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SPECTROSCOPY OF ATOMS AND MOLECULES

FTIR Spectroscopic and Quantum-Chemical Studies on Some Tribromoindenes and Their Isomers[1]

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Abstract—Combined experimental and computational studies on molecular structure of newly synthesised *transtirans* 1,2,3-tribromo-1,2,3-trihydro-^{1}H-benz[f]indene (TTTBI) were reported. Also, only computational studies were done for *cis-trans*-1,2,3-tribromo-1,2,3-trihydro-^{1}H-benz[f]indene (CTTBI) and *cis-cis*-1,2,3-tribromo-1,2,3-trihydro-^{1}H-benz[f]indene (CCTBI) in order to understand the vibrational spectra and molecular parameters of them. The geometry optimization and vibrational wave numbers of the title molecules were carried out with the Gaussian98 program package by using Hartree–Fock (HF) and Density Functional Theory (DFT) with B3LYP functional and 6-31G (d) basis set. All calculations were done for the title compounds in their ground states. Especially for CTTBI and CCTBI, which could not be synthesized yet, these kind of pre-calculations take an important role for their synthesis process. Also crystal structural parameters of TTTBI by single-crystal X-ray diffraction method was used as input for computational study of it. Observed and calculated vibrational wave numbers were compared. Because the use of benz[f]indene as a cyclopentadienyl ligand attracted much attention because an annulated benzo ring might increase both the stereocontrol and productivity of catalytic system, TTTBI and other computationally studied and modeled two molecules may play an important role of other types of compounds as a starting structures.

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INTRODUCTION

Benz[f]indenones and benz[f]indenes are potentially useful building blocks in organic and organometallic synthesis. However, their chemistry has not been much explored. Recently, benz[f]indenones were used as important starting materials in the synthesis of kinamycin antibiotics, which showed excellent activity against gram-positive bacteria [1]. The use of benz[f]indene as a cyclopentadienyl ligand attracted much attention because an annulated benzo ring might increase both the stereocontrol and productivity of catalytic system [2]. Lately, benz[f]indenones and benz[f]indenes were used as target molecules for computational chemistry [3]. The zirconocene compounds of benz[f]indenes are used as catalyst in the ethylene polymerization [4]. The bromination of hydrocarbons is an important process, since it leads to useful intermediates for the synthesis of a large variety of bromoorganic compounds [5–8]. Although their wide usage and importance mentioned above there is no quantum chemical calculations on the title molecules. Therefore, a quantum chemical study has been carried out to investigate the structure and vibrational frequencies in detail. The aim of the present study is to predict the structure and harmonic vibrational spectra by means of the HF and DFT/B3LYP level of theory and to analyze the vibrational wave numbers of title compounds. The IR spectra of the title compounds were reported and compared with those of the theoretical ones. In this study, optimized molecular geometry and vibrational spectrum of TTTBI, CTTBI and CCTBI were computed by Gaussian98 program [9] (Tables 1–3). Also vibrational study was done and compared with X-ray diffraction data [10] for the geometric structure of TTTBI.

METHODS OF CALCULATION

Quantum chemical calculations were carried out with the Gaussian98 software. The optimized geometries of the title compounds in their ground states were obtained using restricted Hartree-Fock (RHF) and the Becke-3-Lee-Yang-Parr (B3LYP) hybrid three-parameter exchange-correlation functional [11, 12] supplemented with the standard 6-31 G (d) basis set. The other isomers were also studied and their IR spec-

[1] The article is published in the original.

Table 1. Geometry of TTTBI calculated at the RHF and DFT/B3LYP theory levels using 6-31G(d) basis set for the selected geometric parameters (R: bond lengths in Ångström, A: bond angles in degrees, D: dihedral angles in degrees)

