

The FTIR spectra of substituted tetraoxa[8]circulenes and their assignments based on DFT calculations

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ABSTRACT

The FTIR spectrum of symmetrical derivative of the tetraoxa[8]circulene, named *para*-dinaphthylene-2,3,10,11-tetraundecyldiphenylenetetrauran (*p*-2B2N4R, R = *n*-C₁₁H₂₃) has been recorded and interpreted using density functional theory (DFT) calculations for the model compounds *p*-2B2N4R (R = H, C₂H₅). The unsubstituted tetraoxa[8]circulene, namely *para*-dinaphthylenodiphenylenetetrauran (*p*-2B2N) and *para*-dinaphthylene-2,3,10,11-tetraethyldiphenylenetetrauran (*p*-2B2N4R, R = C₂H₅) belong to the *D*_{2h} and *D*₂ symmetry point groups, respectively. The equilibrium molecular geometry, harmonic vibrational frequencies and infrared intensities have been calculated utilizing the DFT/B3LYP method with the 6–31G(d) basis set using the symmetry constraints. Comparison of the calculated vibrational spectra with the experimental data provides a reliable assignment of the observed bands in the FTIR spectra. The results of quantum-chemical calculations provide a complete interpretation of vibrational modes based on a good agreement with all details of the experimental spectra.

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1. Introduction

The synthesis and properties of the tetraoxa[8]circulenes family have attracted significant attention in recent time [1–8]. Tetraoxa[8]circulenes (Fig. 1) are highly stable compounds. For the simplest tetraoxa[8]circulene a central eight-membered ring is surrounded by four benzene rings and four furan rings in an alternating manner (Fig. 1, compound 1). All tetraoxa[8]circulenes are planar π -extended molecules with circular system of condensed furan and aromatic rings. As a result, the planar cyclooctatetraene ring in the center of the tetraoxa[8]circulene molecules is formed. Some tetraoxa[8]circulenes and other hetero[8]circulenes (e.g. octathia[8]circulene and tetrathiatetraselena[8]circulene) have been used in materials science with a great success during construction of various devices used in molecular electronics, such as OLEDs and OFETs devices [1,9,10].

In particular, the tetraoxa[8]circulenes have been used to prepare the discotic liquid crystals [3], blue organic light emitting diodes (OLEDs) [1] and stable radical-cation salts [11]; their

aggregation behavior both in the solid state and in solution has been demonstrated recently [5]. In general, one can say that the questions concerning tetraoxa[8]circulenes structure and their spectral properties represent a wide area of the upcoming studies in comparison with the well-studied problems related to thiacyclenes and selenacyclenes [9,10]. Vibrational (IR and Raman) spectra of symmetrical compounds 1 and 2 which belong to the *D*_{4h} point group (Fig. 1) have been studied recently with account of complete theoretical interpretation by DFT method [2].

In the present paper the experimentally measured FTIR spectrum of the newly synthesized tetraoxa[8]circulene *p*-2B2N4R (R = *n*-C₁₁H₂₃, Fig. 2) is discussed in comparison with the FTIR spectra of the similar tetraoxa[8]circulenes (Fig. 1), accounting our quantum-chemical predictions. The results of the quantum-chemical DFT calculations presented in this paper illustrates a complete assignment of the FTIR spectrum of the tetraoxa[8]circulene *p*-2B2N4R (R = *n*-C₁₁H₂₃). A short discussion of some relevant Raman bands is also presented; a detailed analysis will be given elsewhere.

2. Experimental

The π -extended tetraoxa[8]circulene (Fig. 2) *para*-dinaphthylene-2,3,10,11-tetraundecyldiphenylenetetrauran (*p*

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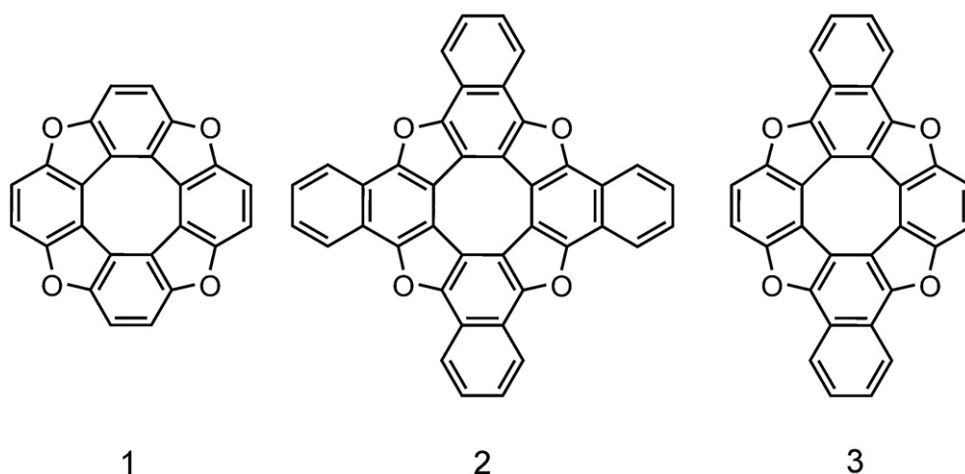


Fig. 1. Structure of the some π -extended tetraoxa[8]circulenes, named as 4B (I), 4N (II) and *p*-2B2N (III).

-2B2N4R, $R=n\text{-C}_{11}\text{H}_{23}$) has been prepared by the statistical condensation of 2,3-*bis*-undecyl-1,4-benzoquinone and naphthoquinone according to our previously published procedure, and the various isomers have been purified by the column chromatography on silica gel [1]. The FTIR spectra were recorded on a Bruker Alpha-P FTIR spectrometer (Bruker Optic GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector; a temperature-controlled single-bounce diamond attenuated total reflectance (ATR) crystal, and a pressure application device for solid samples.

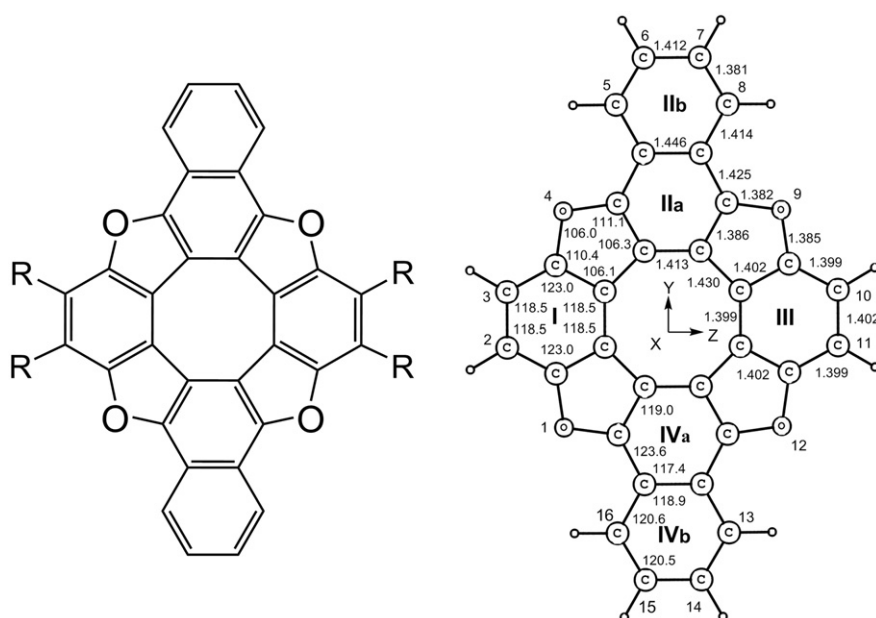
3. Method of calculation

The structure of the *p*-2B2N molecule was optimized at the B3LYP/6-31G(d) [12,13] level of the density functional theory with the control of possible symmetry constraints using the Gaussian 03 package [14]. The vibrational frequencies and the corresponding IR intensities were calculated for the optimized geometry in the framework of the same DFT method. All vibrational frequencies were found real which indicates the true minimum of the

total energy finding. The calculated vibrational frequencies were scaled in order to provide direct comparison with the experimental spectra. A satisfactory agreement between the computed and experimental frequencies can be obtained by using different scaling factors for different optical regions (or types of vibrations): 0.950 for the high frequency region (C–H stretching) and 0.969 for the rest of the spectrum (C=C bond stretching in aromatic rings, in-plane and out-of-plane deformation vibrations). The scale factors have been calculated as an averaged ratio between the experimentally observed and predicted frequency of all bands in a particular region of the IR and Raman spectra of the studied tetraoxa[8]circulenes. It should be noted that similar values of the scale factors are typical and well-known for the corresponding spectral regions [15].

For economy of computation resources the *n*-undecyl substituents in the *p*-2B2N4R molecule ($R=\text{C}_{11}\text{H}_{23}$) are replaced by the ethyl groups (*p*-2B2N4R, $R=\text{C}_2\text{H}_5$) and by hydrogen atoms (*p*-2B2N4R, $R=\text{H}$, Fig. 2, which is simply denoted as *p*-2B2N in the following).

The comparison of the calculated vibrational spectra of the *p*-2B2N4R ($R=\text{C}_2\text{H}_5$) and *p*-2B2N molecules with the experimental



FTIR spectrum of the *p*-2B2N4R molecule ($R = C_{11}H_{23}$) allows us additionally to search and assign the vibrational bands which correspond to the alkyl substituents vibrations.

The calculated IR spectra of the studied tetraoxa[8]circulenes are constructed with the SWizard program [16] (half-width is 15 cm^{-1} using the Lorentz distribution function). The detailed vibrational assignments of fundamental modes were performed on the ground of the calculated vibrational modes animation with GaussView 5.0 program [14].

4. Results and discussion

4.1. Molecular geometry of symmetrical tetraoxa[8]circulene molecules

Substitution of the two benzene rings in the parent all-benzene tetraoxa[8]circulene molecule (Fig. 1, compound 1) by the naphthalene fragments (Fig. 1, compound 3) creates the *p*-2B2N molecule which belongs to the D_{2h} symmetry point group. In this case the geometry parameters of the naphthalene fragments (the rings II(a,b) and IV(a,b)) are quite close to the corresponding parameters in the 4N molecule (Fig. 1, compound 2) and the benzene substituent parameters (the rings I and III in the *p*-2B2N molecule, Fig. 2) are close to those of the 4B molecule. At the same time the furan rings become non-symmetrical and the C–C bonds in the entire cyclooctatetraene-type circle are not strictly alternate (Fig. 2) in comparison with the tetraoxa[8]circulene molecule 4B [2]. In the series of the 4B, *p*-2B2N and 4N molecules the perimeter of the entire and outer π -conjugated circuits increases.

Appearance of the ethyl substituents at the 2, 3, 10 and 11 positions of the outer perimeter of the *p*-2B2N4R molecule leads to increase of the $C^{(3)}-C^\alpha$, $C^\alpha-O$, C^2-C^3 bond lengths by 0.008, 0.005 and 0.014 Å respectively in comparison with the unsubstituted *p*-2B2N species, but the $C^\alpha-C^\beta$ bond lengths decrease by 0.004 Å, which is a manifestation of the weak positive inductive effect of the ethyl substituents.

Accounting for the fact that the benzene, furan and naphthalene rings in the studied tetraoxa[8]circulenes are involved in the united extended π -system, one can expect in the FTIR spectra an existence of not only individual characteristic modes of these constituents but also an occurrence of the mixed vibrations.

4.2. IR spectrum of the *p*-2B2N molecule

We have calculated the *p*-2B2N4R molecule with $R = H$ and $R = C_2H_5$ in order to make a qualitative assignment of all extra bands in a real experimental FTIR spectrum detected for the species with $R = C_{11}H_{23}$. Comparison of all calculated and experimental spectra with account of the known typical qualitative assignments for aliphatic chains affords us to make a complete interpretation of the experimental measurements.

The *p*-2B2N tetraoxa[8]circulene molecule consists of 48 atoms and has 138 normal modes of vibrations. These 138 normal vibrational modes of the *p*-2B2N molecule in the D_{2h} point group (the molecule is in the yz plane) are distributed by the symmetry types as the following:

$$\Gamma_{vib} = 12A_u + 11B_{1g}(R) + 11B_{3u}(IR) + 11B_{2g}(R) + 23B_{2u}(IR) + 23B_{1u}(IR) + 23B_{3g}(R) + 24A_g(R).$$

The in-plane vibrations of the B_{1u} and B_{2u} symmetry and the out-of-plane vibrations of the B_{3u} type are allowed in the IR spectrum. In the Raman spectrum the in-plane vibrations of the A_g , B_{3g} symmetry and the out-of-plane B_{1g} , B_{2g} vibrations are active (Table SM 1). The in-plane A_u modes are forbidden in both IR and Raman spectra.

