The Effect of a Heteroatom on the Structure and Vibrational Spectra of Heteroannulated Tetraphenylenes

V. A. Minaeva[a], G. V. Baryshnikov[a], and B. F. Minaev[a,b,c]

[a] *Khmelnitskii Cherkassy National University, Cherkassy, 18031 Ukraine*
[b] *Tomsk State University, Tomsk, 634050 Russia*
[c] *Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190 China*
e-mail: minaeva@cdu.edu.ua, glebchem@rambler.ru, bfmin@rambler.ru

Received March 11, 2015

Abstract—Based on calculations by the DFT method, we have theoretically compared IR absorption and Raman spectra of tetraoxa[8]circulene (4O) and its analogs that contain sulfur (4S) and selenium (4Se) atoms. Calculations have shown that the structure of investigated molecules and observed shifts of similar vibrations in their IR and Raman spectra are interrelated. We have constructed correlation schemes of frequency shifts of normal vibrations upon passage from planar 4O circulene to its 4S and 4Se nonplanar analogs. The obtained data are of fundamental interest both from the point of view of specific selection rules and in the context of the novelty of the force field, where the conjugation of the internal and external macrocycles with heteroatoms manifests itself.

1. INTRODUCTION

In the large variety of polyaromatic compounds, heterocyclic circulenes represent a specific class of molecules due to their unusual electronic structure and promising spectral–luminescent properties [1–4]. Combinations of six- and five-membered cycles, which are characteristic of circulenes, also occur in the structure of some fullerenes and nanotubes [4–7]. One of the most important particular features of heterocirculenes is a high symmetry of their molecules [1]. Thus, molecules of hetero[8]circulenes, the basis of which contains a completely annulated eight-membered carbon framework, possess various forms of molecular symmetry and belong to the following point groups: D_{8h} (octathia[8]circulene), D_{4h} (tetraoxa[8]circulene), D_{2h} (diazadioxa[8]circulene), C_{4h} (tetra-*tert*-butyltetraoxa[8]circulene), C_{2v} (azatrioxa[8]circulene), and so on [1]. All the above-listed hetero[8]circulenes contain in their composition a planar octatetraene nucleus. In addition, these highly symmetrical molecules can act as combination structural parts of graphene-like two-dimensional polymers and nanotubes [8–10]. Until recently, the number of nonplanar (saddle-shaped) hetero[8]circulenes was limited by only a few theoretical predictions based on quantum-chemical calculations of hypothetic structures [11–13]. However, recently [14], the synthesis and results of physicochemical investigations of new hetero[8]circulenes, 4S-8OMe and 4Se-8OMe (Fig. 1), have been presented. Molecules of these compounds contain four sulfur or selenium atoms in the external conjugated perimeter, and these atoms are arranged symmetrically between benzene fragments. X-ray diffraction analysis showed that these compounds have a slightly bent (saddle-shaped) configuration. Without taking into account side substituents, they appear as is shown in Fig. 1 (4S, 4Se) and belong to the D_{2d} point symmetry group, which has not been observed for hetero[8]circulenes (4S-8OMe and 4Se-8OMe molecules correspond to the D_2 point group). However, 4S and 4Se molecules themselves have not been obtained synthetically and are model objects. Their simplest analog is represented by tetraoxa[8]circulene (4O), which was synthesized in 1968 by Högberg almost half a century ago by cyclooligomerization of *p*-benzoquinone in the presence of strong mineral acids [15]. However, its vibrational spectra have been studied and interpreted only comparatively recently [16–19].

In particular, it has been noted [18] that the IR and Raman spectra of tetraoxa[8]circulene 4O and its derivatives are of fundamental interest both from the point of view of specific selection rules and in the context of the novelty of the force field and importance of the analysis of vibrational modes of a new class of molecules, which are rich in manifestations of vibronic effects in UV spectra of these circulenes [1, 4]. In this work, we analyze in detail vibrational (IR and Raman) spectra of compounds 4O, 4S, and 4Se in terms of the density functional theory (DFT) in conjunction with
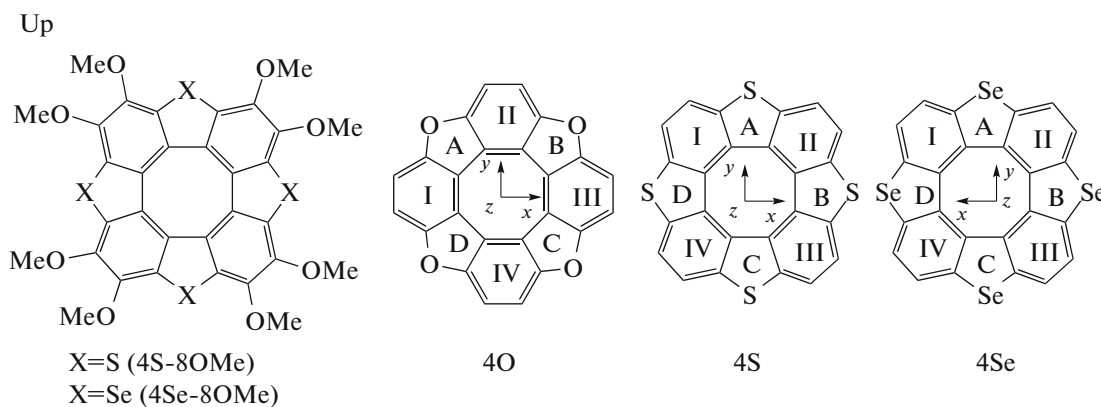
Fig. 1. Structural formulas of molecules of synthesized compounds: tetrathia-(4S-8OMe), tetraselena-(4Se-8OMe), and tetra-oxa[8]circulene (4O), as well as model compounds: tetrathia[8]circulene (4S) and tetraselena[8]circulene (4Se) without substituents and with the chosen notation of rings and choice of axes.

the group-theoretical analysis of vibrational modes with structural characteristics of molecules. We have found that the lowering of the space symmetry group of 4S and 4Se molecules affects the shape of their vibrational spectra to a lesser degree compared to those for 4O planar circulene than change of the type of the heteroatom in the five-membered ring does. Introduction of sulfur and selenium heteroatoms not only shifts predictably bands of C–S and C–Se stretching vibrations, but also causes changes in frequencies and intensity redistributions of skeletal vibrations, in particular, stretching and bending vibrations of C=C and C–H bonds of benzene fragments. Our analysis establishes interrelations between vibrational spectra of related chalcogen-containing 4O, 4S, and 4Se circulenes and is of interest for assignment of lines and their systematization in experimental IR and Raman spectra of other hetero[8]circulenes. 4S and 4Se molecules are simpler prototypes of already synthesized compounds [14], and our DFT-calculations yield undeniable predictions of their stability and possibility of future verifying of their spectral properties.

2. METHOD OF CALCULATION

Structural parameters of 4O, 4S, and 4Se molecules were optimized by the B3LYP/6-311++G(d,p) density functional method [20–22] using the Gaussian 09 software package [23] and taking into account symmetry characteristics (the D_{4h} point group for 4O molecules and the D_{2d} point group for 4S and 4Se molecules). On the basis of this same method, we also calculated frequencies and shapes of normal vibrations of molecules under investigation. All frequencies of vibrations prove to be real, which indicates the location of the true minimum on the hypersurface of the total energy of the molecule. Calculated frequencies of normal vibrations were corrected using the following scaling factors: 0.96 for the high-frequency range and

0.98 for the rest of the spectrum. These values make it possible to reach the best agreement between calculated frequencies of vibrations and experimentally observed spectra [1, 14].

In order to convert the calculated Raman activity into the corresponding intensity for the ith normal mode (I_i), we used the following recalculation formula [24, 1, 19]:

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(-\dfrac{hc_0\nu_i}{kT} \right) \right]},$$

where ν_0 is the laser excitation frequency (9398.5 cm^{-1} [16]), ν_i is the frequency of the ith normal mode (cm^{-1}), c_0 is the speed of light in vacuum (2.9979 × 10^{10} cm/s), h is the Planck constant (6.6261 × 10^{-27} erg s), k is the Boltzmann constant (1.3806 × 10^{-16} erg/K), and f is the conversion factor of intensities of all the peaks to conditional unity. This is necessary to correctly compare calculated and observed Raman spectra.

The calculated spectra of investigated 4O, 4S, and 4Se molecules were constructed using the SWizard program [25] (the line halfwidth was 7 cm^{-1}, and the Lorentz distribution function was used). Assignments of normal vibrations were performed on the ground of animation of the calculated normal vibrations shape.