Selected bond lengths, bond angles and dihedral angles	X-ray, [10]	RHF	B3LYP	Selected bond lengths, bond angles and dihedral angles	X-ray, [10]	RHF	B3LYP
R(1,14)	1.96	1.97	2.00	A(14,11,20)	–	112.9	113.5
R(2,16)	1.97	1.97	2.01	A(13,12,15)	122.0	120.3	120.3
R(3,11)	1.96	1.97	2.01	A(9,13,12)	118.7	120.3	120.3
R(4,8)	1.40	1.41	1.42	A(1,14,11)	108.0	107.6	107.2
R(4,10)	1.32	1.35	1.37	A(1,14,16)	106.9	107.6	107.2
R(4,11)	1.49	1.49	1.49	A(1,14,23)	–	105.2	105.1
R(5,6)	1.38	1.41	1.42	A(11,14,16)	106.1	106.2	106.1
R(5,8)	1.36	1.35	1.37	A(11,14,23)	–	114.7	115.3
R(5,17)	0.93	1.07	1.08	A(16,14,23)	–	114.7	115.3
R(6,7)	1.41	1.41	1.43	A(6,15,12)	120.3	120.7	120.8
R(6,15)	1.42	1.42	1.42	A(2,16,8)	109.8	111.4	110.8
R(7,9)	1.41	1.42	1.42	A(2,16,14)	110.1	110.0	109.2
R(7,10)	1.41	1.41	1.42	A(2,16,25)	–	103.8	103.2
R(8,16)	1.48	1.49	1.49	A(8,16,14)	103.5	103.8	104.1
R(9,13)	1.35	1.35	1.37	A(8,16,25)	–	114.9	115.8
R(9,18)	0.93	1.07	1.08	A(14,16,25)	–	112.9	113.5
R(10,19)	0.93	1.07	1.08	D(11,4,8,16)	–	−0.01	−0.005
R(11,14)	1.51	1.53	1.53	D(8,4,11,3)	–	104.1	103.4
R(11,20)	0.98	1.07	1.08	D(8,4,11,14)	–	−14.2	−13.9
R(12,13)	1.40	1.41	1.41	D(8,4,11,20)	–	−138.0	−139.4
R(12,15)	1.34	1.35	1.37	D(10,4,11,3)	–	−77.0	−77.4
R(12,21)	0.93	1.07	1.08	D(10,4,11,14)	–	164.5	165.3
R(13,22)	0.93	1.07	1.08	D(10,4,11,20)	–	40.7	39.8
R(14,16)	1.52	1.53	1.53	D(4,8,16,2)	–	−104.1	−103.4
R(14,23)	0.98	1.07	1.08	D(4,8,16,14)	–	14.2	13.9
R(15,24)	0.93	1.07	1.08	D(4,8,16,25)	–	138.0	139.4
R(16,25)	0.98	1.07	1.08	D(5,8,16,2)	–	76.9	77.4
A(8,4,10)	121.6	121.0	120.9	D(5,8,16,14)	–	−164.5	−165.3
A(8,4,11)	108.5	110.2	110.1	D(5,8,16,25)	–	−40.8	−39.8
A(10,4,11)	129.9	128.6	128.8	D(3,11,14,1)	–	148.1	149.1
A(6,5,8)	120.5	119.4	119.6	D(3,11,14,16)	–	−96.6	−96.4
A(5,6,7)	118.9	119.5	119.4	D(3,11,14,23)	–	31.2	32.4
A(5,6,15)	122.5	121.5	121.7	D(4,11,14,1)	–	−92.4	−92.4
A(7,6,15)	118.6	118.9	118.7	D(4,11,14,16)	–	22.6	22.0
A(6,7,9)	118.5	118.9	118.7	D(4,11,14,23)	–	150.6	150.9
A(6,7,10)	119.3	119.5	119.4	D(20,11,14,1)	–	32.5	34.5
A(9,7,10)	122.2	121.5	121.7	D(20,11,14,16)	–	147.7	148.9
A(4,8,5)	119.8	121.0	120.9	D(20,11,14,23)	–	−84.2	−82.1
A(4,8,16)	111.3	110.2	110.1	D(1,14,16,2)	–	−148.1	−149.1
A(5,8,16)	128.9	128.6	128.8	D(1,14,16,8)	–	92.5	92.4
A(7,9,13)	121.9	120.7	120.8	D(1,14,16,25)	–	−32.5	−34.5
A(4,10,7)	119.9	119.4	119.6	D(11,14,16,2)	–	96.7	96.4
A(3,11,4)	111.9	111.4	110.8	D(11,14,16,8)	–	−22.6	−22.0
A(3,11,14)	110.4	110.0	109.2	D(11,14,16,25)	–	−147.7	−148.9
A(3,11,20)	–	103.8	103.2	D(23,14,16,2)	–	−31.2	−32.4
A(4,11,14)	104.7	103.8	104.1	D(23,14,16,8)	–	−150.6	−150.9
A(4,11,20)	–	114.9	115.8	D(23,14,16,25)	–	84.3	82.1

Table 2. Geometry of CTTBI calculated at the RHF and DFT/B3LYP theory levels using 6-31G(d) basis set for the selected geometric parameters. (R: bond lengths in Ångström, A: bond angles in degrees, D: dihedral angles in degrees)

Selected bond lengths, bond angles and dihedral angles	RHF	B3LYP	Selected bond lengths, bond angles and dihedral angles	RHF	B3LYP
R(1,14)	1.93	1.98	A(1,14,16)	116.6	112.1
R(2,16)	1.97	1.96	A(1,14,24)	105.1	105.7
R(3,11)	1.94	2.03	A(11,14,16)	104.2	102.9
R(4,8)	1.41	1.42	A(11,14,24)	108.8	114.8
R(4,10)	1.35	1.37	A(16,14,24)	107.1	114.6
R(4,11)	1.50	1.49	A(2,16,8)	109.7	115.1
R(5,6)	1.42	1.42	A(2,16,14)	112.8	115.9
R(5,8)	1.35	1.36	A(2,16,25)	104.8	103.6
R(5,23)	1.07	1.08	A(8,16,14)	101.2	103.4
R(6,7)	1.41	1.43	A(8,16,25)	115.4	110.8
R(6,15)	1.42	1.42	A(14,16,25)	112.9	107.7
R(7,9)	1.42	1.42	D(8,4,11,3)	−143.9	−96.3
R(7,10)	1.42	1.42	D(8,4,11,14)	−22.9	18.1
R(8,16)	1.50	1.50	D(8,4,11,19)	96.3	145.5
R(9,13)	1.35	1.37	D(10,4,11,3)	36.3	84.2
R(9,21)	1.07	1.08	D(10,4,11,14)	157.3	−161.2
R(10,20)	1.07	1.08	D(10,4,11,19)	−83.4	−33.9
R(11,14)	1.52	1.53	D(4,8,16,25)	144.0	92.4
R(11,19)	1.07	1.08	D(5,8,16,2)	82.5	31.9
R(12,13)	1.41	1.41	D(5,8,16,14)	−158.0	159.5
R(12,15)	1.35	1.37	D(5,8,16,25)	−35.6	−85.3
R(12,18)	1.07	1.08	D(3,11,14,1)	−73.1	−156.2
R(13,17)	1.07	1.08	D(3,11,14,16)	158.2	85.7
R(14,16)	1.53	1.54	D(3,11,14,24)	44.1	−39.5
R(14,24)	1.07	1.08	D(4,11,14,1)	164.5	86.9
R(15,22)	1.07	1.08	D(4,11,14,16)	35.9	−31.2
R(16,25)	1.07	1.09	D(4,11,14,24)	−78.0	−156.4
A(8,4,10)	120.92	121.0	D(19,11,14,1)	44.6	−41.9
A(8,4,11)	108.9	109.6	D(19,11,14,16)	−83.9	−159.5
A(10,4,11)	130.1	129.4	D(19,11,14,24)	161.9	74.8
A(4,8,5)	121.1	121.1	D(1,14,16,2)	−45.4	45.7
A(4,8,16)	109.8	108.5	D(1,14,16,8)	−162.6	−81.3
A(5,8,16)	128.9	130.3	D(1,14,16,25)	73.2	161.3
A(3,11,4)	114.0	110.4	D(11,14,16,2)	81.7	159.9
A(3,11,14)	112.2	107.1	D(11,14,16,8)	−35.4	32.9
A(3,11,19)	105.2	103.4	D(11,14,16,25)	−159.5	−84.6
A(4,11,14)	101.6	103.9	D(24,14,16,2)	−162.9	−74.7
A(4,11,19)	112.4	114.5	D(24,14,16,8)	79.8	158.2
A(14,11,19)	111.4	114.5	D(24,14,16,25)	−44.2	40.8
A(1,14,11)	114.4	106.5			

