

## SPECTROSCOPY OF ATOMS AND MOLECULES

# Raman Spectra of Alkyl-Substituted Azaoxa[8]circulenes: DFT Calculation and Experiment

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**Abstract**—Raman lines in spectra of recently synthesized azaoxa[8]circulenes have been assigned in detail on the basis of obtained experimental data and B3LYP/6-31G(d) calculations. Particular features of the structure of three azaoxa[8]circulenes have been considered based on data of X-ray structural analysis and DFT calculations. Regularities in changes of the geometric parameters have been found for benzene, furan, pyrrole, and naphthalene rings that occur upon formation of the macroring in comparison with free molecules. Raman spectra of macrorings have been shown to contain a characteristic set of lines the frequencies of which differ from those of analogous lines in Raman spectra of benzene, pyrrole, furan, and naphthalene. Results of quantum-chemical calculations agree well with experimental data with respect to line frequencies and intensities due to recalculation of Raman activities of normal vibrations into intensities of Raman lines.

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### INTRODUCTION

Azaoxa[8]circulenes form a new class of polyaromatic compounds, which consist of eight condensed aromatic rings, with one or two of them being the pyrrole ring [1]. At present, two representatives of azatrioxa[8]circulenes have been synthesized and identified (Fig. 1)—*N*-propyl-tetra-*tert*-butylazatrioxa[8]circulene, which will be further referred to as **C1**, and *N*-propyl-di-*tert*-butylazatrioxa[8]circulene, which will be further referred to as **C3**—as well as one representative of diazadioxo[8]circulenes, *N,N*-dipropyl-tetra-*tert*-butyldiazadioxo[8]circulene, which will be further referred to as **C2**. Azaoxa[8]circulenes, as well as the related tetraoxa[8]circulenes [2–10], are interesting

for applications in technology of organic light-emitting diodes for preparing electroluminescent layers [3]. In addition, azaoxa[8]circulenes can be put to an evaluation test as a material for organic field transistors, by analogy with the known related “sulflower” (octathia[8]circulene) [11].

Azaoxa[8]circulenes are little-studied compounds. Their electronic structure and aromatic properties, electronic absorption and luminescence spectra, as well as IR and Raman spectra, are of special interest. In this work, we will present a complete assignment of lines in the Raman spectra of the examined azaoxa[8]circulenes **C1**–**C3** based on quantum-chemical calculations comparison with experiment. In addi-

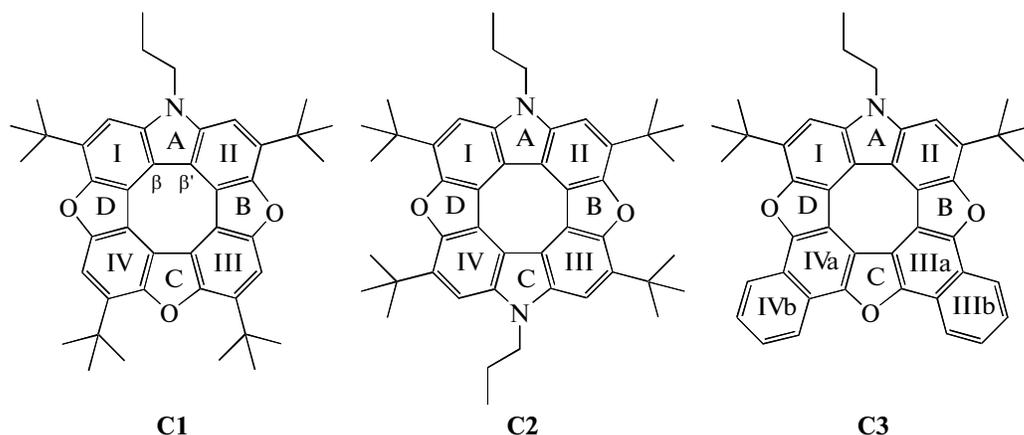


Fig. 1. Structures of molecules of compounds **C1**–**C3** and notation of rings.

tion, we will analyze the geometric structure of the **C1–C3** molecules based on our calculations and the X-ray diffraction data. It will be shown that the polyaromatic macroring of azaoxa[8]circulenes is characterized by an individual Raman spectrum, which differs from the spectra of constituent free molecules of benzene, furan, pyrrole, and naphthalene. Application of the generally accepted corrections for anharmonicity of vibrations and recalculation of activity of normal vibrations into intensity allowed us to obtain a good agreement between the calculated and experimental spectra with respect to the frequencies and intensities of Raman lines. Calculated geometric parameters of compounds **C1–C3** also agree well with experiment; in the majority of examples, the discrepancies in bond lengths do not exceed 0.005 Å. On such background we provide an exact interpretation of the structure and optical properties of this new class of compounds.

## EXPERIMENT

The azaoxa[8]circulenes under study were synthesized from a common precursor, *N*-propyl-2,7-di-*tert*-butyl-3,6-dihydroxycarbazole, according to an original technique [1]. In the case of compound **C1**, only one regioisomer is formed with respect to the *tert*-butyl substituents, which is evidenced by the <sup>1</sup>N NMR data: signals that correspond to two types of aromatic protons and two types of *tert*-butyl substituents are observed in the spectrum.

Raman spectra were recorded on a BRUKER IFS66 NIR-FT spectrometer that was equipped with an FRA106 unit. As an excitation source, we used a YAG:Nd laser that emits at a wavelength of 1064 nm with an output power of 300 mW; as a detector, we used a germanium diode cooled to liquid-nitrogen temperature.

## METHOD OF CALCULATION

The structure of the **C1–C3** molecules was optimized by the B3LYP/6-31G(d) density fluctuation method [12, 13] using the Gaussian 03 software package [14] and monitoring the maximal possible symmetry. Based on this method, we also calculated frequencies of corresponding normal vibrations. All frequencies of vibrations were real-valued quantities, which indicates that the true minimum on the hypersurface of the total energy of molecules was found. To compare the calculated frequencies with experimental ones, the former were slightly corrected with a scaling factor. For the high-frequency spectral range, we used the scaling factor of 0.950; for the remainder of the spectrum, the scaling factor was 0.969. The scaling factors were obtained as an average value of the ratios of experimental and calculated vibration frequencies of all fragments in a certain range of the spectrum. These values of the scaling factors are typical for the

corresponding spectral ranges [15] and are widely used in modern quantum theory of molecular vibrations.

The values of activities of the normal modes in the Raman spectra ( $S_i$ ) are not identical to the Raman intensities observed in the experiment. It is known that the Raman activity of vibrations is calculated via the derivative of the polarizability of the electronic shell. In the density functional theory that we use, all the parameters of the molecular electronic shells are calculated ab initio along with the minimization of the total energy in terms of the given B3LYP functional. To transform the Raman activity into the corresponding intensity for the  $i$ th normal mode ( $I_i$ ), we used the recalculation formula that was applied in [16],

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[ 1 - \exp\left(-\frac{hc_0 v_i}{kT}\right) \right]}, \quad (1)$$

where  $v_0$  is the laser excitation frequency (9398.5 cm<sup>-1</sup>),  $v_i$  is the frequency of the  $i$ th normal mode (cm<sup>-1</sup>),  $c_0$  is velocity of light in vacuum ( $2.9979 \times 10^{10}$  cm/s),  $h$  is the Planck constant ( $6.6261 \times 10^{-27}$  erg s),  $k$  is the Boltzmann constant ( $1.3806 \times 10^{-16}$  erg/K), and  $f$  is an arbitrarily chosen recalculation factor of intensities of all peaks (was taken equal to 1).

The calculated values of  $I_i$  were expressed in fractions of unity for comparison with corresponding experimental spectra. The calculated Raman spectra of the studied azaoxa[8]circulenes were plotted using the program SWizard [17] (the line halfwidth was 15 cm<sup>-1</sup>, and the Lorentz distribution function was used). It is interesting to note that for the **C3** molecule, the relative intensity of Raman lines of low-frequency normal vibrations is approximately 10–30 times lower than the intensity of similar lines calculated for the **C1** and **C2** molecules. This is related, first of all, to the peculiarity of transformation of the absolute activity of the normal vibration into the intensity by Eq. (1).

Analysis of Eq. (1) shows that the factor  $\exp(-hc_0 v_i/kT)$  decreases exponentially with an increase of vibration frequency  $v_i$  and has a substantial contribution (greater than 0.1) at values of  $v_i$  that do not exceed 476 cm<sup>-1</sup>. Precisely for this reason, the calculated intensity of low-frequency Raman lines is at least an order of magnitude higher than the corresponding activity values. In the rest of the Raman spectrum (from 477 to 4000 cm<sup>-1</sup>), the value of the factor  $\exp(-hc_0 v_i/kT)$  becomes so small that it can be neglected and the denominator of formula (1) can be assumed to be  $v_i$ . Therefore, the most influential factor that determines the absolute value of  $I_i$  in the midrange of frequencies is precisely the factor  $(v_0 - v_i)^4$ , which decreases very rapidly with increasing  $v_i$  and with approaching resonance; the ratio  $S_i/v_i$  is a factor of the second order in determining the

intensity of Raman lines, being almost insignificant at  $S_i > 100 \text{ \AA}^4/\text{amu}$ .