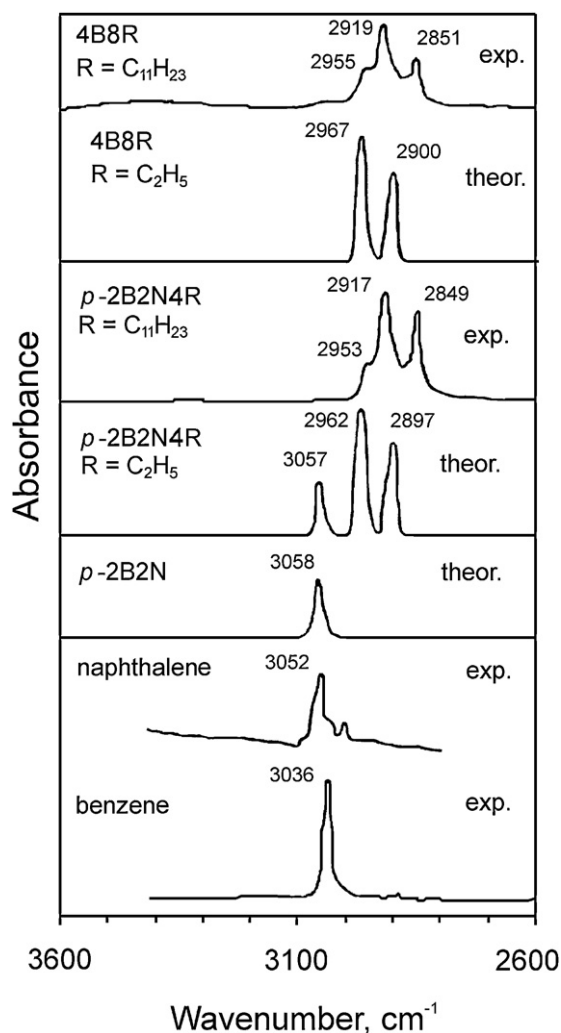


Fig. 3. IR spectra for *p*-2B2N ($R = H, C_2H_5, C_{11}H_{23}$), 4B ($R = C_2H_5, C_{11}H_{23}$), benzene, and naphthalene molecules in high-frequency region.

The calculated vibrational frequencies and IR intensities together with the normal modes assignment in the *p*-2B2N4R molecules ($R = H$ and C_2H_5) are presented in Table 1 and Table 2, respectively. In Tables 1 and 2 a comparison with the experimental FTIR spectrum of the parent *p*-2B2N4R ($R = C_{11}H_{23}$) tetraoxa[8]circulene molecule is given.

The spectral regions 3600–2600 and 1700–400 cm^{-1} are shown in Figs. 3 and 4, respectively for all studied and calculated molecules including the benzene, furan and naphthalene for comparison. For the *p*-2B2N4R ($R = C_{11}H_{23}$) molecule the experimental FTIR spectrum is presented in these two Figures.

4.2.1. CH vibrations

The carbon–hydrogen vibrations in aromatic compounds can be found in the range 3080–3030 cm^{-1} (CH stretching), 1225–950 cm^{-1} (in-plane CH deformations), and below 900 cm^{-1} (out-of-plane CH deformation vibrations) [17,18].

4.2.1.1. The CH stretching vibrations, ν (CH). In the IR spectrum of the unsubstituted tetraoxa[8]circulene *p*-2B2N there are six vibrational modes of the B_{1u} and B_{2u} symmetry, which belong to the C–H bonds stretching vibrations. Such vibrations in benzene rings (modes ν_{137} , ν_{136}) are predicted by our DFT calculation to appear at higher frequency in comparison with the naphthalene modes ν_{133} , ν_{132} and ν_{129} , ν_{128} (Table 1). The symmetric C–H stretching

Table 1
Calculated data of selected vibrational modes for *p*-2B2N molecule.

Num.	Sym.	Fre.	I_{IR}	$I_{IR, rel.}$	Exp. <i>p</i> -2B2N4R, R = C ₁₁ H ₂₃	Assignment
ν_{137}	B_{2u}	3072	13.4	$7.1 \cdot 10^{-2}$	3057(IR)	CH str., s., I, III, oph.
ν_{136}	B_{1u}	3060	0.01	$3.5 \cdot 10^{-5}$		CH str., as., I, III
ν_{133}	B_{1u}	3058	63.6	$3.4 \cdot 10^{-1}$		CH str., s., II, IV, oph.
ν_{132}	B_{2u}	3054	23.6	$1.3 \cdot 10^{-1}$		CH str., as., II, IV
ν_{129}	B_{1u}	3043	25.5	$1.4 \cdot 10^{-1}$	1709(IR)	CH str., as., II, IV
ν_{128}	B_{2u}	3031	3.2	$1.7 \cdot 10^{-2}$		CH str., as., II, IV
ν_{125}	B_{2u}	1637	1.6	$8.4 \cdot 10^{-3}$		CC str., s., I, III, oph.
ν_{123}	B_{2u}	1625	0.1	$6.8 \cdot 10^{-4}$		CC str., s., II, IV, iph.
ν_{122}	B_{1u}	1617	0.9	$5.0 \cdot 10^{-3}$	1583(IR)	CC str., s., II, IV, oph.
ν_{121}	B_{3g}	1600	–	0.0		CC str., s., I, III oph.; C α C β str., as.
ν_{120}	B_{1u}	1590	0.4	$2.1 \cdot 10^{-3}$		CC str., s., I, III, iph.; CC str., s., II, IV, oph.; C α C β str., s.
ν_{117}	B_{2u}	1575	11.3	$6.0 \cdot 10^{-2}$		CC str., s., IIa, IVa, iph.; CC str., as., IIb, IVb, iph.; CC str., s., I, III, oph.
ν_{116}	B_{1u}	1541	0.2	$1.3 \cdot 10^{-3}$	1464 IR	CC str., as., II, IV, oph.; C β C β' str.
ν_{113}	B_{2u}	1464	2.8	$1.4 \cdot 10^{-4}$		CC str., as., I, III, oph.
ν_{112}	B_{1u}	1460	69.6	$3.7 \cdot 10^{-1}$		CC str., as., II, IV, oph.; C β C β' str.
ν_{111}	B_{3g}	1452	–	0.0		CC str., as., I, III; IIa, IVa ip. def. as.
ν_{109}	B_{2u}	1429	0.03	$1.4 \cdot 10^{-4}$	1415 IR	CC str., as., II, IV, iph., I, III, oph.
ν_{108}	B_{1u}	1424	187.2	1.0		CC str., as., I, III; CC str., as., Kekule IIa, IVa.
ν_{105}	B_{1u}	1397	38.8	$2.1 \cdot 10^{-1}$		CC str., as., Kekule, IIa, IVa; C α C β str., s.
ν_{104}	B_{2u}	1384	105.7	$5.6 \cdot 10^{-1}$		CC str., as., Kekule, I, III; C α C β str., as.
ν_{101}	B_{1u}	1346	10.2	$5.4 \cdot 10^{-2}$	1376(IR)	CO str., half furan ring; CC str., as., Kekule, IIb, IVb, oph.; C β C β' str.
ν_{100}	B_{2u}	1338	77.1	$4.1 \cdot 10^{-1}$		CC str., as., Kekule, I, III; CO str. half furan ring
ν_{97}	B_{1u}	1290	28.3	$1.5 \cdot 10^{-1}$		CC str., as., Kekule, IIb, IVb; CO str.; C β C β' str.
ν_{95}	B_{2u}	1273	0.7	$3.6 \cdot 10^{-3}$		CH ip. bend., I-IV; I, III str., oph.
ν_{93}	B_{2u}	1246	0.2	$9.3 \cdot 10^{-4}$	1250(IR)	CH ip. bend., I-IV; I, III str., oph.
ν_{92}	B_{1u}	1220	55.8	$3.0 \cdot 10^{-1}$		CH ip. bend., I, III, iph.; CO str., s., half furan ring; I, III def., iph.
ν_{89}	B_{2u}	1172	21.6	$1.2 \cdot 10^{-1}$		CH ip. bend., I-IV; CO str., s.; I, III str., oph.
ν_{87}	B_{1u}	1158	3.9	$2.1 \cdot 10^{-2}$		CH ip. bend., II, IV, oph.
ν_{86}	B_{1u}	1149	16.3	$8.7 \cdot 10^{-2}$	1099(IR)	CH ip. bend.; CO str., as., half furan ring; I, III, IIa, IVa def.
ν_{84}	B_{2u}	1129	64.7	$3.5 \cdot 10^{-1}$		CH ip. bend., I-IV; CO str., as.
ν_{81}	B_{2u}	1070	5.1	$2.7 \cdot 10^{-2}$		CH ip. bend., I, III, oph.; CO str., s.
ν_{80}	B_{1u}	1054	61.1	$3.3 \cdot 10^{-1}$		CH ip. bend.; CO str., as.; I, III ip. def., as.; II, IV ip. def., s.
ν_{78}	B_{2u}	1029	104.3	$5.6 \cdot 10^{-1}$	1041(IR)	CH ip. bend., I, III; CO str., as.; IIb, IVb, ct., ip. def., as.
ν_{76}	B_{1u}	1022	58.4	$3.1 \cdot 10^{-1}$		CO str., as; IIb, IVb, ip. def.; CH ip. bend.
ν_{74}	B_{1u}	985	47.1	$2.5 \cdot 10^{-1}$		II, IV, fu. bre.; I, III, ct. ip. def., as.
ν_{70}	B_{3u}	928	1.4	$7.7 \cdot 10^{-3}$		CH op. bend., as., II, IV, oph.
ν_{68}	B_{2u}	905	50.1	$2.7 \cdot 10^{-1}$	914(IR)	I, fu. and III, fu. str., oph.; IIb, IVb, ip. def., as.
ν_{62}	B_{1u}	828	20.3	$1.1 \cdot 10^{-1}$		II, IV bre., oph.; fu. str.
ν_{61}	B_{2u}	827	2.7	$1.4 \cdot 10^{-2}$		II, IV, def., as.; I, III str., oph.; ct. def., as.
ν_{59}	B_{3u}	782	58.0	$3.1 \cdot 10^{-1}$		CH op. bend., s., I, III, iph.
ν_{55}	B_{3u}	755	98.3	$5.3 \cdot 10^{-1}$	755(IR)	CH op. bend., s., II, IV, iph.
ν_{50}	B_{1u}	685	3.6	$1.9 \cdot 10^{-2}$		II, IV bre., oph.
ν_{49}	B_{2u}	684	1.2	$6.2 \cdot 10^{-3}$		I, III ip. def., s., oph.; IIb, IVb ip. def., as.
ν_{46}	B_{3u}	659	20.2	$1.1 \cdot 10^{-1}$		IIa, IVa op. def.; CH op. bend., iph.
ν_{42}	B_{3u}	637	0.1	$3.9 \cdot 10^{-4}$	718(IR)	CH op. bend., s., I, III, iph.; I, III, fu. op. def., iph.
ν_{40}	B_{1u}	623	1.3	$7.2 \cdot 10^{-3}$		IIa and IIb str., oph.; IVa and IVb str., oph.
ν_{39}	B_{2u}	621	6.7	$3.6 \cdot 10^{-2}$		II and IV ip. def., iph.
ν_{36}	B_{1u}	576	10.8	$5.8 \cdot 10^{-2}$		IIb, IVb ip. def., s., oph.; I, III def., as.
ν_{32}	B_{2u}	512	0.8	$4.0 \cdot 10^{-3}$	462(IR)	I and III ip. def., s., oph.; II and IV ip. def., as.
ν_{28}	B_{3u}	462	5.6	$3.0 \cdot 10^{-2}$		II and IV op. def., iph.; CH op. bend.
ν_{24}	B_{1u}	422	3.1	$1.7 \cdot 10^{-2}$		II and IV ip. def., s., oph.
ν_{20}	B_{2u}	369	0.1	$4.8 \cdot 10^{-4}$		II and IV sw., iph.
ν_{18}	B_{3u}	332	0.4	$2.1 \cdot 10^{-3}$	636(IR)	I-IV op. def.
ν_{17}	B_{1u}	328	0.3	$1.7 \cdot 10^{-3}$		II and IV str., oph.
ν_{14}	B_{3u}	275	3.9	$2.1 \cdot 10^{-2}$		Skeleton op. def., iph.
ν_8	B_{3u}	163	0.6	$3.4 \cdot 10^{-3}$		I, III and II, IV op. def., oph.
ν_6	B_{2u}	143	0.7	$3.9 \cdot 10^{-3}$	462(IR)	IIb, IVb ip. sw., iph.
ν_4	B_{3u}	82	0.7	$3.8 \cdot 10^{-3}$		I-IV, ct and fu. op. def., oph.
ν_1	B_{3u}	35	0.5	$2.9 \cdot 10^{-3}$		Skeleton op. waving, iph.