Table 3. Geometry of CCTBI calculated at the RHF and DFT/B3LYP theory levels using 6-31G(d) basis set for the selected geometric parameters. (R: bond lengths in Ångström, A: bond angles in degrees, D: dihedral angles in degrees)

Selected bond lengths, bond angles and dihedral angles	RHF	B3LYP	Selected bond lengths, bond angles and dihedral angles	RHF	B3LYP
R(1,13)	1.9287	1.95	A(3,10,6)	110.9733	110.5
R(2,7)	1.9638	1.99	A(3,10,13)	114.5856	113.6
R(3,10)	1.964	1.99	A(3,10,24)	104.1804	103.5
R(4,5)	1.3559	1.3739	A(6,10,13)	101.3255	101.8
R(4,14)	1.4193	1.4207	A(6,10,24)	114.4841	115.3
R(4,22)	1.0758	1.0873	A(13,10,24)	111.6789	112.5
R(5,6)	1.4165	1.4237	A(1,13,7)	116.87	116.6
R(5,7)	1.5033	1.4999	A(1,13,10)	116.8492	116.6
R(6,9)	1.3559	1.3739	A(1,13,25)	104.1013	104.0
R(6,10)	1.5033	1.4998	D(5,6,10,24)	−139.2616	−140.6142
R(7,13)	1.5357	1.5409	D(9,6,10,3)	−78.2979	−79.2665
R(7,23)	1.076	1.0883	D(6,5,7,2)	−103.2321	−102.5
R(8,11)	1.3574	1.3761	D(3,10,13,7)	−89.0028	−89.0872
R(8,14)	1.4211	1.4212	D(3,10,13,25)	158.9377	158.0253
R(8,17)	1.0757	1.0872	D(6,10,13,1)	163.3016	161.606
R(9,16)	1.4193	1.4207	D(6,10,13,7)	30.5398	29.7732
R(9,21)	1.0758	1.0873	D(23,7,13,1)	74.4536	74.5
R(10,13)	1.5356	1.5407	D(23,7,13,10)	−152.7961	−153.7
R(10,24)	1.0759	1.0882	D(5,7,13,10)	−30.5283	−29.7634
R(11,12)	1.4171	1.417	D(2,7,13,25)	−158.8926	−157.9744
R(11,18)	1.075	1.0864	D(5,7,13,1)	−163.2787	−161.5951
R(12,15)	1.3574	1.3761	D(23,7,13,25)	−40.7344	−40.7
R(12,19)	1.075	1.0864	D(2,7,13,1)	−43.7047	−42.7041
R(13,25)	1.0814	1.0946	D(4,5,7,2)	78.2423	79.2
R(14,16)	1.4134	1.4385	D(4,5,7,13)	−159.6351	−159.7
R(15,16)	1.4211	1.4212	A(7,13,10)	106.5543	106.2
R(15,20)	1.0757	1.0872	A(7,13,25)	105.6506	106.2
A(6,5,7)	110.347	110.3	A(10,13,25)	105.6537	106.3
A(5,6,10)	110.3388	110.3	D(7,5,6,9)	−178.6484	−178.4
A(9,6,10)	128.6667	128.8	D(7,5,6,10)	0.0171	0.0119
A(2,7,5)	110.992	110.6	D(4,5,7,23)	−39.3286	−37.7
A(2,7,13)	114.6121	113.6	D(5,6,10,3)	103.1675	102.4764
A(2,7,23)	104.1822	103.5	D(6,5,7,23)	139.197	140.5
A(5,7,13)	101.3192	101.8	D(6,5,7,13)	18.8905	18.5
A(5,7,23)	114.4609	115.2	D(9,6,10,24)	39.273	37.6429
A(13,7,23)	111.6616	112.4	D(9,6,10,13)	159.6159	159.715

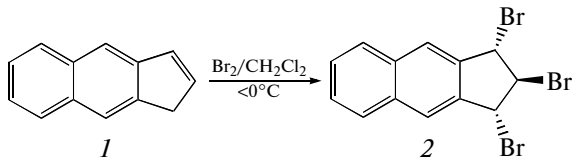


Fig. 1. Illustration of synthesis process.

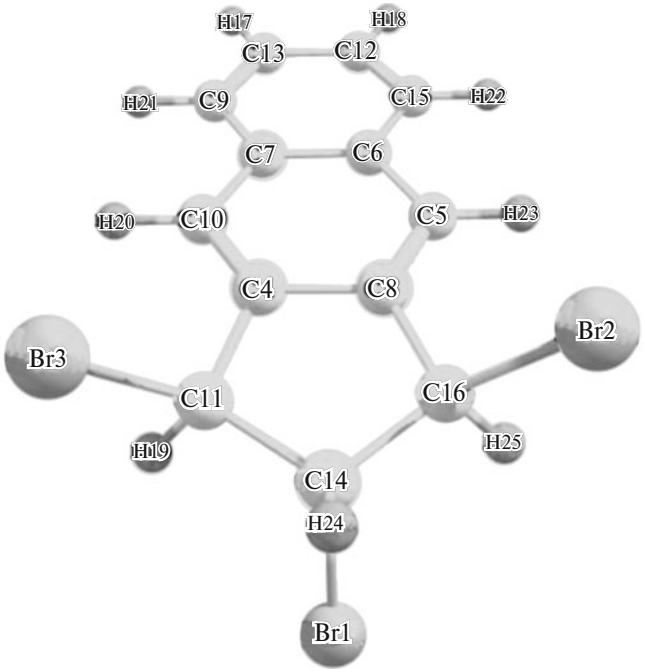


Fig. 2. Optimized geometric structure of TTTBI.

