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Boron nitride substituted 12-crown-4 ether: Theoretical study of structural, thermochemical, and nonlinear optical properties

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ABSTRACT

The structures and stability of 531 novel boron nitride substituted isomers of 12-crown-4 ether verified theoretically. For a collection of 23 selected BN isomers, structural geometry, vibrational stability, energy gaps, natural bond population analysis, and nonlinear optical responses investigated theoretically. The changes of standard enthalpies for ionization reactions and electron affinity reactions studied as well. The presence of double bonds in BN isomers of 12c4 might develop their host-guest chemistry. Moreover, the results of ionization potentials and electron affinities calculated by single point calculations showed good correlation with those of thermochemistry ones. The observed correlations clearly suggest a lower cost of computations for the mentioned physical properties. The polarizability and hyperpolarizability results introduced some BN substituted crown ethers as efficient candidates for construction of practical devices for optical harmonic generation and signal processing.

Keywords: Boron nitride crown ethers; 12-crown-4 ether; Density functional theory; NBO analysis; Nonlinear optical response

INTRODUCTION

Macrocyclic compounds have attracted significant attention because of their ability to form a binding host cavity for specific ligands (guests). Crown ethers – multidentate macrocyclic compounds- as "host" prototypes entrap various guest species providing insight into the molecular recognition [1-5] especially in biological systems and biochemical processes. The host-guest interactions are dependent on the size of the crown ether, the type of donor atom (oxygen, nitrogen or sulfur), and polarity of solvent. After the first characterization of crown ethers [6, 7] they have found extensive applications in biology [8, 9] and science [10-14]. There are many studies on vibrational spectra of 12-crown-4 (12c4 or 1,4,7,10-tetraoxacyclododecane), and its alkali metal cation complexes [15-21].

The structure and binding energies of 18-crown-6 complexes with alkaline earth cations were examined at RHF and MP2 levels of theory using 6-31+G basis set [22]. Proton affinity of some free crown ether were calculated at MP2/6-31+G**

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level [23]. The vibrational spectra of 12-crown-4-alkali metals complexes were evaluated at MP2 level and using 6-311++G** basis set [24]. Armentrout *et al* studied quantitative interactions of alkali metal cations with the cyclic 12-crown-4 polyether ligand [25] theoretically and experimentally. The bond dissociation energies of complexes determined using threshold collision-induced dissociation of these complexes with xenon in a guided ion beam tandem mass spectrometer. Density functional theory was employed to study the interaction of alkali metal cations with crown ether-bridged Z-stilbene. Density functional theory through B3LYP hybrid functional with 6-31G(d) and, LANL2DZ basis set used [26]. Klipfel and the co-workers treated some crown ethers and their cation complexes by ab initio density functional theory. They applied a genetic algorithm (GA) to achieve the minimum energy of the structures [27] due to floppy structure of selected crown ethers. In an experimental and theoretical study at 2011, isolated complexes of 18-crown-6 ethers with alkaline-earth metal cations were investigated [28]. It has been shown that computations at the B3LYP/6-311++G(2d,2p), and B3LYP/aug-cc-pVDZ levels of theory agree well with the most salient features of the experimental spectra. Density functional theory calculations performed for crown ether complexes of tin(II) trifluoromethane sulfonate to evaluate the observed structural features experimentally [29].

Quantum chemical investigations on a series of crown ethers with narrow cavities bound to alkali metal ions were performed. The hybrid functional of DFT; B3LYP along with large split valence 6-311++G(d,p) basis set were applied [30]. Yanez and his co-workers theoretically studied the structural and bonding properties of neutral and anionic Five-membered rings containing BN Bonds. They also used EOM-CCSD method to obtain the ^{15}N-^{11}B and ^{1}H-^{11}B spin-spin coupling constants[31]. As boron nitride compounds are isoelectronic to carbon materials with similar structure, the present study is devoted to a theoretical investigation of some novel boron nitride derivatives of 12-crown-4 ether. Such compounds have not been studied yet. In this work we will use DFT method to investigate stability and various properties of the novel BN crown ethers. Among 531 BN isomers of 12-crown-4 ether, we considered those with an equal number of boron and nitrogen atoms. After verification the stability of all BN isomers, we selected 23 BN isomers for the study of various molecular properties like vibrational stabilities, NBO analysis, and thermochemistry of electron exchange reactions, polarizabilities, and nonlinear optical responses.

