.5	3103	5.1	3113	5.9	3109	8
	3091	3.6	3093	16	3079	10.9	3090	13.1
	3091	15.3	3089	12.8	3079	11	3090	30
	3091	17.9	3087	8	3078	11.4	3087	7
	3090	6.2	3086	11	3078	11.2	3087	0.2
	3043	35.5	3044	25.2	3040	26.9	3044	42.6
	3040	37.1	3042	27.4	3038	33.9	3040	20.5
3026	3040	40.8	3041	34.9	3038	28	3039	51.4
	3039	30.1	3040	22.6	3038	41.4	3039	20.1
	3039	17.7	3037	14.3	3038	29.9	3038	31
	3038	5.8	3036	13.2	3036	4.5	3037	16.2
	3038	30	3036	40	3036	31.7	3036	18.8
	3033	88.3	3032	120.7	3034	11.5	3033	80.6
2956	3032	140.8	3032	45.8	3033	9.9	3032	103.2
	3029	29	3026	4.5	3031	41.2	3031	137
	3026	8.5	3025	5.8	3025	19.4	3025	18.7
	3024	6.1	3022	9	3023	6.6	3024	10.5
2935	3023	9.8	3022	8	3001	12.5	3023	6.9
2904	3022	14.6	2996	6.4	3001	5.8	2982	15.3
	2979	24.6	2983	20.3	2964	29	2979	4.8
2868	2977	18.7	2963	23	2964	65.3	2964	36.2
	2963	67	2958	4.8	2957	31.5	2958	21.5
	2957	35.2	2954	23.7	2949	2.4	2955	32.3
	2955	36.3	2948	22.4	2948	4.3	2945	36.1
	1604	0	1601	1.7	1594	0	1603	1.5
1606	1602	31.5	1597	0.3	1591	3.5	1602	5.4
	1590	2	1586	0.3	1581	0.2	1587	0
	1518	35.4	1476	102.4	1477	36.1	1475	8.9
	1475	62.8	1471	75.5	1473	182.6	1472	44.5
1483	1474	167.8	1471	64.4	1473	67	1472	60.1
	1470	4.6	1466	24	1467	16	1465	18.4
1464	1467	27.7	1464	19.4	1466	27.7	1465	15.5
	1457	7.9	1455	7.8	1455	11.1	1454	20.1
	1453	15.8	1440	3.3	1446	4.1	1441	2.8
1448	1445	41.1	1440	28.4	1441	2.3	1441	2.3
	1438	8.7	1434	0.4	1436	0.1	1436	1.6
	1434	1.6	1431	0.1	1432	0.1	1431	1.9
	1431	0.2	1415	1.1	1410	0	1420	17.7
1429	1429	23.7	1413	6.9	1406	3.4	1414	37.2
	1425	0.5	1405	4.4	1401	0	1397	2.9
	1406	0.6	1397	25	1377	3.5	1385	1.2
	1398	34.1	1378	10.1	1374	4.8	1383	51.3
1392	1397	37.9	1376	4.7	1374	4.4	1374	9.8
	1376	6	1373	6.1	1360	54.8	1373	4.4
	1344	2.3	1344	22	1344	9.1	1342	21
	1330	3.4	1303	15	1303	19.9	1311	0.7

(*Continued*)

Table 4. Continued.

	Computational							
	Cone		Partial cone		1,3-alternate		1,2-alternate	
Experimental	*ν*	*I*	*ν*	*I*	*ν*	*I*	*ν*	*I*
1306	1319	0	1300	12.5	1300	0	1309	13.5
	1286	2.8	1289	28.9	1290	9.3	1299	60.3
1285	1285	29.3	1288	45.9	1290	9.1	1280	42.7
	1274	4	1274	3.5	1267	0	1275	13.1
	1270	27.5	1266	29.4	1262	3.1	1262	5.4
	1265	0.2	1258	15.6	1260	50.9	1261	13.5
1258	1250	7.8	1251	10.4	1248	11	1252	6.3
	1245	0.2	1249	7.3	1243	4.1	1252	15.9
1243	1244	13.4	1239	23.9	1243	4.4	1235	8.7
	1236	0	1224	6.8	1206	17.3	1226	19.1
	1228	17.6	1211	11	1204	2.7	1221	1.2
	1218	0.1	1209	0.7	1204	2.9	1218	4.5
1202	1200	34.6	1202	95.8	1201	143.3	1202	123.9
	1196	21.6	1199	22.6	1200	11.3	1198	21.4
	1189	0	1189	22.7	1189	6.8	1191	6.1
	1187	9.5	1185	6.2	1187	0.3	1187	24.1
	1155	3.1	1175	4.2	1171	9.4	1185	8.6
1158	1154	2.7	1153	2.6	1171	9.5	1152	0
1124	1113	4	1111	18.3	1108	20.2	1113	1.1
1104	1097	7.2	1109	1.6	1105	1.9	1112	24.8
	1083	0	1093	2.3	1102	0	1097	0.1
1039	1016	0	1018	0.2	1015	0.4	1016	0.7
1028	1014	0.1	1016	0.2	1014	0	1013	1.1
	1012	0	1011	1.1	1011	0.2	1010	0.4
	969	7.5	972	2.1	970	0.4	982	0.2
	969	11.5	968	6.2	970	0.4	961	7.2
977	967	50.7	947	10.2	945	36.1	950	0
	946	954	0	941	10.4	943	2.2	0
946	954	0	941	10.4	943	2.2	941	0
	931	0	929	0	933	0.7	929	1.3
	925	0.2	921	4.5	920	0.3	918	3.2
917	918	0.6	917	0.3	917	2.7	916	3.3
	915	0.6	909	7	909	4.2	908	2.1
	907	0.8	906	2.4	906	1	905	19
	903	2.8	903	0.2	904	4.6	904	8
887	896	32.6	876	1.8	871	3.7	877	2.3
872	871	3.7	868	8.8	868	0.1	871	9.4
	856	23	851	13.9	860	40.7	849	23.2
854	853	0.9	812	7	811	1	813	10.5
817	807	27.7	792	40.3	774	0	778	0
	803	6.4	765	26.7	756	14.6	744	2.5
782	787	0	757	21	746	11.1	744	10.5
740	744	0	729	3	724	3.7	722	10.9
	722	14.1	687	1.3	679	0.7	676	0.1
710	710	0.1	670	6.2	679	0.7	663	0.4
	684	0	661	4.1	628	4.2	649	2.5
675	666	2.1	660	3.5	618	4.7	633	110.2
618	664	2.8	626	0.8	618	4.8	621	0.7
604	661	0.3	616	9.1	588	1.7	620	44.3
	609	1.3	591	6	581	0	591	10.9
593	588	12.5	583	5.5	563	0.1	586	20.8
569	557	0	556	25.3	549	52.7	555	12.1
554	555	7.2	550	6.3	548	52.7	542	0
	540	0.7	527	4.4	529	2.4	523	3.1

