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BeO analogues of annulated cyclooctatetraene and cyclodecapentaene as new inorganic species with unusual multiple hypervalent O···O interactions

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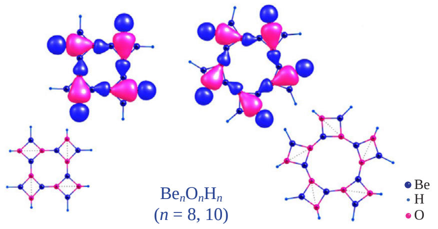
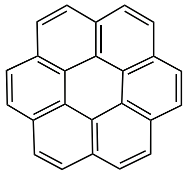
Density functional theory calculations at the level of B3LYP/6-311+G(df,p) and wB97XD/6-311+G(df,p) predict stability of the BeO analogues of annulated cyclooctatetraene and cyclodecapentaene, $Be_nO_nH_n$ (n = 8, 10), which uniquely feature the presence of multiple hypervalent diagonal O···O interactions within the four-membered rings.



Keywords: beryllium oxide, BeO-based nanostructures, annulated cyclooctatetraene derivatives, hypervalent interaction, hyperbonding, hypercoordination, oxygen–oxygen interactions, non-classical systems, planar tetracoordinated oxygen, inorganic building block.

The development of approaches to the design of new 2D structures is currently one of the active areas of experimental and theoretical research, inspired by the interesting properties of such type systems.[1,2] Among the discovered technologically useful properties of two-dimensional crystalline systems are superconductivity, unique magnetic and optical parameters, high hardness, rigidity and others. The building blocks of most polycyclic nanosystems are simple annulated compounds (such as circulenes) containing a central cyclic fragment partially or completely fused to other rings. For example, the molecules of coronene **1**, cyclobutadiene-annulated cyclooctatetraene **2** and antikekulene **3** can be considered as the building blocks of



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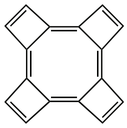

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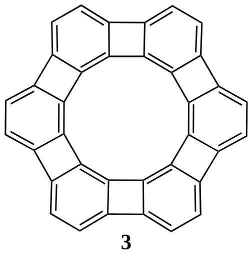

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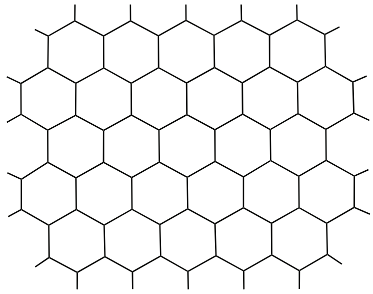

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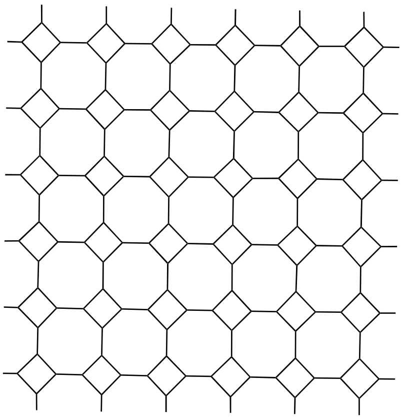

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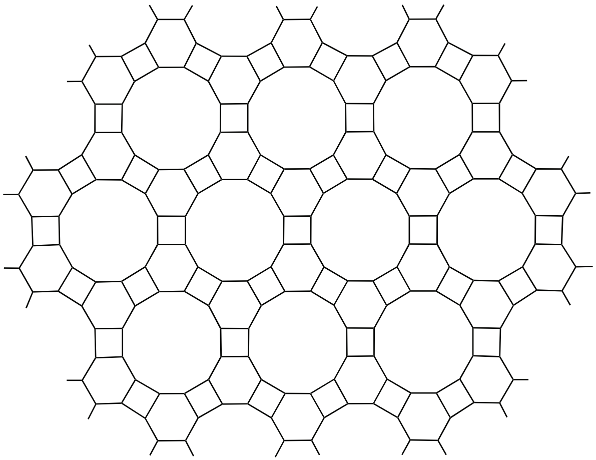