THEORETICAL METHODS

Boron nitride compounds are isoelectronic to carbon materials with similar structures. To construct novel boron nitride derivatives of 12-crown-4 ether (Fig. 1), the carbon atoms of the crown ether substituted with B and N atoms. The total number of boron atoms and nitrogen atoms chose to be equal. The numbers of isomers are shown in Table 1.

First, all of 531 BN isomers fully optimized to achieve the proper equilibrium geometries. Then the vibrational frequencies were calculated to identify probable imaginary frequencies of the isomers. The both mentioned calculations were performed with B3LYP [32, 33] hybrid functional of DFT along with 6-31+G(d,p) basis set [34, 35]. To reduce the number of final computations in each category we considered the isomers with the same number of boron and nitrogen atoms. The selections of BN isomers included the isomer with the most favorable electronic energy and also the isomer with the alternate arrangement of substituted boron and nitrogen atoms (See Figs 1-4).

Table 1. Molecular formula (M.F.), category of isomers, different combinations of substituted BN atoms for each category of BN isomers, number of isomers of 12-crown-4 ether

M.F.	Category of Isomers	Combinations	# Isomers
$C_6H_{14}B_aN_bO_4$	(a+b=2)	(1B,1N)	4
$C_4H_{12}B_aN_bO_4$	(a+b=4)	(1B,3N), (2B,2N), (3B,1N)	145
$C_2H_{10}B_aN_bO_4$	(a+b=6)	(1B,5N), (2B,4N), (3B,3N), (4B,2N), (5B,1N)	303
$H_8B_aN_bO_4$	(a+b=8)	(1B,7N), (2B,6N), (3B,5N), (4B,4N), (5B,3N), (6B,2N), (7B,1N)	79

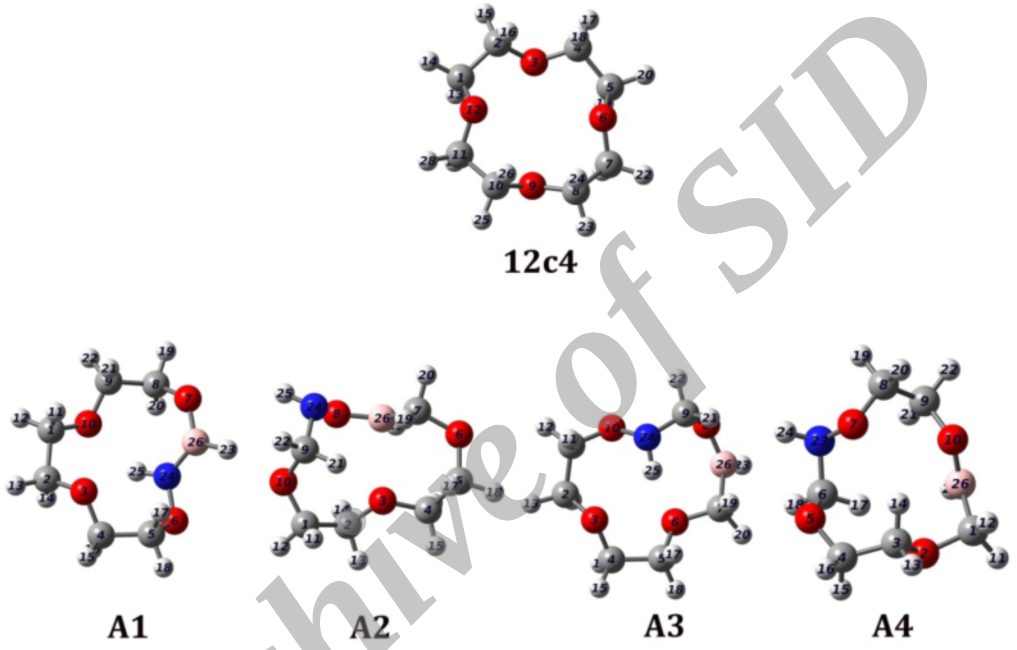

Fig. 1. Spatial representations of 12c4 ether, and category 1 isomers of 12c4 ether.

