Planar Four-Coordinate Carbon
in Star-Like Perlithioannulenes C_nLi_n (n = 3–6)

V. I. Minkin, R. M. Minyaev, A. G. Starikov, and T. N. Gribanova

Institute of Physical and Organic Chemistry, Rostov State University, pr. Stachki 194/2, Rostov-on-Don, 344090, Russia
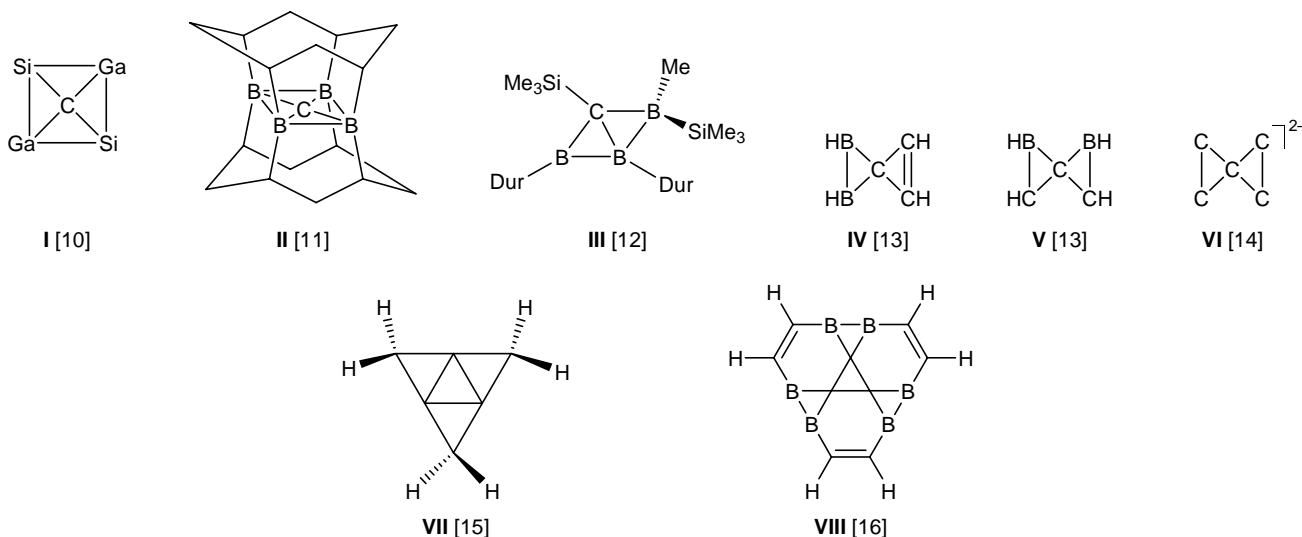*e-mail: minyaev@ipoc.rsu.ru*

Abstract—The structure and stability of perlithioannulenes C_nLi_n (n = 3–6) were examined *ab initio* [MP2(full)/6-311+G**] and in terms of the density functional theory (B3LYP/6-311+G**). The systems with n = 3, 5, and 6 may be stabilized as planar star-like structures with bridging lithium atoms and hypercoordinate carbon atoms. Star-like structures are the most stable isomers of odd-numbered annulenes (n = 3, 5), while the most stable isomers of even-numbered annulenes (n = 4, 6) have less symmetric nonplanar structures.

The concept of planar structure of a four-coordinate carbon center, which was discarded as early as 1874 by Van't Hoff [1] and Le Bel [2] because of its inability to rationalize isomerism of methane derivatives, was recovered almost 100 years later by Hoffmann, Alder, and Wilcox [3] who predicted that such a structure may be stabilized if some stereoelectronic conditions are met. This paradoxical (at first glance) problem remains so far one of the most intriguing challenges to imagination and capabilities of theoretical and experimental chemists [4–9]. The conditions necessary for stabilization of a planar four-coordinate carbon atom include mainly introduction of substituents which possess π-acceptor and σ-donor properties and are capable of delocalizing unshared electron pair of the planar carbon center over the ligand environment, as well as steric enforcement of the planar bond configuration. In the past decade, a number of fascinating results were obtained in this field, which implied almost all possible ways (among those proposed previously) of stabilization of a planar four-coordinate carbon center (for review, see [4–9]); some examples (structures **I**–**VIII**) are shown below.