Num.: number of modes; Sym.: symmetry of modes; Fre.: scaled frequency value, cm⁻¹; I_{IR} – IR intensity, km/mol; $I_{IR, rel.}$ – relative IR intensity; def.: deformation; bre: breathing; s.: symmetrical vibrations; as.: asymmetrical vibrations; iph.: in phase vibrations; oph.: out-of-phase vibration; I, III, benzene ring numbers; II(a,b), IV(a,b), naphthalene ring numbers (Fig. 2); bend.: bending vibrations; sw.: swinging vibrations; fu.: furan; ct: cyclooctatetraene ring; str.: stretching; ip.: in plane vibration; op.: out-of-plane vibration.

vibrations in aromatics are observed usually at higher frequencies and show larger intensity in comparison with the asymmetric C–H stretching modes. In the calculated IR spectrum of the *p*-2B2N molecule they are observed as a medium band at 3072–3031 cm⁻¹ with the maximum at 3058 cm⁻¹ (Fig. 3). We have not obtained frequency shift of the C–H stretching vibrations of the *p*-2B2N molecule in comparison with the calculated IR spectra of the 4B and 4N molecules [2]. In the calculated IR spectrum of benzene (the D_{6h} symmetry point group) the analogous asymmetric CH vibrations of

the E_{1u} type are predicted at the same frequency (3041 cm⁻¹) with the identical IR absorption intensity (51.9 km/mole). The observed IR spectrum of benzene in gas phase exhibits an intense band at 3064 cm⁻¹ [19] and at 3036 cm⁻¹ in a condensed phase (Fig. 3) [20]. In the naphthalene IR spectrum (D_{2h} symmetry point group, yz is a molecular σ_h plane) the symmetric CH stretching vibrations of the B_{2u} symmetry are calculated at 3047 cm⁻¹ ($I = 59.4$ km/mole); the asymmetric CH stretching in naphthalene are also slightly shifted (3036 cm⁻¹) and provide together one line with the similar

Table 2
Calculated data for vibrational modes of the *p*-2B2N4R (R = C₂H₅) molecule.

Num.	Sym.	Fre.	<i>I</i> _{IR}	<i>I</i> _{IR} , rel.	Exp. R = C ₁₁ H ₂₃	Assignment
ν_{209}	<i>B</i> ₂	3057	68.0	$3.6 \cdot 10^{-1}$	3057(IR)	CH str., s., II, IV, oph.
ν_{208}	<i>B</i> ₃	3052	27.6	$1.5 \cdot 10^{-1}$		CH str., as., II, IV, iph.
ν_{207}	<i>B</i> ₁	3052	0.001	$2.1 \cdot 10^{-6}$		CH str., as., II, IV, oph.
ν_{205}	<i>B</i> ₂	3040	25.9	$1.4 \cdot 10^{-1}$		CH str., as., II, IV, oph.
ν_{204}	<i>B</i> ₃	3030	2.4	$1.3 \cdot 10^{-2}$		CH str., as., II, IV, iph.
ν_{203}	<i>B</i> ₁	3030	0.001	$1.1 \cdot 10^{-6}$		CH str., as., II, IV, oph.
ν_{201}	<i>B</i> ₃	2975	113.0	$6.0 \cdot 10^{-1}$	2953(IR)	CH ₂ , CH ₃ str., as.
ν_{200}	<i>B</i> ₂	2974	34.0	$1.8 \cdot 10^{-1}$		CH ₂ , CH ₃ str., as.
ν_{199}	<i>B</i> ₁	2974	2.4	$1.3 \cdot 10^{-2}$		CH ₂ , CH ₃ str., as.
ν_{197}	<i>B</i> ₃	2963	72.3	$3.8 \cdot 10^{-1}$		CH ₂ , CH ₃ str., as.
ν_{196}	<i>B</i> ₂	2962	91.8	$4.9 \cdot 10^{-1}$	2917(IR)	CH ₂ , CH ₃ str., as.
ν_{195}	<i>B</i> ₁	2962	15.4	$8.2 \cdot 10^{-2}$	2921(R)	CH ₂ , CH ₃ str., as.
ν_{193}	<i>B</i> ₃	2948	24.4	$1.3 \cdot 10^{-1}$		CH ₂ , CH ₃ str., as.
ν_{192}	<i>B</i> ₂	2943	5.2	$2.8 \cdot 10^{-2}$		CH ₂ , CH ₃ str., as.
ν_{191}	<i>B</i> ₁	2943	1.7	$8.9 \cdot 10^{-3}$		CH ₂ , CH ₃ str., as.
ν_{189}	<i>B</i> ₃	2916	32.3	$1.7 \cdot 10^{-1}$		CH ₂ str., s., I, III, oph.
ν_{188}	<i>B</i> ₁	2912	52.6	$2.8 \cdot 10^{-1}$		CH ₂ str., s., I, oph, III, oph.
ν_{187}	<i>B</i> ₂	2912	4.9	$2.6 \cdot 10^{-2}$		CH ₂ str., s., I, oph, III, oph.
ν_{185}	<i>B</i> ₁	2898	56.5	$3.0 \cdot 10^{-1}$		CH ₃ str., s., I, oph, III, oph.
ν_{184}	<i>B</i> ₂	2897	20.7	$1.1 \cdot 10^{-1}$		CH ₃ str., s., I, oph, III, oph.
ν_{183}	<i>B</i> ₃	2897	82.8	$4.4 \cdot 10^{-1}$	2849(IR)	CH ₃ str., s., I, III, oph.
ν_{181}	<i>B</i> ₃	1638	7.2	$3.8 \cdot 10^{-2}$	1709(IR)	CC str., s., I, III, oph.
ν_{180}	<i>B</i> ₁	1628	0.001	$4.3 \cdot 10^{-6}$	1637(R)	CC str., s., II, IV, oph.
ν_{179}	<i>B</i> ₃	1625	2.8	$1.5 \cdot 10^{-2}$		CC str., s., II, IV, iph.
ν_{178}	<i>B</i> ₂	1617	0.1	$5.3 \cdot 10^{-4}$		CC str., s., II, IV, oph.
ν_{177}	<i>B</i> ₁	1603	0.1	$4.4 \cdot 10^{-4}$	1613(R)	CC str., s., I, III, oph.; C ^α C ^β str., as.
ν_{176}	<i>B</i> ₂	1593	0.2	$1.3 \cdot 10^{-3}$		CC str., s., I, III, iph.; CC str., s., II, IV, oph.; C ^α C ^β str., s.
ν_{174}	<i>B</i> ₁	1581	0.02	$9.1 \cdot 10^{-5}$	1584(R)	CC str., IIa, IVa, s., IIb, IVb, as.; COC ip. bend.
ν_{173}	<i>B</i> ₃	1576	14.8	$7.9 \cdot 10^{-2}$	1583(IR)	CC str., s., IIa, IVa, iph.; CC str., as., IIb, IVb, iph.
ν_{172}	<i>B</i> ₂	1541	0.1	$7.2 \cdot 10^{-4}$		CC str., as., II, IV, oph.; C ^β C ^{β'} str.
ν_{169}	<i>B</i> ₃	1499	1.2	$6.3 \cdot 10^{-3}$		CH ₂ scis., oph.; CH ₃ bend, as.
ν_{168}	<i>B</i> ₁	1489	7.3	$3.9 \cdot 10^{-2}$	1499(IR)	CH ₂ scis., oph.; CH ₃ bend, as.
ν_{167}	<i>B</i> ₂	1489	1.4	$7.6 \cdot 10^{-3}$		CH ₂ scis., iph.
ν_{165}	<i>B</i> ₃	1484	0.4	$2.3 \cdot 10^{-3}$		CH ₃ bend, as.; CH ₂ scis., oph, II, IV.
ν_{164}	<i>B</i> ₁	1480	0.1	$6.4 \cdot 10^{-4}$		CH ₃ bend, as.
ν_{163}	<i>B</i> ₂	1480	11.8	$6.3 \cdot 10^{-2}$	1464(IR)	CH ₃ bend, as.
ν_{161}	<i>B</i> ₃	1480	4.3	$2.3 \cdot 10^{-2}$		CH ₃ bend, as.
ν_{159}	<i>B</i> ₂	1465	0.4	$2.0 \cdot 10^{-3}$	1466(R)	CH ₂ scis., I, III, iph.
ν_{158}	<i>B</i> ₁	1465	3.5	$1.9 \cdot 10^{-2}$		CH ₂ scis., I, III, oph.
ν_{157}	<i>B</i> ₃	1465	0.003	$1.7 \cdot 10^{-5}$		CC str., as., I, III oph.
ν_{156}	<i>B</i> ₂	1460	44.7	$2.4 \cdot 10^{-1}$	1464(IR)	CC str., as., II, IV oph.; C ^β C ^{β'} str.
ν_{155}	<i>B</i> ₁	1446	0.02	$1.3 \cdot 10^{-4}$		IIa, IVa, ip. def., as.; CC str., as., I, III; C ^α C ^β , C ^α C ^{β'} str., s.
ν_{153}	<i>B</i> ₃	1429	0.3	$1.6 \cdot 10^{-3}$		CC str., as., II, IV, iph., I, III, oph.
ν_{151}	<i>B</i> ₂	1404	185.1	$9.8 \cdot 10^{-1}$	1415(IR)	CC str., as., I, III; CC str., as., Kekule, IIa, IVa.
ν_{150}	<i>B</i> ₁	1404	1.4	$7.2 \cdot 10^{-3}$		C ^β C ^{β'} str.
ν_{149}	<i>B</i> ₂	1392	0.02	$1.1 \cdot 10^{-4}$		CH ₃ bend, s., I, III, iph.
ν_{148}	<i>B</i> ₁	1391	7.2	$3.8 \cdot 10^{-2}$		CH ₃ bend, s., I, III, oph.
ν_{147}	<i>B</i> ₃	1391	3.1	$1.6 \cdot 10^{-2}$		CH ₃ bend, s., I, III, oph.
ν_{145}	<i>B</i> ₃	1378	126.8	$6.7 \cdot 10^{-1}$	1376(IR)	CC str., as., Kekule, I, III; CH ₂ twist.; C ^α C ^β str., as.
ν_{144}	<i>B</i> ₂	1365	22.8	$1.2 \cdot 10^{-1}$		CC str., as., I, III and II, IV; CH ₂ twist.; C ^α C ^β str., s.
ν_{142}	<i>B</i> ₁	1361	0.1	$2.5 \cdot 10^{-4}$		C ^β C ^{β'} str.
ν_{141}	<i>B</i> ₂	1344	2.2	$1.2 \cdot 10^{-2}$		CO str., half furan ring; CC str., as., Kekule, IIb, IVb, oph.; C ^β C ^{β'} str.
ν_{140}	<i>B</i> ₃	1341	103.9	$5.5 \cdot 10^{-1}$	1335(IR)	CC str., as., Kekule I, III; CO str., half furan ring
ν_{138}	<i>B</i> ₁	1335	0.15	$8.2 \cdot 10^{-4}$	1346(R)	IIa, IVa, def., as., ip.; CO str., s.; C ^β C ^{β'} str.
ν_{137}	<i>B</i> ₃	1332	5.0	$2.7 \cdot 10^{-2}$		CH ₂ wag.
ν_{136}	<i>B</i> ₂	1332	6.8	$3.6 \cdot 10^{-2}$		CH ₂ wag.
ν_{134}	<i>B</i> ₁	1328	1.5	$7.8 \cdot 10^{-3}$		CH ₂ wag., oph.
ν_{133}	<i>B</i> ₃	1301	5.1	$2.7 \cdot 10^{-2}$		C–CH ₂ str.; I, III str., oph.
ν_{132}	<i>B</i> ₂	1291	16.3	$8.7 \cdot 10^{-2}$		CC str., as., Kekule, IIb, IVb; CO str.; C ^β C ^{β'} str.
ν_{130}	<i>B</i> ₁	1267	0.001	$1.1 \cdot 10^{-6}$		CH ₂ twist.
ν_{129}	<i>B</i> ₃	1266	2.8	$1.5 \cdot 10^{-2}$		I, III, str., oph.; CH ip. bend., II, IV; CO str., s., oph.
ν_{128}	<i>B</i> ₂	1266	6.7	$3.6 \cdot 10^{-2}$	1250(IR)	CH ₂ twist.
ν_{126}	<i>B</i> ₃	1253	4.0	$2.2 \cdot 10^{-2}$		CH ₂ twist.; I, III str., oph.
ν_{125}	<i>B</i> ₁	1245	0.03	$1.6 \cdot 10^{-4}$		CH ip. bend, II, IV.
ν_{123}	<i>B</i> ₂	1223	12.2	$6.5 \cdot 10^{-2}$	1217(IR)	CO str., half furan ring; C _{benz} –CH ₂ str.; CH ₂ wag.; I, III def., iph.
ν_{122}	<i>B</i> ₁	1167	1.5	$8.2 \cdot 10^{-3}$		CO str., as.; CH ₂ wag.
ν_{121}	<i>B</i> ₃	1166	3.0	$1.6 \cdot 10^{-2}$	1159(IR)	CH ip.bend, II, IV; CO str., s.; I, III str., oph.
ν_{119}	<i>B</i> ₂	1157	1.4	$7.6 \cdot 10^{-3}$		CH ip.bend, II, IV, oph.
ν_{118}	<i>B</i> ₁	1137	0.01	$2.5 \cdot 10^{-5}$		CH ip.bend, II, IV, oph.; CO str., as.
ν_{117}	<i>B</i> ₂	1108	6.9	$3.7 \cdot 10^{-2}$	1108(IR)	CH ₂ twist.
ν_{116}	<i>B</i> ₁	1107	0.001	$1.1 \cdot 10^{-6}$		CH ₂ twist.
ν_{115}	<i>B</i> ₂	1102	95.0	$5.1 \cdot 10^{-1}$	1099(IR)	CO str., half furan ring; I, III, IIa, IVa def.
ν_{114}	<i>B</i> ₃	1099	56.9	$3.0 \cdot 10^{-1}$	1099(IR)	CH ip.bend, II, IV, iph.; CO str., as.; I–IV ip. def.
ν_{112}	<i>B</i> ₃	1089	0.3	$1.4 \cdot 10^{-3}$		CH ₂ and CH ₃ twist.; CO str.
ν_{109}	<i>B</i> ₃	1060	39.4	$2.1 \cdot 10^{-1}$		CH ₂ wag, CH ₃ twist.
ν_{108}	<i>B</i> ₂	1051	1.4	$7.5 \cdot 10^{-3}$		CH ₃ twist.; CH ₂ wag.; CH ip. bend.; CO str., as.; I–IV ip. def.