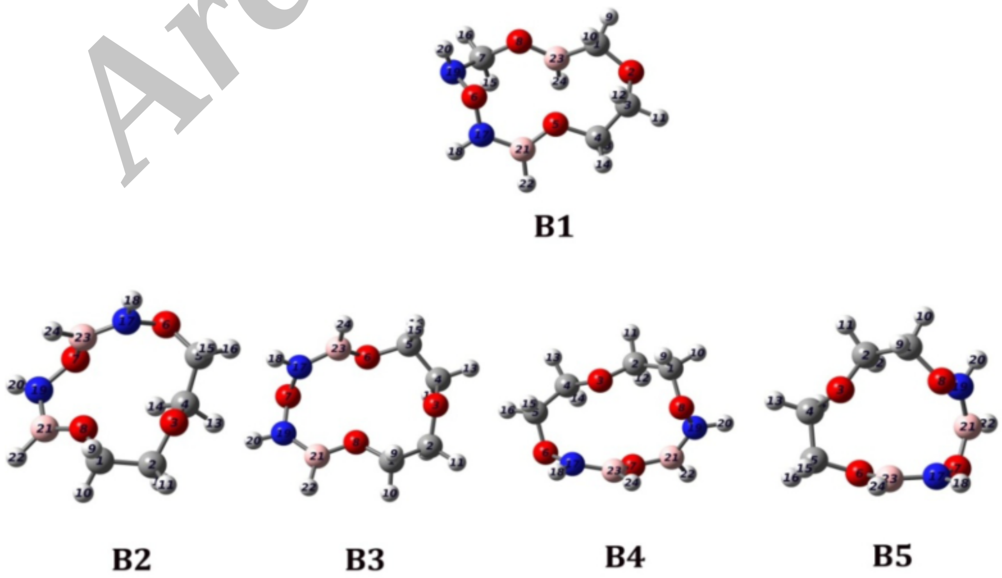

Fig. 2. Spatial representations of category 2 isomers of 12c4 ether.

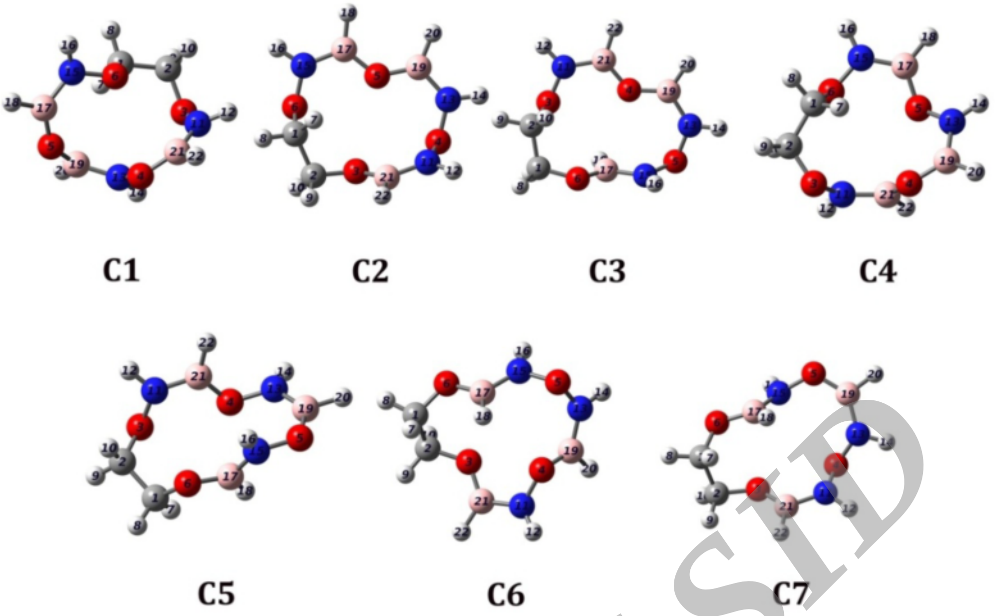

Fig. 3. Spatial representations of category 3 isomers of 12c4 ether.