The ligand environment of the planar four-coordinate center in all systems **I**–**VIII** consists of Group III and IV elements. Less attention was given to the
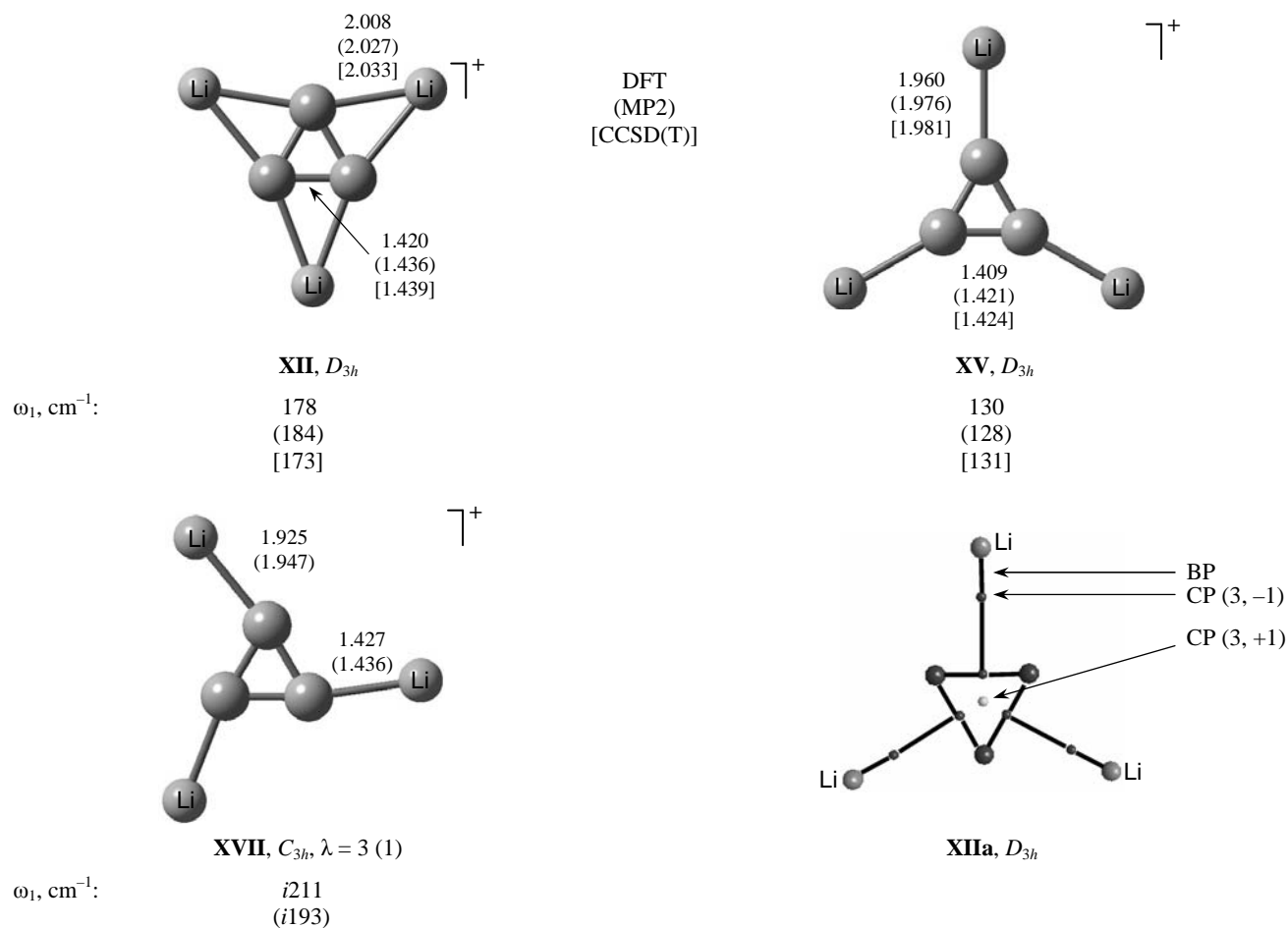

I [10]   **II** [11]   **III** [12]   **IV** [13]   **V** [13]   **VI** [14]

VII [15]   **VIII** [16]

DFT
(MP2)
[CCSD(T)]

2.008
(2.027)
[2.033]

1.420
(1.436)
[1.439]