3. RESULTS AND DISCUSSION

3.1. Structure of 4O, 4S, and 4Se Circulenes

The optimized structures of 4O, 4S, and 4Se molecules are shown in Fig. 2 in the order of increasing curvature of the surface of the macrocycle. In accordance with data of X-ray diffraction analysis, the bending angles of the internal eight-membered cycle with respect to the completely planar 4O circulene were found to be 0.07° and 4.1° for substituted 4S-8OMe and 4Se-8OMe circulenes, respectively [14].
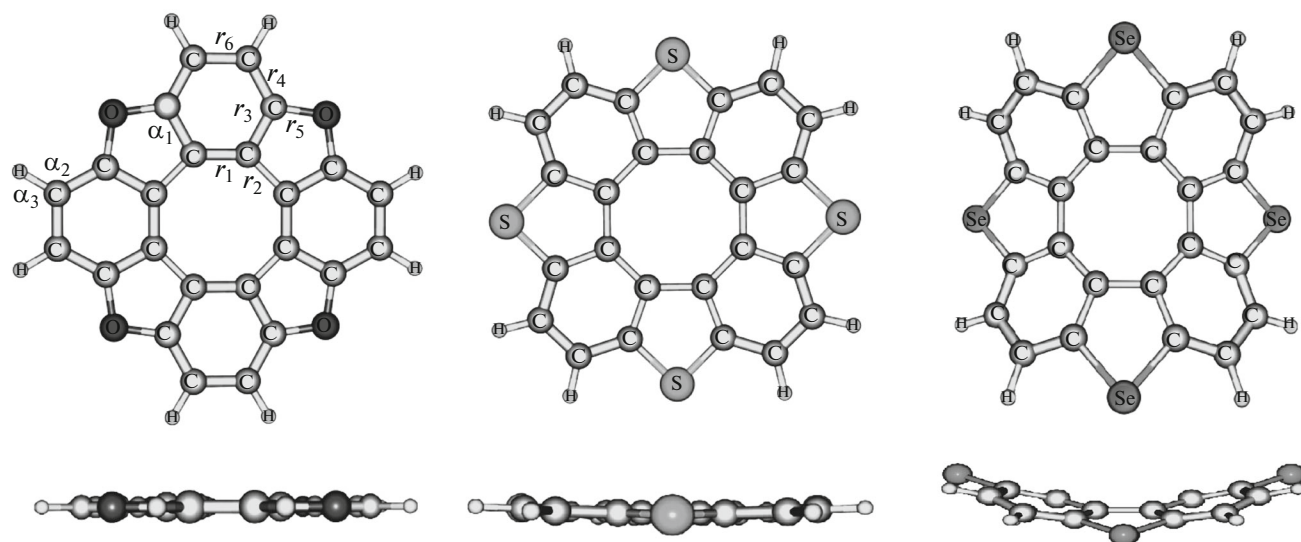
Fig. 2. Structures of the 4O, 4S, and 4Se molecules (top view and lateral view) based on results of optimization by the B3LYP/6-311++G(d,p) method.

Our DFT-calculation for 4S and 4Se molecules yields 0.04° and 5.9°, respectively, which is very close to theoretical results for substituted circulenes. A characteristic feature of these three molecules, as well as of all remaining hetero[8]circulenes [1], is an insignificant alternation of r_1 and r_2 bonds in the internal eight-membered cycle (Fig. 2; Table 1), which, as a consequence, has a weakly pronounced anti-aromatic character [2] in comparison with typical anti-aromatic systems, such as cyclobutadiene or planar cyclooctatetraene.

Radial bonds r_3 for the 4S and 4Se molecules are considerably longer than those for the 4O molecule, whereas bonds r_6 are shorter. As a consequence, benzene fragments in the 4S and 4Se molecules are strongly deformed; namely, external half-ring $r_4r_6r_4$ significantly differs from internal half-ring $r_3r_1r_3$ and it is observed that, in the series $r_1 > r_3 > r_4 > r_6$, bonds tend to be monotonically shorten. All this leads to a situation that skeletal stretching vibrations of C=C bonds of the 4S and 4Se molecules experience a strong frequency shift and changes in IR and Raman intensities compared to similar vibrations of planar 4O circulene. Valence angles CXC (X is a heteroatom), which

are denoted in Fig. 2 as α_1, predictably decrease with an increase in the atomic radius of the heteroatom, which is also observed for free nonannulated furan, thiophene, and selenophene molecules. In the general case, geometrical parameters of five-membered heterocycles in the composition of 4O, 4S, and 4Se circulenes change little upon conjugation with benzene cycles. In turn, the latter compounds experience the strongest deformations upon forming of the circulene macrocycle, which is clearly observed in characteristic frequency shifts of "benzene" vibrations. Notably, an increase in the degree of deformation of benzene fragments (twisting of cycles with changing of valence angles α_2 and α_3) also strongly affects frequencies of bending vibrations of CH bonds, which will be discussed further.

3.2. Vibrational Spectra of 4O, 4S, and 4Se Molecules

The vibrational spectra of 4O, 4S, and 4Se molecules, which consist of 36 atoms, contain 102 normal vibrations each. The distribution of normal vibrations among symmetry species in the D_{4h} (4O molecule) and D_{2d} (4S and 4Se molecules) point groups and their

Table 1. Basic structural parameters of the 4O, 4S, and 4Se molecules based on optimization data by the B3LYP/6-311++G(d,p) method

Circulene	r_1	r_2	r_3	r_4	r_5	r_6	α_1	α_2	α_3
4O	1.395	1.430	1.398	1.398	1.384	1.401	106.2	120.6	120.9
4S	1.447	1.481	1.426	1.397	1.730	1.364	90.1	120.4	121.9
4Se	1.447	1.483	1.422	1.395	1.879	1.369	84.8	120.7	121.4

Parameter r denotes the bond in accordance with Fig. 2 (the bond length is expressed in Å); α is the valence angle, deg (Fig. 2).
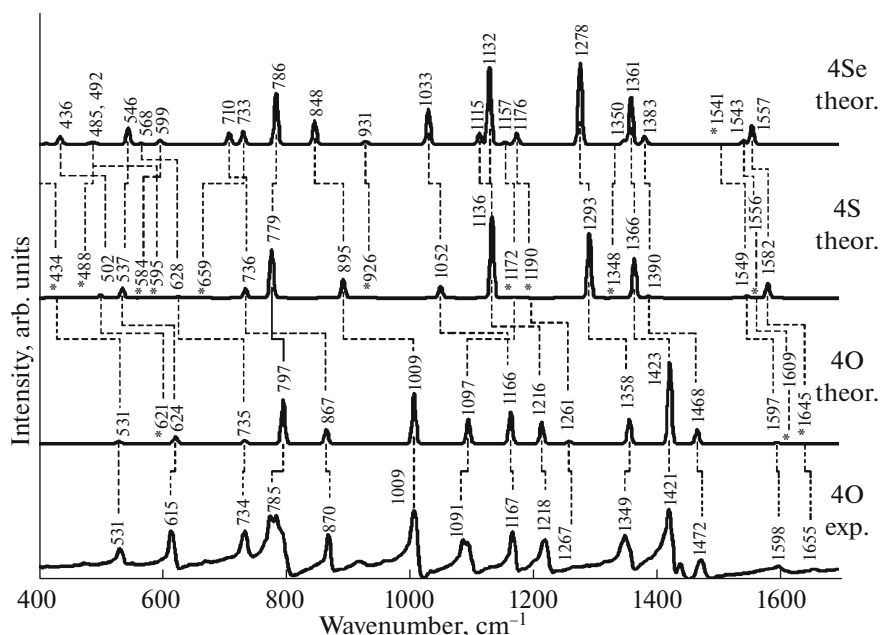
Fig. 3. IR spectra of the 4O, 4S, and 4Se molecules calculated by the B3LYP/6-311++G(d,p) method. Normal vibrations with intensities close to zero are indicated by asterisks; dashed lines show the correspondence between bands of identical vibrations.

activities in IR and Raman spectra are presented in Table 2.

The calculated frequencies and shapes of normal vibrations for all the three investigated molecules are compared in Table 3. For degenerate vibrations, the number of the second pair mode is shown in the parentheses. Vibrations of the a_{2g} and b_{2u} symmetry in the 4O molecule and corresponding a_2 vibrations in

the 4S and 4Se molecules are forbidden in the IR and Raman spectra, and, therefore, are not shown in Table 3.