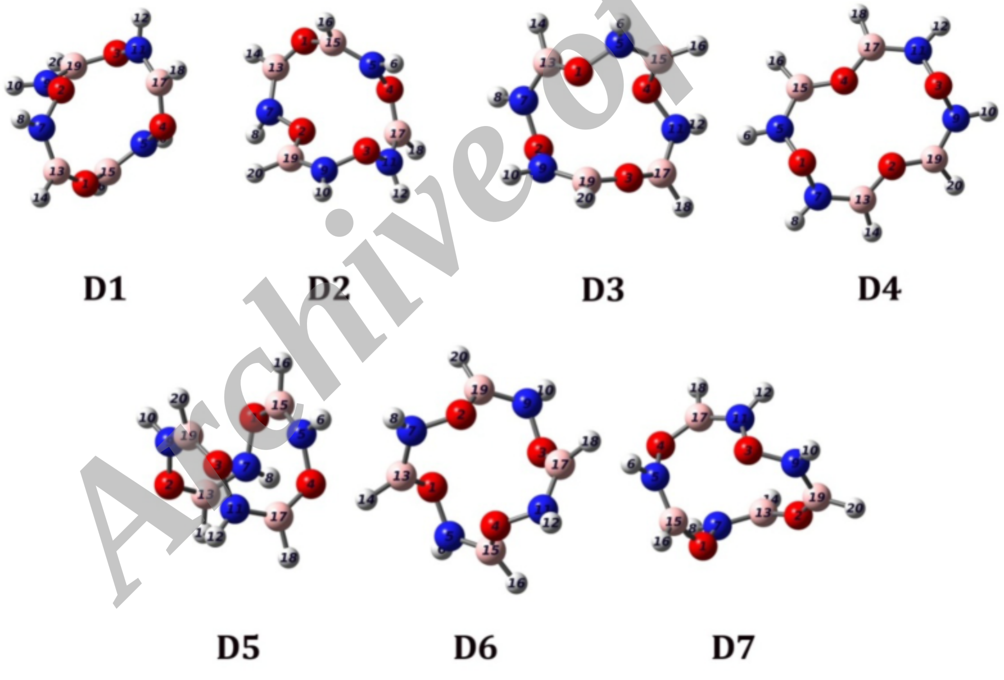

Fig. 4. Spatial representations of category 4 isomers of 12c4 ether.

Then selected BN isomers optimized using B3LYP hybrid functional with 6-311++G(d,p) large basis set [36]. B3LYP is the most widely used hybrid generalized gradient approximation (GGA) functional [37-41]. The natural bonding orbitals (NBO) calculations [42]performed using NBO 3.1 program as implemented in the Gaussian 98 package. The NBO calculations carried out at the same level of theory with a tight convergence criterion. The hyperconjugative interaction energy deduced from the second-order perturbation approach [43]. We also calculated changes of enthalpies of ionization and electron affinities of BN crown ethers at the level of B3LYP/6-311++G (d, p) at 298.15 K and 1 atm.