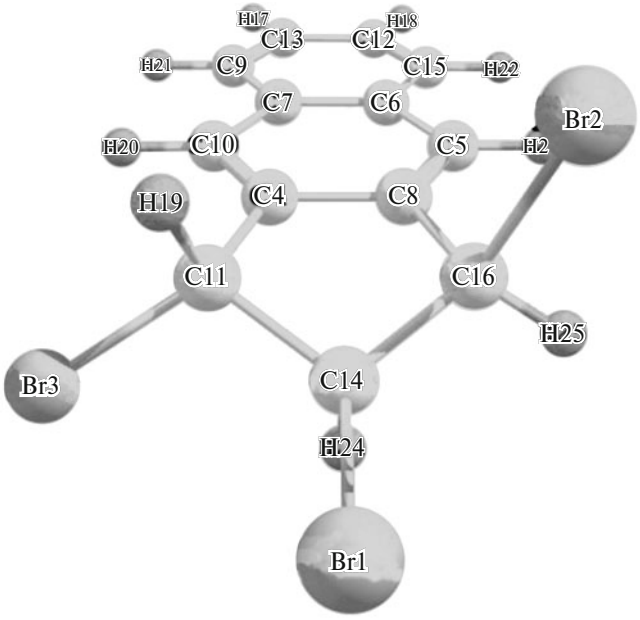


Fig. 3. Optimized geometric structure of CTTBI.

tra were calculated by the gradient method to determine the true minimum of the total energy and wavenumbers of vibrations. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters. Vibrational spectra were calculated using the theories mentioned above.

MATERIALS AND METHOD

Experimentally, to a magnetically stirred solution of benz[f]indene (*1* in Fig. 1) [13] (0.2 g, 1.2 mmol) in CH_2Cl_2 (10 ml) cooled to 0°C (ice bath) was added drop-wise a solution of bromine (0.21 g, 1.3 mmol) in CH_2Cl_2 (3 ml). The reaction mixture was left in the fridge for a night. After the removing of the solvent in vacuo, the crude product was submitted to column chromatography (silica gel) eluting with hexane to give the product (*2* in Fig. 1) (97 mg, 20%). The structure of TTTBI was used by single-crystal X-ray diffraction. Data were collected on a CrysAlis CCD, Oxford Diffraction Ltd. with an imaging-plate detector diffractometer using graphite-monochromated Mo$K\alpha$ radiation with the ω scan mode. The collected data were reduced by using CrysAlis RED, and empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied. CCTBI and CTTBI could not be synthesized thus only quantum chemical calculations

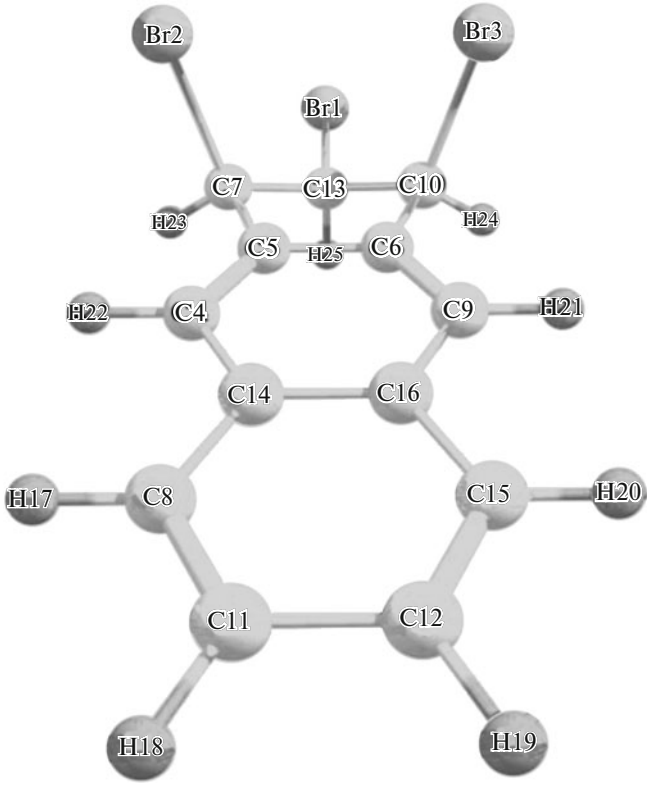


Fig. 4. Optimized geometric structure of CCTBI.