Table 2 (Continued)

Num.	Sym.	Fre.	I_{IR}	$I_{IR, rel.}$	Exp. R = C ₁₁ H ₂₃	Assignment
ν_{107}	B_1	1051	0.1	$5.6 \cdot 10^{-4}$		CH ₃ twist.; CH ₂ wag.
ν_{106}	B_3	1036	188.0	1.00	1041(IR)	CO str., as.; CH ₂ twist.; IIb, IVb ip. def., as.
ν_{104}	B_2	1034	0.9	$4.6 \cdot 10^{-3}$		CO str.; IIb, IVb, ip. def.; CH ip. bend.
ν_{103}	B_1	1031	0.01	$5.0 \cdot 10^{-5}$		CO str.; IIb, IVb., ct., ip. def., as.
ν_{101}	B_2	1008	16.9	$9.0 \cdot 10^{-2}$		CH ₂ –CH ₃ str.; IIb, IVb str., oph.
ν_{100}	B_3	985	12.2	$6.5 \cdot 10^{-2}$	985(R)	CH ₂ –CH ₃ str. I, III, oph.
ν_{99}	B_1	967	0.1	$5.5 \cdot 10^{-4}$		Fu. bre., oph.; II, IV, ct., ip. def.; CH ₂ –CH ₃ str.
ν_{98}	B_2	963	32.9	$1.7 \cdot 10^{-1}$	941(IR)	II, IV, fu. bre.; ct. ip. def., as.
ν_{96}	B_2	958	0.001	$5.9 \cdot 10^{-6}$		CH op. bend., as., II, IV, iph.
ν_{94}	B_1	926	1.2	$6.1 \cdot 10^{-3}$		CH op. bend., as., II, IV, iph.
ν_{93}	B_3	926	0.000	0.00		CH op. bend., as., II, IV, iph.
ν_{92}	B_3	910	22.0	$1.2 \cdot 10^{-1}$	914(IR)	I, fu. and III, fu. str., oph.; IIb, IVb, ip. def., as.; CH ₂ –CH ₃ str.
ν_{91}	B_1	904	0.004	$1.9 \cdot 10^{-5}$	891(R)	IIb, IVb, fu., ct. def., as.; CH ₂ –CH ₃
ν_{90}	B_2	899	61.8	$3.3 \cdot 10^{-1}$	891(R) 890(IR)	Fu. str.; I, III, ip. def., as.; ct. def., as.; CH ₂ –CH ₃ str.
ν_{89}	B_1	896	0.000	0.00	891(R)	Fu. str.; I, III, ip. def.; as., ct. def., as.; CH ₂ –CH ₃ str.
ν_{88}	B_3	895	36.7	$2.0 \cdot 10^{-1}$	860(IR)	II, IV ip. def., as.; ct. def., as.; I, III, str., oph.; CH ₂ –CH ₃ str.
ν_{86}	B_2	854	0.002	$1.0 \cdot 10^{-5}$	857(R)	CH op. bend., as., II, IV, iph.
ν_{84}	B_2	820	0.6	$3.2 \cdot 10^{-3}$	802(IR)	II, IV bre., oph.; fu. str.; CH ₂ rock., CH ₃ rock.
ν_{83}	B_1	816	0.02	$8.1 \cdot 10^{-5}$		CH ₂ rock., CH ₃ rock.
ν_{82}	B_3	774	8.8	$4.7 \cdot 10^{-2}$	789(IR)	CH ₂ rock., CH ₃ rock.
ν_{80}	B_1	763	0.01	$7.0 \cdot 10^{-5}$		I, III, IIa, IVa, def., as.; ct. sw.
ν_{79}	B_2	761	6.8	$3.6 \cdot 10^{-2}$		II, IV bre., oph.; CH ₂ rock., CH ₃ rock.
ν_{78}	B_3	755	0.07	$3.6 \cdot 10^{-4}$		CH op. bend., s.; II, IV, iph.
ν_{77}	B_1	754	72.7	$3.9 \cdot 10^{-1}$	755(IR)	CH op. bend., s.; II, IV, iph.
ν_{76}	B_3	745	2.7	$1.5 \cdot 10^{-2}$		CH ₂ rock.; CH ₃ rock.
ν_{74}	B_2	730	0.001	$6.4 \cdot 10^{-6}$		CH op. bend., as.; II, IV op. def., iph.
ν_{73}	B_1	713	0.01	$7.5 \cdot 10^{-5}$		CH ₂ rock.; IIb, IVb ip. def., as.
ν_{71}	B_3	706	0.1	$5.1 \cdot 10^{-4}$		I, III, op. def., iph.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{70}	B_3	679	4.7	$2.5 \cdot 10^{-2}$		I, III, ip. def., s., oph.; IIb, IVb, ct. def., as.
ν_{68}	B_1	676	13.7	$7.3 \cdot 10^{-2}$	718(IR)	I, III, fu. op. def.
ν_{67}	B_2	674	0.04	$1.9 \cdot 10^{-4}$		I, III def., op., oph.; fu. op. def.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{66}	B_1	668	1.5	$7.8 \cdot 10^{-3}$	682(R)	CH ₂ rock.; II, IV ip. def., as.
ν_{65}	B_2	664	0.1	$7.7 \cdot 10^{-4}$		IIa and IIb str., oph.; IVa and IVb str., oph.; CH ₂ rock.
ν_{64}	B_1	655	15.3	$8.1 \cdot 10^{-2}$	667(IR)	CH op. bend., II, IV, iph.; IIa, IVa op. def., iph.
ν_{63}	B_3	650	0.06	$3.3 \cdot 10^{-4}$		CH op. bend., II, IV, iph.; IIa, IVa op. def., oph.
ν_{62}	B_2	639	12.2	$6.5 \cdot 10^{-2}$	636(IR)	IIb, IVb ip. def., s., oph.; I, III def., as.
ν_{61}	B_2	638	0.8	$4.3 \cdot 10^{-3}$		IIa, IVa op. def.
ν_{59}	B_3	620	0.1	$7.7 \cdot 10^{-4}$		I and III op. def., iph.; II, IV op. def., oph.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{56}	B_2	548	0.5	$2.8 \cdot 10^{-3}$		I, III ip. def., iph.; IIb and IVb str., oph.; CH ₃ rock.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{54}	B_3	543	0.3	$1.7 \cdot 10^{-3}$		I and III ip. def., s., oph.; II and IV ip. def., as.
ν_{53}	B_1	537	0.001	$3.7 \cdot 10^{-6}$		I–IV ip. def., as.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{52}	B_2	522	0.05	$2.5 \cdot 10^{-4}$		II, IV, ct. op. def., iph.
ν_{49}	B_3	494	4.0	$2.1 \cdot 10^{-2}$		I, III str., oph.; CH ₃ rock.
ν_{48}	B_1	482	0.004	$2.1 \cdot 10^{-5}$		I–IV ip. def., as.
ν_{47}	B_2	476	0.04	$2.6 \cdot 10^{-4}$		II and IV ip. def., s., oph.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{46}	B_3	472	0.3	$1.8 \cdot 10^{-3}$		I, III op. def., iph.; II, IV op. def., oph.
ν_{45}	B_1	466	2.3	$1.2 \cdot 10^{-2}$	462(IR)	II and IV op. def., iph.; CH op. bend.
ν_{44}	B_2	447	0.3	$1.8 \cdot 10^{-3}$		I, III op. def., oph.; CH ₂ rock.
ν_{43}	B_1	438	2.2	$1.2 \cdot 10^{-2}$		I, III op. def., iph.; CH ₂ rock.
ν_{41}	B_3	404	0.004	$2.1 \cdot 10^{-5}$		I–IV, fu. op. def.
ν_{39}	B_2	392	0.2	$8.6 \cdot 10^{-4}$		I–IV, fu. op. def.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{38}	B_3	376	0.06	$3.1 \cdot 10^{-4}$		II and IV sw., iph.
ν_{36}	B_2	335	0.4	$1.9 \cdot 10^{-3}$		II and IV str., oph.
ν_{35}	B_1	330	0.01	$4.0 \cdot 10^{-5}$		I–IV op. def.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{34}	B_3	325	1.1	$5.7 \cdot 10^{-3}$		CH ₂ and CH ₃ rock.; IIb and IVb ip. sw., oph.
ν_{32}	B_3	294	0.3	$1.6 \cdot 10^{-3}$		Ct. op. def.; CH ₃ rock.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{31}	B_1	290	0.02	$1.2 \cdot 10^{-4}$		CH ₂ rock.; CH ₃ twist.; skeleton ip. sw.
ν_{30}	B_2	274	0.04	$2.0 \cdot 10^{-4}$		I and III op. def., oph.; II and IV op. def., iph.
ν_{29}	B_1	274	0.1	$6.5 \cdot 10^{-4}$		CH ₃ rock.; skeleton op. def.
ν_{28}	B_3	271	0.2	$9.3 \cdot 10^{-4}$	273(R)	II and IV op. def., oph.; C _{benz} –CH ₂ –CH ₃ bend.
ν_{26}	B_2	247	0.3	$1.5 \cdot 10^{-3}$		CH ₃ twist.
ν_{25}	B_1	239	1.1	$5.6 \cdot 10^{-3}$		Skeleton op. def., iph.
ν_{24}	B_3	218	0.2	$1.2 \cdot 10^{-3}$		CH ₃ twist.
ν_{22}	B_1	214	0.1	$7.2 \cdot 10^{-4}$		Skeleton ip. sw., CH ₃ twist.
ν_{20}	B_3	209	0.0001	$5.3 \cdot 10^{-7}$		I–IV, fu., ct. op. def.
ν_{19}	B_2	198	0.02	$1.0 \cdot 10^{-4}$	192(R)	I–IV, ct. op. def.
ν_{18}	B_1	169	1.6	$8.3 \cdot 10^{-3}$		I, III and II, IV op. def., oph.
ν_{17}	B_2	169	0.7	$3.8 \cdot 10^{-3}$		CH ₃ twist.
ν_{15}	B_1	141	0.002	$8.0 \cdot 10^{-6}$		CH ₂ and CH ₃ rock.; IIb and IVb sw., oph.
ν_{14}	B_3	140	0.5	$2.5 \cdot 10^{-3}$		IIb, IVb ip. sw., iph.
ν_{13}	B_1	127	0.01	$7.8 \cdot 10^{-5}$		I–IV, ct and fu. op. def., oph.
ν_{12}	B_2	125	0.003	$1.3 \cdot 10^{-5}$	115(R)	IIb, IVb op. waving, iph.
ν_{10}	B_3	87	0.001	$7.4 \cdot 10^{-6}$	84(R)	IIb, IVb op. waving, oph.
ν_9	B_2	72	0.002	$1.2 \cdot 10^{-5}$		CH ₂ and CH ₃ rock.; skeleton waving, oph.
ν_8	B_3	72	0.07	$3.6 \cdot 10^{-4}$		CH ₂ and CH ₃ rock.; skeleton waving, oph.
ν_6	B_1	49	0.1	$5.9 \cdot 10^{-4}$		CH ₂ and CH ₃ rock.