XII, D_{3h}

ω_1, cm^{-1}:   178
(184)
[173]

1.960
(1.976)
[1.981]

1.409
(1.421)
[1.424]

XV, D_{3h}

130
(128)
[131]

1.925
(1.947)

1.427
(1.436)

XVII, C_{3h}, $\lambda = 3$ (1)

ω_1, cm^{-1}: i211
(i193)
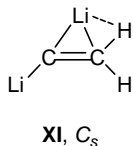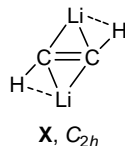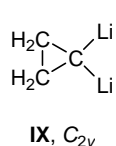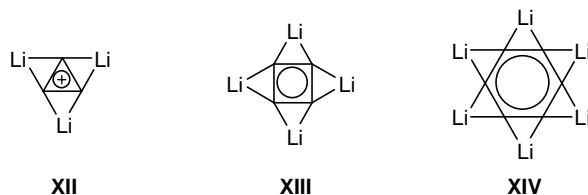
BP
CP (3, –1)
CP (3, +1)

XIIa, D_{3h}

Fig. 1. Geometric parameters and least (or imaginary) harmonic vibration frequencies of structures **XII**, **XV**, and **XVII**, according to DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G** and CCSD(T)/6-311+G**] calculations. Hereinafter, the bond lengths are given in Angstroem units; the values calculated by the MP2 and CCSD(T) methods are given in parentheses and brackets, respectively. Bader's molecular graphs for all structures are indexed with "a." BP stands for Bader's bond path, CP (3, –1) denotes stationary point on bond path, and CP (3, +1) denotes ring stationary point.

lithium atom as substituent in the ligand environment of a planar four-coordinate center, though just organolithium structures were formerly considered to be the most promising compounds having a planar four-coordinate carbon atom [9]. For example, according to quantum-chemical calculations, stable isomers **IX**–**XI** of 1,1-dilithiocyclopropane, 1,1-dilithioethene, and 1,2-dilithioethene have planar four-coordinate carbon centers [9].

IX, C_{2v} **X**, C_{2h} **XI**, C_s

We previously performed MNDO and RHF/3-21G studies [17, 18] of the structure and stability of

perlithioannulenes **XII**–**XIV** and found that the most stable are bridged star-like isomers in which all ring carbon atoms are characterized by planar four-coordinate configuration.

XII   **XIII**   **XIV**

More recent *ab initio* (MP2/TZP) calculations [19, 20] confirmed the stability of planar star-like structure of hexalithiobenzene (**XIV**); however, another more stable (by about 100 kcal/mol) nonplanar isomer was revealed [20]. On the other hand, no other isomers than those having a star-like structure were found for

ω₁, cm⁻¹:

XX, C_{2h}
188
(162)

XXI, D_{2d}
122
(69)