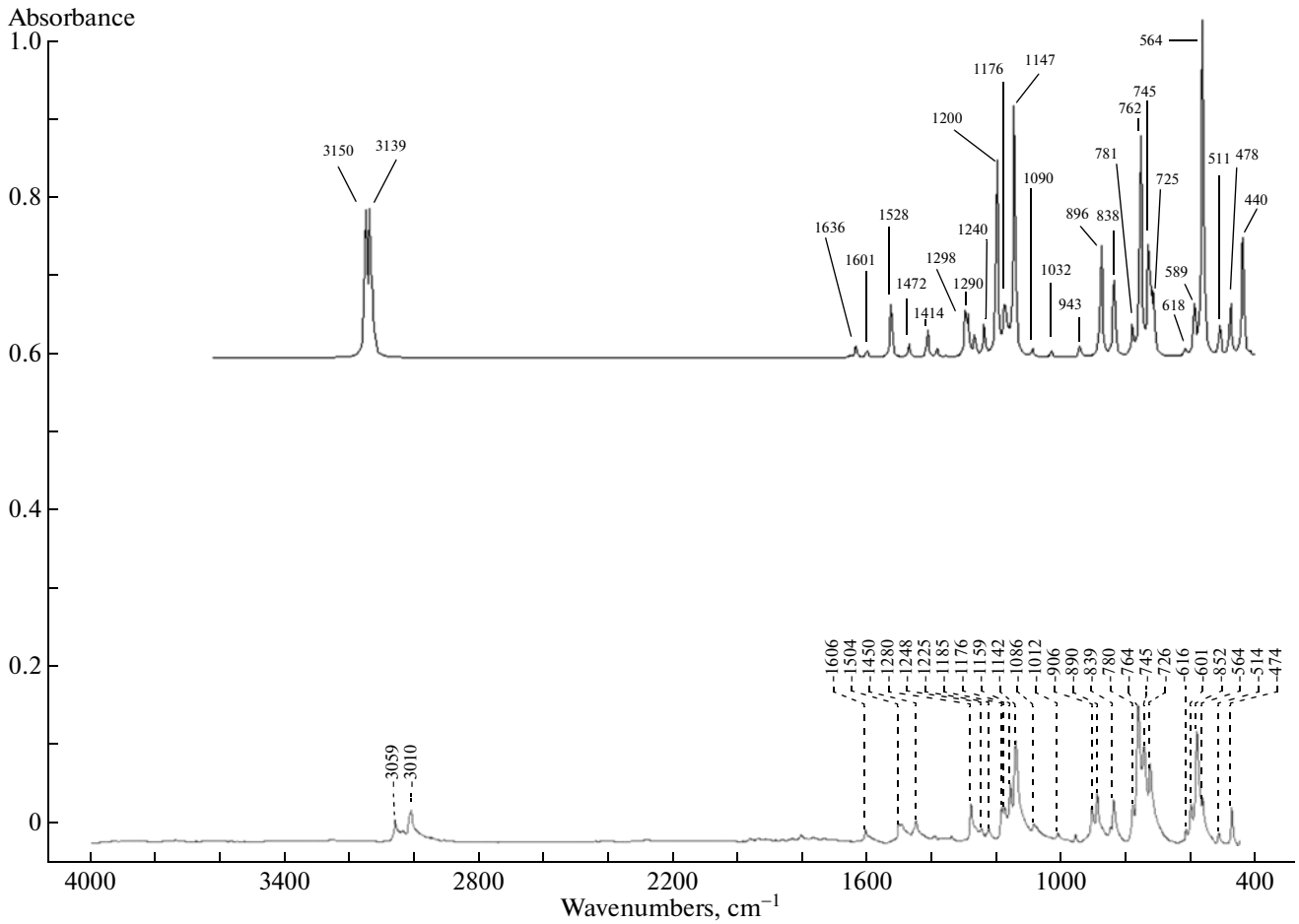


Fig. 5. Comparison of experimental and calculated IR spectra of TTTBI (top—calculated, below—experimental).

were done for these compounds. FTIR spectrum of TTTBI was also recorded by using KBr technique between 4000 cm^{-1} and 400 cm^{-1} spectral region.

RESULTS AND DISCUSSION

From the X-ray diffraction data and computational data, it can be seen the mean plane of the two fused-six membered rings is essentially planar, with the maximum deviations for atoms C_5, C_{12} and C_4, of –0.017(8), 0.014(9) and 0.011(7) Å respectively, for TTTBI. The C-C-Br angles are in the range 106.9° (5)–111.9° (5). The C-Br bonds are in the range 1.961(9)–1.970(8) Å. The repulsive interactions between the Br atoms may affect the molecular structure. The values of the other geometric parameters in the TTTBI are normal. Dipole-dipole and van der Waals interactions are effective in the molecular packing of the TTTBI. The TTTBI and two isomers of it consist of 25 atoms, which has 69 normal modes. The 69 normal modes of the title molecules have been assigned according to the detailed motion of the individual atoms. All normal modes assigned to one of 11 types of motion (C-C, C-H and C-Br stretches; H-C-C, C-C-C, C-C-Br and Br-C-H bendings and Br-C-C-H, C-C-C-C, C-C-C-H and C-C-C-Br torsions) were predicted by a calculational analysis. To the best of our knowledge, there are no experimental parameters and quantum chemical studies for the molecular structure of CTTBI and CCTBI. Therefore we could not compare our calculated results for the geometries of CCTBI and CTTBI with those of X-ray data. The molecular structures and atomic numbering of the compounds were given in Figs. 2–4. Firstly, the optimized geometries of the title compounds were calculated using RHF and B3LYP levels of theory using 6-31 G(d) standard basis set. The selected calculated geometric parameters and definitions of the natural coordinates for the molecules are summarized in Tables 1–3 for TTTBI, CTTBI, CCTBI, respectively. From B3LYP calculations C-Br bond lengths were calculated as 2 Å, which differs from the X-ray data by only 0.04 Å. From RHF calculations these bond lengths were calculated as 1.97 Å which are closer (0.01 Å) to X-ray data than those of B3LYP results. It indicates that RHF method estimated the bond lengths better than B3LYP method for TTTBI. On the