The above considerations show that, for the **C3** compound, the most intense maximum at  $1428 \text{ cm}^{-1}$  (the normal vibration  $\nu_{171}$ ;  $S_i = 2147.8 \text{ \AA}^4/\text{amu}$ ) exhibits a considerably higher (approximately by two orders of magnitude) intensity in the Raman spectrum than the most intense maxima in the spectra of compounds **C1** and **C2** at  $1635 \text{ cm}^{-1}$  (the normal vibration  $\nu_{229}$ ;  $S_i = 1916.8 \text{ \AA}^4/\text{amu}$ ) and  $1624 \text{ cm}^{-1}$  (the normal vibration  $\nu_{252}$ ;  $S_i = 1681.3 \text{ \AA}^4/\text{amu}$ ). Upon recalculation of calculated absolute intensities into relative ones, we put the absolute intensity of vibrations  $\nu_{171}$ ,  $\nu_{229}$ , and  $\nu_{252}$  equal to unity, while all the remaining lines in the Raman spectra have a relative intensity expressed in fractions of unity. In this case, the ratio of the line intensities in each Raman spectrum is preserved and low-frequency Raman lines in the spectrum of compound **C3** have a considerably lower relative intensity than do similar lines in the Raman spectra of compounds **C1** and **C2**.

## RESULTS AND DISCUSSION

### *The Molecular Structure of Alkyl-Substituted Azaoxa[8]circulenes*

The structures of molecules **C1–C3** and notation of rings are presented in Fig. 1. To enumerate benzene rings, we used Roman numerals I–IV; heterocycles were denoted by capital letters. The geometric parameters of the **C1–C3** molecules were compared with the data of X-ray diffraction analysis and the calculation results by the same method for free molecules of benzene, furan, pyrrole, and naphthalene. The analysis indicates that the C–O and C–N bonds are subjected to elongation to a greater extent upon condensation than the C=C bonds in benzene fragments; however, in general, there is observed a tendency to expansion of benzene, furan, and pyrrole rings in the condensed cyclic system compared to corresponding free molecules and to leveling the C=C, C–O, and C–N bond lengths in the outer perimeter. The structure of rings IIIa (IVa) of the naphthalene fragment in compound **C3** differs little from that in free naphthalene, except for bond lengths involved in condensation:  $1.377 \text{ \AA}$  in free state and  $1.388 \text{ \AA}$  in compound **C3**. In rings IIIb (IVb), bond lengths change to a greater extent.

Leveling bond lengths in the outer perimeter of azacirculenes is one piece of evidence of their aromatic character, as well as characteristic signals of “aromatic” protons in PMR spectra [1]. However, for the central octatetraene ring of **C1–C3** molecules, a strict alternation of C=C bond lengths is observed, which is indicative of a very weak cyclic conjugation. As a consequence, the octatetraene ring, even while remaining planar, has an antiaromatic character. This is also supported by recent calculations [1, 18, 19] of

nucleus-independent chemical shifts that were performed at the center of the octatetraene ring in hetero[8]circulenes and above the center by  $1 \text{ \AA}$ , which are positive and point to the occurrence of paratropic circular currents in the ring, i.e., to its antiaromaticity.

Comparison of bond lengths that we calculated with the data of X-ray diffraction analysis shows their good agreement. The discrepancy between theoretical and experimental absolute values of the bond lengths does not exceed  $0.015 \text{ \AA}$  and, for the majority of bonds, is much smaller.

Comparison of the geometric parameters of the pyrrole fragments in **C1–C3** molecules shows that they are not equivalent, although they are rather close to each other. Thus, the lengths of the C–N bonds in **C1** and **C3** molecules differ from each other only by  $0.001 \text{ \AA}$ , while, in **C1** and **C2**, by  $0.003 \text{ \AA}$ . The lengths of the condensed (side) C=C bonds of the pyrrole rings are  $1.412$ ,  $1.415$ , and  $1.413 \text{ \AA}$  for compounds **C1**, **C2**, and **C3**, respectively, whereas the lengths of the bases of the pyrrole rings are  $1.430$ ,  $1.436$ , and  $1.431 \text{ \AA}$ , respectively. Therefore, we can see that the pyrrole rings in molecule **C2** are more expanded compared to **C1** and **C3**. This affects the values of the force constants of bonds, which should be reflected in shifts of corresponding bands in the Raman spectrum of compound **C2** compared to compounds **C1** and **C3**.

The furan fragments in molecules **C1–C3** are also not identical. Thus, the lengths of the C–O bonds in rings *B* and *D* of **C1** and **C3** molecules are pairwise nonsymmetric ( $1.380$  and  $1.392 \text{ \AA}$  for **C1** molecule and  $1.376$  and  $1.392 \text{ \AA}$  for **C3**), which is a consequence of the manifestation of the induction effect of the irregularly arranged *tert*-butyl substituents in the **C1** molecule and of the occurrence of the naphthalene fragments in the **C3** molecule (this effect is transferred over the  $\pi$ -system). In the **C2** molecule the C–O bonds of the furan rings *B* and *D* are pairwise and almost do not differ from each other, which can be explained by a symmetric arrangement of the two pyrrole rings and regular arrangement of the *tert*-butyl substituents. Deformation of furan rings *B* and *D* is also observed with respect to the C=C side bond lengths. For the **C3** molecule, this is more pronounced, which is predominantly caused by the redistribution of the electron density over the  $\pi$ -system in the presence of the naphthalene fragments.

Furan rings *C* in the **C1** and **C3** molecules do not have analogs in the **C2** molecule. The lengths of the two C–O bonds in the ring *C* of the **C1** molecule are equal to each other and are  $1.390 \text{ \AA}$ , while, in the **C3** molecule, they decrease to  $1.380 \text{ \AA}$ , which is caused by the conjugation effect over the  $\pi$ -system in the presence of the naphthalene fragments. Similar changes are also characteristic of the two C=C side bonds; namely, in the **C3** molecule, they are shorter by  $0.013 \text{ \AA}$  than for **C1**. Therefore, ring *C* in the **C3** molecule is significantly narrowed compared to its analog

in molecule **C1**, which should manifest itself in the positions and intensities of corresponding bands in the Raman spectrum.

Differences in the structure of the **C1–C3** molecules also cause insignificant differences in the lengths of the C=C bonds of the benzene fragments, which, in the majority of cases, do not exceed 0.002 Å.

### *Raman Spectra of Alkyl-Substituted Azaxa[8]circulenes*

The vibrational spectrum of the molecule of compound **C1**, which consists of 94 atoms, has 276 normal vibrations, which belong to the  $A'$  and  $A''$  symmetry species in the  $C_s$  symmetry point group. Almost all normal vibrations that yield lines observed in the Raman spectrum are in-phase and are totally symmetric ( $A'$ ). The table presents form of vibrational modes, calculated frequencies, and activities of the normal vibrations in the Raman spectra, as well as the calculated relative intensities of Raman lines, and gives assignments of lines in the experimental spectrum of compound **C1**. Only the most active normal vibrations are presented in this table. For **C1–C3** compounds, the calculated and experimental frequencies of the Raman lines are shown in Fig. 2. Complete tables of calculated normal vibrations for all three investigated molecules are available from the authors by request.

### *Vibrations of Aromatic Rings*

**C–H vibrations of aromatic rings.** CH vibrations in Raman spectra of aromatic compounds can be identified in the ranges 3080–3010 (C–H stretching vibrations), 1290–990  $\text{cm}^{-1}$  (in-plane bending vibrations) and below 900  $\text{cm}^{-1}$  (out-of-plane bending vibrations) [20].

**C–H stretching vibrations of aromatic rings,  $\nu\text{CH}$ .** To stretching vibrations of the C–H bonds in the Raman spectrum of molecule **C1**, the four  $\nu\text{CH}$  normal vibrations of benzene fragments belong, of which only two are Raman active, which is observed in the experimental spectrum as a weak doublet (3091 and 3076  $\text{cm}^{-1}$ ; table; Fig. 2). In the calculated Raman spectrum of the **C1** molecule (Fig. 2), a weak line at 3085  $\text{cm}^{-1}$ , which is formed by the doublet of the lines at 3085 and 3070  $\text{cm}^{-1}$  of symmetric C–H vibrations in benzene rings III, IV and I, II, respectively, is attributed to stretching vibrations of C–H bonds.

We also obtained the same splitting in the calculated and experimental spectra for  $\nu\text{CH}$  vibrations in the upper (I, II) and lower (III, IV) benzene rings of the **C2** molecule (calculation: 3072 and 3048  $\text{cm}^{-1}$ ; experiment: 3089 and 3049  $\text{cm}^{-1}$ ), which contradicts the symmetric structure shown in Fig. 1. When optimizing geometry of the **C2** molecule, we started from the symmetric structure; however, the final calculation yielded a molecule with small differences in valence

angles (up to 5°) of the *tert*-butyl groups at the upper and lower benzene rings. Spontaneous violation of symmetry in the arrangement of these groups is caused by a peculiar pseudo-Jahn–Teller effect. In the presence of hyperconjugation of the *tert*-butyl groups and aromaticity of the outer ring, vibronic perturbations substantially deform the force field of the **C2** molecule. The C–H stretching vibrations in the outer ring proved to be very sensitive to these deformations, which led to the above-indicated splitting of the frequencies of vibrations of the upper and lower CH-groups. Replacement of the two benzene fragments in molecule **C1** with naphthalene fragments (molecule **C3**) does not lead to a shift of the frequency 3072  $\text{cm}^{-1}$  of the C–H bonds vibrations in benzene fragments; only the total intensity of the line in the spectrum decreases. The line that corresponds to them has an intensity that is too low to be observed in the calculated Raman spectrum.  $\nu\text{CH}$  vibrations of naphthalene fragments in the Raman spectrum of molecule **C3** yield two lines, 3057 and 3040  $\text{cm}^{-1}$ , which overlap each other to merge into a band at 3057  $\text{cm}^{-1}$  (experiment: 3055  $\text{cm}^{-1}$ ). Compared to the symmetric  $\nu\text{CH}$  vibrations that we calculated in the Raman spectra of benzene (calculation: 3053 and 3027  $\text{cm}^{-1}$ ) and naphthalene (calculation: 3049 and 3027  $\text{cm}^{-1}$ ), upon formation of molecules of azacirculenes under study, a small shift toward higher frequencies is observed, which is a consequence of strengthening of C–H bonds upon condensation in benzene and naphthalene rings.