XXII, D_{2h}, λ = 1
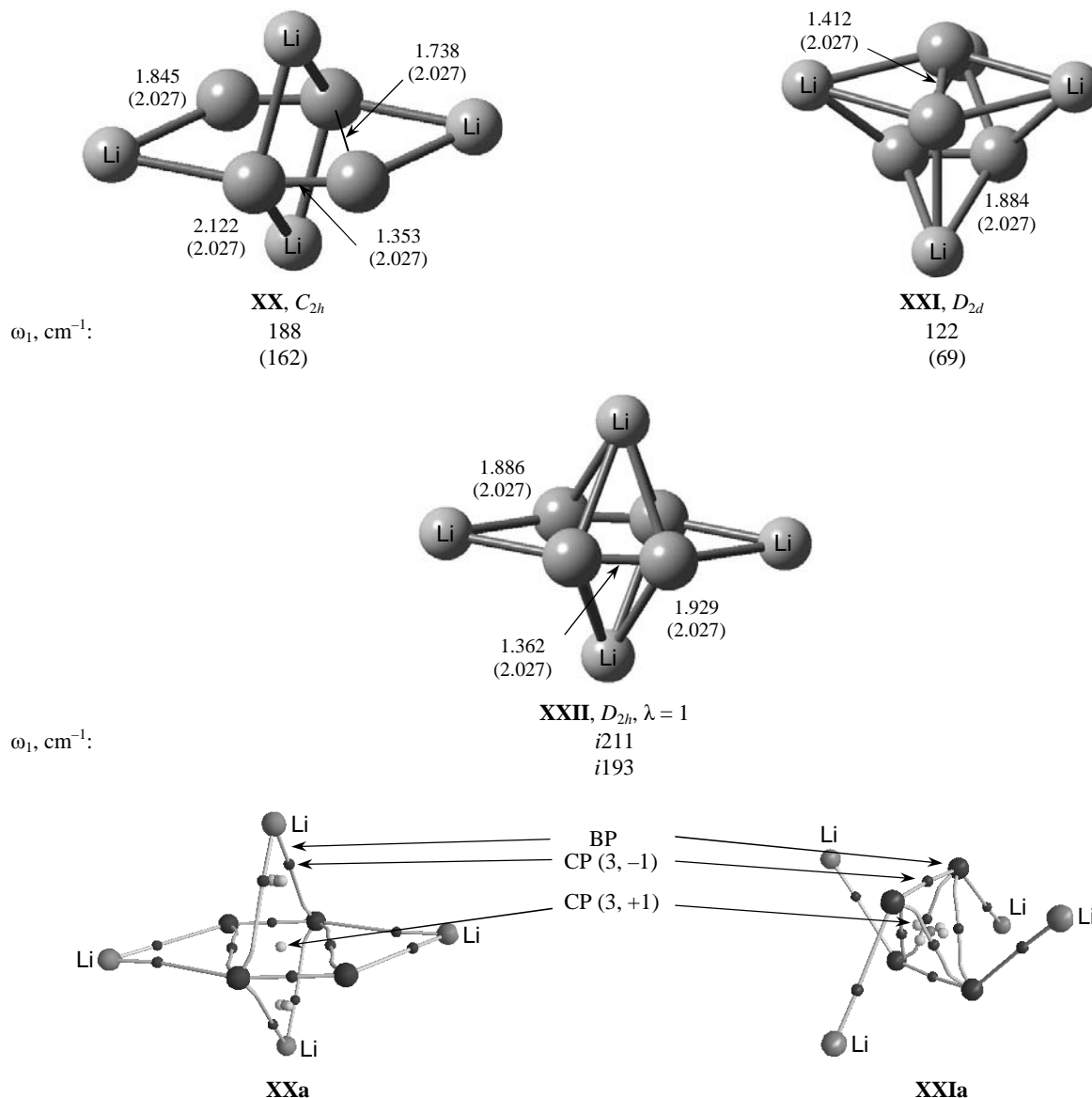i211
i193

XXa

XXIa

Fig. 2. Geometric parameters and least (or imaginary) harmonic vibration frequencies of structures **XX–XXII**, according to DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G**] calculations.

perlithiated cyclopropenyl cation by RHF/3-21G non-empirical calculations [17, 18]. It is known that the RHF/3-21G level is insufficient to reliably describe aromatic systems where electronic correlation effects are crucial [21]. We examined the structure of per-lithioannulenes by quantum-chemical methods which take into account electronic correlation, namely *ab initio* [MP2/TZP and CCSD(T)] and DFT (B3LYP/6-311+G**); the electronic and steric structures of the whole series of perlithioannulenes C_nLi_n (n = 3–6) were studied.

The calculations were performed in terms of the restricted Hartree–Fock (RHF) approach with account

taken of correlation of valence and core electrons according to the second-order Moeller–Plesset perturbation theory [MP2(full)] and in terms of the density functional theory (DFT B3LYP) with the valence-split 6-311+G** basis set; Gaussian-98 [22] and Gamess [23] software packages were used. Perlithiocyclopropenyl cation $C_3Li_3^+$ was also calculated by the coupled cluster method involving perturbative singles, doubles, and triples [CCDS(T)] with the 6-311+G** basis set, which is the most accurate among modern nonempirical methods [23]. The results given below indicate that the three methods demonstrate a good consistency; therefore, perlithioannulenes with n = 4–6 were calcu-

lated only by the DFT and MP2 methods. Complete geometry optimization of molecular structures corresponding to energy minima ($\lambda = 0$; λ is the number of negative Hessian eigenvalues in a given stationary point) and saddle points ($\lambda = 1$) on the potential energy surface (PES) was performed in the *tight* mode of Gaussian and to a gradient of 10^{-5} hartree/bohr in GAMESS. The molecular structures shown in figures were plotted using Gauss View [24].