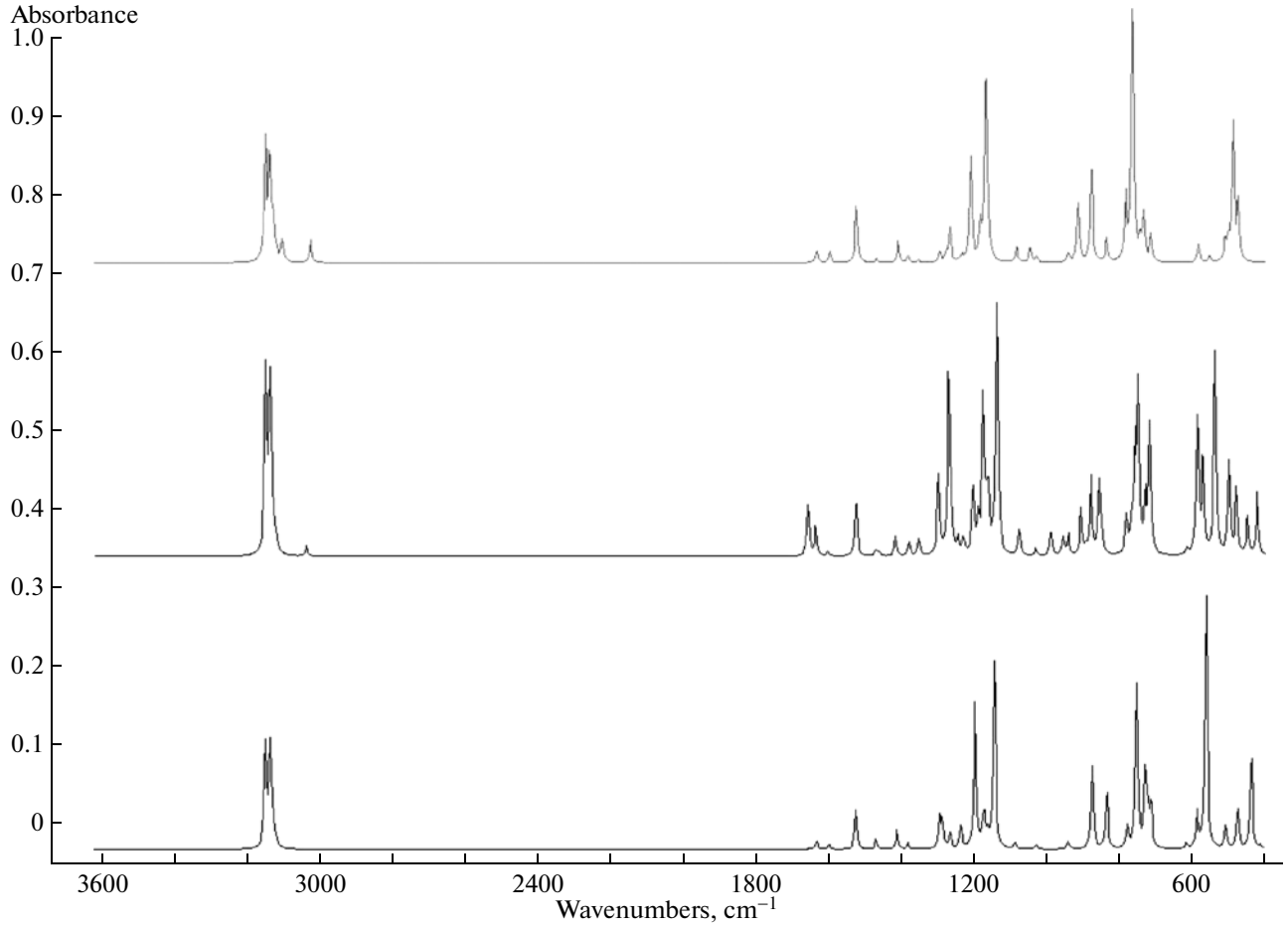


Fig. 6. Comparison of calculated IR spectra between TTTBI and two isomers (top—CCTBI, middle—CTTBI, bottom—TTTBI).

other hand, B3LYP estimated the bond angles better than RHF method. All aromatic ring angles (including CCC and CCH angles) are almost 120° for all compounds. Two aromatic ring is almost planar with small deviations. For CTTBI a comparison of optimized geometries (Table 2) with respect to the methods showed us that RHF value of (4, 11, 14, 1) dihedral angle is 164.5° while it was 86.9° for B3LYP. Also (3, 11, 4, 8) is −143.9° for RHF while it was −96.3° for B3LYP. And finally (2, 4, 8, 16) is −97.7° for RHF while it was −150.3° for B3LYP. These values are distinguishable than the others for those of the CCTBI and TTTBI so we can understand the difference between the optimized geometries calculated by different methods by analyzing them for CTTBI. It can be easily seen that from the optimized geometries one of the C atoms (C_{14}) of the five-membered ring is above the plane for RHF while the same atom was below the plane for B3LYP. It indicates that taking into consideration electron correlation effects used in B3LYP method plays an important role for the molecular structure. Because the electronic interactions has been taken into account repulsive interactions between the Br atoms actively took part of resulting structure. RHE/6-31 G(d) and B3LYP/6-31 G(d) levels of theory with the optimized geometries have been used to calculate all parameters of the title compounds.

Well known scale factors in the literature [14] were used to compare how close the calculated values of wave numbers with those of the observed ones. From Table 4 it can be seen that B3LYP is better in estimating the wave numbers than RHF. To avoid complexity of huge data, calculated B3LYP results for vibrational wave numbers will be given in parenthesis immediately after experimental values for the rest of the text. The numerical harmonic vibrational analysis was done for the optimized geometries. The absence of negative wave numbers and negative eigenvalues of the Hessian matrices for the stationary points found at the molecular potential energy hyper-surfaces confirms that this structure correspond to real minimum. The difference between the experimental and calculated, results is due to the basis set incompleteness and the neglect of anharmonicity. From the results, it has been seen both

Table 4. Comparison of calculated (RHF/6-31G(d) and B3LYP/6-31G(d)) and experimental vibrational wave numbers (cm^{-1}) of the title compounds