**CH in-plane bending vibrations of aromatic rings,  $\delta\text{CH}$ .** In the Raman spectra of the molecules under study, we calculated these vibrations in the range 1254–1040  $\text{cm}^{-1}$  (table). In the experimental spectrum of compound **C1**,  $\delta\text{CH}_{\text{benz}}$  vibrations contribute to lines at 1257 (calculation: 1254), 1198 (calculation: 1195), 1134 (calculation: 1126), and 1034  $\text{cm}^{-1}$  (calculation: 1043  $\text{cm}^{-1}$ ). In the Raman spectrum of molecule **C2** (Fig. 2), the experimental lines at 1255 (calculation: 1254), 1188 (calculation: 1194 and 1180), and 1047  $\text{cm}^{-1}$  (calculation: 1044  $\text{cm}^{-1}$ ) correspond to these lines. The frequencies of  $\delta\text{CH}_{\text{benz}}$  vibrations calculated in the Raman spectrum of molecule **C3** were also close to those of **C2** (Fig. 2), but some of these lines are not observed in the experimental spectrum because of their low intensity. The line  $\delta\text{CH}_{\text{benz}}$  with a contribution from the skeletal vibration of the N–CH<sub>2</sub> bond was calculated in molecule **C1** at 1126  $\text{cm}^{-1}$ ; in the Raman spectrum of molecule **C2**, it experiences a strong shift to 1180  $\text{cm}^{-1}$ . A similar shift, to 1188  $\text{cm}^{-1}$ , was also observed in the Raman spectrum of molecule **C3**, benzene rings III and IV of which do not contain CH groups; however, this normal vibration, along with the  $\delta\text{CH}_{\text{benz}}$  vibrations in rings I and II, involves  $\delta\text{CH}_{\text{naphth}}$  vibrations. The closely located lines at 1180 and 1194  $\text{cm}^{-1}$  in the Raman spectrum of molecule

Calculated data of Raman-active normal vibrations of molecule C1

Vibration	$\nu$ , $\text{cm}^{-1}$	$\frac{S_i}{\text{\AA}^4/\text{amu}}$	$I_i$	Experiment	Vibration species
$\nu_{276}$	3085	186.9	$2.1 \times 10^{-2}$	3091	$\nu_s\text{CH}$ benz III, IV, in-phase
$\nu_{274}$	3070	168.5	$1.9 \times 10^{-2}$	3076	$\nu_s\text{CH}$ benz I, II, in-phase
$\nu_{272}$	2996	188.1	$2.3 \times 10^{-2}$	3005	$\nu_{as}\text{CH}_3$ <i>t</i> -but at III, IV, in-phase
$\nu_{271}$	2994	109.7	$1.3 \times 10^{-2}$	3005	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I, II, in-phase
$\nu_{264}$	2965	118.8	$1.5 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>n</i> -propyl, $\nu_{as}\text{CH}_2$
$\nu_{263}$	2962	503.3	$6.3 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I–IV, in-phase
$\nu_{262}$	2962	148.1	$1.8 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at III, IV, ooph
$\nu_{261}$	2962	14.5	$1.8 \times 10^{-3}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at III, IV, in-phase
$\nu_{260}$	2960	79.9	$9.8 \times 10^{-3}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at III, IV, ooph
$\nu_{259}$	2960	537.3	$6.7 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I, II, in-phase
$\nu_{258}$	2960	115.0	$1.4 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I, II, ooph
$\nu_{257}$	2958	34.4	$4.3 \times 10^{-3}$	2960	$\nu_{as}\text{CH}_3$ <i>n</i> -propyl, $\nu_{as}\text{CH}_2$
$\nu_{256}$	2957	73.8	$9.2 \times 10^{-3}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I, II, in-phase
$\nu_{255}$	2957	13.4	$1.7 \times 10^{-3}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I, II, ooph, $\nu_{as}\text{CH}_3$ <i>n</i> -propyl, $\nu_{as}\text{CH}_2$
$\nu_{254}$	2953	100.0	$1.3 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at III, IV, in-phase
$\nu_{250}$	2952	112.7	$1.4 \times 10^{-2}$	2960	$\nu_{as}\text{CH}_3$ <i>t</i> -but at I, II, in-phase
$\nu_{246}$	2942	2.9	$4.0 \times 10^{-4}$		$\nu_{as}\text{CH}_3$ <i>n</i> -propyl, $\nu_{as}\text{CH}_2$
$\nu_{245}$	2923	90.4	$1.2 \times 10^{-2}$	2926	$\nu_{as}\text{CH}_3$ <i>n</i> -propyl, $\nu_{as}\text{CH}_2$
$\nu_{244}$	2906	49.7	$6.5 \times 10^{-3}$	2906	$\nu_s\text{CH}_3$ <i>n</i> -propyl, $\nu_s\text{CH}_2$
$\nu_{243}$	2901	935.0	$1.2 \times 10^{-1}$	2906	$\nu_s\text{CH}_3$ <i>t</i> -but at III, IV, in-phase
$\nu_{242}$	2900	57.9	$7.7 \times 10^{-3}$	2906	$\nu_s\text{CH}_3$ <i>t</i> -but at III, IV, ooph
$\nu_{241}$	2899	763.5	$1.0 \times 10^{-1}$	2906	$\nu_s\text{CH}_3$ <i>t</i> -but at I, II, in-phase
$\nu_{240}$	2899	49.8	$6.6 \times 10^{-3}$	2906	$\nu_s\text{CH}_3$ <i>t</i> -but at I, II, ooph
$\nu_{239}$	2896	94.4	$1.3 \times 10^{-2}$		$\nu_s\text{CH}_2$ <i>n</i> -propyl, in-phase
$\nu_{232}$	2892	95.0	$1.3 \times 10^{-2}$		$\nu_s\text{CH}_3$ <i>n</i> -propyl
$\nu_{229}$	1635	1917.0	1.0	1653	$\nu_s\text{C}=\text{C}$ benz I–IV, in-phase, $\nu\text{C}^\beta-\text{C}^{\beta'}$ pyr, fur
$\nu_{228}$	1628	310.4	$1.6 \times 10^{-1}$	1653	$\nu_s\text{C}=\text{C}$ benz I, II and III, IV, ooph, $\nu\text{C}^\beta-\text{C}^{\beta'}$ pyr, fur, $\nu_s\text{C}-\text{N}$
$\nu_{225}$	1591	1129.0	$6.2 \times 10^{-1}$	1605	$\nu_{as}\text{C}=\text{C}$ benz III, IV, $\delta\text{COC}$ B, C, D, $\nu\text{C}^\beta-\text{C}^{\beta'}$ , $\nu_s\text{C}^\alpha=\text{C}^\beta$ fur C
$\nu_{223}$	1570	397.1	$2.2 \times 10^{-1}$	1581	$\nu_{as}\text{C}=\text{C}$ benz I, II, $\delta\text{CNC}$ , $\nu_s\text{C}^\alpha=\text{C}^\beta$ fur C, $\nu\text{C}^\beta-\text{C}^{\beta'}$ fur B, D, $\delta\text{COC}$ fur C
$\nu_{217}$	1493	29.2	$1.8 \times 10^{-2}$		$\delta_{as}\text{CH}_3$ <i>n</i> -propyl, $\delta\text{CH}_2$
$\nu_{216}$	1492	224.0	$1.4 \times 10^{-1}$	1502	$\delta_{as}\text{CH}_3$ <i>t</i> -but, <i>n</i> -propyl, $\delta\text{CH}_2$ , $\nu_s\text{C}^\alpha=\text{C}^\beta$ pyr, $\delta\text{CNC}$
$\nu_{208}$	1484	25.0	$1.6 \times 10^{-2}$		$\delta_{as}\text{CH}_3$ <i>n</i> -propyl
$\nu_{207}$	1483	3.2	$2.0 \times 10^{-3}$		$\delta_{as}\text{CH}_3$ <i>t</i> -but, <i>n</i> -propyl
$\nu_{205}$	1478	25.9	$1.6 \times 10^{-2}$	1479	$\delta_{as}\text{CH}_3$ <i>t</i> -but, <i>n</i> -propyl, $\delta\text{CH}_2$
$\nu_{204}$	1478	8.3	$1.4 \times 10^{-3}$		$\delta_{as}\text{CH}_3$ <i>n</i> -propyl, $\delta\text{CH}_2$
$\nu_{202}$	1478	28.9	$1.8 \times 10^{-2}$	1481	$\delta_{as}\text{CH}_3$ <i>t</i> -but at I, II, $\delta_{as}\text{CH}_3$ <i>n</i> -propyl, $\delta\text{CH}_2$
$\nu_{198}$	1473	41.8	$2.6 \times 10^{-2}$	1481	$\delta_{as}\text{CH}_3$ <i>n</i> -propyl, $\delta\text{CH}_2$
$\nu_{195}$	1471	74.7	$4.7 \times 10^{-2}$	1462	$\delta_{as}\text{CH}_3$ <i>t</i> -but, <i>n</i> -propyl, $\delta\text{CH}_2$ , $\nu_s\text{C}^\alpha=\text{C}^\beta$ , $\nu\text{C}^\beta-\text{C}^{\beta'}$ pyr, $\delta\text{CNC}$
$\nu_{188}$	1419	69.4	$4.7 \times 10^{-2}$	1421	$\nu_{as}\text{C}=\text{C}$ benz I, II, $\delta_s\text{CH}_3$ <i>t</i> -but at I, II, $\omega\text{CH}_2$ , $\nu_s\text{C}-\text{N}$ , $\delta\text{COC}$ B, C, D
$\nu_{184}$	1407	110.8	$7.6 \times 10^{-2}$	1404	$\nu_{as}\text{C}=\text{C}$ benz, $\delta_s\text{CH}_3$ <i>t</i> -but at I–IV, $\nu_s\text{C}-\text{N}$ , $\omega\text{CH}_2$ , $\nu_s\text{C}^\alpha=\text{C}^\beta$ fur B, C, D
$\nu_{182}$	1389	146.3	$1.0 \times 10^{-1}$	1383	Vibrations of benzene rings, as., $\delta_{as}\text{CH}_3$ <i>t</i> -but, <i>n</i> -propyl, $\delta\text{CH}_2$ , $\nu\text{C}^\beta-\text{C}^{\beta'}$ pyr, fur, $\nu_s\text{C}^\alpha=\text{C}^\beta$ fur C, $\nu_s\text{C}-\text{O}$ B, D, $\delta\text{COC}$ fur C, $\delta\text{CNC}$

Table. (Contd.)