Table 2 (Continued)

Num.	Sym.	Fre.	I_{IR}	$I_{IR, rel.}$	Exp. R = C ₁₁ H ₂₃	Assignment
ν_5	B_3	49	0.03	$1.8 \cdot 10^{-4}$		CH ₂ and CH ₃ rock.
ν_4	B_2	46	0.01	$7.8 \cdot 10^{-5}$		CH ₂ and CH ₃ rock.
ν_2	B_1	34	0.7	$3.6 \cdot 10^{-3}$		Skeleton op. waving, iph.
ν_1	B_1	33	0.2	$9.4 \cdot 10^{-4}$		Skeleton op. waving, iph.

Exp.: experimental; Num.: number of modes; Sym.: symmetry of modes; Fre.: scaled frequency value, cm⁻¹; I_{IR} – IR intensity, km/mol; $I_{IR, rel.}$ – relative IR intensity; def.: deformation; bre.: breathing; s.: symmetrical vibrations; as.: asymmetrical vibrations; iph.: in phase vibrations; oph.: out-of-phase vibration; I, III, benzene ring numbers; II(a,b), IV(a,b), naphthalene ring numbers (Fig. 2); bend.: bending vibrations; sw.: swinging vibrations; fu.: furan; ct.: cyclooctatetraene ring; str.: stretching; ip.: in plane vibration; op.: out-of-plane vibration; twist.: twisting; scis.: scissoring; wag.: wagging; rock.: rocking.

maximum. The observed IR spectrum of naphthalene exhibits an intense band at 3052 cm⁻¹ in KBr pellets (Fig. 3) [20]. Thus we can explain a small high-frequency shift of benzene and naphthalene CH stretching vibrations, their splitting and intensity quenching in the parent *p*-2B2N tetraoxa[8]circulene molecule.

4.2.1.2. The planar CCH deformation vibrations of the benzene and naphthalene rings, δ (CH). The planar deformation vibrations, δ (CH), in the *p*-2B2N molecule are calculated in the range 1273–1022 cm⁻¹ (Table 1). As a rule, these vibrations are mixed with ν (CO) and/or with the in-plane rings deformation. In the calculated IR spectrum of benzene (Fig. 4) the δ (CH) vibrational band is predicted at 1036 cm⁻¹ (the E_{1u} mode) which coincides with the experimental value [19,20]; the corresponding band in the 4B

molecule (the E_u mode) is found at 1093 cm⁻¹ (exp.: 1091 cm⁻¹), thus demonstrating a strong frequency shift. Besides that, contribution of the δ (CH) vibrations in the calculated IR spectrum of 4B molecule is presented in the modes $\nu_{73}(72)$, $\nu_{70}(69)$, $\nu_{65}(64)$, $\nu_{57}(56)$ with the calculated frequencies 1260, 1218, 1166 and 1009 cm⁻¹, respectively. The band of the δ (CH) vibrations, predicted in the benzene IR spectrum at 1036 cm⁻¹, is shifted to the low-frequency in the IR spectrum of the *p*-2B2N molecule (B_{2u} (ν_{81}), calc.: 1070 cm⁻¹, Table 1). But because of the low absorption intensity (5.1 km/mol) in IR spectrum it is not observed in Fig. 4. This band is also absent in the IR spectra of the *p*-2B2N4R (R = C₂H₅ and C₁₁H₂₃) molecules (Fig. 4). The intense mode ν_{69} , calculated in IR spectrum of the 4B molecule at 1218 cm⁻¹ (exp.: 1218 cm⁻¹), which includes mixing of vibrations δ (CH) and ν (CO), is observed in the IR spectrum of the *p*-2B2N molecule as a strong band at the close frequency (1220 cm⁻¹). In IR spectra of the substituted *p*-2B2N4R molecules (R = C₂H₅ and C₁₁H₂₃) this band shows weaker intensity and belongs only to the ν (CO) vibrations of furan rings.

The deformation E_u mode of 4N calculated at 1264 cm⁻¹ (exp.: 1268 cm⁻¹) corresponds to the B_{2u} (ν_{31}) vibration in the IR spectrum of naphthalene (calc.: 1257 cm⁻¹, Fig. 4). E_u mode of 4N calculated at 1164 cm⁻¹ (exp.: 1172 cm⁻¹) corresponds to the B_{2u} (ν_{25}) vibration in IR spectrum of naphthalene (calc.: 1121 cm⁻¹; exp.: 1123 cm⁻¹).

The E_u mode of 4N with very low absorption intensity (0.1 km/mol) calculated at 1158 cm⁻¹ (Table 1 and Fig. 5) belongs only to the planar CCH deformation vibrations, δ (CH), and corresponds to the B_{1u} (ν_{27}) vibration in IR spectrum of naphthalene [2] (calc.: 1147 cm⁻¹). In the IR spectrum of *p*-2B2N (Table 1 and Fig. 5) this type of vibrations provides a weak band (B_{1u} (ν_{87}), calc.: 1158 cm⁻¹); the respective band in the substituted *p*-2B2N4R (R = C₂H₅) molecule (Table 2 and Fig. 5) is calculated at the same frequency (B_2 (ν_{119}), calc.: 1157 cm⁻¹). The deformation E_u modes of 4N calculated at 1056 and 1023 cm⁻¹ correspond to the B_{1u} (ν_{80} and ν_{76}) vibration in the IR spectrum of *p*-2B2N (calculated values are 1054 and 1022 cm⁻¹, respectively), where ν_{80} mode produce a band of the middle intensity and the ν_{76} mode is overlapped by more intensive ν_{78} mode. However, in the *p*-2B2N4R (R = C₂H₅) molecule the corresponding bands (B_2 (ν_{108} and ν_{104})) lost their intensity (Table 2). One should note that these bands belong not only to the planar CCH deformation vibrations of the naphthalene rings, but also the ν (CO) vibrations of furan rings.

The B_{2u} ν_{93} , ν_{89} , ν_{84} , ν_{78} modes and the B_{1u} ν_{86} mode contain a mixed contribution of the δ (CH) vibrations from benzene and naphthalene rings (Fig. 5 and Table 1). This leads to a shift of the corresponding IR bands in the spectrum of *p*-2B2N in comparison with the 4B and 4N spectra (and also in the alkyl substituted *p*-2B2N4R molecules in comparison with the unsubstituted *p*-2B2N species).

The mixing of the IR-active planar CCH deformation vibrational modes of the 4B and 4N molecules with the corresponding vibrational modes of the *p*-2B2N and *p*-2B2N4R (R = C₂H₅) molecules in their IR spectra is shown in Fig. 5.

In the Raman spectrum of *p*-2B2N molecule (Table SM 1) the δ (CH) vibrations contribute both to the A_g modes viz. (ν_{96} , ν_{90} , ν_{83} ,

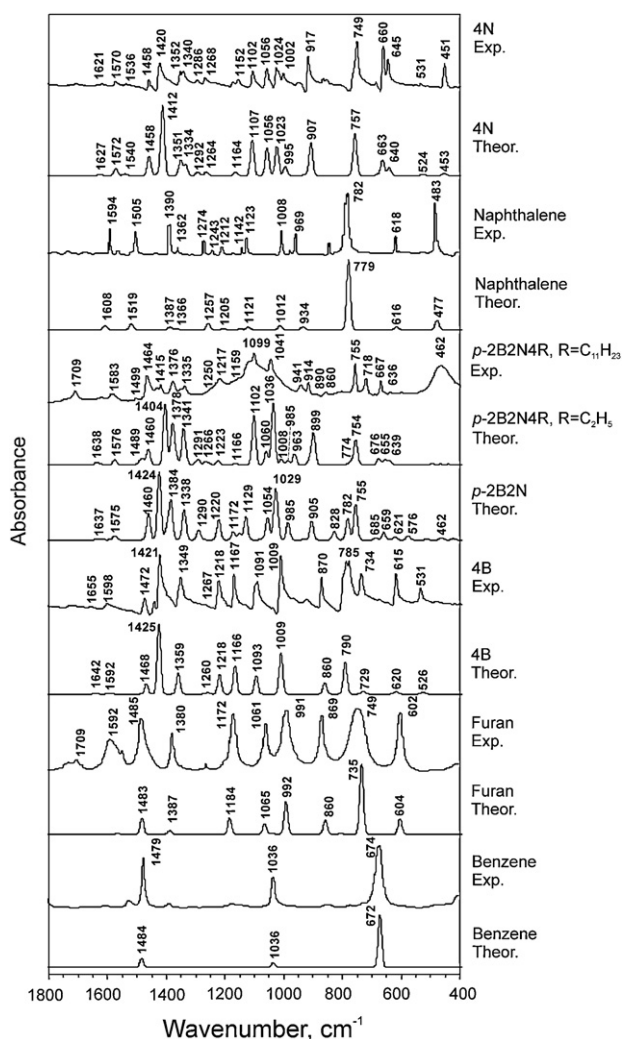


Fig. 4. Calculated and experimental IR spectra for symmetrical tetraoxa[8]circulenes, benzene, furan and naphthalene molecules.

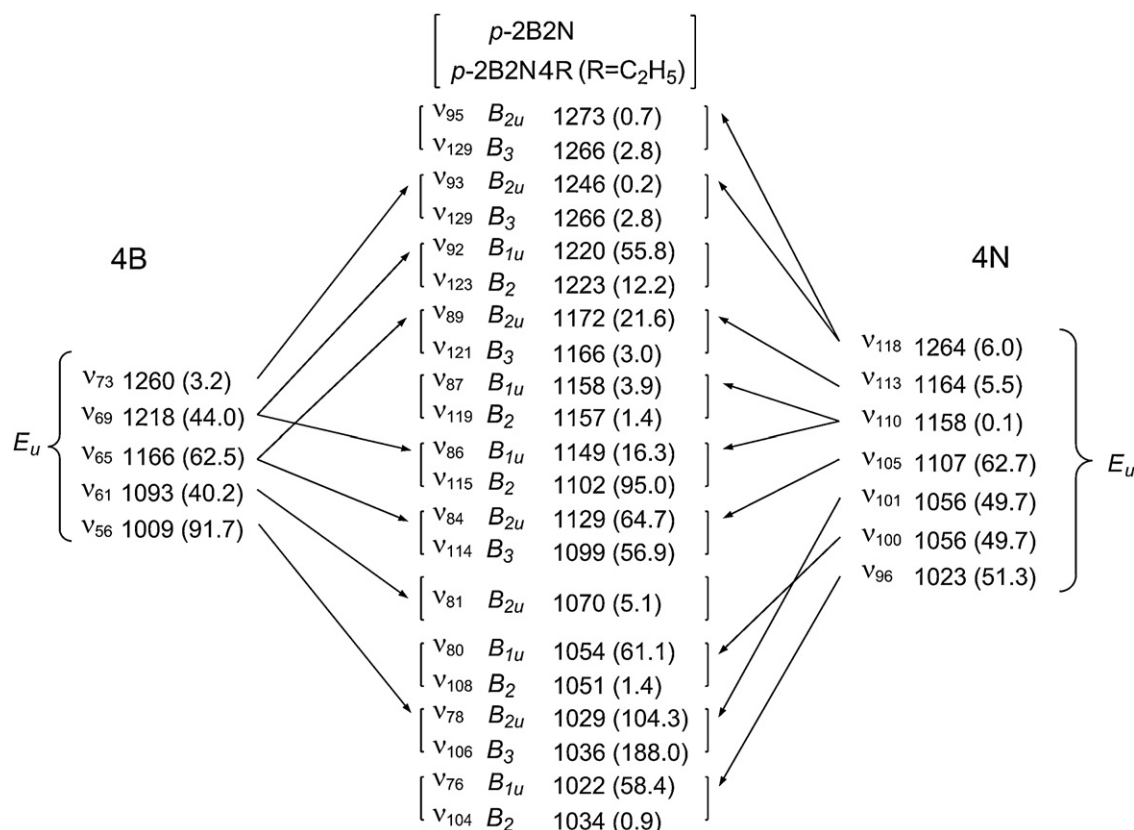


Fig. 5. The correlation diagrams for the IR-active $\delta(\text{CH})$ vibrational modes of benzene moieties in 4B molecule and naphthalene moieties in 4N molecule upon formation of the *p*-2B2N molecule vibrations (numbers in parentheses after the wavenumber values corresponds to calculated IR intensities, km/mol).