Perlithiocyclopropenyl cation $C_3Li_3^+$. Two most stable structures, bridged **XII** and classical **XV** were found for $C_3Li_3^+$ cation; they occupy energy minima ($\lambda = 0$) on the PES. Bridged structure **XII** is more favorable than **XV** by 9.1 (DFT), 12.2 (MP2), or 11.2 kcal/mol (CCD). Although structures like **XVI** correspond to energy minima on the potential energy surface, they are less stable than the bridged form by more than 30 kcal/mol; therefore, these structures are not considered here.

XV, D_{3h} **XVI**, C_{2v} **XVII**, C_{3h}
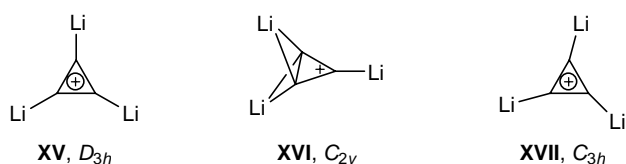
According to the DFT calculations, structure **XVII** having a C_{3h} symmetry corresponds to apex of a three-dimensional hill ($\lambda = 3$), while MP2 calculations localize that structure as transition state ($\lambda = 1$) in the rearrangement **XV** $\rightleftarrows$ **XVII** $\rightleftarrows$ **XII** with an activation barrier of 3.4 (DFT) or 1.9 kcal/mol (MP2). The calculated geometric and energy parameters of structures **XII**, **XV**, and **XVII** are given in Fig. 1.

A good agreement is observed for the geometric parameters calculated by the three methods: the differences do not exceed 0.02 Å. The C–C bond in structures **XV** and **XII** is longer than in cyclopropenyl cation $C_3H_3^+$ (1.373 Å [25]), indicating a weaker aromatic stabilization in the lithium-substituted ring. The molecular graph of structure **XII** (**XIIa**, Fig. 1) includes a cyclic critical point and shows that the lithium atoms are linked not to carbon atoms but to the mid C–C bond like a specific π-complex.

Perlithiocyclobutadiene C_4Li_4. Classical form **XVIII** of perlithiated cyclobutadiene is unstable ($\lambda = 5$), while bridged structure **XIX**, though it occupies a local minimum, is less stable than nonplanar structure **XX** by almost 18 kcal/mol. The geometric parameters of the latter are given in Fig. 2 together with structure **XXI** whose energy is higher than the energy of **XX** by only 5 kcal/mol. Structure **XX** is stereochemically nonrigid, and reorientation of the apical lithium atoms from one couple of carbon atoms to the other is characterized by a low barrier (0.4 kcal/mol; Scheme 1).

XVIII, D_{2h} **XIX**, D_{2h}
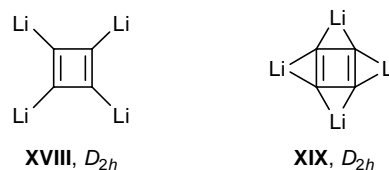
The molecular graphs of structures **XX** and **XXI** (Fig. 2) indicate the presence of hypercoordinate carbon atoms therein (five-coordinate in **XX** and pyramidal four-coordinate in **XXI**). Addition of two lithium atoms to unstable structure **XVIII** stabilizes it as symmetrical D_{4h} form **XXIII** with four pyramidal
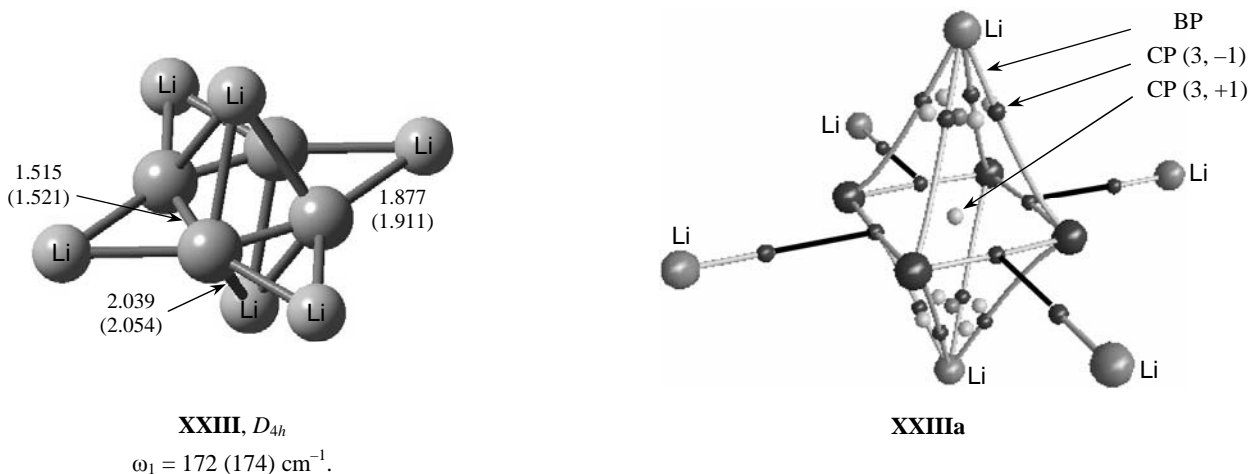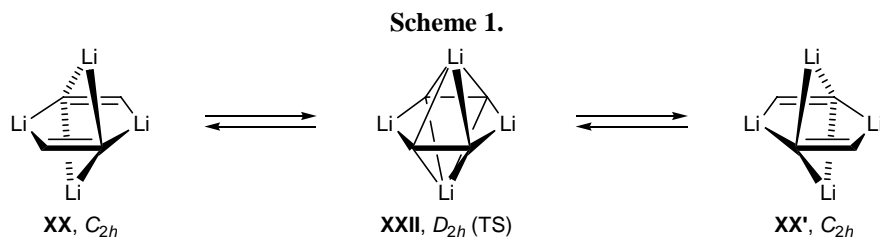