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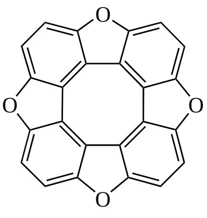
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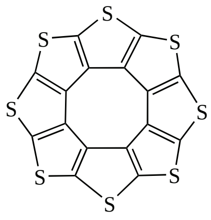
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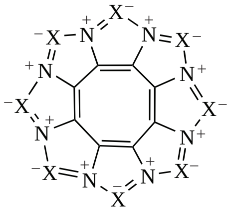
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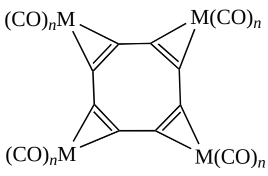

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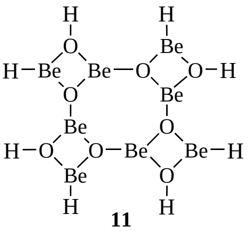
graphene **4** and its allotropic modifications **5** and **6**, respectively.[3,4]

The use of systems with unusual geometric and electronic structures as building blocks is especially interesting, since it ensures the formation of nanostructures with extraordinary physical and chemical properties. For example, octagraphene (T-graphene) **5**, which includes cyclooctatetraene structural blocks in a non-standard planar configuration, is, according to theoretical studies,[5] one of the hardest materials characterized by record superconductivity. The study of parent polycyclic annulated systems, which are the building blocks of nanosystems, allows a better understanding of the nature of bonding and stability and helps to specifically regulate their properties. Annulated systems of type **1**–**3** are also interesting as ligands for the formation of complex molecular systems, for example, of the sandwich type.[6,7]

One of the effective approaches to the search for new compounds is the approach based on the construction of heterosubstituted systems, which makes it possible to significantly expand the range of characteristics and properties of the parent hydrocarbon compounds. Many series of new heterocyclic and organometallic derivatives have been formed and studied based on the planar annulated cyclooctatetraene framework. Examples of experimentally obtained derivatives are tetraoxa[8]circulene **7**, including polymeric forms,[8] as well as octathia[8]circulene **8** and other chalcogen-heterosubstituted derivatives.[9] Theoretically studied systems are pnictogen-substituted systems **9** (X = P, As, BF_2),[10,11] metal carbonyl derivatives **10**[12] with $Cr(CO)_5$, $Fe(CO)_4$, $Ni(CO)_3$ and $Ni(CO)_2$ moieties and a number of other systems.[13,14] The planar cyclooctatetraene derivatives have found wide application in modern optoelectronic devices, such as organic light-emitting diodes and organic field-effect transistors.[13]

BeO derivatives are isoelectronic analogues of carbon systems where each CC group is replaced by a BeO group. The actively studied[15–18] BeO-based nanostructures are characterized by excellent mechanical, thermal and optical properties. A further insight into the structure and stability of small polycyclic BeO compounds may open additional opportunities for the design of new unusual BeO-based nanostructures. In this paper, we present the results of a study of the structure and stability of BeO analogues of annulated cyclooctatetraene and cyclodecapentaene (the $Be_8O_8H_8$ **11** and $Be_{10}O_{10}H_{10}$ **12** systems, respectively).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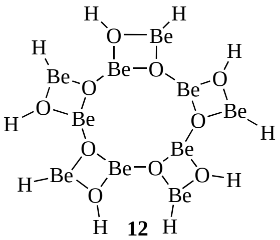
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Density functional theory calculations were performed with the B3LYP[19] and wB97XD[20] functionals and the valence-split basis set 6-311+G(df,p)[21] using the Gaussian 16 program package.[22] Stationary points on the potential energy surfaces were localized with full geometry optimization, identified by calculating the matrix of second derivatives (force constants) and checked for stability of Hartree–Fock solutions. Natural bond orbital (NBO) analysis[23] was performed with the help of the NBO 6.0 program.[24] The AIM (Atoms in Molecules) analysis[25] was carried out using the AIMAll Professional program.[26] The drawings were made using the ChemCraft[27] program suite with the calculated atomic coordinates as the input parameters.