The single point computations of ionization potentials and electron affinities give vertical ionization potentials and the vertical electron affinities from the bottom of the potential well of the neutral species, respectively. Single point computations performed at B3LYP/6-311++G (d,p) level with tight convergence criterion using the optimized geometries of the neutral molecules [44]. Polarizabilities and hyperpolarizabilities for all crown ethers have been performed using B3LYP/6-311++G (d, p) model chemistry. We computed the polarizabilities and hyperpolarizabilitiesby coupled-perturbed HF (CPHF) [45] method. The definition for the isotropic polarizability is [46]:

$$\alpha= (1/3)(\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}) \tag{1}$$

the polarizability anisotropy invariant is:

$$\Delta\alpha= (1/2)\ [(\alpha_{XX}-\alpha_{YY})^2 + (\alpha_{YY}-\alpha_{ZZ})^2 + (\alpha_{ZZ}-\alpha_{XX})^2]^{1/2} \tag{2}$$

And the average hyperpolarizability is:

$$\beta_{\|}= (1/5)\Sigma_i(\beta_{iiZ}+\beta_{iZi}+\beta_{Zii}) \tag{3}$$

All calculations carried out by Gaussian98 program [47].

RESULTS AND DISCUSSION

1. Structures and frequencies

All optimized geometries of 23 selected BN isomers stemmed from 12-crown-4 ether are displayed in Figs 1-4. Replacing carbon atoms of 12-crown-4 ether with B and N atoms broke or changed the symmetry of original ether. The exceptions were D5 and D6 isomers (Fig. 4) with S_4 point group like 12-crown-4 ether. The optimizations of selected structures performed by B3LYP method of DFT with 6-311++G (d, p) basis set. The DFT method marked the lowest energy isomer in each category: A1 from $C_6(BN)H_{14}O_4$ (Fig. 1), B4 from $C_4(BN)_2H_{12}O_4$ (Fig. 2), C2 from $C_2(BN)_3H_{10}O_4$ (Fig. 3), and D4 from $(BN)_4H_8O_4$ (Fig. 4) (Table 2). Fig. 1 shows the structures with the lowest electronic energy. In the lowest energy structure of $C_6(BN)H_{14}O_4$ category, B and N atoms were neighbors joining with a chemical bond. But in other categories the B and N arrays the structure with the lowest electronic energy did not have an alternative order.

The calculated ZPE-corrected energies also reflected the same trend as total electronic energies in each category. None of selected BN isomers of 12-crown-4 ether showed imaginary frequencies at B3LYP/6-311++G (d, p) level of theory. Calculated relative energies of isomers in each category were small (Table 2) indicating that all isomers in each category could be existed. Isomer B3 in $C_4B_2N_2H_{12}O_4$ category and isomer C3 in $C_2B_3N_3H_{10}O_4$ category showed very small relative energies among isomers of related category. The Table also shows a narrower range of relative energy in $C_2B_3N_3H_{10}O_4$ category in comparison with the others. The ZPE-corrected relative energies showed the same trend as E_rs (Table 2).

A closer look at isomers in $B_4N_4H_8O_4$ category revealed D5 and D6 as conformers (Fig. 4). D5 with atotal electronic energy of -624.39364 au is more favorable conformer (Table 2). The change of enthalpy of conversion for D5→D6 reaction at 1.00 atm and 298.15 K was Δ_rH^0= 63.77 kJ/mol. The change of enthalpy of conversion for cyclohexane Boat→Chair conversion was Δ_rH^0= 27.21 kJ/mol at the same level of theory and thermodynamic conditions. The source of this difference might be related to boron-nitrogen double bonds in the mentioned structures. These double bonds tend to lock each conformer in its relaxed geometry and make rotations around related π-bonds more difficult than cyclohexane.

Table 2. Total electronic energies (in a.u.), ZPE-corrected energies (in a.u.), relative energies (E_r, in kcal/mol), ZPE-corrected relative energies (in kcal/mol) of BN-derivatives of 12-crown-4 ether at B3LYP/6-311++G (d,p) level of theory*