Vibration	$\nu, \text{cm}^{-1}$	$S_i, \text{\AA}^4/\text{amu}$	$I_i$	Experiment	Vibration species
$\nu_{171}$	1372	204.8	$1.5 \times 10^{-1}$	1365	Vibrations of benzene rings, as., $\omega\text{CH}_2$ , $\nu_s\text{C}-\text{N}$ , $\nu\text{C}^\beta-\text{C}^{\beta'}$ fur B, D and C, ooph
$\nu_{170}$	1357	32.3	$2.4 \times 10^{-2}$	1346	Vibrations of benzene rings, as., $\delta_s\text{CH}_3$ <i>t</i> -but at I, II, $\nu\text{C}-\text{O}$ semiring B, D, $\tau\text{CH}_2$ , $\nu\text{C}^\beta-\text{C}^{\beta'}$ fur B and D, ooph, $\nu_{\text{as}}\text{C}^\alpha=\text{C}^\beta$ pyr
$\nu_{169}$	1357	92.8	$6.8 \times 10^{-2}$	1346	Vibrations of benzene rings, as., $\delta_s\text{CH}_3$ <i>t</i> -but at III, IV, breathing pyr, $\nu_s\text{C}-\text{O}$ fur, $\nu\text{C}^\beta-\text{C}^{\beta'}$ fur C, pyr, in-phase
$\nu_{168}$	1341	92.1	$6.8 \times 10^{-2}$	1346	$\nu_{\text{as}}$ Kekule C=C benz I, II, $\delta\text{CNC}$ , $\delta\text{COC}$ fur C, $\nu\text{N}-\text{CH}_2$ , $\delta_s\text{CH}_3$ <i>t</i> -but
$\nu_{167}$	1327	174.7	$1.3 \times 10^{-1}$	1329	$\nu_{\text{as}}$ Kekule C=C benz III, IV, $\tau\text{CH}_2$
$\nu_{166}$	1324	216.3	$1.6 \times 10^{-1}$	1329	Vibrations of benzene rings, as., breathing pyr, $\nu_s\text{C}-\text{O}$ fur C, semiring B, D, $\nu\text{N}-\text{CH}_2$
$\nu_{165}$	1311	140.0	$1.1 \times 10^{-1}$	1304	Vibrations of benzene rings, as., $\nu_{\text{as}}\text{C}^\alpha=\text{C}^\beta$ pyr, $\tau\text{CH}_2$
$\nu_{164}$	1302	8.7	$6.8 \times 10^{-3}$		$\omega\text{CH}_2$
$\nu_{159}$	1254	308.3	$2.6 \times 10^{-1}$	1257	$\delta\text{CH}$ benz I, II, $\nu\text{C}_{\text{benz}}-\text{C}t$ -but, $\nu\text{N}-\text{CH}_2$ , $\nu\text{C}^\beta-\text{C}^{\beta'}$ pyr
$\nu_{157}$	1232	47.1	$4.0 \times 10^{-2}$		$\delta\text{CH}$ benz III, IV, $\nu_{\text{as}}\text{C}-(\text{CH}_3)$ , $\nu_{\text{as}}\text{C}-\text{O}$ fur B, D, $\nu\text{C}^\beta-\text{C}^{\beta'}$ pyr
$\nu_{156}$	1225	453.8	$3.9 \times 10^{-1}$	1228	$\delta\text{CH}$ benz, breathing benz I-IV, in-phase and ct out-of-phase, $\nu_{\text{as}}\text{C}-(\text{CH}_3)$ , $\nu\text{C}-\text{O}$
$\nu_{146}$	1195	126.8	$1.1 \times 10^{-1}$	1198	$\delta\text{CH}$ benz
$\nu_{145}$	1195	52.0	$4.7 \times 10^{-2}$	1198	$\delta\text{CH}$ benz, $\nu_s\text{C}-\text{O}$ fur C, $\nu\text{C}-\text{O}$ semiring B, D, $\tau\text{CH}_2$ , $\tau\text{CH}_3$ <i>n</i> -propyl
$\nu_{141}$	1140	30.1	$2.9 \times 10^{-2}$	1134	$\delta\text{CH}$ benz III, IV, $\nu\text{C}-\text{O}$ semiring B, D
$\nu_{140}$	1126	82.0	$8.1 \times 10^{-2}$	1134	$\delta\text{CH}$ benz, $\nu\text{N}-\text{CH}_2$ , $\nu_s\text{C}-\text{O}$ fur C, $\nu\text{C}-\text{O}$ semiring B, D, def benz, ct
$\nu_{138}$	1096	11.5	$1.2 \times 10^{-2}$	1101	$\tau\text{CH}_3$ <i>n</i> -propyl, $\delta\text{CH}_2-\text{CH}_2-\text{CH}_3$ , $\nu\text{N}-\text{CH}_2$
$\nu_{136}$	1052	45.4	$5.0 \times 10^{-2}$	1053	$\nu\text{C}^\beta-\text{C}^{\beta'}$ fur C, $\tau\text{CH}_3$ <i>t</i> -but, $\nu_{\text{as}}\text{C}-\text{O}$ fur B, D
$\nu_{135}$	1043	6.7	$7.5 \times 10^{-3}$	1034	$\delta\text{CH}$ benz I, II, $\nu\text{C}_{\text{benz}}-\text{C}t$ -but, breathing fur B, D and C, ooph
$\nu_{127}$	1019	61.0	$7.1 \times 10^{-2}$	1020	$\nu\text{CH}_2-\text{CH}_3$ <i>n</i> -propyl, $\tau\text{CH}_3$ <i>t</i> -but
$\nu_{125}$	1002	29.8	$3.6 \times 10^{-2}$	1020	Breathing fur C, $\nu_s\text{C}-\text{O}$ B, C, D, $\nu\text{N}-\text{CH}_2$ , $\nu\text{CH}_2-\text{CH}_2$ , def benz, as.
$\nu_{117}$	920	21.9	$3.0 \times 10^{-2}$	926	$\nu_{\text{as}}\text{C}-(\text{CH}_3)$
$\nu_{109}$	879	16.7	$2.5 \times 10^{-2}$		$\nu\text{CH}_2-\text{CH}_2$ , $\tau\text{CH}_3$ <i>n</i> -propyl
$\nu_{107}$	853	5.0	$7.5 \times 10^{-3}$	858	$\nu\text{C}_{\text{benz}}-\text{C}t$ -but, $\nu\text{CH}_2-\text{CH}_2$
$\nu_{106}$	847	3.9	$5.9 \times 10^{-3}$	858	$\delta\text{COC}$ fur B, D, ooph, $\nu\text{C}_{\text{benz}}-\text{C}t$ -but, def benz, as. I, II
$\nu_{101}$	822	13.6	$2.2 \times 10^{-2}$	835	$\delta\text{CNC}$ , breathing pyr, def benz, s.
$\nu_{98}$	778	9.3	$1.6 \times 10^{-2}$	781	$\nu_s\text{C}-(\text{CH}_3)$ at I-IV, $\nu\text{N}-\text{CH}_2$ , def benz, s.
$\nu_{96}$	763	24.0	$4.3 \times 10^{-2}$	781	$\nu_s\text{C}-(\text{CH}_3)$ at I-IV, $\nu\text{N}-\text{CH}_2$ , def benz
$\nu_{87}$	683	9.5	$2.0 \times 10^{-2}$	690	$\delta\text{CNC}$ , I, II benz and B, D fur twisting, $\delta\text{CH}_2-\text{CH}_2-\text{CH}_3$ , $\delta\text{N}-\text{CH}_2-\text{CH}_2$
$\nu_{86}$	676	1.3	$2.8 \times 10^{-2}$		$\nu\text{C}_{\text{benz}}-\text{C}t$ -but at III, IV, $\nu\text{C}-(\text{CH}_3)$ <i>t</i> -but, def benz, as.
$\nu_{81}$	629	6.9	$1.6 \times 10^{-2}$	634	$\nu_s\text{C}-(\text{CH}_3)$ , in-phase
$\nu_{78}$	586	7.3	$1.9 \times 10^{-2}$	596	Def benz, as.
$\nu_{74}$	546	8.1	$2.3 \times 10^{-2}$	549	$r\text{CH}_2$ , def benz I, II
$\nu_{73}$	534	7.7	$2.3 \times 10^{-2}$	534	$\delta\text{CH}_3-\text{C}-\text{CH}_3$ <i>t</i> -but at III, IV, def macroring, $\delta\text{N}_{\text{pyr}}-\text{CH}_2-\text{CH}_2$ , $\delta\text{CH}_2-\text{CH}_2-\text{CH}_3$
$\nu_{72}$	523	8.0	$2.4 \times 10^{-2}$	523	$r\text{CH}_2$ , $r\text{CH}_3$ <i>t</i> -but at I, II, $\delta\text{CH}_3-\text{C}-\text{CH}_3$ <i>t</i> -but
$\nu_{69}$	472	24.7	$8.8 \times 10^{-2}$	484	Breathing macroring, $\delta\text{CH}_3-\text{C}-\text{CH}_3$ , $\delta\text{N}_{\text{pyr}}-\text{CH}_2-\text{CH}_2$ , $\delta\text{CH}_2-\text{CH}_2-\text{CH}_3$
$\nu_{56}$	378	2.1	$1.1 \times 10^{-2}$	372	$\delta\text{CH}_3-\text{C}-\text{CH}_3$ <i>t</i> -but at III, IV, skel $\text{CH}_3$ <i>t</i> -but

Table. (Contd.)