ν_{82} , ν_{77}) and to the B_{3g} modes viz. (ν_{94} , ν_{91} , ν_{85} , ν_{79}). The mode ν_{88} of the A_g symmetry ($\nu_{\text{calc.}} = 1159 \text{ cm}^{-1}$) corresponds to the $\delta(\text{CH})$ vibrations only.

4.2.1.3. Out-of-plane CCH deformation vibrations of benzene and naphthalene rings, $\gamma(\text{CH})$. The non-planar deformation vibrations, $\gamma(\text{CH})$, in the IR spectrum of the *p*-2B2N molecule are calculated in the range $928\text{--}460 \text{ cm}^{-1}$ (Table 1). All of them belong to the B_{3u} symmetry.

The modes ν_{59} (calc.: 782 cm^{-1}) and ν_{42} (calc.: 637 cm^{-1}) in the IR spectrum of the *p*-2B2N molecule belong to $\gamma(\text{CH})$ vibrations of benzene rings. The ν_{42} mode of very low intensity (0.1 km/mol) includes not only the out-of-plane CH deformation but also the out-of-plane deformations of benzene rings and of the COC fragments of furans. The corresponding out-of-plane HCOCH vibrations of the B_1 symmetry in the IR spectrum of furan (Fig. 4) are calculated at 604 cm^{-1} (exp: 602 cm^{-1} [20]). The mode ν_{59} in the calculated IR spectrum of the *p*-2B2N (Table 1) molecule produces a middle intensity band at 782 cm^{-1} (Fig. 4). In the IR spectra of the substituted molecules *p*-2B2N4R (R = C_2H_5 and $\text{C}_{11}\text{H}_{23}$) the corresponding band is absent, which provides a support of our calculations and conclusions.

In the IR spectrum of the 4B molecule (Fig. 4) we also observe a strong band ν_{46} at 790 cm^{-1} (exp: 785 cm^{-1}) and a weak band ν_{30} at 620 cm^{-1} (exp: 615 cm^{-1}); both belong to the out-of-plane deformation vibrations, of the A_{2u} symmetry. The $\gamma(\text{CH})$ vibration in the benzene molecule according to our calculations occurs at 672 cm^{-1} (exp: 674 cm^{-1} [19,20]) and provides the most intense absorption band in the IR spectrum of benzene (Fig. 4).

The ν_{14} (B_{3u} symmetry) mode of the naphthalene molecule (in-phase $\gamma(\text{CH})$ vibrations; calc.: 779 cm^{-1}) is split in the IR spectrum of 4N into four modes, which provide absorption band of moderate

intensity at 660 cm^{-1} (calc.: 663 cm^{-1}) and a strong band observed at 749 cm^{-1} (calc.: 757 cm^{-1}); other modes are not active.

Thus, under condensation of benzene rings into the tetraoxa[8]circulene 4B molecule and of naphthalene rings into the 4N structure a strong splitting of the non-planar CH vibrations occurs. At the same time under the substitution of the two benzene rings by the naphthalene fragments in the parent all-benzene tetraoxa[8]circulene molecule only a small shift of the corresponding IR bands takes place, since the geometry parameters of the naphthalene fragments in the *p*-2B2N molecule are quite close to the corresponding parameters in the 4N molecule and the benzene substituents parameters in the *p*-2B2N molecule are close to those of the 4B molecule. The out-of-plane CCH deformation vibrations of the benzene and naphthalene rings (the B_{1g} and B_{2g} symmetry) have low activity in the Raman spectrum of the *p*-2B2N molecule (Table SM 1).

4.2.2. Ring vibrations

4.2.2.1. The benzene and naphthalene fragments CC stretching vibrations. The IR bands of the skeleton vibrations of the aromatic CC bonds are usually observed in the region $1650\text{--}1430 \text{ cm}^{-1}$ [17,18]. The $\nu(\text{CC})$ vibrations in the IR spectrum of the *p*-2B2N molecule are calculated in the range $1637\text{--}1290 \text{ cm}^{-1}$ (Table 1).

At higher frequencies ($1637\text{--}1541 \text{ cm}^{-1}$) the IR-active CC stretching vibrational modes of the benzene and naphthalene moieties are mixed together upon formation of the *p*-2B2N molecule vibrations. This is indicated in Fig. 6, where behind the main contributions of the $\nu(\text{CC})$ vibrations (solid line), presented in Table 1, the small contributions of $\nu(\text{CC})$ vibrations of other aromatic rings are shown by dashed line.

A very weak band ν_{125} (B_{2u} symmetry) at 1637 cm^{-1} in the IR spectrum of the *p*-2B2N molecule belongs to symmetric vibrations

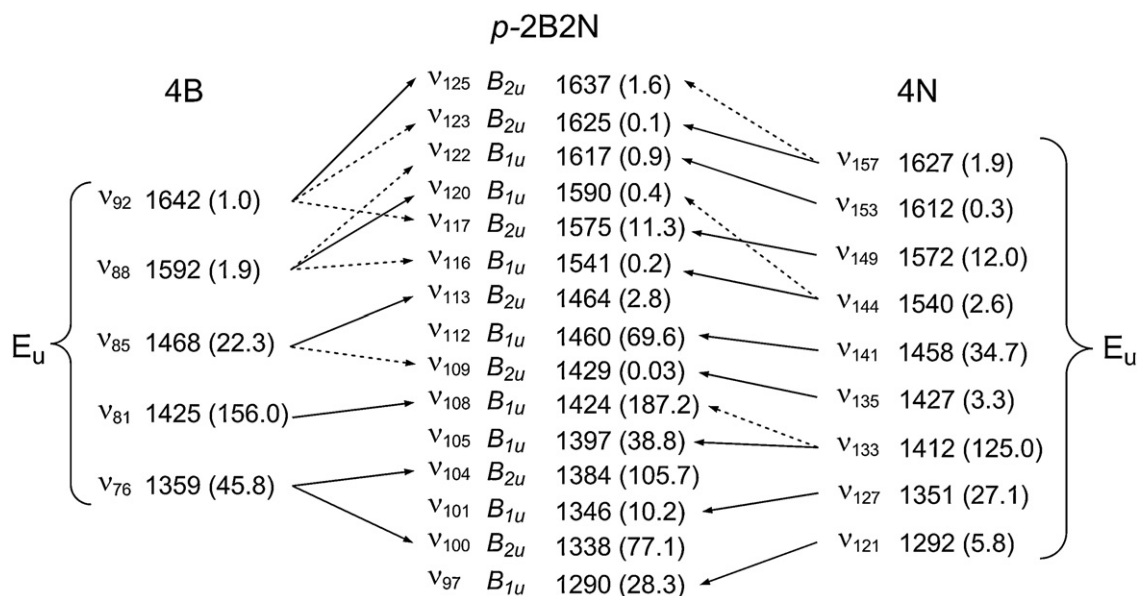


Fig. 6. The correlation diagrams for the IR-active CC bond stretching modes of benzene moieties in 4B molecule and naphthalene moieties in 4N molecule upon formation of the p-2B2N molecule vibrations (numbers in parentheses after the wavenumber values corresponds to calculated IR intensities, km/mol).

of the $\nu(C^2C^3)$ and $\nu(C^2'C^3')$ bonds in the ring I and to the out-of-phase $\nu(C^{10}C^{11})$ and $\nu(C^{10'}C^{11'})$ vibrations in the ring III. This band is similar (by the type of $\nu(CC)$ vibrations) to the calculated band ν_{92} at 1642 cm^{-1} (exp.: 1655 cm^{-1}) in the IR spectrum of the 4B molecule (Fig. 4), but includes a small contribution of the CC stretching vibrational modes ν_{157} of the 4N species (Fig. 6).

A very strong band ν_{108} (B_{1u} symmetry) at 1424 cm^{-1} in the IR spectrum of the p-2B2N molecule belongs to asymmetric vibrations of the condensed bonds $\nu(CC)$ in benzene and furan rings. These vibrations occur in-phase in the rings I and III; a strong deformation of the CCH angles in benzene fragments takes place at the same time. The band ν_{108} of the type $\nu(CC)$ is similar to the calculated band ν_{81} at 1425 cm^{-1} (exp.: 1421 cm^{-1}) in the IR spectrum of the 4B molecule, but it has a significant contribution of the strong CC stretching (Kekule vibrations) mode ν_{133} of the 4N molecule (calc.: 1412 cm^{-1} , exp.: 1420 cm^{-1}).

A strong band ν_{104} (calc.: 1384 cm^{-1}) and the band ν_{100} (calc.: 1338 cm^{-1}) of the medium intensity in the IR spectrum of the p-2B2N molecule belong to the skeleton vibrations of the benzene rings, which include subsequent alternations of the CC bonds stretching and compression of large amplitude (Kekule vibrations). The band ν_{100} contains contribution of the $\nu(CO)$ vibrations in furan rings. These two bands are formed as a result of the ν_{76} band splitting described before in the IR spectrum of the 4B molecule [2], upon substitution of the two benzene rings in the parent all-benzene tetraoxa[8]circulene molecule by the naphthalene fragments. Upon the hydrogen atoms substitution in benzene rings by alkyl substituents C_2H_5 and $C_{11}H_{23}$ these bands are shifted by 3–6 cm^{-1} , at least.

A very weak band ν_{113} (B_{2u} symmetry) at 1464 cm^{-1} in the IR spectrum of the p-2B2N molecule is also determined by the CC bond vibrations in benzene rings, but it is not observed in the IR spectrum, since it is overlapped by the absorption band of the asymmetric vibrations of the CC bonds in naphthalene rings (ν_{112} , Table 1). Since the permanent dipole moment of the benzene molecule is equal to zero, only asymmetric CC vibrations are allowed in its IR spectrum (E_{1u} vibrations, calc.: 1484 cm^{-1} ; gas phase IR spectrum: 1484 cm^{-1} [19], in condensed phase: 1479 cm^{-1} [20], Fig. 4).

The bands ν_{122} , ν_{112} , ν_{105} , ν_{101} , ν_{97} of the B_{1u} symmetry in the IR spectrum of the p-2B2N molecule are determined by CC bond vibrations in the naphthalene fragments. A very weak band ν_{122} is

not presented in the IR spectrum shown in Fig. 4; the bands ν_{105} and ν_{101} are overlapped by more strong benzene bands ν_{104} and ν_{100} . In the IR spectrum of the p-2B2N molecule, presented in Fig. 4, the ν_{112} band at 1460 cm^{-1} of middle intensity and a weak band ν_{97} at 1290 cm^{-1} , both belong to CC bonds of the naphthalene fragments. The latter band is formed by asymmetric Kekule vibrations of the “b” rings in two opposite naphthalene fragments. A weak band ν_{117} of the B_{2u} symmetry at 1575 cm^{-1} in the IR spectrum of the p-2B2N molecule has contributions of the CC bond vibrations in benzene and naphthalene fragments. The CC bond vibrations in naphthalene rings do not exhibit frequency shifts upon substitution of the two opposite naphthalene fragments by benzene fragments in the 4N molecule, as it follows from Figs. 4 and 6.

4.2.2.2. Furan CC and CO stretching vibrations. Vibration of the $C^B C^B$ bond of the A_1 symmetry in the free furan molecule (C_{2v} point group) which is active in both IR and Raman spectra occurs at 1380 cm^{-1} (calc.: 1387 cm^{-1} [2]). This vibration is split in the IR spectrum of the p-2B2N molecule (B_{1u} modes ν_{116} , ν_{112} , ν_{101} and ν_{97}) (Table 1 and Fig. 4). The band ν_{116} has a very low intensity (0.2 km/mol), and the band ν_{101} is overlapped by the stronger band ν_{100} (Table 1); thus vibration of the $C^B C^B$ bond in IR spectrum of the p-2B2N molecule really produce contributions into the ν_{112} and ν_{97} bands at 1460 and 1290 cm^{-1} , respectively (Fig. 4).