(*Continued*)

Table 4. Continued.

	Computational							
	Cone		Partial cone		1,3-alternate		1,2-alternate	
Experimental	ν	I	ν	I	ν	I	ν	I
523	509	6	507	2.8	498	3	507	10.4
512	503	0.4	502	8.7	497	2.8	497	0.4
	466	5.4	469	4	465	1.2	467	3.6
474	434	7.7	463	1.4	464	1.1	464	3.8
443	433	8.6	434	1.9	432	0.7	435	0.8
431	432	0.3	432	1.9	432	0.3	434	0
	419	7	413	3	408	1.2	412	0.4
	401	0	402	1	390	1.9	403	0

the partial cone conformer three hydrogen bonds are formed, and four ν(OH) bands at 3149, 3313, 3358 and 3481 $\mathrm{cm^{-1}}$ are shown in the computed IR spectra. The shoulder at 2940 $\mathrm{cm^{-1}}$ refers to asymmetric CH stretch of methylene groups. The medium-intensity bands at 2907 and 2872 $\mathrm{cm^{-1}}$ in the experimental IR spectra of are linked to symmetric CH vibrations of methyl and methylene groups.

The bands at 1604, 1480, 1368, and 1298 $\mathrm{cm^{-1}}$ of experimental spectra refer to aromatic ring CC stretch and CCH bending. The relatively weak bands at 3050 and 3020 $\mathrm{cm^{-1}}$ in the experimental IR spectra are linked to aromatic CH stretch. The strong band at 2957 $\mathrm{cm^{-1}}$ should be related to asymmetric CH stretch of methyl groups.

The bands at 1239, 1198, 1199, 1040, and 941 $\mathrm{cm^{-1}}$ are due to aromatic CH in plane bend. The bands at 867, 819 and 780 $\mathrm{cm^{-1}}$ in the experimental IR spectra corresponds to aromatic CH and CC out-of-plane bend. The doublet of medium-intensity bands at 1243, 1258 $\mathrm{cm^{-1}}$ and the strong band at 1205 $\mathrm{cm^{-1}}$ in the experimental IR spectra communicate to CO, CC stretching and CCH bending vibrations. The very weak bands at 854, 917, 946, and 977 $\mathrm{cm^{-1}}$relate to out-of-plane and in plane CH bending mixed with CC stretching vibrations. The medium-intensity bands at 874, 787 $\mathrm{cm^{-1}}$ in the IR spectra are related to out-of-plane CH, CC bending and CC stretching vibrations. The medium-intensity band at 819 $\mathrm{cm^{-1}}$ is connected with CC stretching vibrations. Band at 711 $\mathrm{cm^{-1}}$ refer to out-of-plane CH bending vibration. Various weak bands in the region 450–750 $\mathrm{cm^{-1}}$ in the IR spectra are assigned to CCC bending vibrations.

5. Conclusion

In summary, IR spectra studied in conjunction with normal mode calculations provide details of conformation studied of calixarene compounds. The analysis of the band intensities in the four main conformers of the calix[4]arene molecule, IR spectra shows the high sensibility to detect the phenolic units reorientation.

The analytical bands for each conformation of calix[4]arene may be separated. The calculation appears that the basic parameters, frequencies and the assignment of bands, obtained by both theoretical and experimental approach are in good agreement. It shows that sufficiently satisfactory results may be obtained in the frame of relatively simple HF model with substantial gain of computer time and resources.

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