The calculated IR and Raman spectra of 4O, 4S, and 4Se molecules are presented in Figs. 3 and 4, respectively and are compared with the experimental IR and Raman spectra of the 4O compound. The assignment of bands in the experimental IR and

Table 2. Correlation of symmetry of normal vibrations in the D_{4h} and D_{2d} point groups

D_{4h} [a]			D_{2d} [a]			In-plane/out-of-plane normal vibration
symmetry[b]	method		symmetry[b]	method		
	IR	Raman		IR	Raman	
e_u (34)	+	−	e	+	+	In-plane
e_g (16)	−	+	e	+	+	Out-of-plane
a_{2u} (4)	+	−	b_2	+	+	Out-of-plane
b_{2g} (9)	−	+	b_2	+	+	In-plane
a_{1g} (9)	−	+	a_1	−	+	In-plane
b_{1u} (5)	−	−	a_1	−	+	Out-of-plane
b_{1g} (9)	−	+	b_1	−	+	In-plane
a_{1u} (4)	−	−	b_1	−	+	Out-of-plane
a_{2g} (8)	−	−	a_2	−	−	In-plane
b_{2u} (4)	−	−	a_2	−	−	Out-of-plane

[a] Notation of axes is given in Fig. 1.
[b] In the parentheses, the number of vibrations of the given type is presented.
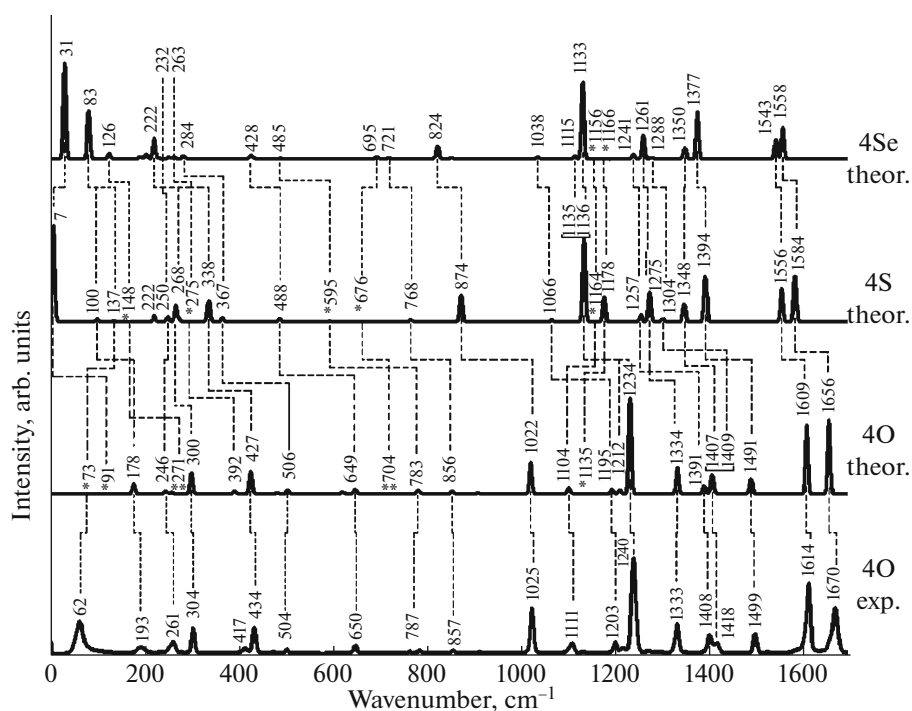
Fig. 4. Raman spectra of the 4O, 4S, and 4Se molecules calculated by the B3LYP/6-311++G(d,p) method. Normal vibrations with intensities close to zero are denoted by single asterisks; double asterisks denote symmetry forbidden normal vibrations; dashed lines show the correspondence between bands of identical vibrations.

Raman spectra of tetraoxa[8]circulene is given in Table 3.

3.2.1. Vibrations of aromatic cycles.

3.2.1.1. Vibrations of CH bonds of aromatic cycles. Vibrations of CH bonds in IR and Raman spectra of aromatic compounds can be identified in the ranges $3080-3010$ cm^{-1} (stretching vibrations, νC$-$H), $1290-990$ cm^{-1} (in-plane CH-bends, δCH), and below 900 cm^{-1} (out-of-plane CH-bends, γCH) [26].

Eight normal vibrations, $\nu_{102}-\nu_{95}$, belong to stretching vibrations of the C$-$H bonds in vibrational spectra of investigated molecules. Among them, the normal vibration ν_{95} with the smallest frequency, which is of the a_{2g} symmetry in the 4O molecule and of the a_2 symmetry in the 4S and 4Se molecules, is forbidden. Modes of symmetric vibrations are more intense and are observed at higher frequencies compared to asymmetric ones (Table 3). In the calculated IR spectrum of the 4O molecule, only symmetric νC$-$H vibrations do form a weak absorption band at 3080 cm^{-1} (exp. 3080 cm^{-1} [16]). Compared to tetraoxa[8]circulene, in the IR spectra of the 4S and 4Se molecules, the νC$-$H band is slightly shifted toward smaller frequencies (by 14 cm^{-1}), which is a consequence of changes in geometrical parameters of benzene fragments upon their condensation with heterocycles. Thus, e.g., the lengths of C$-$H bonds in the 4S and 4Se molecules (1.0832 and 1.0831 Å, respectively)

are somewhat longer than those in the 4O molecule (1.0824 Å).

In the calculated Raman spectra, symmetric νC$-$H vibrations (normal vibration ν_{102} of the a_{1g} symmetry and vibration ν_{99} of the b_{1g} symmetry) form a weak line with the same frequency as in the IR spectrum. Asymmetric νC$-$H vibrations form weak lines at 3068 (exp. 3051 cm^{-1}), 3051, and 3050 cm^{-1} in the Raman spectra of the 4O, 4S, and 4Se molecules, respectively.

In-plane bending vibrations, δCH, are, as a rule, mixed with νC$-$X vibrations of furan (thiophene, selenophene) cycles and/or with bending vibrations of the rings. In the calculated IR spectrum of the 4O molecule (Fig. 3), the band at 1097 cm^{-1} of the medium intensity, which is formed by degenerate normal vibrations ν_{61} and ν_{60} of the e_u symmetry, belongs solely to δCH vibrations. In the experimental IR spectrum (Fig. 3), the band that corresponds to it is the vibration at 1091 cm^{-1}, which is also of medium intensity, showing good agreement with theoretical predictions. Corresponding vibrations $\nu_{69(68)}$ (of the e symmetry) in the IR spectra of the 4S and 4Se molecules are of weak activity (Fig. 3) and are shifted in frequency by 75 and 60 cm^{-1} toward the range of higher frequencies (Table 3). We attribute these changes in the spectra of the 4S and 4Se molecules compared to the spectrum of the 4O molecule to changes in angles α_2 and α_3, belonging to C$-$H bonds (Table 2).

Table 3. Comparison of normal vibrations in molecules of tetraoxa-, tetrathia-, and tetraselena[8]circulene