Vibration	$\nu$ , $\text{cm}^{-1}$	$S_i$ , $\text{\AA}^4/\text{amu}$	$I_i$	Experiment	Vibration species
$\nu_{55}$	375	4.3	$2.2 \times 10^{-2}$	372	$\delta\text{CH}_3\text{-C-CH}_3$ <i>t</i> -but at I, II, skel. $\text{CH}_3$ <i>t</i> -but, twisting benz
$\nu_{51}$	333	1.1	$6.8 \times 10^{-3}$	341	Out-of-plane skeletal vibration benz
$\nu_{50}$	331	1.6	$9.7 \times 10^{-3}$	341	Out-of-plane skeletal vibration pyr, fur C
$\nu_{38}$	278	5.2	$4.1 \times 10^{-2}$	285	Twisting $\text{CH}_3$ <i>t</i> -but
$\nu_{24}$	216	11.1	$1.3 \times 10^{-2}$	229	Twisting $\text{CH}_3$ <i>t</i> -but, s.
$\nu_{21}$	195	6.5	$9.3 \times 10^{-2}$	204	Torsion vibration of <i>t</i> -but groups at III, IV
$\nu_{14}$	108	1.7	$7.0 \times 10^{-2}$	118	Torsion vibration of <i>t</i> -but groups at I–IV
$\nu_{10}$	67	1.6	$1.5 \times 10^{-1}$	83	Out-of-plane bending of macroring
$\nu_9$	66	1.9	$1.9 \times 10^{-1}$	83	Out-of-plane twisting of macroring
$\nu_8$	56	0.05	$6.1 \times 10^{-3}$		Twisting of <i>t</i> -but groups at III, IV
$\nu_7$	52	0.001	$1.0 \times 10^{-4}$		Twisting of <i>t</i> -but groups at I, II
$\nu_6$	46	0.2	$4.5 \times 10^{-2}$		Twisting of <i>t</i> -but groups at I, II
$\nu_5$	36	0.03	$9.0 \times 10^{-3}$		Twisting of <i>t</i> -but groups at III, IV
$\nu_4$	33	0.02	$6.0 \times 10^{-3}$		Out-of-plane vibration of macroring
$\nu_3$	31	0.4	$1.8 \times 10^{-2}$		Torsion vibration of <i>n</i> -propyl groups
$\nu_2$	26	0.2	$1.4 \times 10^{-2}$		Torsion vibration of <i>n</i> -propyl groups
$\nu_1$	26	0.03	$2.1 \times 10^{-2}$		Torsion vibration of <i>t</i> -but and <i>n</i> -propyl groups

Note:  $S_i$  denotes the activity of the normal vibration,  $I_i$  is the relative intensity of Raman lines, I–IV enumerate benzene rings, *benz* denotes the benzene ring, *ct* stands for the cyclooctatetraene ring, *fur* designates the furan ring, *pyr* denotes the pyrrole ring, *t-but* is the *tert*-butyl, *def* denotes deformation, *skel* designates the skeletal vibration, *ooph* denotes out-of-phase,  $\nu$  is the stretching vibration,  $\delta$  designates the in-plane bending vibration,  $\gamma$  denotes the out-of-plane vibration,  $\delta\text{CH}_2$  is the scissor vibration of methylene groups,  $\omega\text{CH}_2$  is the wagging vibration of methylene groups,  $b\text{CH}_2$  is the scissor vibration of methylene groups,  $r\text{CH}_2$  and  $r\text{CH}_3$  stand for rocking vibrations, and  $\tau\text{CH}_2$   $\tau\text{CH}_3$  designate twisting vibrations.

**C2**, as well as the lines at 1188 and 1196  $\text{cm}^{-1}$  in the spectrum of molecule **C3**, overlap each other and form a strong line at 1188  $\text{cm}^{-1}$  in the experimental spectrum of compound **C2**, while, in the spectrum of compound **C3**, this is a weak line at 1192  $\text{cm}^{-1}$  (Fig. 2). Experimental  $\delta\text{CH}$  lines of naphthalene fragments in the spectrum of molecule **C3** are observed at 1263 (calculation: 1254,  $\nu_{144}$ ), 1225 (calculation: 1223), 1155 (calculation: 1156 and 1147), and 1074  $\text{cm}^{-1}$  (calculation: 1066  $\text{cm}^{-1}$ ) with an intensity that is lower than the average intensity.

As a rule,  $\delta\text{CH}$  vibrations are mixed with C–O, C–N, and C–C stretching vibrations and with in-plane vibrations of rings. The normal vibration  $\nu_{146}$  in molecule **C1** with the calculated frequency of 1195  $\text{cm}^{-1}$  (in **C2** and **C3**, it lies at 1194 and 1196  $\text{cm}^{-1}$ , respectively) belongs only to in-plane deformations  $\text{CH}_{\text{benz}}$  (does not have contributions from other vibrations) and shows a strong shift toward higher frequencies (by about  $\approx 25 \text{ cm}^{-1}$ ) compared to the corresponding band at 1171  $\text{cm}^{-1}$  in benzene (experiment: 1178  $\text{cm}^{-1}$  [21]). Normal vibration  $\nu_{132}$  in molecule **C3** with a calculated frequency of 1156  $\text{cm}^{-1}$  belongs solely to  $\delta\text{CH}$  vibrations of naphthalene fragments. In the Raman spectrum of the naphthalene molecule,  $\delta\text{CH}$  vibra-

tions were calculated to be at 1238, 1145, and 1023  $\text{cm}^{-1}$ .

**CH out-of-plane bending vibrations of aromatic rings,  $\gamma\text{CH}$ .** In the Raman spectrum of molecule **C1**,  $\gamma\text{CH}_{\text{benz}}$  were calculated at 843 (in rings III and IV) and 828 and 829  $\text{cm}^{-1}$  (in rings I and II). The activity of out-of-plane CH bending vibrations is low, and they are not observed in the Raman spectrum; they also are not presented in the table. In the Raman spectrum of molecule **C2**,  $\gamma\text{CH}_{\text{benz}}$  were calculated only at 827 and 826  $\text{cm}^{-1}$ , since *tert*-butyl substituents are introduced into rings III and IV in a regular order. For molecule **C3**, obtained  $\gamma\text{CH}_{\text{benz}}$  frequencies are similar to those found for **C2**. The obtained calculation data confirm once more the well-known statement that frequencies of out-of-plane bending vibrations are determined by the number of attached hydrogen atoms in the ring [20].  $\gamma\text{CH}$  vibrations of naphthalene fragments were calculated to be in the range 957–752  $\text{cm}^{-1}$ . According to our calculations,  $\gamma\text{CH}$  vibrations of the  $E_{1g}$  symmetry in the Raman spectrum of the benzene molecule should occur at 837  $\text{cm}^{-1}$ , and  $\gamma\text{CH}$  vibrations of naphthalene of the  $B_{1g}$  and  $B_{2g}$  symmetry should occur at 873, 761, and 712  $\text{cm}^{-1}$ . Out-of-plane CH deformations with the displacement from the plane of carbon