As the calculation results show, the C_{4h}-symmetric structure **11** with a central eight-membered cycle and the C_{5h}-symmetric structure **12** with a central ten-membered cycle correspond to energy minima ($\lambda = 0$, where λ denotes the number of negative eigenvalues of the matrix of second derivatives) on the potential energy surface. The geometric and energy parameters of structures **11** and **12** are presented in Figure 1 and Table 1.

Both systems are characterized by a planar structure with pronounced alternation of Be–O bonds within the central ring. The calculated Be–O bond lengths are 1.48–1.60 Å, which is shorter than 1.89 Å[28] in bulk binary BeO compounds of the rock salt type and fall within the range of the Be–O bond lengths in theoretically studied monolayers, such as 1.66 Å in graphene-like hexagonal BeO.[16]

The calculated diagonal O···O distances within the four-membered cycles in both systems are almost identical, amounting to 2.4 Å, and are significantly shorter than the sum of the van der Waals radii (2.8 Å[29]). The Be–O–Be and O–Be–O bond angles of the four-membered fragments are ~90° and are significantly smaller than the parameters of the three-coordinated sp^2-hybridized units (120°), indicating significant steric strain in

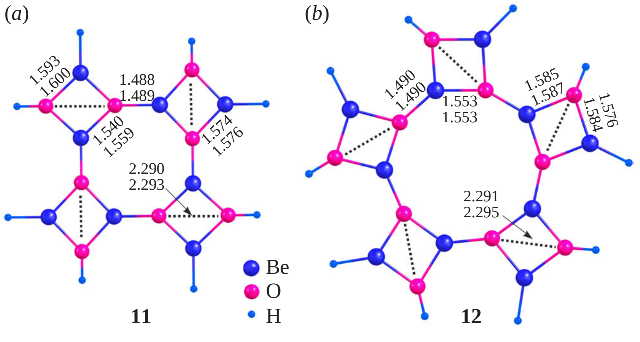

Figure 1 Bond lengths (Å) in systems (*a*) **11** (C_{4h}) and (*b*) **12** (C_{5h}) calculated using the B3LYP (values in roman font) and wB97XD (values in italics) methods with the 6-311+G(df,p) basis set.

Table 1 Energy parameters of systems **11** and **12** calculated using the B3LYP and wB97XD methods with the 6-311+G(df,p) basis set.

Structure	Symmetry	Method	$E_{tot}{}^a$/a.u.	ZPE^b/a.u.	λ^c	$\omega_1{}^d$/cm^{-1}	$\Delta_{H-L}{}^e$/eV
11	C_{4h}	B3LYP	−725.952753	0.129536	0	29.8	6.9
		wB97XD	−725.663812	0.129550	0	33.3	10.6
12	C_{5h}	B3LYP	−907.441219	0.162572	0	19.9	7.0
		wB97XD	−907.081668	0.161893	0	23.3	10.7

[a] Total energy. [b] Harmonic zero-point energy correction. [c] Number of negative eigenvalues of the Hessian. [d] Value of the lowest harmonic vibration frequencies. [e] HOMO–LUMO energy gap.

Table 2 NICS(1) indices for central and four-membered cycles in systems **11** and **12** calculated using the B3LYP and wB97XD methods with the 6-311+G(df,p) basis set.

Method	NICS(1) (ppm)			
	System **11**		System **12**	
	Central cycle	Four-membered cycle	Central cycle	Four-membered cycle
B3LYP	−0.1	−2.9	0.1	−2.9
wB97XD	−0.1	−2.8	0.1	−2.7

the four-membered rings. Thus, as in the case of carbon derivatives, one of the factors stabilizing the planar forms **11** and **12** is steric constraint associated with the annulation of the central ring by strained four-membered rings.