4O			4S		4Se		Type of vibration
vibration	ν, cm^{-1}	experiment [16]	vibration	ν, cm^{-1}	vibration	ν, cm^{-1}	
$\nu_{102}\,a_{1g}$	3080	3078 Raman	$\nu_{99}\,a_1$	3066	ν_{99}	3066	ν_sC−H benzene cycle I−IV, in-phase
$\nu_{101(100)}\,e_u$	3080	3090 IR	$\nu_{101(100)}\,e$	3067	$\nu_{101(100)}$	3066	ν_sC−H benzene cycle I, III, out-of-phase (II, IV, out-of-phase)
$\nu_{99}\,b_{1g}$	3080	3078 Raman	$\nu_{102}\,b_1$	3067	ν_{102}	3066	ν_sC−H benzene cycle I, III and II, IV, out-of-phase
$\nu_{98}\,b_{2g}$	3068	3051 Raman	$\nu_{98}\,b_2$	3051	ν_{96}	3050	ν_{as}C−H benzene cycle I, III, out-of-phase, II, IV, out-of-phase
$\nu_{97(96)}\,e_u$	3068	3056 IR	$\nu_{97(96)}\,e$	3051	$\nu_{98(97)}$	3050	ν_{as}C−H benzene cycle I, III (II, IV), in-phase
$\nu_{94}\,a_{1g}$	1656	1670 Raman	$\nu_{93}\,a_1$	1584	ν_{93}	1558	ν_sC=C benzene cycle I−IV, in-phase, νC$^\beta$−C$^{\beta'}$, in-phase
$\nu_{93(92)}\,e_u$	1645	1655 IR	$\nu_{92(91)}\,e$	1582	$\nu_{92(91)}$	1557	ν_sC=C benzene cycle I, III, out-of-phase (II, IV, out-of-phase)
$\nu_{91}\,b_{2g}$	1609	1614 Raman	$\nu_{90}\,b_2$	1556	ν_{90}	1543	δCXC, ν_sC=C benzene cycle I−IV
$\nu_{90}\,b_{1g}$	1609	−	$\nu_{94}\,b_1$	1585	ν_{94}	1559	ν_sC=C benzene cycle I, III and II, IV, out-of-phase, ν_{as}C$^\alpha$=C$^\beta$ and C$^{\alpha'}$=C$^{\beta'}$
$\nu_{88(87)}\,e_u$	1597	1598 IR	$\nu_{89(88)}\,e$	1549	$\nu_{88(87)}$	1541	ν_sC=C benzene cycle II, IV, in-phase (I, III, in-phase)
$\nu_{86}\,a_{1g}$	1491	1499 Raman	$\nu_{85}\,a_1$	1394	ν_{83}	1377	ν_{as}C=C benzene cycle I−IV, νC$^\beta$−C$^{\beta'}$, in-phase, δCXC, in-phase, ν_{as}C$^\alpha$=C$^\beta$ and C$^{\alpha'}$=C$^{\beta'}$
$\nu_{85(84)}\,e_u$	1468	1472 IR	$\nu_{84(83)}\,e$	1390	$\nu_{85(84)}$	1383	ν_{as}C=C benzene cycle II, IV, out-of-phase (I, III, out-of-phase), νC$^\beta$−C$^{\beta'}$ A, C, out-of-phase (B, D, out-of-phase)
$\nu_{82(81)}\,e_u$	1423	1421 IR	$\nu_{82(81)}\,e$	1366	$\nu_{82,81}$	1361	ν_{as}C=C benzene cycle I, III (II, IV)
$\nu_{80}\,b_{1g}$	1418	−	$\nu_{80}\,b_1$	1359	ν_{79}	1349	ν_{as}C=C benzene cycle I, III and II, IV, out-of-phase
$\nu_{79}\,a_{1g}$	1409	1418 Raman	$\nu_{78}\,a_1$	1304	ν_{78}	1288	ν_{as}C=C benzene cycle Kekule I−IV, νC$^\beta$−C$^{\beta'}$, in-phase, δCXC, in-phase
$\nu_{78}\,b_{2g}$	1407	1418 Raman	$\nu_{79}\,b_2$	1348	ν_{80}	1350	ν_sC$^\alpha$=C$^\beta$ and C$^{\alpha'}$=C$^{\beta'}$, A, C and B, D, out-of-phase
$\nu_{77}\,b_{2g}$	1391	1403 Raman	$\nu_{74}\,b_2$	1257	ν_{74}	1241	νC$^\beta$−C$^{\beta'}$ A, C and B, D, out-of-phase, vibrations of benzene rings, as.
$\nu_{76(75)}\,e_u$	1358	1349 IR	$\nu_{77(76)}\,e$	1293	$\nu_{77(76)}$	1278	ν_{as}C=C benzene cycle Kekule I, III, out-of-phase (II, IV, out-of-phase)
$\nu_{74}\,b_{1g}$	1334	1333 Raman	$\nu_{75}\,b_1$	1275	ν_{75}	1261	ν_{as}C=C benzene cycle Kekule, I, III and II, IV, out-of-phase
$\nu_{73(72)}\,e_u$	1261	1267 IR	$\nu_{72(71)}\,e$	1190	$\nu_{72(71)}$	1176	ν_{as}C−X, δCH, vibrations of benzene rings I, III, out-of-phase (II, IV, out-of-phase)
$\nu_{71}\,a_{1g}$	1234	1240 Raman	$\nu_{66}\,a_1$	1136	ν_{66}	1133	δCH benzene cycle, ν_sC−X, in-phase, νC$^\beta$−C$^{\beta'}$, in-phase
$\nu_{70(69)}\,e_u$	1216	1218 IR	$\nu_{65(64)}\,e$	1136	$\nu_{65(64)}$	1132	δCH benzene cycle, ν_sC−X, A, C, out-of-phase (B, D, out-of-phase)

Table 3. (Contd.)

4O			4S		4Se		Type of vibration
vibration	ν, cm^{-1}	experiment [16]	vibration	ν, cm^{-1}	vibration	ν, cm^{-1}	
$\nu_{68}\,b_{2g}$	1212	1219 Raman	$\nu_{63}\,b_2$	1135	ν_{63}	1115	δCH benzene cycle, ν_sC–X, A, C, in-phase, B, D, in-phase
$\nu_{66}\,b_{1g}$	1195	1203 Raman	$\nu_{62}\,b_1$	1066	ν_{62}	1038	ν_{as}C–X, vibrations of benzene rings I, III and II, IV, out-of-phase
$\nu_{65(64)}\,e_u$	1166	1167 IR	$\nu_{61(60)}\,e$	1052	$\nu_{61(60)}$	1033	δCH benzene cycle, ν_{as}C–X, vibrations of benzene rings II, IV, out-of-phase (I, III, out-of-phase)
$\nu_{63}\,a_{1g}$	1135	–	$\nu_{70}\,a_1$	1178	ν_{70}	1166	δCH benzene cycle, in-phase
$\nu_{62}\,b_{1g}$	1104	1111 Raman	$\nu_{67}\,b_1$	1164	ν_{67}	1156	δCH benzene cycle, I, III and II, IV, out-of-phase
$\nu_{61(60)}\,e_u$	1097	1091 IR	$\nu_{69(68)}\,e$	1172	$\nu_{69(68)}$	1157	δCH benzene cycle, II, IV, out-of-phase (I, III, out-of-phase)
$\nu_{58}\,a_{1g}$	1022	1025 Raman	$\nu_{52}\,a_1$	874	ν_{51}	824	δCH benzene cycle, ν_sC–X, breathing otc, vibrations of benzene rings I–IV, hc of rings A, B, C, D
$\nu_{57(56)}\,e_u$	1009	1009 IR	$\nu_{54(53)}\,e$	895	$\nu_{53(52)}$	848	δCH benzene cycle, ν_{as}C–X, vibrations of benzene rings II, IV, out-of-phase (I, III, out-of-phase)
$\nu_{55}\,b_{2g}$	988	–	$\nu_{51}\,b_2$	873	ν_{54}	854	Def benzene cycle I–IV, as., vibrations hc rings A, C and B, D, out-of-phase
$\nu_{54}\,b_{1u}$	912	–	$\nu_{55}\,a_1$	926	ν_{55}	931	γ_{as}CH benzene cycle
$\nu_{53}\,a_{1u}$	911	–	$\nu_{58}\,b_1$	927	ν_{58}	931	γ_{as}CH benzene cycle
$\nu_{52(51)}\,e_g$	911	–	$\nu_{57(56)}\,e$	926	$\nu_{57(56)}$	931	γ_{as}CH benzene cycle II, IV (I, III)
$\nu_{50(49)}\,e_u$	867	870 IR	$\nu_{45(44)}\,e$	736	$\nu_{42(41)}$	710	Vibrations of benzene rings II, IV, out-of-phase (I, III, out-of-phase), vibrations of hc rings A, B, C, D
$\nu_{48}\,b_{1g}$	856	857 Raman	$\nu_{46}\,b_1$	768	ν_{43}	721	Vibrations of benzene rings I, III and II, IV, out-of-phase, def otc, s, ν_{as}C–X
$\nu_{46}\,a_{2u}$	797	785 IR	$\nu_{50}\,b_2$	779	ν_{50}	786	γCH benzene cycle, in-phase
$\nu_{45(44)}\,e_g$	790	–	$\nu_{49(48)}\,e$	779	$\nu_{49(48)}$	785	γ_sCH benzene cycle II, IV out-of-phase (I, III out-of-phase)
$\nu_{43}\,b_{2u}$	785	–	$\nu_{47}\,a_2$	778	ν_{47}	785	γ_sCH benzene cycle I, III and II, IV, out-of-phase
$\nu_{42}\,b_{2g}$	783	787 Raman	$\nu_{34}\,b_2$	595	ν_{27}	485	δCXC, def benzene cycle I–IV, as
$\nu_{41(40)}\,e_u$	735	734 IR	$\nu_{39(38)}\,e$	628	$\nu_{34(33)}$	568	Def benzene cycle II, IV (I, III), as
$\nu_{39}\,b_{1u}$	704	–	$\nu_{42}\,a_1$	676	ν_{40}	695	Out-of-plane def benzene cycle I–IV, hc rings A, B, C, D
$\nu_{38(37)}\,e_g$	675	–	$\nu_{41(40)}\,e$	659	$\nu_{45(44)}$	733	Out-of-plane def benzene cycle I, III (II, IV)
$\nu_{35}\,a_{1g}$	649	650 Raman	$\nu_{26}\,a_1$	488	ν_{24}	428	δCXC, in-phase
$\nu_{34}\,b_{2u}$	643	–	$\nu_{35}\,a_2$	604	ν_{38}	651	Out-of-plane def benzene cycle I, III and II, IV, out-of-phase
$\nu_{33}\,a_{2u}$	624	615 IR	$\nu_{30}\,b_2$	537	ν_{32}	546	γCH benzene cycle, in-phase, out-of-plane def hc rings A, B, C, D
$\nu_{32(31)}\,e_g$	622	–	$\nu_{33(32)}\,e$	584	$\nu_{37(36)}$	599	Out-of-plane def benzene cycle I, III, out-of-phase (II, IV, out-of-phase)

Table 3. (Contd.)