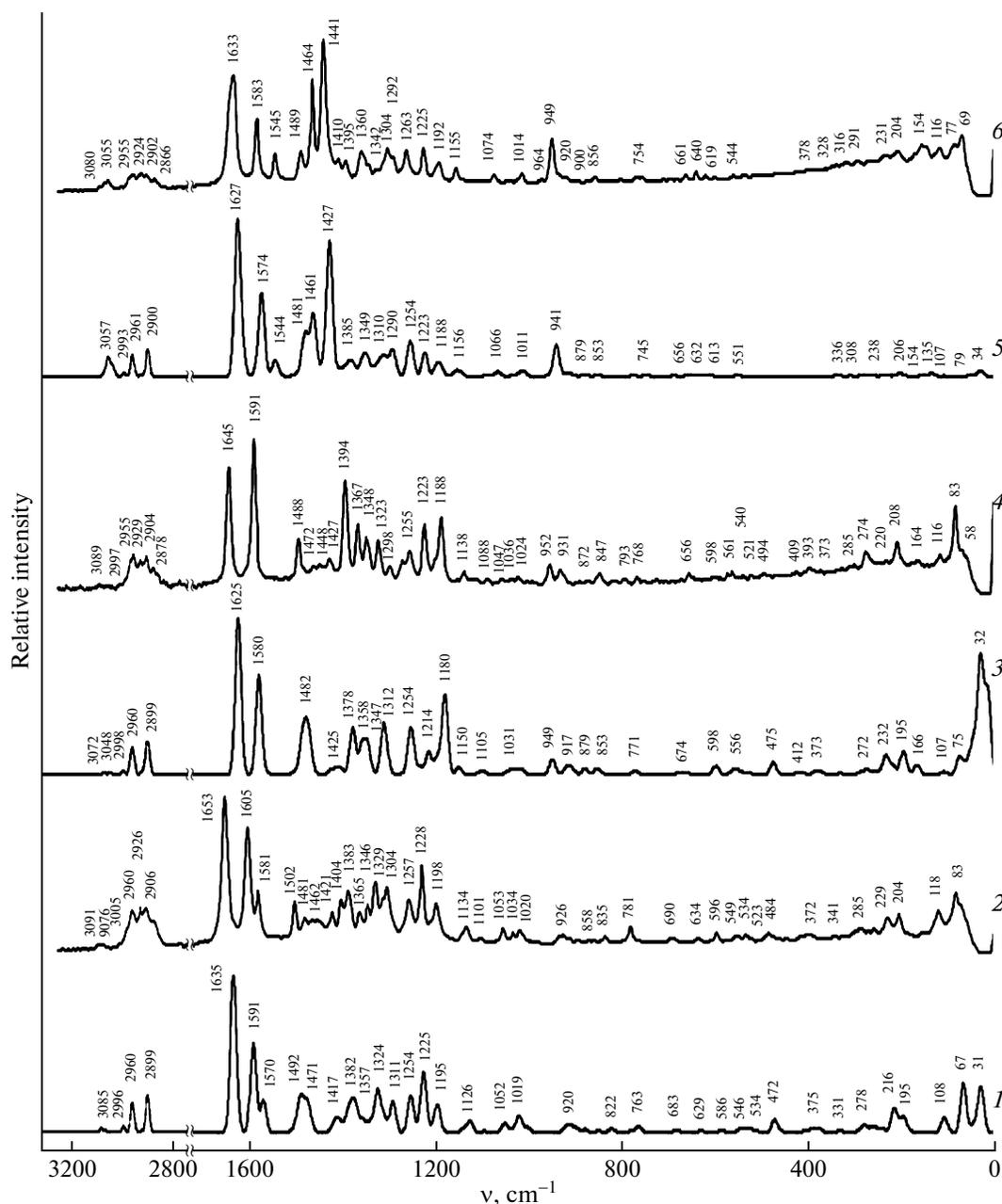


Fig. 2. (1, 3, 5) Calculated and (2, 4, 6) experimental Raman spectra of compounds (1, 2) **C1**, (3, 4) **C2**, and (5, 6) **C3**.

atoms of benzene rings in azacirculenes under study were calculated to be in the range 712–557  $\text{cm}^{-1}$  and, for naphthalene fragments, in the range 703–525  $\text{cm}^{-1}$ .

**Stretching vibrations of C=C bonds of aromatic rings,  $\nu_{\text{CC}}$ .** Vibrations of this type are observed in the experimental spectra in the range 1625–1430  $\text{cm}^{-1}$  [20]. In the Raman spectrum of benzene, our calculation shows that  $\nu_{\text{CC}}$  vibrations of the  $E_{2g}$  symmetry are located at 1603  $\text{cm}^{-1}$  and, in the spectrum of naphthalene, they lie at 1636 and 1460  $\text{cm}^{-1}$  ( $B_{3g}$  symmetry) and at 1580, 1463, and 1373  $\text{cm}^{-1}$  ( $A_g$  symmetry).

The frequencies of  $\nu_{\text{CC}_{\text{benz}}}$  vibrations in the spectrum of molecule **C1** were calculated to be in the range 1635–1327  $\text{cm}^{-1}$  (table), and they form two strong lines at 1635 and 1591  $\text{cm}^{-1}$  and a satellite at 1570  $\text{cm}^{-1}$  (Fig. 2). The band in the range 1419–1407  $\text{cm}^{-1}$  and the line of  $\nu_{\text{CC}_{\text{benz}}}$  Kekule vibrations at 1327  $\text{cm}^{-1}$  also pertain to these lines. In the experimental spectrum of compound **C1**, the lines at 1653, 1605, 1581, 1421, and 1404  $\text{cm}^{-1}$ , as well as the lines of Kekule vibrations at 1346 and 1329  $\text{cm}^{-1}$ , correspond to them. The strongest line at 1635  $\text{cm}^{-1}$  is formed by superposition

of the modes  $\nu_{229}$  and  $\nu_{228}$  (table). In the spectrum of molecule **C2**, this band is shifted by  $10\text{ cm}^{-1}$  toward lower frequencies, which, in our opinion, is related to a change in the lengths of C=C bonds involved in this vibration that takes place upon introduction of the pyrrole fragment into the ring *C* instead of the furan fragment and because of regularly ordered *tert*-butyl substituents.

The frequencies of vibrations of C=C bonds in **C1** (which are lateral sides of heterorings) were calculated to be  $1591\text{ cm}^{-1}$  (vibrations in rings III and IV) and  $1570\text{ cm}^{-1}$  (vibrations in rings I and II), whereas, in molecule **C2**, they occur simultaneously in all the benzene rings and yield a line at  $1580\text{ cm}^{-1}$  in the spectrum. Here, we also reveal a  $10\text{-cm}^{-1}$  shift (in two directions), which is indicative of a universal change of the force field of C=C bonds in the heteroring. A normal vibration with a frequency of  $1343\text{ cm}^{-1}$  corresponds to the Kekule vibrations that occur simultaneously in rings I–IV of molecule **C2**, but the corresponding line in the Raman spectrum is weak and is overlapped with broadened lines of other vibrations (table; Fig. 2).

Strong lines at  $1627$  (experiment:  $1633$ ) and  $1574\text{ cm}^{-1}$  (experiment:  $1583\text{ cm}^{-1}$ ) in the Raman spectrum of molecule **C3** belong to mixed vibrations of C=C bonds of the benzene and naphthalene fragments (the remaining lines of mixed  $\text{C}=\text{C}_{\text{benz}}$  and  $\text{C}=\text{C}_{\text{naphth}}$  vibrations are weak and not observed in the spectrum of **C3**). A weak line at  $1544\text{ cm}^{-1}$  (experiment:  $1545\text{ cm}^{-1}$ ), a medium-intensity line at  $1461\text{ cm}^{-1}$  (experiment: a strong line at  $1464\text{ cm}^{-1}$ ), and a very strong line at  $1427\text{ cm}^{-1}$  (experiment:  $1441\text{ cm}^{-1}$ ), the relative intensity of which is taken to be unity, belong to stretching vibrations of C=C bonds of naphthalene fragments alone. We attributed the latter line to Kekule vibrations in naphthalene rings IIIa and IVa. Compared to naphthalene, upon formation of molecule **C3**, this line is shifted by  $54\text{ cm}^{-1}$  toward higher frequencies, which is a consequence of strengthening of C=C bonds upon condensation of naphthalene rings. The Kekule vibration in naphthalene rings IIIb and IVb, which is mixed with  $\nu\text{CC}_{\text{benz}}$ , was calculated in this work to be at  $1330\text{ cm}^{-1}$ ; however, the intensity of the corresponding line is too weak to be observed in the spectrum. The Kekule vibration in the benzene fragments alone of molecule **C3** was calculated to occur at  $1349\text{ cm}^{-1}$  (experiment:  $1342\text{ cm}^{-1}$ ).

**Bending vibrations of aromatic rings.** In-plane skeletal bending vibrations of benzene and naphthalene fragments are observed as breathinglike vibrations, vibrations of rings, and their deformations (table). Many of them are mixed with vibrations of other types. It should be noted that the breathing vibration is a symmetric motion of all the nuclei in the ring; vibra-

tions of the ring imply a simultaneous, but not necessarily symmetric, motion of all the nuclei in the ring.

In-plane skeletal vibrations of rings in the Raman spectra of molecules **C1–C3** were calculated to occur lower than  $1378\text{ cm}^{-1}$ . As a rule, they are mixed with  $\nu\text{CO}$  and/or  $\delta\text{CH}$ .

For molecules **C1**, **C2**, and **C3**, the in-phase breathing vibration of all the benzene rings was calculated to be at  $1225$ ,  $1214$ , and  $1223\text{ cm}^{-1}$  (benzene rings I and II), respectively. In the experimental spectrum, these normal vibrations yield lines, with intensities close to the average intensity, at  $1228$ ,  $1223$ , and  $1225\text{ cm}^{-1}$ , respectively. The in-phase vibration of the entire macroring is observed for molecule **C1** at  $472\text{ cm}^{-1}$  (experiment:  $484\text{ cm}^{-1}$ ), for molecule **C2** at  $475\text{ cm}^{-1}$  (experiment:  $494\text{ cm}^{-1}$ ), and for molecule **C3** at  $493\text{ cm}^{-1}$  (in the naphthalene fragment of the macroring, the breathing vibration occurs only in rings IIIa and IVa and, because of its weak intensity, is not observed in the Raman spectrum). The breathing vibration in naphthalene rings IIIa and IVa was noted in this work to be at  $1290\text{ cm}^{-1}$ , which is close to the observed weak peak at  $1292\text{ cm}^{-1}$ . Characteristically, the breathing vibrations in rings IIIb and IVb of molecule **C3** and in its octatetraene ring (in phase) are mixed, which yields an intense line at  $941\text{ cm}^{-1}$  (experiment:  $949\text{ cm}^{-1}$ ).

In the calculated Raman spectra of the benzene and naphthalene molecules, the breathing of their rings yields strong lines at, respectively,  $988$  (the  $A_{1g}$  symmetry) and  $752\text{ cm}^{-1}$  (the  $A_g$  symmetry). As can be seen from the obtained data, upon formation of molecules **C1–C3**, the breathing normal vibrations experience strong frequency shifts and changes in their activity, which is related to the specifics of the  $\pi$ -conjugation in macrorings.