Asymmetric vibrations of the $C^\alpha C^\beta$ bonds of the B_2 symmetry are allowed in both IR and Raman spectra of furan and are calculated in the free furan molecule at 1565 cm^{-1} [2]. The corresponding mode has a very low absorption intensity (0.6 km/mol). In IR spectrum of the p-2B2N molecule the $\nu_{as}(C^\alpha C^\beta)$ vibration is predicted by our DFT calculations at 1384 cm^{-1} (B_{2u} mode ν_{104}) as a contribution to the strong asymmetric mode $\nu(CC)$ in benzene rings (the Kekule vibrations). In the substituted p-2B2N4R ($R = C_2H_5$) molecule the corresponding mode ν_{145} of the B_3 symmetry indicates additionally a twisting vibration contribution from the methylene groups and exhibits a shift by 6 cm^{-1} to the low-frequency region (Table 2). The modes ν_{121} and ν_{111} of the B_{3g} symmetry are calculated in vibrational spectrum of the p-2B2N molecule at 1600 and 1452 cm^{-1} (Table 1); they are forbidden in IR spectrum but are allowed by symmetry in the Raman spectrum (Table SM 1).

Symmetric vibrations of the $C^\alpha C^\beta$ bonds of the A_1 symmetry are allowed in both IR and Raman spectra of furan [2] and are calculated in the free furan molecule at 1483 cm^{-1} (exp.: 1485 cm^{-1} , Fig. 4). In the IR spectra of the *p*-2B2N molecule the $\nu_s(C^\alpha C^\beta)$ vibrations are calculated at 1590 and 1397 cm^{-1} (Table 1, the B_{1u} modes ν_{120} and ν_{105}). A main contribution to these modes provides the skeleton vibrations of the aromatic CC bonds. In the IR spectrum of the *p*-2B2N molecule the corresponding modes are not observed (Fig. 4), since the band ν_{120} is very weak and the band ν_{105} is overlapped by a stronger band ν_{104} .

Symmetric vibrations of the CO bond of the A_1 symmetry and asymmetric vibrations of the B_2 symmetry in the free furan molecule, which are active in both IR and Raman spectra, occurs at the calculated frequencies 1065 and 992 cm^{-1} ($\nu_s(\text{CO})$), 1184 and 1040 cm^{-1} ($\nu_{as}(\text{CO})$). The band at 1040 cm^{-1} is not presented in Fig. 4 because of the low intensity (1.1 km/mol). This vibration is split in IR spectrum of the *p*-2B2N molecule and is mixed with the in-plane $\delta(\text{CH})$, CC stretching vibrations in benzene and naphthalene fragments and with other vibrations (Table 1), providing modes of the B_{2u} and B_{1u} symmetry in the range 1346 – 1055 cm^{-1} (the D_{2h} point group, the molecule *p*-2B2N is situated in the *yz* plane). Besides that, the $\nu(\text{CO})$ vibrations of the B_2 and A_1 symmetry in furan produce upon splitting new vibrations of the B_{3g} and A_g symmetry, respectively, which are forbidden in the IR spectrum, but are allowed in the Raman spectra of the *p*-2B2N molecule (Table SM 1). The CC stretching vibrations in benzene and naphthalene fragments and deformation vibrations of these rings lead to the fact, that in the modes ν_{101} , ν_{100} , ν_{92} and ν_{86} the $\nu(\text{CO})$ vibrations are localized only inside the half furan ring.

In the calculated IR spectrum of the *p*-2B2N molecule, presented in Fig. 4, the $\nu(\text{CO})$ band are predicted at 1338 (ν_{100}), 1220 (ν_{92}), 1172 (ν_{89}), 1149 (ν_{86}), 1129 (ν_{84}), 1054 (ν_{80}) and 1029 (ν_{78}) cm^{-1} .

4.2.2.3. Deformation vibrations of the rings. The planar skeleton deformations of benzene, naphthalene, furan and cyclooctatetraene rings are observed in breathing and stretchings vibrations of the rings (Table 1). Many of them are mixed with other types of vibrations. It should be noted, that the ring breathing is a symmetric movement of all nuclei in the ring; the ring stretching includes also simultaneous movements but not necessary symmetrical for all deformations.

The planar skeleton rings deformations in the IR spectrum of *p*-2B2N are calculated at lower frequencies than 1276 cm^{-1} . These modes consist of symmetric and asymmetric deformations, breathing of rings and in the range 1273 – 1022 cm^{-1} they are mixed with $\delta(\text{CH})$, $\nu(\text{CO})$ vibrations or with the COC angles deformation (Table 1). The weak bands ν_{74} , ν_{62} and ν_{50} in the calculated IR spectrum of the *p*-2B2N molecule at 985 , 828 and 685 cm^{-1} belong to breathing vibration of the naphthalene rings. The band ν_{74} has also admixture of the breathing vibration of the furan rings. In a free furan the breathing vibrations of the A_1 symmetry are calculated by our DFT approach at 1139 and 1065 cm^{-1} [2]. Very weak bands ν_{50} at 685 cm^{-1} and ν_{17} at 328 cm^{-1} in the IR spectrum of *p*-2B2N belong to breathing vibration entirely in the naphthalene rings.

The out-of-plane deformations of the rings of the B_{3u} symmetry, which are allowed in the IR spectrum of *p*-2B2N have their frequencies to be lower than 660 cm^{-1} (Table 1), are observed in the out-of-plane deformations of the separate fragments: ν_{46} (calc.: 659 cm^{-1}), ν_{42} (calc.: 637 cm^{-1}), ν_{28} (calc.: 462 cm^{-1}), ν_{18} (calc.: 332 cm^{-1}), ν_8 (calc.: 163 cm^{-1}), ν_4 (calc.: 82 cm^{-1}), and in the form of skeleton deformations of the whole molecule (ν_{14} , ν_1). Weak bands in the IR spectrum of *p*-2B2N at 659 and 462 cm^{-1} belong to the out-of-plane deformations of the rings, and those at 621 and 576 cm^{-1} – belong to in-plane deformations of the rings (Fig. 4).

In general the DFT calculations explain all visible features in experimental spectra and predict some new ones in low-frequency region.

4.3. IR spectrum of the *p*-2B2N4R ($R = C_2H_5$) molecule

The *p*-2B2N4R ($R = C_2H_5$) tetraoxa[8]circulene molecule consists of 78 atoms and has 210 normal modes of vibrations. These 210 normal vibrational modes in the D_2 point group (the molecule is in the *xy* plane) are distributed by the symmetry types as the following: $54A$, $52B_1$, $52B_2$, $52B_3$. In the IR spectrum the B_1 , B_2 and B_3 vibrations are allowed. In the Raman spectrum all modes are allowed, but the most active are the totally symmetrical A modes (Table SM 2).

4.3.1. The CH stretching vibrations, $\nu(\text{CH})$

In the calculated IR spectrum of the substituted circulene molecule *p*-2B2N4R ($R = C_2H_5$) the CH stretching vibration band is predicted at the same frequency ($\nu_{\text{max}} = 3057\text{ cm}^{-1}$) as it is predicted for the unsubstituted circulene molecule *p*-2B2N ($\nu_{\text{max}} = 3058\text{ cm}^{-1}$). However, in the experimental IR spectrum of the substituted circulene *p*-2B2N4R ($R = C_{11}H_{23}$) the CH band of the naphthalene rings has lost its intensity and is not observed in Fig. 3 in the IR spectrum of the 2B2N4R ($R = C_{11}H_{23}$), but it has been observed as a very weak peak at 3057 cm^{-1} in the IR spectrum of the 2B2N4R ($R = C_{11}H_{23}$) in Fig. SM 1. The intense bands at the calculated frequencies 2962 and 2897 cm^{-1} belong to CH stretching vibrations in the CH_2 and CH_3 groups of the substituents. In the experimental IR spectrum of *p*-2B2N4R ($R = C_{11}H_{23}$) circulene these two bands are shifted to the low-frequency region and are observed at 2917 , 2849 cm^{-1} and as a shoulder at 2953 cm^{-1} . Analogous bands in the experimental IR spectrum in the fully substituted 4B8R ($R = C_{11}H_{23}$) circulene are observed in the similar region (2919 , 2851 cm^{-1} and shoulder at 2955 cm^{-1}), and for the 4B8R ($R = C_2H_5$) molecule in the gas phase they are predicted at 2967 and 2900 cm^{-1} (Fig. 3). Such a shift is determined by intermolecular interactions between long aliphatic chains in the crystal. The crystal packing provides a pressure on these chains and induces the frequency shift of CH vibrations in the CH_2 and CH_3 groups.

4.3.2. Out-of-plane deformation vibrations of benzene and naphthalene rings, $\gamma(\text{CH})$

Substitution of the hydrogen atoms in benzene rings by ethyl groups leads to increase by 39 cm^{-1} of the frequency of the mode, which corresponds to the ν_{42} mode in the IR spectrum of *p*-2B2N molecule (and to increase of its intensity). In the IR spectrum of *p*-2B2N4R ($R = C_2H_5$) the corresponding band (ν_{68}) of the B_1 symmetry is calculated at 676 cm^{-1} . In the experimental FTIR spectrum of *p*-2B2N4R ($R = C_{11}H_{23}$) this band is observed at 718 cm^{-1} .

The $\gamma(\text{CH})$ vibration of the naphthalene rings in the *p*-2B2N4R ($R = H$, C_2H_5) molecules are predicted in our DFT calculations at the same frequencies as in the 4N molecule (755 and 659 cm^{-1} in the *p*-2B2N); 754 and 655 cm^{-1} in the *p*-2B2N4R ($R = C_2H_5$). In the experimental FTIR spectrum of *p*-2B2N4R ($R = C_{11}H_{23}$) their corresponding analogous are at 755 and 667 cm^{-1} . The calculated CH vibration frequencies (stretching and deformation) in the substituted *p*-2B2N4R tetraoxa[8]circulene molecule ($R = C_{11}H_{23}$) are in a good agreement with the measured spectra.

4.3.3. Deformation vibrations of the methyl and methylene groups of the alkyl substituents

Asymmetric deformation vibrations of the methyl group are usually observed near 1460 cm^{-1} [17]. Our calculations show that such deformation modes are mixed with scissor vibrations of the CH_2 -group of ethyl-substituent in the *p*-2B2N4R ($R = C_2H_5$) molecule, which correspond to weak vibration bands B_3 (ν_{169} , ν_{165}) and B_1 (ν_{168}) with the frequency 1499 , 1484 and 1489 cm^{-1} .

(Table 2). Vibrational modes $B_1 \nu_{164}$, $B_2 \nu_{163}$ and $B_3 \nu_{161}$ with the frequency 1480 cm^{-1} are formed only by asymmetric deformation vibrations of the methyl group ($\delta(\text{CH}_3)$). The corresponding weak band in the calculated IR spectrum of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$) is revealed as a left shoulder of the middle-intense band with a maximum at 1460 cm^{-1} , which belongs to the CC stretching vibrations in naphthalene fragments of the $p\text{-}2\text{B}2\text{N}$ molecule (Fig. 4). In the experimental IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$) molecule the observed band, which corresponds to the scissor vibrations of the CH_2 -group and to the asymmetric deformation vibrations of the methyl group, $\delta(\text{CH}_3)$, is detected at 1499 cm^{-1} (calculated in the $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$) molecule at 1499 and 1489 cm^{-1}). Its intensity is very weak.

In the calculated IR spectrum of the undecane molecule (Table SM 3) the asymmetric deformation vibrations of the methyl group, which are mixed with the scissor vibrations of the CH_2 -group is predicted to be at 1499 cm^{-1} ($\nu_{\text{exp}}=1468\text{ cm}^{-1}$); intrinsic methyl group asymmetric deformation vibrations are calculated at 1482 cm^{-1} ($\nu_{\text{exp}}=1461\text{ cm}^{-1}$).

The symmetric deformation vibrations of the methyl group are usually observed in the narrow frequency region from 1385 to 1370 cm^{-1} [17]. In the calculated vibrational spectrum of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$) this vibrations of the methyl group are predicted at 1391 cm^{-1} ; they are not mixed with other vibrations. In the calculated IR spectrum of the undecane molecule the symmetric deformation vibrations are found at 1397 cm^{-1} . As follows from Table 2 and Table SM 3, the symmetric deformation vibrations of the methyl group have low absorption intensity and do not form a special separate band in the experimental and theoretical spectra.