An assessment of the aromaticity of systems **11** and **12** using the NICS(1) indices,[30] which are nucleus-independent chemical shifts at a point 1 Å above the ring center, shows (Table 2) that the central rings of both systems (the eight-membered ring in system **11** and the ten-membered ring in system **12**) can be characterized as non-aromatic, since the NICS(1) index values are close to zero. The peripheral four-membered rings are characterized by negative NICS(1) indices and are weakly aromatic, which is an additional factor in the stabilization of the BeO derivatives under consideration.

The analysis of the nature of the bonding using the AIM approach shows that each oxygen atom in systems **11** and **12** forms four bond paths, three of which correspond to the interaction with the beryllium environment, and one corresponds to the interaction with the opposite oxygen center in the four-membered fragment (Figure 2). Thus, the oxygen atoms in the systems under consideration can be characterized as non-classical planar four-coordinated centers. The stabilization of these non-classical centers is ensured by the combined influence of steric (inclusion in strained rings) and electronic (σ-donor and π-acceptor environment and aromaticity of the rings) factors,[31–33] which are fully realized in systems **11** and **12**. The diagonal interaction between the oxygen atoms within the four-membered cycles, discovered within the AIM approach, is another (rather unusual) factor determining the structure of the considered BeO systems.

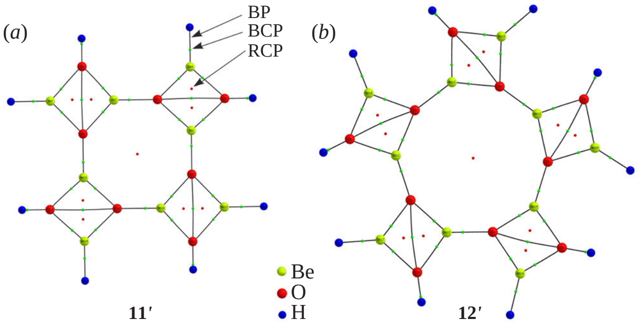

Figure 2 Bader molecular graphs **11′** and **12′** of structures (*a*) **11** and (*b*) **12**, respectively, indicating Bader bond paths (BPs), bond path critical points (BCPs) and ring critical points (RCPs).

The critical points of the bond paths corresponding to the O···Be interactions are characterized by positive values of the Laplacian of the electron density and low values of the electron density (Table 3), which corresponds to ionic type interactions (closed shells).[34] Another criterion to evaluate the covalent character of the bonds is the ratio of the kinetic and potential energy densities, $-G(r)/V(r)$.[35] If this ratio is greater than 1, the interaction is non-covalent. Between 0.5 and 1, the interaction is partially covalent, and when this ratio is less than 0.5, the interaction is covalent. A ratio of $-G(r)/V(r)$ close to 1 confirms the predominantly ionic nature with a partially covalent character of the O–Be interactions. The negative sign of the total electron energy density $H(r)$ also indicates some degree of covalence of the bonds. Likewise, O···O interactions can be interpreted as predominantly closed-shell interactions with a partially covalent character, which is confirmed by the positive values of the Laplacian, low values of the total electron density, the $-G(r)/V(r)$ ratio close to 1 and the negative sign of the total electron energy density $H(r)$ at the bond critical points.

As shown by the data of MO and NBO analyses, the intramolecular O···O interaction in the four-membered rings is due to the donation of electron density from the lone electron pair of oxygen to the antibonding orbital of the OH σ-bond (Figure 3). This mechanism is identical to that of the hypervalent interaction between electron-rich centers in systems of a wide variety of structural types.[31,36–38] In the systems under consideration, almost ideal steric conditions for such interaction are realized, which are ensured by the optimal mutual orientation of the interacting orbitals in the four-membered rings, as well as the forced approach of the oxygen centers. Due to the high

Table 3 Wiberg bond indices, bond lengths and AIM parameters for bond critical points in systems **11** and **12** calculated using the B3LYP and wB97XD methods with the 6-311+G(df,p) basis set.