4O			4S		4Se		Type of vibration
vibration	ν, cm^{-1}	experiment [16]	vibration	ν, cm^{-1}	vibration	ν, cm^{-1}	
$\nu_{30(29)}\,e_u$	621	615 IR	$\nu_{28(27)}\,e$	502	$\nu_{26(25)}$	436	Rocking benzene rings II, IV out-of-phase (I, III out-of-phase)
$\nu_{27}\,a_{1u}$	529	–	$\nu_{31}\,b_1$	547	ν_{31}	546	Out-of-plane def benzene cycle I–IV
$\nu_{26(25)}\,e_u$	531	531 IR	$\nu_{21(20)}\,e$	434	$\nu_{21(20)}$	351	Def benzene cycle II, IV (I, III), as
$\nu_{24}\,b_{1g}$	506	504 Raman	$\nu_{19}\,b_1$	367	ν_{18}	284	Rocking hc rings A, B, C, D, def otc
$\nu_{23(22)}\,e_g$	483	476 Raman	$\nu_{25(24)}$	488	$\nu_{30(29)}$	492	Out-of-plane def benzene cycle I, III, in-phase (II, IV, in-phase)
$\nu_{21}\,b_{1u}$	474	–	$\nu_{23}\,a_1$	467	ν_{28}	490	Out-of-plane def benzene cycle I–IV
$\nu_{20}\,b_{2g}$	473	–	$\nu_{22}\,b_2$	455	$\nu_{23}\,b_2$	413	Rocking benzene rings I–IV
$\nu_{19}\,a_{1g}$	427	434 Raman	$\nu_{18}\,a_1$	338	ν_{12}	222	Breathing of macrocycle
$\nu_{18}\,b_{1u}$	426	–	$\nu_{14}\,a_1$	285	ν_{15}	253	Out-of-plane def hc rings A, C, out-of-phase, B, D, out-of-phase
$\nu_{17(16)}\,e_g$	392	417 Raman	$\nu_{13(12)}\,e$	275	$\nu_{17(16)}$	263	Out-of-plane def benzene cycle II, IV, in-phase (I, III in-phase)
$\nu_{15(14)}\,e_u$	367	–	$\nu_{16(15)}\,e$	307	$\nu_{8(7)}$	193	Rocking benzene rings I, III (II, IV)
$\nu_{13}\,a_{1u}$	363	–	$\nu_{10}\,b_1$	252	ν_9	205	Out-of-plane def benzene cycle I–IV
$\nu_{12}\,b_{1g}$	300	304 Raman	$\nu_{11}\,b_1$	268	ν_{11}	221	Def otc, s
$\nu_{10}\,a_{2u}$	271	–	$\nu_6\,b_2$	148	ν_6	126	Out-of-plane vibration of macrocycle
$\nu_9\,b_{2g}$	258	–	$\nu_7\,b_2$	222	ν_{10}	218	Def otc, s
$\nu_{8(7)}\,e_g$	246	261 Raman	$\nu_{9(8)}\,e$	250	$\nu_{14(13)}$	232	Out-of-plane vibration of macrocycle with def benzene cycle II, IV, out-of-phase (I, III, out-of-phase)
$\nu_{6(5)}\,e_g$	178	193 Raman	$\nu_{4(3)}\,e$	100	$\nu_{5(4)}$	83	Out-of-plane vibration of macrocycle with bending benzene cycle II, IV, out-of-phase (I, III, out-of-phase)
$\nu_4\,b_{1u}$	91	–	$\nu_1\,a_1$	7	ν_2	31	Out-of-plane vibration of macrocycle with bending
$\nu_1\,a_{2u}$	73	–	$\nu_5\,b_2$	137	ν_3	83	Out-of-plane butterfly vibration of macrocycle

X denotes heteroatom (O, S, or Se); I, II, III, and IV—enumeration of benzene rings (Fig. 1); A, B, C, and D—notation of furan (thiophene, selenophene) rings (Fig. 1); hc—heterocycle; otc—octatetraene cycle; def—deformation; s—symmetric vibration; as—asymmetric vibration; ν—frequency (wavenumber), as well as ν—stretching vibration; δ—in-plane deformation vibration (change of angle); γ—out-of-plane vibration.

We showed that the weak line of δCH deformations in benzene fragments, which was calculated to be at 1104 cm^{-1} in the Raman spectrum of the 4O molecule (exp. 1111 cm^{-1}), should not be observed in the Raman spectra of the 4S and 4Se compounds because of its predicted low intensity (its relative intensity I_R is about 10^{-4}). In the Raman spectrum of the 4S molecule, normal vibration ν_{70}, which also does not contain contributions from other vibrations, forms a line at 1178 cm^{-1}, the intensity of which is close to the medium intensity (Fig. 4). In the Raman spectra of the 4O and 4Se compounds, the corresponding lines of δCH vibrations at 1135 cm^{-1} (ν_{63}) and 1166 cm^{-1} (ν_{70}) have considerably lower intensities (the values of I_R are 1.1×10^{-3} and 1.3×10^{-3}), whereas in the IR spectra of the investigated compounds, this normal vibration is symmetry forbidden (a_{1g} and a_1).

Contributions of δCH vibrations to the IR spectrum of the 4O molecule are made by the bands at 1216 (exp. 1218 cm^{-1}), 1166 (exp. 1167 cm^{-1}), and 1009 cm^{-1} (exp. 1009 cm^{-1}). The corresponding bands in the IR spectra of the 4S (1136, 1052, and 895 cm^{-1}) and 4Se molecules (1132, 1033, and 848 cm^{-1}) are considerably shifted to the range of lower frequencies (by 114 cm^{-1}

in tetrathia[8]circulene and by 161 cm^{-1} in tetraselena[8]circulene, Fig. 3). The bands at 1136 and 1132 cm^{-1} in the IR spectra of the 4S and 4Se molecules, respectively (Fig. 3), have higher absorption intensities (101.2 and 69.8 km/mol) compared to the intensity of the band at 1216 cm^{-1} (40.8 km/mol) in the IR spectrum of the 4O molecule.

In the calculated Raman spectra of the 4S and 4Se molecules, the lines of strong, weak, and close-to-medium intensities with the frequencies, respectively, at 1136, 1135, and 874 cm^{-1} and at 1133, 1115, and 824 cm^{-1} (Fig. 4) have contributions of δCH vibrations, as well as of νC−X vibrations of thiophene (selenophene) cycles and in-plane bending vibrations of rings (Table 3). They are also considerably shifted to the range of smaller frequencies compared to the corresponding lines in the Raman spectrum of tetraoxa[8]circulene: 1234 (exp. 1240), 1212 (exp. 1219), and 1022 cm^{-1} (exp. 1025 cm^{-1}). The line at 1135 cm^{-1} with a calculated relative intensity of 0.1 in the Raman spectrum of tetrathia[8]circulene should be overlapped by a stronger line at 1136 cm^{-1} ($I_R = 0.7584$). A considerable shift of bands of δCH vibrations, which have contributions of stretching vibrations of C−X bonds, is related, to a large degree, to differences in the lengths of C−X bonds (Table 1).

Out-of-plane CH bending vibrations of benzene rings (in phase) of the b_2 symmetry in the IR spectra of the 4S and 4Se molecules were calculated in this work to be at 779 and 786 cm^{-1}, respectively (Fig. 3; Table 3, normal vibration ν_{50}). The corresponding absorption band of a medium intensity in the IR spectrum of tetraoxa[8]circulene was calculated to be at 797 cm^{-1} (normal vibration ν_{46} of the a_{2u} symmetry) and was experimentally observed at 785 cm^{-1} as a doublet band (Fig. 3). Bending deformation vibrations γCH, which are mixed with out-of-plane bending deformations of heterocyclic fragments, were calculated in the IR spectra of the 4S and 4Se molecules at lower frequencies: 537 and 546 cm^{-1}, respectively (Table 3). The corresponding band in the IR spectrum of tetraoxa[8]circulene was calculated to be at 624 cm^{-1}. The intensity of this absorption band in the experimental IR spectrum of the 4O compound is significantly higher than the theoretically calculated intensity (Fig. 3).

In the Raman spectrum of the 4O compound, γCH vibrations of the a_{2u} symmetry are forbidden (Table 2), whereas, in the calculated Raman spectra of the 4S and 4Se molecules, lines of out-of-plane CH vibrations are not presented because of their extremely low intensities.