The twisting vibrations of methyl groups are calculated in the $1089\text{--}1051\text{ cm}^{-1}$ range and in the low-frequency region $290\text{--}169\text{ cm}^{-1}$; the rocking vibrations are below 820 cm^{-1} . These modes are determined mainly by the skeleton deformations of the rings and produce a very weak absorption bands (Table 2). The scissoring vibrations of the CH_2 -group are calculated at 1465 cm^{-1} (exp.: 1467 cm^{-1} [17]); they do not mix with other types of vibrations. The low-intense modes $B_2 \nu_{159}$ and $B_1 \nu_{158}$ belong to them; the corresponding band is not observed in the substituted $p\text{-}2\text{B}2\text{N}4\text{R}$ molecules.

The wagging and twisting vibrations of the CH_2 -group are calculated in the range $1332\text{--}1060\text{ cm}^{-1}$ and have low intensity. In the IR spectrum of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$), presented in Fig. 4, the twisting vibrations produce a very weak band ν_{121} at 1166 cm^{-1} , which corresponds to a left shoulder at 1159 cm^{-1} in the wide band with a maximum at 1099 cm^{-1} in the experimental IR spectrum of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$). The right shoulder of the same band belongs to the wagging vibrations of the methylene groups, which are mixed with the twisting vibrations of methyl groups. According to our calculations in the IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$) species the corresponding band (ν_{109}) at 1060 cm^{-1} exhibits the highest absorption intensity in comparison with wagging and twisting vibrations of the methylene groups. In the calculated IR spectrum of the undecane molecule this type of vibrations is predicted to be at 1094 cm^{-1} .

The twisting vibrations of the CH_2 -group provide contributions into a strong band ν_{145} at 1378 cm^{-1} (exp.: 1376 cm^{-1}), ν_{106} at 1036 cm^{-1} (exp.: 1041 cm^{-1}), and also into other (very weak) bands (Table 2). Rocking vibrations of the methylene groups, as a rule, are mixed with above described rocking vibrations of the methyl groups (ν_{82} at 774 cm^{-1} (exp.: 789 cm^{-1}), Table 2). The rocking vibrations of the methylene groups in the calculated IR spectrum of the undecane molecule are lying at 717 cm^{-1} (exp.: 721 cm^{-1} [20]).

Thus, the replacement of the undecyl substituents by the ethyl groups in the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule provides the adequate positions of the IR bands which correspond to alkyl substituents.

4.3.4. Ring vibrations

4.3.4.1. *The benzene and naphthalene fragments CC stretching vibrations.* Calculation shows, that upon substitution of the hydrogen atoms in benzene rings by ethyl groups, no shift of this band (calc.: 1638 cm^{-1}) occurs. However, in the experimental IR spectra of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$) molecule (Fig. 4) and in the completely substituted $4\text{B}8\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$) molecule this band takes place at 1709 cm^{-1} . Such a great frequency shift can be connected with a geometry distortion of the studied molecules being a result of intermolecular interactions between the long aliphatic chains during crystallization. Such distortion has to influence a position of this band in the IR spectrum because of involvement of the C^2C^3 and $\text{C}^{10}\text{C}^{11}$ bonds. Just these bonds are very sensitive to aliphatic substituents, which being similar to long antenna transfer the influence of intermolecular interactions in a condensed phase.

Upon the hydrogen atoms substitution in benzene rings by ethyl groups a hindrance of the $\nu(\text{CC})$ vibrations in benzenes occurs (and also of the C_2H_5 vibrations) and increase of the $\nu(\text{CC})$ amplitude. The corresponding band in the IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$) of the B_2 symmetry is shifted by 20 cm^{-1} to the low-frequency side. In the experimental IR spectrum of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$) this band (exp.: 1415 cm^{-1}) lost its intensity.

In the substituted $p\text{-}2\text{B}2\text{N}4\text{R}$ molecules ($\text{R}=\text{C}_2\text{H}_5$ and $\text{C}_{11}\text{H}_{23}$) CC bond vibrations in naphthalene rings are observed at the frequencies which are close to those of the parent $p\text{-}2\text{B}2\text{N}$ molecule. The largest shift (8 cm^{-1}) is observed for the band at 1583 cm^{-1} in the experimental IR spectrum of the substituted $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$) circulene, which corresponds to a weak band at 1575 cm^{-1} in the unsubstituted $p\text{-}2\text{B}2\text{N}$ molecule. As mentioned above (Fig. 6), this band has a contribution of the C^2C^3 and $\text{C}^{10}\text{C}^{11}$ bonds of benzene rings, which are very sensitive to aliphatic substitutions. The calculated IR band at 1290 cm^{-1} in the $p\text{-}2\text{B}2\text{N}$ molecule has lost its intensity in the experimental IR spectrum of the synthesized compound $p\text{-}2\text{B}2\text{N}4\text{R}$ with $\text{R}=\text{C}_{11}\text{H}_{23}$.

4.3.4.2. *Furan CC and CO stretching vibrations.* In the substituted $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$) molecule the mode ν_{144} of the B_2 symmetry, which corresponds to the ν_{105} mode in $p\text{-}2\text{B}2\text{N}$, indicates also a contribution of the twisting vibrations in the methylene groups of ethyl substituents and is shifted by 32 cm^{-1} to the low-frequency region (Table 2). The $\nu(\text{CO})$ bands in IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$) are predicted at $1341(\nu_{140})$, $1223(\nu_{123})$, $1166(\nu_{121})$, $1102(\nu_{115})$, $1099(\nu_{114})$, $1051(\nu_{108})$ and $1036(\nu_{106})\text{ cm}^{-1}$. Under the ethyl substitution we predict the largest shift in the modes ν_{115} and ν_{114} (by 47 and 30 cm^{-1} , respectively); in the IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$) in Fig. 4 they produce just one strong band at 1102 cm^{-1} . The band ν_{108} (calc.: 1051 cm^{-1}) in IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$) is not observed in Fig. 4 because of the weak intensity (1.4 kJ/mol). In the experimental IR spectrum of the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule with $\text{R}=\text{C}_{11}\text{H}_{23}$ to the calculated above-mentioned bands with a large $\nu(\text{CO})$ contribution do correspond the bands at 1335 , 1217 , 1159 , 1099 and 1041 cm^{-1} . Thus the shift of the considered experimental bands in the real $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_{11}\text{H}_{23}$) molecule is rather small ($3\text{--}7\text{ cm}^{-1}$) in comparison with the calculated bands in the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$).

The breathing vibrations in the $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$) ν_{98} , ν_{84} and ν_{79} are at 963 (exp.: 941 cm^{-1}), 820 and 761 cm^{-1} . The two last bands are weak ($I=0.6$ and 6.8 kJ/mol) and are not observed in the IR spectrum.

In the model $p\text{-}2\text{B}2\text{N}4\text{R}$ molecule ($\text{R}=\text{C}_2\text{H}_5$) the ν_{79} mode (Table 2) corresponding to ν_{50} band (Table 1) has a contribution of rocking vibrations of the methylene and methyl groups; thus it experiences a strong shift to the higher frequencies (by 76 cm^{-1}).

The band ν_{64} at 655 cm^{-1} in the IR spectrum of $p\text{-}2\text{B}2\text{N}4\text{R}$ ($\text{R}=\text{C}_2\text{H}_5$) (Table 2, exp.: 667 cm^{-1}) corresponds to the band ν_{46}

at 659 cm^{-1} of the *p*-2B2N molecule (Table 1). The band ν_{45} at 466 cm^{-1} (Table 2) corresponds the band ν_{28} at 462 cm^{-1} (Table 1). The interesting band ν_{36} at 576 cm^{-1} in the IR spectrum of *p*-2B2N (Table 1), which belongs to the in-plane deformations in benzene and naphthalene rings, is shifted by 63 cm^{-1} to higher frequency upon ethyl substitution (calc.: 639 cm^{-1} , Table 2).

In general the DFT calculations explain all visible features in experimental spectra and predict some new ones in low-frequency region.

4.3.5. CC vibrations of the alkyl substituents

The skeleton CC stretching vibrations of ethyl groups ($\text{CH}_2\text{—CH}_3$ stretching) occur in the range $1008\text{--}895\text{ cm}^{-1}$. These vibrations are mixed with the skeleton deformations of benzene, naphthalene, furan and cyclooctatetraene rings. They provide in the IR spectrum of the *p*-2B2N4R molecule ($\text{R}=\text{C}_2\text{H}_5$) the weak bands at 1008 and 985 cm^{-1} and a strong band at 899 cm^{-1} , which is formed by the overlap of three vibrational modes: ν_{92} (calc.: 910 cm^{-1}), ν_{90} (calc.: 899 cm^{-1}) and ν_{88} (calc.: 895 cm^{-1}) (Table 2). In the experimental IR spectrum of the *p*-2B2N4R molecule with $\text{R}=\text{C}_{11}\text{H}_{23}$ a right shoulder of the strong band at 1041 cm^{-1} corresponds to the above-mentioned weak bands (Fig. 4 and Table 2). The strong band at 899 cm^{-1} in the spectrum of the species with $\text{R}=\text{C}_2\text{H}_5$ is split in the real molecule ($\text{R}=\text{C}_{11}\text{H}_{23}$) to the three weak satellites at 914 , 890 and 860 cm^{-1} .

Deformations of the angles $\text{C}_{\text{benz}}\text{—CH}_2\text{—CH}_3$ are calculated in the range $620\text{--}271\text{ cm}^{-1}$ (Table 2), but the corresponding IR bands intensity is very weak (not more than 0.5 km/mol). The stretching vibration of the $\text{C}_{\text{benz}}\text{—CH}_2$ bond occurs at higher frequency and contributes to a weak band ν_{123} , which belongs mostly to the furan half-ring vibrations of the CO bonds (Fig. 4 and Table 1, calc.: 1223 cm^{-1} , exp.: 1217 cm^{-1}).

5. Conclusions

We have detected FTIR spectrum of symmetrical derivative of the tetraoxa[8]circulene *para*-dinaphthylene-2,3,10,11-tetraundecyldiphenylenetetrauran (*p*-2B2N4R, $\text{R}=\text{n-C}_{11}\text{H}_{23}$) and have interpreted it the density functional theory (DFT). The unsubstituted *para*-dinaphthylenodiphenylenetetrauran (*p*-2B2N) and the *para*-dinaphthylene-2,3,10,11-tetraethyldiphenylenetetrauran (*p*-2B2N4R, $\text{R}=\text{C}_2\text{H}_5$) molecules which belong to the D_{2h} and D_2 symmetry point groups, respectively, have been studied as the model simulating compounds and their equilibrium molecular structures, harmonic vibrational frequencies, IR absorption intensities have been calculated by the DFT/B3LYP method with the 6-31G(d) basis set. All 138 normal modes of unsubstituted *para*-dinaphthylenodiphenylenetetrauran and 210 modes of the *para*-dinaphthylene-2,3,10,11-tetraethyldiphenylenetetrauran molecules were calculated and analyzed. IR active 57 modes of *p*-2B2N and 156 IR active modes of *p*-2B2N4R ($\text{R}=\text{C}_2\text{H}_5$) are presented in the Tables 1 and 2 with a complete assignment of their structural nature. In order to classify vibrational origins of the tetraoxa[8]circulene modes we have compared them with the calculated modes and the IR spectra of benzene, naphthalene, furan, tetraphenylenetetrauran (4B) and tetranaphthylenetetrauran (4N). Some forbidden modes of these compounds are allowed in the unsubstituted and substituted tetraoxa[8]circulenes *p*-2B2N, which is observed in the spectra. The replacement of the undecyl substituents by the ethyl ones in the *p*-2B2N4R molecule has been proven by direct calculation of undecane molecule and a good correlation obtained between calculated and observed spectra.

The symmetry correlation diagrams for vibrational modes in the present and the previously studied molecules have been used

in the intensity and frequency analysis. Comparison of the calculated vibrational spectra with the experimental data provides very reliable assignments of all observed bands in FTIR spectra of the tetraoxa[8]circulenes *p*-2B2N and help in additional interpretation of some forbidden modes of the constituent molecules. The corresponding frequency shifts are well reproduced. The reference spectra also help in the assignment of the close lying bands from different fragments, which almost coincide in the observed spectra.

Upon introduction of the substituents a significant shift occurs for those modes, which belong to vibration of the bonds being sensitive to aliphatic substitution. The calculated vibration frequencies (stretching and deformation) in the substituted *p*-2B2N tetraoxa[8]circulene molecule are in a good agreement with the measured spectra taking into account the deviation, which corresponds to the crystal packing effects.

The detailed analysis of all IR active bands is necessary from the point of fundamental importance of these symmetric tetraoxa[8]circulenes vibration assignment.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.vibspec.2013.01.001>.

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