Out-of-plane bending vibrations of the molecules under study are observed in their Raman spectra as deformations of individual fragments and as skeleton waving of the entire molecule. Out-of-plane skeletal vibrations of benzene and pyrrole rings were calculated at  $333$  and  $331\text{ cm}^{-1}$  for molecule **C1** and at  $336\text{ cm}^{-1}$  for molecule **C3**; bending of the macroring skeleton was found to be below  $115\text{ cm}^{-1}$ . All these normal vibrations are of low activity in Raman spectra.

#### *Vibrations of Five-Membered Aromatic Heterorings*

The occurrence of pyrrole fragments distinguishes our compounds from previously studied tetraoxa[8]circulenes [6–10]; therefore, vibrations of pyrrole fragments deserve special analysis.

**Vibrations of pyrrole rings.** Heteroaromatic compounds, such as pyrrole and furan, commonly have three Raman lines, which are observed at  $1580$ ,  $1490$ , and  $1400\text{ cm}^{-1}$  and belong to the stretching vibrations of C=C bonds [22]. In the spectrum of molecule **C1**,

the first of these three lines of vibrations of the bond  $C^\beta-C^{\beta'}$  is completely overlapped by  $C=C$  bands of benzene fragments and is mixed with one of them (table). The normal vibration of the bond  $C^\beta-C^{\beta'}$ , which was calculated in the pyrrole molecule to occur at  $1394\text{ cm}^{-1}$  (experiment:  $1382\text{ cm}^{-1}$  [22]), in the spectrum of molecule **C1**, was calculated in this work to be at  $1389\text{ cm}^{-1}$  (experiment:  $1383\text{ cm}^{-1}$ ) and found to have a complicated nature (table). In molecule **C2**, we have two normal vibrations, at  $1378$  and  $1381\text{ cm}^{-1}$  (corresponding lines are overlapped with the line at  $1376\text{ cm}^{-1}$ , which belongs to wagging vibrations of methylene groups and to the vibration of the bonds  $C^\beta-C^{\beta'}$  in furan fragments and which yield a strong line at  $1394\text{ cm}^{-1}$  in the experimental spectrum). In molecule **C3**, the vibration  $\nu C^\beta C^{\beta'}$  was calculated at  $1385\text{ cm}^{-1}$ ; the corresponding line is overlapped with the line at  $1395\text{ cm}^{-1}$  of Kekule vibrations in naphthalene fragments. The normal vibrations that have contributions from vibrations  $\nu C^\beta C^{\beta'}$  contain  $\nu CC$  vibrations of furan rings, vibrations of benzene rings, and vibrations of alkyl substituents.

Asymmetric vibrations of bonds  $C^\alpha=C^\beta$  have a low activity both in the free pyrrole molecule ( $1549\text{ cm}^{-1}$ ) and in compounds **C1–C3** and are not observed in the Raman spectra because of their low intensity. In the macrorings of molecules **C1–C3**, the bonds  $C^\alpha=C^\beta$  of pyrrole (as well as of furan) fragments are simultaneously  $C=C$  bonds of benzene rings; therefore, it often does not seem possible to consider these vibrations separately. Symmetric and asymmetric changes in  $C-N$  bond lengths in pyrrole fragments occur during vibrations of  $C=C$  bonds of benzene rings, as well as during rocking and twisting vibrations of methylene groups of the *n*-propyl substituent.

As distinct from pyrrole, where the breathing of the ring yields a very strong line at  $1145\text{ cm}^{-1}$  in the Raman spectrum (experiment:  $1142\text{ cm}^{-1}$  [22]), the breathing vibrations of the pyrrole fragment of molecules **C1** and **C3** were calculated in this work to occur, respectively, at  $1324$  (experiment:  $1329$ ) and  $1321\text{ cm}^{-1}$  (experiment:  $1321\text{ cm}^{-1}$ ; the shoulder on the left wing of the band at  $1304\text{ cm}^{-1}$ ). For the **C2** molecule, there are two normal vibrations with the frequencies at  $1312$  (the in-phase breathing vibration in rings *A* and *C*; experiment:  $1323\text{ cm}^{-1}$ ) and  $1328\text{ cm}^{-1}$  (the out-of-phase breathing vibration in rings *A* and *C*). The latter vibration has a weak activity in the Raman spectrum.

Analysis of normal vibrations of pyrrole fragments shows that, in the Raman spectrum, corresponding bands of compound **C2** are indeed shifted compared to compounds **C1** and **C3**.

**Vibrations of furan rings.** The normal vibration of the bond  $C^\beta-C^{\beta'}$  in free furan, which is both IR and Raman active, was calculated in this work to occur at  $1387\text{ cm}^{-1}$  (experiment:  $1380\text{ cm}^{-1}$  [23]); the  $\nu C^\beta C^{\beta'}$

also contributes to the normal vibration  $\nu_s CO$  with the frequency of  $1065\text{ cm}^{-1}$ . In the Raman spectra of molecules **C1–C3**, these vibrations are split and are mixed in the range  $1635\text{--}1350\text{ cm}^{-1}$  with  $\nu CC$  vibrations of benzene and naphthalene fragments and vibrations of other types. Normal vibrations  $\nu_{182}$ ,  $\nu_{137}$ , and  $\nu_{136}$  in the spectrum of molecule **C1** with calculated frequencies of  $1389$ ,  $1052$ , and  $1052\text{ cm}^{-1}$  and normal vibrations of the similar shape in the spectra of molecules **C2** (calculation:  $1378$  and  $1057\text{ cm}^{-1}$ ) and **C3** (calculation:  $1385$ ,  $1113$ , and  $1034\text{ cm}^{-1}$ ) do not have contributions from vibrations of aromatic  $C=C$  bonds and are close to calculated frequencies  $\nu C^\beta C^{\beta'}$  in free furan.

The asymmetric vibration of the  $C^\alpha=C^\beta$  bonds in the free furan molecule was calculated at  $1565\text{ cm}^{-1}$ ; however, its activity in the Raman spectrum of the furan molecule is low and is not observed. Similar vibrations  $\nu_{as} C^\alpha C^\beta$  in the spectrum of molecule **C1** are considerably shifted (table). Because of their low intensity, these normal vibrations do not yield observable lines in the Raman spectrum.

Symmetric vibrations of bonds  $C^\alpha=C^\beta$  in the free furan molecule yield a strong band at  $1483\text{ cm}^{-1}$  (experiment:  $1485\text{ cm}^{-1}$  [23]). In molecules **C1** and **C2**, vibrations  $\nu_s C^\alpha C^\beta$  were calculated in this work at  $1407\text{ cm}^{-1}$ . In the experimental spectrum of compound **C1**, this vibration is observed at  $1404\text{ cm}^{-1}$  (Fig. 2; table), while, in the spectrum of the **C2** molecule, the corresponding line is overlapped. In molecule **C3**, this  $\nu_s C^\alpha C^\beta$  vibration is mixed with the Kekule normal vibration in naphthalene, which yields a very strong Raman line at  $1427\text{ cm}^{-1}$  in the spectrum of **C3**.

Symmetric vibrations of  $C-O$  bonds of the  $A_1$  symmetry and asymmetric vibrations of the  $B_2$  symmetry, which are active in the IR and Raman spectra of the free furan molecule, were calculated in this work to occur at  $1065$  and  $992$  ( $\nu_s CO$ ) and at  $1184$  and  $1040\text{ cm}^{-1}$  ( $\nu_{as} CO$ ). In the Raman spectra of molecules **C1–C3**, these vibrations are split and are mixed with  $\delta CH$ , planar deformations of rings, and vibrations of other types in the range  $1389\text{--}953\text{ cm}^{-1}$ . The nonequivalence of the bond lengths  $C^\alpha-O$  in ring *B*, as well as in ring *D*, leads to the stretching vibrations of the  $C^\alpha-O$  bonds in rings *B* and *D* of molecules **C1** and **C3** occurring mainly in semirings of furan fragments, which is not characteristic for the **C2** molecule. In the Raman spectrum of compound **C3**, the calculated line at  $1147\text{ cm}^{-1}$ , which is combined with the  $\delta CH_{naphth}$  line at  $1156\text{ cm}^{-1}$  (experiment:  $1155\text{ cm}^{-1}$ ), is contributed by  $\nu CO$  vibrations, which occur only in furan ring *C* with identical lengths of its  $C-O$  bonds ( $1.380\text{ \AA}$ ). Many normal vibrations that have contributions from

$\nu\text{CO}$  do not yield observable bands in the Raman spectra because of their low intensity.

In-plane vibrations of valence angles COC, which were calculated in the spectrum of furan at  $859\text{ cm}^{-1}$ , in the spectra of molecules **C1**–**C3** under study, are shifted in frequency, respectively, to 847, 836, and  $845\text{ cm}^{-1}$  (in furan rings *B* and *D*). In the ring *C* for molecules **C1** and **C3**, these vibrations were calculated at 897 and  $905\text{ cm}^{-1}$ , respectively. As in the case of the free furan molecule, the corresponding lines have very low intensities and are not presented in the Raman spectra.

The breathing vibrations of furan ring *C* in the Raman spectra of molecules **C1** and **C3** were calculated at  $1002$  and  $1024\text{ cm}^{-1}$ , respectively. As distinct from furan, where the breathing vibration of the ring yields a strong band at  $1139\text{ cm}^{-1}$  in the Raman spectrum, normal vibrations that have contributions from the breathing vibration of furan ring *C* are of weak activity and manifest themselves in the macroring at lower frequencies. We have not revealed clearly pronounced breathing vibrations of rings *B* and *D* in the calculated normal vibrations of molecules **C1**–**C3**; instead, only sluggish deformations of rings were observed. Such changes in the shape of vibrations of the rings *B* and *D* are related to the specifics of  $\pi$  systems of macrorings.