System	Bond	Method	Bond length/Å	WBI[a]	$\rho(r)$[b]/a.u.	$\nabla^2\rho(r)$[c]/a.u.	$V(r)$[d]/a.u.	$G(r)$[e]/a.u.	$H(r)$[f]/a.u.	$-G(r)/V(r)$
11	O–O	B3LYP	2.290	0.02	0.053	0.220	−0.060	0.057	−0.003	0.95
		wB97XD	2.293	0.01	0.052	0.220	−0.060	0.057	−0.002	0.95
	O–Be(1)	B3LYP	1.574	0.14	0.089	0.618	−0.168	0.161	−0.007	0.96
		wB97XD	1.577	0.13	0.087	0.625	−0.165	0.161	−0.004	0.98
	O–Be(2)	B3LYP	1.560	0.15	0.093	0.645	−0.181	0.171	−0.010	0.94
		wB97XD	1.559	0.15	0.093	0.663	−0.180	0.173	−0.007	0.96
	O–Be(3)	B3LYP	1.488	0.18	0.113	0.826	−0.236	0.221	−0.015	0.94
		wB97XD	1.489	0.18	0.112	0.840	−0.234	0.222	−0.012	0.95
12	O–O	B3LYP	2.291	0.01	0.053	0.217	−0.061	0.057	−0.003	0.93
		wB97XD	2.295	0.01	0.053	0.218	−0.060	0.057	−0.003	0.95
	O–Be(1)	B3LYP	1.585	0.14	0.087	0.595	−0.163	0.156	−0.007	0.96
		wB97XD	1.589	0.13	0.085	0.603	−0.160	0.156	−0.005	0.98
	O–Be(2)	B3LYP	1.553	0.15	0.094	0.661	−0.184	0.174	−0.010	0.95
		wB97XD	1.553	0.15	0.093	0.678	−0.183	0.176	−0.007	0.96
	O–Be(3)	B3LYP	1.490	0.18	0.113	0.822	−0.234	0.220	−0.014	0.94
		wB97XD	1.490	0.18	0.111	0.838	−0.233	0.221	−0.012	0.95

[a] Wiberg bond index. [b] Electron density. [c] Laplacian of electron density. [d] Potential electron energy density. [e] Kinetic electron energy density. [f] Total electron energy density.

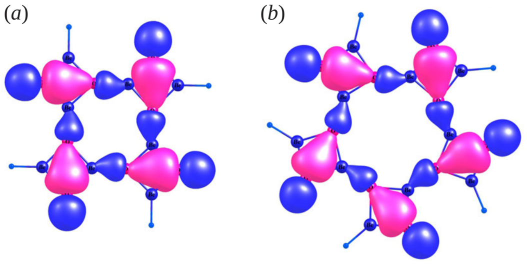

Figure 3 Orbital interactions $n_O \rightarrow \sigma^*_{OH}$ in systems (*a*) **11** and (*b*) **12**, providing the formation of hypervalent O···O bonds.

electronegativity of oxygen, its hypervalent bonds are much less common than those formed by sulfur and phosphorus. Therefore, the presented systems containing several hypervalent O···O bonds are rather unusual. The aromatic nature of the four-membered rings also facilitates the implementation of hypervalent interactions.

Thus, compounds **11** and **12** represent the first examples of BeO analogues of annulated derivatives of cyclooctatetraene and cyclodecapentaene, which can serve as ligands or building blocks for constructing complex systems. The stabilization of planar structures is determined by steric (surrounding the central ring by sterically strained fragments) and electronic (aromaticity of four-membered rings and hypervalent interactions in them) effects. The presented systems are an unusual example of compounds in which multiple hypervalent O···O interactions are simultaneously realized.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.10.010.

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