TTTBI					CTTBI				CCTBI					
Mode	RHF	B3LYP	RHF*	B3LYP**	RHF	B3LYP	RHF*	B3LYP**	RHF	B3LYP	RHF*	B3LYP**	Exp. (TTTBI)	Mode descriptions
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	3403	3216	3124	3154	3391	3213	3113	3151	3391	3213	3113	3151	–	ν(CH) (s.) (R1)
2	3391	3213	3113	3150	3385	3202	3108	3140	3378	3201	3101	3139	–	ν(CH) (as.) (R1)
3	3379	3201	3102	3139	3378	3200	3101	3138	3371	3193	3095	3131	–	ν(CH) (s.) (R2)
4	3378	3194	3101	3132	3369	3199	3093	3137	3368	3192	3092	3130	3059	ν(CH) (as.) (R2)
5	3377	3192	3100	3130	3363	3193	3088	3131	3362	3187	3087	3125	–	ν(CH) as. R1 + ν(CH) (s.-R2)
6	3371	3191	3095	3129	3358	3191	3083	3129	3357	3183	3082	3121	–	ν(CH) (as.) (R1)
7	3369	3190	3093	3128	3355	3187	3080	3125	3347	3166	3073	3105	3010	ν(CH) (as.) (R3)
8	3363	3187	3088	3125	3329	3183	3056	3121	3345	3165	3071	3104	–	ν(CH) (as.) (R3)
9	3357	3184	3082	3122	3309	3098	3038	3038	3276	3087	3008	3027	–	ν(CH) (s.) (R3)
10	1851	1686	1699	1653	1854	1691	1702	1658	1851	1686	1699	1653	–	δ(Ring) Def. (R2)
11	1819	1668	1670	1636	1819	1670	1670	1638	1818	1668	1669	1636	–	δ(Ring) Def. (R1)
12	1784	1633	1638	1601	1784	1635	1638	1603	1783	1631	1637	1599	1606	ν(Ring) (s.)
13	1674	1557	1537	1527	1672	1557	1535	1527	1673	1556	1536	1526	1504	ν(Ring) breath. (R2)
14	1624	1501	1491	1472	1618	1501	1485	1472	1621	1500	1488	1471	1450	ν(Ring) (as.)(1-2-3)
15	1616	1500	1484	1471	1614	1493	1482	1464	1615	1498	1483	1469	–	ν(Ring) Def. (R2)
16	1527	1442	1402	1414	1526	1446	1401	1418	1522	1439	1397	1411	1504	ν(Ring) (R1 + R2)
17	1494	1412	1372	1385	1493	1408	1371	1381	1493	1412	1371	1385	1392	ν(Ring) (R1 + R2)
18	1484	1384	1362	1357	1481	1381	1360	1354	1485	1383	1363	1356	–	ν(Ring) (R1 + R2 + R3)
19	1449	1323	1330	1297	1476	1326	1355	1300	1456	1323	1337	1297	1391	δ(CH) (R1 + R2)
20	1437	1314	1319	1289	1400	1298	1285	1273	1431	1304	1314	1279	1280	δ(CH) (R3)
21	1385	1294	1272	1269	1388	1292	1274	1267	1386	1294	1272	1269	1266	δ(Ring) (R3)
22	1372	1271	1260	1246	1384	1271	1271	1246	1373	1271	1261	1246	1248	δ(CH) (R1 + R2 + R3)
23	1363	1264	1251	1240	1362	1256	1250	1232	1370	1260	1258	1236	1225	CH wag. (R3) + δ(CH) (R2)
24	1339	1224	1229	1200	1352	1229	1241	1205	1333	1236	1224	1212	1185	δ(CH) (R2)
25	1324	1203	1216	1180	1319	1215	1211	1191	1325	1209	1216	1186	–	ν (Ring) (R3)
26	1314	1199	1206	1176	1314	1201	1206	1178	1320	1197	1212	1174	1176	CH wag. (R3)
27	1301	1196	1194	1173	1295	1193	1189	1170	1319	1196	1211	1173	–	CH wag. (R3)
28	1284	1187	1179	1164	1284	1187	1179	1164	1286	1191	1181	1168	–	δ(CH) (R1)
29	1270	1178	1166	1155	1270	1175	1166	1152	1272	1186	1168	1163	1159	δ(CH) (1) + CH wag. (3)
30	1194	1169	1096	1147	1192	1162	1094	1139	1193	1180	1095	1157	1142	CH wag. (R3)
31	1186	1112	1089	1090	1182	1099	1085	1078	1185	1107	1088	1086	1086	CH wag. (R3)
32	1125	1052	1033	1032	1171	1053	1075	1033	1170	1068	1074	1047	–	δ(Ring) def. (R3)
33	1124	1036	1032	1016	1126	1010	1034	990	1126	1051	1034	1031	1012	Ring breath. (R1)
34	1096	995	1006	976	1097	995	1007	976	1096	995	1006	976	–	Ring breath. (R3)

Table 4. (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
35	1095	962	1005	943	1095	976	1005	957	1095	962	1005	943	958	τ(Ring) (R1)
36	1036	953	951	935	1061	962	974	943	1031	935	947	917	–	τ(Ring) (R1 + R2)
37	1014	914	931	896	1033	926	948	908	1018	917	935	899	906	Ring breath. (R1 + R3)
38	1009	905	926	887	1016	913	933	895	1008	908	925	890	–	τ(Ring) (as.) (R2)
39	981	895	901	878	985	898	904	881	985	897	904	880	890	τ(Ring) (s.) (R2)
40	961	867	882	850	963	876	884	859	961	868	882	851	–	τ(Ring) (R1)
41	910	855	835	838	931	867	855	850	913	855	838	838	839	Rl-R2 breath. + δ(Ring) (R3) def.
42	853	796	783	781	862	799	791	783	860	801	790	785	780	Ring (Rl)
43	852	777	782	762	857	785	787	770	858	782	788	767	764	τ(Ring) (R3)
44	852	771	782	756	853	775	783	760	854	780	784	765	–	τ(Ring) R(3) + τ(Ring) R(2)
45	830	760	762	745	838	766	769	751	838	761	769	746	745	γ(CH) o.p. (R1)
46	829	746	761	732	821	746	754	732	824	758	757	743		τ(Ring) R3 + δ(ring) (R2) bend
47	791	739	726	725	802	734	736	720	809	751	743	736	726	τ(Ring) (R1-R2-R3)
48	789	730	724	716	791	730	726	716	789	730	724	716	–	τ(Ring) (R1 + R2)
49	670	630	615	618	675	629	620	617	675	634	620	622	616	τ(Ring) (R2-R3)
50	666	601	611	589	661	600	607	588	655	597	601	585	582	δ(Ring) (as.) (R1-R2-R3)
51	639	576	587	565	616	584	566	573	610	566	560	555	–	δ(Ring) (Rl + R3)
52	617	576	566	564	570	551	523	540	572	522	525	512	564	δ(Ring) (R1-R2-R3)
53	572	521	525	511	562	511	516	501	562	513	516	503	514	τ(Ring) Rl-R2
54	531	487	488	478	534	490	490	480	540	500	496	490	474	τ(Ring) (Rl)
55	489	449	449	440	509	459	467	450	530	486	487	477	451	τ(Ring) Rl +R2-R3
56	460	424	422	416	470	432	432	424	471	433	432	425	–	δ(Ring) (R1-R2-R3)
57	439	407	403	399	442	401	406	393	441	402	405	394	–	γ(R2-R3) o.p.
58	346	317	318	311	364	350	334	343	358	330	329	324	–	δ(Ring) (R1-R2-R3)
59	333	306	306	300	323	304	297	298	350	318	321	312	–	τ(Ring) (R1 + R2)
60	283	259	260	254	276	254	253	249	288	263	264	258	–	ν(C-Br) (as.)
61	227	204	208	200	236	238	217	233	241	223	221	219	–	ν(C-Br)
62	192	173	176	170	219	187	201	183	194	178	178	175	–	τ(Ring) Rl-R2-R3
63	159	147	146	144	162	136	149	133	166	152	152	149	–	δ(R1-R2-R3)
64	149	136	137	133	130	121	119	119	123	114	113	112	–	C-Br (as.) wag.
65	109	99	100	97	126	117	116	115	123	113	113	111	–	C-Br (sym.) wag.
66	99	90	91	88	110	94	101	92	109	100	100	98	–	γ(C-Br) o.p.
67	70	66	64	65	71	68	65	67	75	70	69	69	–	C-Br (sym.) wag.
68	58	55	53	54	64	60	59	59	61	58	56	57	–	C-Br (as.) wag.
69	38	36	35	35	37	35	34	34	46	43	42	42	–	γ(C-Br) o.p.