3.2.1.2. Vibrations of aromatic C=C bonds.
Bands of skeletal vibrations of aromatic C=C bonds in IR spectra are usually observed in the range 1650–1430 cm^{-1} [26, 27]. In annulated tetraphenylenes (Fig. 1), they yield characteristic sets of bands. In the

IR spectrum of the 4O molecule, which contains four condensed benzene rings, these vibrations form four doubly degenerate normal vibrations of the e_u symmetry with calculated frequencies at 1645 ($\nu_{93(92)}$), 1597 ($\nu_{88(87)}$), 1468 ($\nu_{85(84)}$), and 1423 ($\nu_{82(81)}$) cm^{-1} (Table 3; Fig. 3). In the experimental IR spectrum, we observe a very strong band at 1421 cm^{-1} and a well-distinguished absorption band at 1472 cm^{-1}, which correspond to two pair modes $\nu_{82(81)}$ and $\nu_{85(84)}$ of asymmetric νC=C vibrations, with the band at 1472 cm^{-1} being contributed by νC$^\beta$−C$^{\beta'}$ vibrations of furan fragments (Table 3). Modes $\nu_{88(87)}$ of νC=C symmetric vibrations in the experimental IR spectrum form a very weak band at 1598 cm^{-1} (Fig. 3). In the calculated IR spectrum of the 4O molecule, normal vibrations $\nu_{93(92)}$ (calc. 1645 cm^{-1}) do not form a noticeable ν_sC=C absorption band because of their low intensity (0.03 km/mol), while, in the experimental spectrum, a very weak absorption at 1655 cm^{-1} is observed.

In the calculated IR spectra of the 4S and 4Se molecules, the corresponding νC=C bands located at 1582 ($\nu_{92(91)}$), 1549 ($\nu_{89(88)}$), 1390 ($\nu_{84(83)}$), and 1366 cm^{-1} ($\nu_{82(81)}$) and at 1557 ($\nu_{92(91)}$), 1541 ($\nu_{88(87)}$), 1383 ($\nu_{85(84)}$), and 1361 cm^{-1} ($\nu_{82(81)}$) considerably shifted to the range of lower frequencies compared to those of the 4O molecule (shifts from 48 to 85 cm^{-1}); in addition, the intensity of this IR absorption also changed significantly (Table 3; Fig. 3). Thus, the intensity of the weakest band, which is located at 1645 cm^{-1} (ν_sC=C) and which has the highest frequency, increased from 0.03 km/mol (in 4O) to 18.8 (16.7) km/mol in 4S (4Se), which yields well-distinguished absorptions at 1582 and 1557 cm^{-1} in the IR spectra of the 4S and 4Se molecules, respectively. The intensity of the strongest 1423-cm^{-1} band (ν_{as}C=C) in the IR spectrum of 4O was decreased approximately by a factor of 3; the intensities of the two remaining νC=C weak bands (1597 and 1468 cm^{-1}) also decrease, and they became weakly distinguishable in the IR spectra of the 4S and 4Se molecules (Fig. 3). A weak band at 1543 cm^{-1} in the IR spectrum of 4Se (Fig. 3) is formed by normal vibration ν_{90} of the b_2 symmetry (Table 3). The calculated absorption intensity of the corresponding normal vibration in the 4S molecule is too low (0.2 km/mol) for this vibration to be observed, while, in the IR spectrum of the 4O molecule, this vibration is symmetry forbidden (calc. 1609 cm^{-1}; Table 3).

In the Raman spectrum of the 4O molecule (Fig. 4), calculated normal vibrations ν_{94} of the a_{1g} symmetry and ν_{91} of the b_{2g} symmetry, which belong to ν_sC=C vibrations of benzene rings, form strong lines at 1656 and 1609 cm^{-1} (exp. 1670 and 1614 cm^{-1}, respectively). In the spectra 4S and 4Se molecules, the corresponding lines at 1584 and 1556 cm^{-1} and at 1558 and 1543 cm^{-1} were predicted to have lower intensi-

ties. Asymmetric ν_{as}C=C vibrations in the Raman spectrum of tetraoxa[8]circulene (Table 3; ν_{86}, calc. 1491 cm^{-1}, exp. 1499 cm^{-1}) are of weak intensities; however, in the spectra of the 4S and 4Se molecules (ν_{85}, calc. 1394 cm^{-1} and ν_{83}, calc. 1377 cm^{-1}, respectively) their intensities become noticeably higher (Fig. 4). Enhancement in the Raman activity for asymmetric stretching C=C vibrations in the 4S and 4Se molecules can be associated with an increase in the polarizability of heavy heteroatoms and its influence on benzene rings.

Degenerate normal vibrations $\nu_{76(75)}$ in the 4O molecule (calc. 1358 cm^{-1}, exp. 1349 cm^{-1}) with the IR intensity that is close to the medium intensity (Table 3; Fig. 3) belong to asymmetric vibrations of C=C bonds of benzene rings with a high amplitude (Kekule vibrations). In the IR and Raman spectra of the benzene molecule, which has the D_{6h} symmetry, vibrations of this type (b_{2u}) are forbidden and have never been observed. Corresponding Kekule vibrations in the 4S and 4Se molecules were predicted in this work to be at lower frequencies (1293 and 1278 cm^{-1}, respectively), but with a higher (roughly, twofold) IR intensity (Fig. 3). In the Raman spectrum of the 4O molecule (Fig. 4), weak lines ν_{79} and ν_{74} with the calculated frequencies at 1409 and 1334 cm^{-1} (exp. 1418 and 1333 cm^{-1}) belong to the Kekule vibrations. The former of them (ν_{78}; Table 3), which was calculated in the Raman spectra of the 4S and 4Se molecules to be at 1304 and 1288 cm^{-1}, respectively, is observed as a very weak line (Fig. 4), whereas the latter line (ν_{75}), which was calculated to be at frequencies of 1275 and 1261 cm^{-1}, respectively, has approximately the same average intensity, as in the Raman spectrum of the 4O molecule. It is obvious that the activity of Raman Kekule vibrations in hetero[8]circulenes is determined by the polarizability of annulated and weakly deformed benzene rings; it depends on only on the character of deformation, which is roughly the same for all circulenes.

All vibrations of aromatic C=C bonds calculated in the Raman spectra, except for the latter one, have contributions of bending deformations of CXC angles and (or) of stretching vibrations of CC bonds of heterocyclic rings.

3.2.1.3. Bending vibrations of the aromatic ring as a whole. As a rule, vibrations of benzene rings in the 4O molecule calculated in the range of 1261–856 cm^{-1} (Table 3) are mixed with δCH and νC–O vibrations of furan rings. In the IR spectrum of the 4O molecule (Fig. 3), they contribute to weak bands at 1261 and 867 cm^{-1} (exp. 1267 (shoulder) and 870 cm^{-1}, respectively) and bands at 1166 and 1009 cm^{-1} of a medium intensity (exp. 1167 and 1009 cm^{-1}). In the Raman spectrum (Fig. 4), weak lines at 1195 and 856 cm^{-1} (exp. 1203 and 857 cm^{-1}) and the line at 1022 cm^{-1} of

a medium intensity, which is formed by normal vibration ν_{58} of the a_{1g} symmetry (exp. 1025 cm^{-1}), correspond to deformation vibrations of rings. The corresponding bands in the IR and Raman spectra of the 4S and 4Se molecules were predicted in this work to be at lower frequencies (Table 3) and, as a rule, with a lower intensity (Figs. 3, 4). Vibration $\nu_{72(71)}$ of the e_u symmetry, which was calculated in the 4S molecule to be at the frequency of 1190 cm^{-1} (Table 3) and which corresponds to normal vibrations $\nu_{73(72)}$ and $\nu_{72(71)}$ in the 4O and 4Se molecules with the frequencies at 1261 and 1176 cm^{-1}, respectively, has a zero intensity of the IR absorption. This is an accidental result and does not reveal any regularity.

The line at 427 cm^{-1} (exp. 434 cm^{-1}) in the Raman spectrum of the 4O molecule and the corresponding lines at 338 and 222 cm^{-1}, which were predicted to occur in the Raman spectra of the 4S and 4Se molecules (Fig. 4), are formed by the "breathing" of the whole macrocycle. The line of this type of vibration experiences a largest shift (by 116 cm^{-1}; Fig. 4) in the Raman spectrum of the 4Se molecule compared to the 4S molecule, which is an obvious consequence of the heteroatom effect, because C–X bonds vibrate together with remaining ones.