#### Vibrations of Alkyl Substituents

For terminal alkyl groups, four types of vibrations are observed, namely, stretching and bending vibrations of C–H and C–C bonds [20]. They are interpreted in detail in the table. This interpretation is important only because alkyl vibrations obstruct characteristic Raman lines of macrorings. Here, we only note C–H stretching vibrations. According to our calculation, *tert*-butyl  $\text{CH}_3$  groups of molecule **C1** should yield in the Raman spectrum three lines of asymmetric stretching vibrations of C–H bonds, which are located at 2996, 2960, and  $2952\text{ cm}^{-1}$ ; however, the latter two lines are overlapped. In the experimental spectrum, the line at  $2960\text{ cm}^{-1}$  and a broadened shoulder on its left wing correspond to all three of these vibrations. The *n*-propyl group yields four normal asymmetric vibrations of C–H bonds of the methyl and methylene groups, which lie in the range  $2965$ – $2923\text{ cm}^{-1}$ ; however, only one of them ( $\nu_{245}$ ; table), the calculated frequency of which is  $2923\text{ cm}^{-1}$ , yields a clearly pronounced shoulder in the experimental Raman spectrum on the broadened line at  $2906\text{ cm}^{-1}$  (calculation:  $2901\text{ cm}^{-1}$ ), which belongs to symmetric vibrations of C–H bonds of *tert*-butyl  $\text{CH}_3$  groups. This band overlaps the line  $\nu_{244}$  with frequency  $2906\text{ cm}^{-1}$  (table), which belongs to symmetric vibrations of C–H bonds of  $\text{CH}_3$  and  $\text{CH}_2$  groups of the *n*-propyl fragment. The normal vibrations  $\nu_{239}$  and  $\nu_{232}$  (table), which belong

to symmetric vibrations of C–H bonds of  $\text{CH}_2$  and  $\text{CH}_3$  groups, respectively, form a shoulder on the right wing of the band at  $2906\text{ cm}^{-1}$  in the experimental spectrum (Fig. 2). In the experimental spectra of compounds **C2** and **C3**, these bands are observed at frequencies close to that in the spectrum of **C1**.

CH bending vibrations of methyl and methylene groups of alkyl substituents yield weak Raman lines and are important only in the IR spectrum.

$\nu\text{C}-(\text{CH}_2)_3$  vibrations were calculated in this work as occurring in the ranges  $1232$ – $1198$ ,  $922$ – $909$ ,  $819$ – $763$ , and  $629$ – $611\text{ cm}^{-1}$  and, in the experimental spectrum of compound **C1**, make contributions to a strong line at  $1228\text{ cm}^{-1}$  and to weak lines at 781 and  $634\text{ cm}^{-1}$ . A weak line at  $926\text{ cm}^{-1}$  (Fig. 2) belongs solely to  $\nu\text{C}-(\text{CH}_2)_3$  skeletal vibrations. In compound **C2**, the lines at 1223, 768, 656, and  $931\text{ cm}^{-1}$  correspond to them; in **C3**, these lines are at 1225, 754, 640, and  $920\text{ cm}^{-1}$ .  $\text{C}_{\text{benz}}-\text{C}_{\text{t-but}}$  vibrations were calculated to be in the range  $1254$ – $847\text{ cm}^{-1}$  and found to make contributions to weak experimental lines at 1257 and 858 (**C1**), 1255 and 847 (**C2**), and 1263 and  $856\text{ cm}^{-1}$  (**C3**).

$\nu\text{CH}_2-\text{CH}_3$  vibrations of *n*-propyl groups occur at  $1019\text{ cm}^{-1}$  for **C1** (experiment:  $1020\text{ cm}^{-1}$ ), at  $1014\text{ cm}^{-1}$  for **C2** (experiment:  $1024\text{ cm}^{-1}$ ), and at  $1011\text{ cm}^{-1}$  for **C3** (experiment:  $1014\text{ cm}^{-1}$ ). For all the three compounds under study, the normal vibrations  $\nu\text{CH}_2-\text{CH}_2$  were calculated at 879 and  $853\text{ cm}^{-1}$  and yield very weak lines in the experimental Raman spectra.

Vibrations of N– $\text{CH}_2$  bonds occur in the range  $1341$ – $763\text{ cm}^{-1}$  and contribute in the spectrum of **C1** to the experimental lines at 1329 and  $1257\text{ cm}^{-1}$ , the intensity of which is closer to the average intensity, and to weak lines at 1346, 1134, 1020, and  $781\text{ cm}^{-1}$ . Corresponding lines in the spectrum of compound **C2** are observed at 1323, 1255, 1367, 1188, 952, and  $768\text{ cm}^{-1}$ ; in the spectrum of compound **C3**, skeletal vibrations  $\nu\text{N}-\text{CH}_2$  contribute to the lines at 1321 (the shoulder on the left wing of the band at 1304), 1263, 1342, 1192, 1024 (calculation), and  $754\text{ cm}^{-1}$ . The experimental lines at 1257, 1255, and  $1263\text{ cm}^{-1}$  in the spectra of compounds **C1**, **C2**, and **C3**, which are observed in both the IR and Raman spectra, correspond to the calculated line at  $1254\text{ cm}^{-1}$  that occurs in the vibrational spectra of all the three compounds. The  $\nu\text{N}-\text{CH}_2$  vibration at a frequency of  $1255\text{ cm}^{-1}$  was also calculated in this work in the spectrum of the molecule *di-tert*-butyl-dimethoxycarbazole. This line of the vibration of the N–C bond near  $1285\text{ cm}^{-1}$  is characteristic of 1-alkyl-substituted pyrroles [20].

A strong shift toward higher frequencies of the line at  $1134\text{ cm}^{-1}$  (table), which has a contribution from in-plane bending vibrations of CH groups of benzene fragments in the spectra of compounds **C2** and **C3** was

discussed above. The shift of the very weak line at  $1020\text{ cm}^{-1}$  (Fig. 2; table), which belongs to breathing vibrations of individual macroring fragments and skeletal vibrations of bonds  $\text{N}-\text{CH}_2$  and  $\text{CH}_2-\text{CH}_3$ , in the Raman spectrum of compound **C2** approximately by  $70\text{ cm}^{-1}$  and increase in its intensity are related to the introduction of the second pyrrole ring into the macroring instead of the furan ring.

Bending vibrations of the angles  $\text{CH}_3-\text{C}-\text{CH}_3$ ,  $\text{N}-\text{CH}_2-\text{CH}_2$ , and  $\text{CH}_2-\text{CH}_2-\text{CH}_3$  in the **C1** molecule were calculated at  $534$  (experiment:  $534$ ) and  $472\text{ cm}^{-1}$  (experiment:  $484\text{ cm}^{-1}$ ). In the spectrum of compound **C2**, the weak experimental lines at  $540$  and  $494\text{ cm}^{-1}$  correspond to them. In molecule **C3**, these lines were calculated to be at  $536$  and  $493\text{ cm}^{-1}$ , but their intensities are low. Bending vibrations of angles  $\text{CH}_3-\text{C}-\text{CH}_3$  were also calculated in the range  $395-350\text{ cm}^{-1}$  (weak experimental lines at  $372$ ,  $373$ , and  $378\text{ cm}^{-1}$  in compounds **C1**, **C2**, and **C3**, respectively). Torsion vibrations of the *n*-propyl group in molecules **C1**, **C2**, and **C3** yield low-frequency lines at  $31$ ,  $32$ , and  $32\text{ cm}^{-1}$ , respectively, in the calculated Raman spectra of these molecules. These and similar vibrations in the range of low frequencies are very intense in the Raman spectrum [24] as a result of recalculation of the activity ( $S_i$ ) of the normal vibration into the intensity by formula (1).

## CONCLUSIONS

Based on the analysis of calculated frequencies, intensities and shapes of normal vibrations of molecules of azaoxa[8]circulenes and their comparison with experimental Raman spectra, as well as on the analysis of the geometric structure of azaoxa[8]circulenes under study, we drew the following conclusions.

1. Cyclic conjugation in molecules of azaoxa[8]circulenes determines their aromatic properties; in this case, bond lengths in the macroring mainly increase noticeably compared to the free benzene, furan, pyrrole, and naphthalene molecules. Consequently, frequencies and shapes of normal vibrations in the macroring should markedly differ from corresponding normal vibrations in free molecules, which is observed in experiment and in our calculation results.

2. In the optimized structure of molecule **C2** (Fig. 1), a spontaneous symmetry violation in the orientation of *tert*-butyl substituents manifests itself. Our attention was drawn to this fact based on analysis of C–H stretching vibrations of benzene fragments, which is also confirmed in a series of other specific features of the Raman spectrum.

3. An antiaromatic character of the inner octatetraene ring with strong alternation of bond lengths manifests itself in changes in the force field and corresponding frequencies in the Raman spectrum. Thus, lines of C=C stretching vibrations of benzene frag-

ments ( $1653-1633\text{ cm}^{-1}$ ), which dominate in all the Raman spectra, are strongly shifted compared to  $E_{2g}$  vibrations in benzene itself ( $1603\text{ cm}^{-1}$ ) and considerably differ in molecules **C1-C3**.

4. For the Raman spectra of three representatives of azaoxa[8]circulenes, we are the first to have performed a complete assignment of all the Raman lines in the experimental spectrum and find that the frequencies and intensities of the majority of lines are strictly specific for the macroring and do not coincide with corresponding normal vibrations for the free benzene, furan, pyrrole, and naphthalene molecules.

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