* Scaled by 0.9181 for RHF, ** scaled by 0.9806 for B3LYP [14], ν: stretching, δ: in plane bending, γ: out of plane bending, τ: torsion, o.p.: out of plane, i.p.: in plane, s.: symmetric, as.: asymmetric, breath.: breathing, def.: deformation, wag.: wagging, R: Ring.

calculated and experimental results were in good agreement.

Comparison of calculated and experimental IR spectrum of TTTBI was give in Fig. 5. Also comparison of calculated IR spectra between TTTBI and two isomers was given in Fig. 6. Bands at 3059 cm^{-1} and 3010 cm^{-1} indicate aromatic C-H stretching, a weak band at 1606 cm^{-1} (1601 cm^{-1}) shows that aromatic C=C bond, the band at 582 cm^{-1} shows the C-Br stretching. Five of CH stretching modes were not observed in IR spectrum of TTTBI but just calculated at 3154 cm^{-1}, 3150 cm^{-1}, 3139 cm^{-1}, 3130 cm^{-1}, 3125 cm^{-1}, and 3122 cm^{-1}. Ring stretching mode for the rings 1-2-3 was observed at 1450 cm^{-1} (1472 cm^{-1}). Ring deformation modes were not observed in IR spectrum but calculated at 1653 cm^{-1}, 1636 cm^{-1}, 1471 cm^{-1}, and 1032 cm^{-1}. Ring breathing mode for Ring 2 was observed at 1504 cm^{-1} (1527 cm^{-1}). Ring breathing mode for Ring 1 was observed at 1012 cm^{-1} (1016 cm^{-1}). Ring breathing mode for both Ring 1 and Ring 3 was observed at 906 cm^{-1} (896 cm^{-1}). Ring breathing mode for both Ring 1 and Ring 2 was observed at 839 cm^{-1} (838 cm^{-1}). Ring stretching modes for Ring 1 and Ring 2 were observed at 1504 cm^{-1} (1414 cm^{-1}) and 1392 cm^{-1} (1385 cm^{-1}) and just calculated for Ring 3 at 1180 cm^{-1}. CH wagging modes were observed at 1225 cm^{-1} (1240 cm^{-1}), 1176 cm^{-1} (1176 cm^{-1}), 1142 cm^{-1} (1147 cm^{-1}) and 1086 cm^{-1} (1090 cm^{-1}) and just calculated at 1173 cm^{-1}. CH in plane bending modes were observed for all rings at 1391 cm^{-1} (1297 cm^{-1}), 1280 cm^{-1} (1289 cm^{-1}), 1248 cm^{-1} (1246 cm^{-1}), 1185 cm^{-1} (1200 cm^{-1}) and 1159 cm^{-1} (1155 cm^{-1}), respectively. CH out of plane bending mode for Ring 1 was observed at 745 cm^{-1} (745 cm^{-1}). Ring bending modes were observed at 1266 cm^{-1} (1269 cm^{-1}), 582 cm^{-1} (589 cm^{-1}) and 564 cm^{-1} (564 cm^{-1}). The rest of the ring bending modes were just calculated at 564 cm^{-1}, 416 cm^{-1} and 311 cm^{-1}. Ring torsion modes were observed at 958 cm^{-1} (943 cm^{-1}), 764 cm^{-1} (762 cm^{-1}), 726 cm^{-1} (725 cm^{-1}), 616 cm^{-1} (618 cm^{-1}), 514 cm^{-1} (511 cm^{-1}), 474 cm^{-1} (478 cm^{-1}) and 451 cm^{-1} (440 cm^{-1}) and just calculated at 935 cm^{-1}, 887 cm^{-1}, 756 cm^{-1}, 732 cm^{-1}, 716 cm^{-1}, 300 cm^{-1} and 170 cm^{-1}. C-Br stretching modes f were just calculated at 254 cm^{-1} and 200 cm^{-1}. C-Br wagging modes were also just calculated at 133 cm^{-1}, 97 cm^{-1}, 65 cm^{-1} and 54 cm^{-1}. C-Br out of plane modes were just calculated at 88 cm^{-1} and 35 cm^{-1}.

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