In the 4O molecule, calculated normal vibrations $\nu_{41(40)}$ and $\nu_{26(25)}$ of asymmetric deformations of benzene rings of the e_u symmetry form weak IR bands at 735 and 531 cm^{-1} (Table 3; Fig. 3). In the experimental spectrum, the corresponding bands at 734 and 531 cm^{-1} are more intense compared to the calculated ones. In the IR spectra of the 4S and 4Se molecules (Table 3; Fig. 3), the corresponding bands at 628, 434, and 568, 351 cm^{-1} (normal vibrations $\nu_{39(38)}$, $\nu_{21(20)}$ and $\nu_{34(33)}$, $\nu_{21(20)}$) have even lower intensities. The very weak line at 783 cm^{-1} (exp. 787 cm^{-1}) in the Raman spectrum of the 4O molecule, which has contributions of asymmetric deformations of benzene rings, in the calculated Raman spectra of the 4S and 4Se molecules, experiences a very strong shift to the range of lower frequencies (Table 3; normal vibrations ν_{34} and ν_{27}; calc. 595 and 485 cm^{-1}, respectively), which is related to the participation of deformations of CXC angles of heterocycles in this type of vibration. The predicted shift of this normal vibration under the influence of the heteroatom can remain unnoticed, because the relative intensities of the lines at 595 and 485 cm^{-1} are extremely low (6.1 × 10^{-3} and 2.1 × 10^{-3}, respectively).

Out-of-plane deformations of benzene rings of the e_g symmetry in the 4O molecule were calculated in this work to be in the range 675–246 cm^{-1}. This type of displacements of nuclei does not have contributions of other vibrations. In the D_{4h} point group, they are allowed only in the Raman spectrum (Table 2) and yield very weak calculated lines at 483, 392, and

246 cm^{-1} (exp. 476, 417, and 261 cm^{-1}, respectively). The lines at 675 and 622 cm^{-1} are not observed in the Raman spectrum because their weak intensity (the values of I_R are lower than 1×10^{-3} and 7.5×10^{-3}, respectively). In the 4S and 4Se molecules, which belong to the D_{2d} point group, this type of vibrations is symmetry allowed in the IR and Raman spectra (Table 2), but the calculated intensities of corresponding normal vibrations $\nu_{41(40)}$, $\nu_{33(32)}$, $\nu_{25(24)}$, $\nu_{13(12)}$, and $\nu_{9(8)}$ of the e symmetry are too low to be observed in the IR and Raman spectra of the 4S molecule, except for vibration $\nu_{9(8)}$, which yields a weak line at 250 cm^{-1} in the calculated Raman spectrum (Fig. 4). In the 4Se molecule, corresponding normal vibrations $\nu_{45(44)}$, $\nu_{37(36)}$, $\nu_{30(29)}$, $\nu_{17(16)}$, and $\nu_{14(13)}$ with the calculated frequencies at 733, 599, 492, 263, and 232 cm^{-1} also have a very weak Raman intensity; however, in the IR spectrum, the bands at 733, 599, and 492 cm^{-1} can be observed (Fig. 3), since the calculated intensity of the IR absorption reaches values of 4−11 km/mol. It should be noted that all the calculated frequencies of these out-of-plane vibrations of benzene rings (733, 599, and 492 cm^{-1}) in the 4Se molecule proved to be higher than the frequencies of the corresponding vibrations of the 4S molecule (659, 584, and 488 cm^{-1}).

Normal vibrations ν_{39}, ν_{21} of the b_{1u} symmetry and vibrations ν_{27}, ν_{13} of the a_{1u} symmetry, which are forbidden in the IR and Raman spectra of the 4O molecule (Table 3) and which also belong to out-of-plane motions of benzene rings, in the D_{2d} point group, become active in the Raman spectrum (Table 2). However, the calculated intensities of normal vibrations are too low for the corresponding lines to be observed in the Raman spectra of the 4S and 4Se molecules. Exceptions are very weak lines at 695 and 205 cm^{-1} in the Raman spectrum of the 4Se molecule, which belong, respectively, to normal vibration ν_{40} of the a_1 symmetry and to normal vibration ν_9 of the b_1 symmetry (Table 3; Fig. 4).

3.2.2. Vibrations of heterocyclic fragments. Internal degrees of freedom of heterocycles in molecules of annulated tetraphenylenes are also of great interest for interpretation of IR and Raman spectra of these compounds.

Vibrations C$^\beta$−C$^{\beta'}$ of the a_1 symmetry (C_{2v} point group), which are weakly active in IR and Raman spectra, were calculated in this work for free molecules of furan, thiophene, and selenophene in the 6-311++G(d,p) basis set. The corresponding frequencies were determined to be at 1374, 1358, 1336 cm^{-1}, respectively (exp. 1380, 1360, and 1341 cm^{-1} [28]). In the 4O, 4S, and 4Se molecules, these vibrations are split and are mixed with νC=C vibrations of benzene rings and vibrations of other types. They contribute to four normal vibrations ν_{94}, ν_{86}, ν_{79}, and ν_{71} of the a_{1g} symmetry in the 4O molecule, and to corresponding

normal vibrations ν_{93}, ν_{85}, ν_{78}, and ν_{66} and ν_{93}, ν_{83}, ν_{78}, and ν_{66} of the a_1 symmetry in the 4S and 4Se molecules, respectively, which are active only in the Raman spectra (Table 3; lines at 1656, 1491, 1409, and 1234 cm^{-1} (4O); at 1584, 1394, 1304, and 1136 cm^{-1} (4S); and at 1558, 1377, 1288, and 1133 cm^{-1} (4Se)). In the IR spectrum, C$^\beta$−C$^{\beta'}$ vibrations contribute to the weak bands at 1468, 1390, and 1383 cm^{-1} of the 4O, 4S, and 4Se molecules, respectively, which belong to ν_{as}C=C asymmetric stretching vibrations of benzene rings.

Symmetric vibrations of C$^\alpha$=C$^\beta$ and C$^{\alpha'}$=C$^{\beta'}$ bonds of the a_1 symmetry, which were calculated in this work for the furan, thiophene, and selenophene molecules to be at 1468, 1407, and 1425 cm^{-1} respectively (exp. 1485, 1408 and 1419 cm^{-1} [28]), are more active in the IR and Raman spectra compared to C$^\beta$−C$^{\beta'}$ vibrations. In the Raman spectra of the 4O, 4S, and 4Se molecules, these vibrations form a weak line, which is located at 1407, 1348, and 1350 cm^{-1}, respectively, and which belongs solely to this type of vibrations. We note that symmetric vibrations of C$^\alpha$=C$^\beta$ and C$^{\alpha'}$='C$^{\beta'}$ bonds of individual heterocyclic fragments in macrocycles have the a_{1g} symmetry for furan fragments and the a_1 symmetry for thiophene (selenophene) fragments, whereas, for the entire macrocycle, this normal vibration has the b_{2g} symmetry in the 4O molecule and the b_2 symmetry in the 4S and 4Se molecules, because vibrations of heterocyclic fragments in rings A, C and B, D are out-of-phase.

For asymmetric vibrations of C$^\alpha$=C$^\beta$ and C$^{\alpha'}$=C$^{\beta'}$ bonds, which were calculated in the furan, thiophene, and selenophene molecules to be at 1550, 1512 (exp. 1505 cm^{-1} [28]), and 1520 cm^{-1} (exp. 1515 cm^{-1} [28]) respectively, upon condensation in the 4O, 4S, and 4Se molecules, their shift to the range of higher frequencies, namely, to 1609, 1585, and 1559 cm^{-1}, respectively, was predicted (Table 3). In the IR spectra, this type of vibrations is symmetry forbidden (b_{1g} in the D_{4h} point group and b_1 in the D_{2d} group, Table 2); in the Raman spectra, corresponding lines are of a low intensity are overlapped by stronger lines of ν_sC=C vibrations of benzene fragments at 1609, 1584, and 1558 cm^{-1} (Fig. 4).

Asymmetric vibrations of C$^\alpha$=C$^\beta$ and C$^{\alpha'}$=C$^{\beta'}$ bonds, mixing with vibrations of C$^\beta$−C$^{\beta'}$ bonds and COC angles, yield normal vibration ν_{86} of the a_{1g} symmetry in the 4O molecule, the calculated frequency of which is 1491 cm^{-1} (exp. 1499 cm^{-1}, Raman). In the 4S and 4Se molecules, normal vibrations ν_{85} and ν_{83} of the a_1 symmetry and with the calculated frequencies at 1394 and 1377 cm^{-1} correspond to them. These vibrations are also contributed by ν_{as}C=C vibrations of benzene rings, because, in the macrocycle, C$^\alpha$=C$^\beta$ bonds

of heterocyclic fragments are simultaneously C=C bonds of benzene rings.

Symmetric and asymmetric vibrations of C−X bonds in the vibrational spectra of investigated molecules were calculated in this work in the range 1261−721 cm^{-1}. Although lengths of C−X bonds in the investigated molecules are considerably different (Table 1), it seems to be impossible to determine their individual influence on the shift of frequencies, because vibrations of C−X bonds are mixed with δCH vibrations, in-plane deformations of benzene rings, and vibrations of other types.