XXIII, D_{4h}
$\omega_1 = 172$ (174) cm^{-1}.
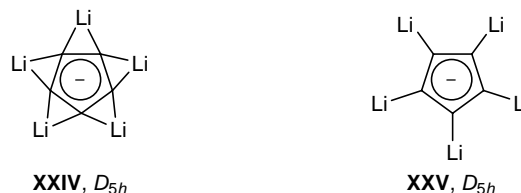

XXIIIa

Fig. 3. Geometric parameters and least harmonic vibration frequencies of structure **XXIII**, according to DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G**] calculations.

Scheme 1.

XX, C_{2h} **XXII**, D_{2h} (TS)   **XX'**, C_{2h}

four-coordinate carbon atoms (Fig. 3). Two lithium atoms in **XXIII** occupy apical positions, and four lithium atoms are equatorial. Topological analysis of electron density distribution according to Bader shows that the apical lithium atoms are linked to all carbon atoms and that equatorial lithium atoms are coordinated to mid C–C bonds, i.e., to the double C=C bonds as in π-complexes (Fig. 3).

Perlithiocyclopentadienyl anion $C_5Li_5^-$. According to the calculations, only bridged structure **XXIV** of perlithiocyclopentadienyl anion $C_5Li_5^-$ is stable, while classical structure **XXV** does not occupy energy minimum ($\lambda = 9$) and is less stable than the bridged form by more than 120 kcal/mol. Introduction of one or two additional lithium atoms into the apical positions gives neutral form **XXVI** or cationic species **XXVII**, respectively, which are stabilized as five-point star-like structures shown in Fig. 4. In going from anion **XXIV** to

neutral form **XXVI** and then to cation **XXVII**, the bond lengths therein almost do not change.

XXIV, D_{5h} **XXV**, D_{5h}

The molecular graphs shown in Fig. 4 indicate that all carbon atoms in structure **XXIV** are planar four-coordinate, in **XXVI**, five-coordinate, and in **XXVII**, six-coordinate.

Perlithiobenzene C_6Li_6. Like four- and five-membered analogs, the classical structure of perlithiobenzene C_6Li_6 (**XXVIII**) is unstable ($\lambda = 12$); its stable planar form **XIV** contains bridging lithium atoms.

XXIV, D_{5h} **XXVI**, C_{5v} **XXVII**, D_{5h}

ω_1, cm^{-1}:   130   136   159
           119   130   158

XXIVa, D_{5h} **XXVIa**, C_{5v} **XXVIIa**, D_{5h}
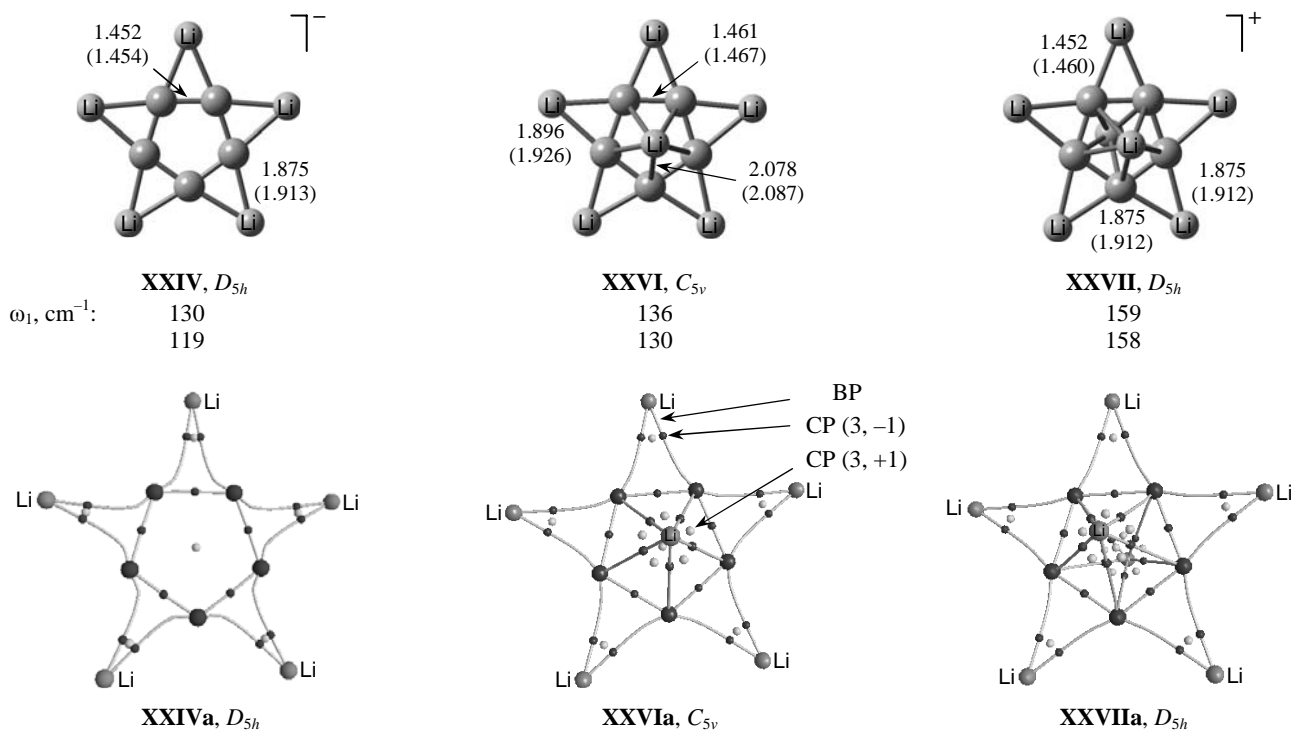
Fig. 4. Geometric parameters and least harmonic vibration frequencies of structures **XXIV–XXVII**, according to DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G**] calculations.
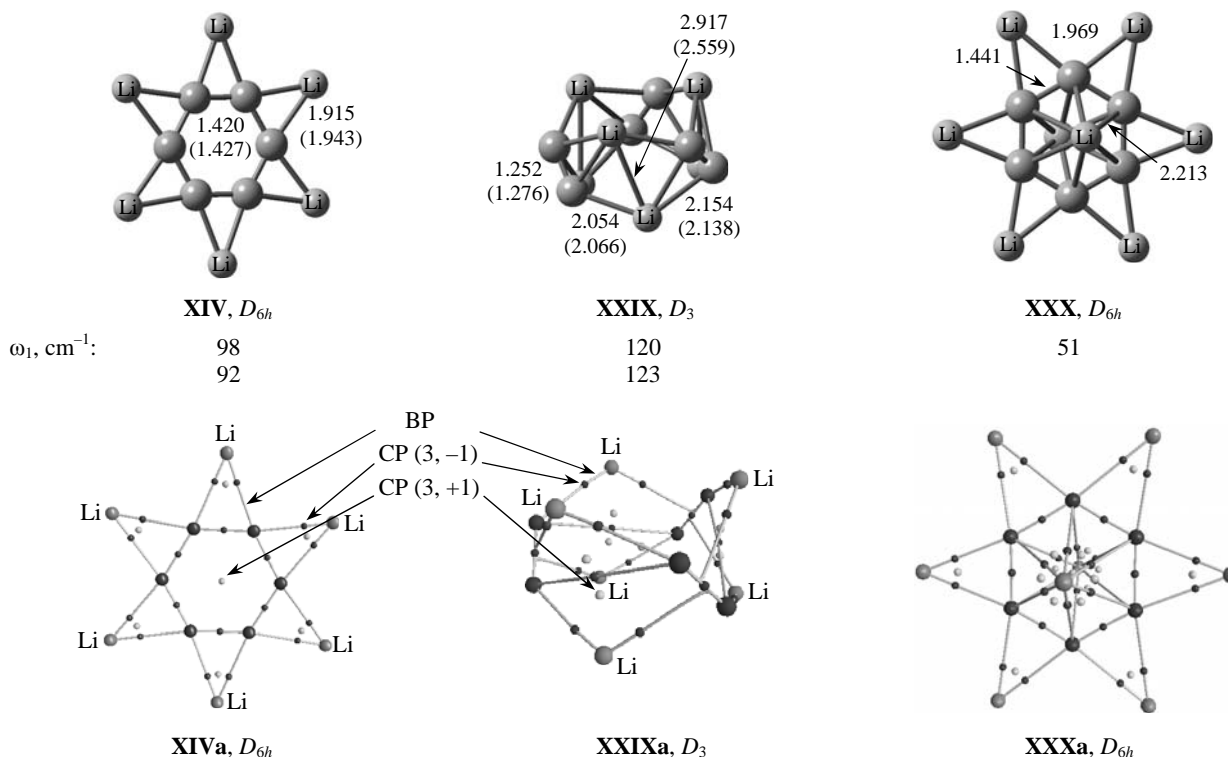
XIV, D_{6h}	**XXIX**, D_3	**XXX**, D_{6h}
ω_1, cm^{-1}: 98	120	51
92	123	