Vibrations ν_{42} and ν_{35} in the 4O molecule and corresponding normal vibrations in the 4S and 4Se molecules (Table 3), which are responsible for deformations of CXC angles of heterocyclic fragments, experience strong shifts in the Raman spectra under the influence of the heteroatom (Fig. 4). This is especially clearly seen upon analysis of vibrations ν_{35}, ν_{26}, and ν_{24} in the 4O, 4S, and 4Se molecules, respectively, the frequencies of which were calculated to be at 649, 488, and 428 cm^{-1}, since this normal vibration does not have contributions from vibrations of other types (Table 3). This shift of lines is related to a strong difference in CXC angles of heterocyclic fragments (Table 1; angle α_1). Thus, in the furan fragment, the CXC angle is 106.2°, and, in the thiophene and selenophene fragments, it is 90.1° and 84.8°, respectively.

Displacement of the heteroatom upon in-plane rocking of heterocycles also considerably affects frequencies of vibrations. Thus, normal vibration ν_{24} in the Raman spectrum of the 4O compound has the frequency of 506 cm^{-1} (exp. 504 cm^{-1}). In the spectra of the 4S and 4Se molecules, corresponding vibrations ν_{19} and ν_{18} are shifted in frequency to 367 and 284 cm^{-1} (Table 3, Fig. 4).

CONCLUSIONS

Modeling of the electronic structure and force fields of hypotonic symmetric molecules of tetrathia- and tetraselena[8]circulenes (4S and 4Se; Fig. 1) based on DFT calculations allowed us to explain changes in their IR and Raman spectra compared to the well-studied tetraoxa[8]circulene molecule (4O; Fig. 1). Characteristic shifts in the IR and Raman spectra (which complement each other) of this new class of compounds of highly symmetrical molecules in the relation to the nature of the heteroatom proved to be nontrivial; they depend on the conjugation between the eight-membered cycle and annulated rings, which confirms a complex character of the aromaticity of these molecules [1, 14]. Thus, in-plane CH bending vibrations (1234 cm^{-1}) with an admixture of C−O stretching vibrations of the a_{1g} symmetry in the 4O molecule, which yield the most intense Raman

line, are of great interest in the context of evolution of Raman spectra of the whole series of molecules. This line is shifted by almost 100 cm^{-1} in the 4S and 4Se circulenes (Fig. 4; ν_{66} of the a_1 symmetry; Table 3).

In this case, it is interesting that IR and Raman active modes, which almost coincide in frequency in the 4S and 4Se molecules (ν_{66} and $\nu_{65(64)}$; Table 3), are strongly spaced apart (by 18 cm^{-1}) in the tetraoxa[8]circulene molecule (4O) (Fig. 3). Thus, in the tetrathia[8]circulene (4S; Figs. 3, 4), these IR and Raman lines coincide, being located at 1136 cm^{-1}. Degenerate modes $\nu_{65(64)}$ of the e symmetry, which are active in the IR spectrum (Table 3), additionally contain out-of-phase vibrations of opposite benzene rings. However, even small admixture of the C−X mode is determining in merging of these IR and Raman lines of the 4S and 4Se molecules, although their nature is mainly determined by CH deformations.

The most clearly pronounced distinction in the IR spectra of molecules of the considered class of compounds is connected with the band at 1009 cm^{-1} of tetraoxa[8]circulene (4O; Fig. 3) of the e_u symmetry. This band is formed by in-plane CH bending vibrations with an admixture of C−O stretching vibrations and out-of-phase vibrations of opposite benzene rings. In the 4S and 4Se molecules, this IR band is shifted by 114 and 161 cm^{-1}, respectively (Fig. 3). Here, the frequency of this band is already strongly affected by the nature of the heteroatom, since the conjugation of all rings manifests itself precisely for these modes.

The line at 434 cm^{-1} observed in the Raman spectrum of the 4O molecule and the corresponding lines at 338 and 222 cm^{-1}, which are predicted in the Raman spectra of the 4S and 4Se molecules (Fig. 4) and which are formed by the breathing of the macrocycle, experience a maximal shift upon passage from the 4S to the 4Se molecule. A large contribution of displacements of the heteroatom to this symmetric vibration of the macrocycle is an important factor of Raman spectra circulenes.

A weak line at 787 cm^{-1} in the Raman spectrum of the 4O molecule, which has a contribution of asymmetric deformations of benzene rings is of great theoretical interest: in the calculated Raman spectra of the 4S and 4Se molecules, it experiences a strong shift to the range of smaller frequencies (595 and 485 cm^{-1}, respectively), which is related to the participation of deformations of CXC angles of heterocycles in the vibration of this type. Despite an extremely low Raman activity, these signals will be important criteria in the interpretation of force fields of this class of molecules.

ACKNOWLEDGMENTS

REFERENCES

1. G. V. Baryshnikov, B. F. Minaev, and V. A. Minaeva, Usp. Khim. **84** (5), 455 (2015).

2. G. Baryshnikov, R. Valiev, N. Karaush, and B. Minaev, Phys. Chem. Chem. Phys. **16** (29), 15367 (2014).

3. G. V. Baryshnikov, N. N. Karaush, and B. F. Minaev, Khim. Geterotsikl. Soedin. **50** (3), 349 (2014).

4. B. F. Minaev, G. V. Baryshnikov, and V. A. Minaeva, Comp. Theor. Chem. **972** (1−3), 68 (2011).

5. R. Pop, M. Medeleanu, M. V. Diudea, B. Szefler, and J. Cioslowski, Cent. Eur. J. Chem. **11** (4), 527 (2013).

6. M. V. Diudea, A. E. Vizitiu, T. Beu, A. Bende, C. L. Nagy, and D. J. Janežič, Mol. Struct. THEOCHEM. **904** (1−3), 28 (2009).

7. J.-C. Charlier, T. W. Ebbesen, and Ph. Lambin, Phys. Rev. B **53** (16), 11108 (1996).

8. G. Baryshnikov, B. Minaev, N. Karaush, and V. Minaeva, Phys. Chem. Chem. Phys. **16** (14), 6555 (2014).

9. G. Baryshnikov, B. Minaev, N. Karaush, and V. Minaeva, RSC Adv. **4** (49), 25843 (2014).

10. J. Yu, Q. Sun, Y. Kawazoe, and P. Jena, Nanoscale **6** (24), 14962 (2014).

11. T. N. Gribanova, N. S. Zefirov, and V. I. Minkin, Doklady Chem. **426** (1), 105 (2009).

12. T. N. Gribanova, N. S. Zefirov, and V. I. Minkin, Pure Appl. Chem. **82** (4), 1011 (2010).

13. T. K. Mandal, D. Jose, A. Nijamudheen, and A. Datta, J. Phys. Chem. C **118** (23), 12115 (2014).

14. X. Xiong, C.-L. Deng, B. F. Minaev, G. V. Baryshnikov, X.-S. Peng, and H. N. C. Wong, Chem. Asian J. **10** (4), 969 (2015).

15. H. Erdtman and H.-E. Hogberg, Tetrahedron Lett. **11** (38), 3389 (1970).

16. V. A. Minaeva, B. F. Minaev, G. V. Baryshnikov, H. Agren, and M. Pittelkow, Vib. Spectrosc. **61**, 156 (2012).

17. V. A. Minaeva, B. F. Minaev, G. V. Baryshnikov, O. M. Romeyko, and M. Pittelkow, Vib. Spectrosc. **65**, 147 (2013).

18. N. N. Karaush, B. F. Minaev, G. V. Baryshnikov, and V. A. Minaeva, Opt. Spectrosc. **116** (1), 33 (2014).

19. V. A. Minaeva, B. F. Minaev, G. V. Baryshnikov, O. N. Romeyko, and M. Pittel'kov, J. Appl. Spectrosc. **79** (5), 695 (2012).

20. A. D. Becke, J. Chem. Phys. **98** (7), 5648 (1993).

21. C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37** (2), 785 (1988).

22. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72** (1), 650 (1980).

23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02 (Gaussian, Inc., Wallingford, 2009).

24. P. L. Polavarapu, J. Phys. Chem. **94** (21), 8106 (1990).

25. S. I. Gorelsky, SWizard program. http://www.sg-chem.net/.

26. G. Socrates, *Infrared and Raman Characteristic Group Frequencies—Tables and Charts*, 3rd ed. (Wiley, Chichester, 2001).

27. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules* (Methuen, London, 1954).

28. J. S. Kwiatkowski, J. Leszczynski, and I. Teca, J. Mol. Struct. **436**, 451 (1997).