XIVa, D_{6h}	**XXIXa**, D_3	**XXXa**, D_{6h}

Fig. 5. Geometric parameters and least harmonic vibration frequencies of structures **XIV**, **XXIX**, and **XXX**, according to DFT (B3LYP/6-311+G**) and *ab initio* [MP2(full)/6-311+G**] calculations.

Here, as in structure **XXIV**, all carbon atoms have planar four-coordinate configuration (see the molecular graph in Fig. 5).

XXVIII, D_{6h}	**XXIX**, D_{6h}
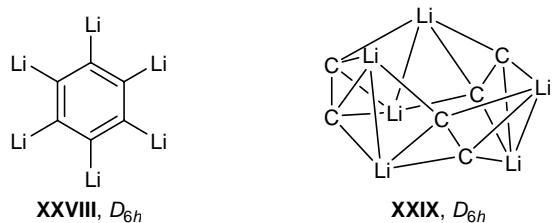
Although star-like structure **XIV** corresponds to a fairly deep local minimum on the PES, the results of calculations [20] predict that the global minimum is occupied by nonplanar structure **XXIX** with a D_3 symmetry. Its geometric parameters and the corresponding molecular graph (**XXIXa**) are shown in Fig. 5. According to our calculations, this structure is energetically more favorable than planar bridging form **XIV** by more than 60 kcal/mol. The other isomeric structures, e.g., like perlithioprismane or substituted benzene with a D_{3h} symmetry, are destabilized by more than 50 kcal/mol relative to structure **XIV**; they are not discussed in the present article. Introduction of two

additional lithium atoms into the apical positions of **XIV** leads to system **XXX** without reduction in the stability of the D_{6h} form, and Bader's topological analysis suggests six-coordinate configuration of all carbon atoms in that system.

Thus the results of our theoretical study indicate that perlithioannulenes are stabilized as planar forms with bridging lithium atoms, yielding attractive three-, five-, and six-point star-like structures with hypercoordinate carbon atoms. These structures are the most stable for perlithioannulenes C_nLi_n with $n = 3$ and 5. The most stable structures for even-numbered annulenes ($n = 4$, 6) are less symmetric dimeric $(C_2Li_2)_2$ (**XX**, $n = 4$) and trimeric $(C_2Li_2)_3$ (**XXIX**, $n = 6$).

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