Compounds	TEE	ZPE-corrected Energy	E_r	ZPE-corrected E_r
		$C_8H_{16}O_4$		
12c4	-615.49737	-615.25349	-	-
		$C_6BNH_{14}O_4$		
A1	-617.72967	-617.51152	0.00	0.00
A2	-617.68441	-617.46639	28.40	28.32
A3	-617.68439	-617.46700	28.41	27.93
A4	-617.68541	-617.46753	27.77	27.60
		$C_4B_2N_2H_{12}O_4$		
B1	-619.92469	-619.73328	24.02	24.00
B2	-619.94969	-619.75841	8.33	8.24
B3	-619.96221	-619.77122	0.47	0.19
B4	-619.96296	-619.77154	0.00	0.00
B5	-619.95449	-619.76279	5.32	5.49
		$C_2B_3N_3H_{10}O_4$		
C1	-622.18121	-622.01636	8.11	8.18
C2	-622.19413	-622.02939	0.00	0.00
C3	-622.19275	-622.02797	0.87	0.90
C4	-622.17863	-622.01437	9.73	9.43
C5	-622.1774	-622.01228	10.5	10.74
C6	-622.18343	-622.01862	6.71	6.76
C7	-622.18088	-622.01593	8.31	8.45
		$B_4N_4H_8O_4$		
D1	-624.40529	-624.26739	14.70	14.82
D2	-624.40666	-624.26915	13.84	13.71
D3	-624.39341	-624.25664	22.16	21.56
D4	-624.42871	-624.29100	0.00	0.00
D5	-624.39364	-624.25446	22.01	22.94
D6	-624.36805	-624.23079	38.06	37.79
D7	-624.40529	-624.26740	14.70	14.82

*For more details refer to Figs 1-4.

2. Energy gaps, Electric dipole moments, and NBO analysis

The energy gaps of BN isomers of 12-crown-4 ether are collected in Table 3. We used TD-DFT [48] with B3LYP/6-311++G (d, p) model chemistry for HOMO-LUMO gaps calculations. Zhang and Musgrave showed that TD-DFT with all functionals accurately predicts the HOMO-LUMO gaps [49]. 12-crown-4 ether had a band gap of about 7.3 eV. Substituting B and N atoms for carbon atoms of 12-crown-4 ether decreased the band gaps but the changes were not significant. The largest change observed for A3 isomer (Fig. 1) from $C_6BNH_{14}O_4$ category. In Fig. 5 one can also find 3D representations of boundary molecular orbitals (HOMO and LUMO) of 12-crown-4 ether and its BN isomers.

One of the key features of crown ethers is their solubility. The solubility of compounds profoundly is affected by their electric dipole moment. Due to the symmetric structure of 12-crown-4 ether the whole structure does not show polarity. As it is known the inner space of the molecule is polar which can interact with positive small species and host them. The outer regions of 12-crown-4 ether are nonpolar which make it soluble in nonpolar solvents.

Table 3. Energy gap (**ΔE**, in eV) Electric Dipole moment ($\boldsymbol{\mu}$ in Debye) and the smallest vibrational frequency ($\boldsymbol{\nu}_{\min}$, in cm^{-1}) calculated in the B3LYP/6-311++G (d, p) level of theory[*]

Category	Crown ether	ΔE	μ_{ED}	$\nu_{\min}$
$C_8H_{16}O_4$	12c4	7.3	0	27
$C_6BNH_{14}O_4$	A1	6.8	4.4	54
	A2	6.3	3.3	53
	A3	5.6	2.9	53
	A4	5.7	1.4	67
$C_4B_2N_2H_{12}O_4$	B1	6.3	1.7	59
	B2	6.3	2.1	25
	B3	6.2	1.2	51
	B4	6.3	3.4	71
	B5	6.2	3.4	44
$C_2B_3N_3H_{10}O_4$	C1	6.3	4.4	50
	C2	6.3	2.7	52
	C3	6.1	2.8	73
	C4	6.3	3.5	47
	C5	6.3	3.0	52
	C6	6.3	2.6	57
	C7	6.3	2.9	55
$B_4N_4H_8O_4$	D1	6.1	2.8	38
	D2	6.2	4.4	54
	D3	6.0	1.8	40
	D4	6.5	1.9	38
	D5	6.4	0.0	53
	D6	6.1	0.0	53
	D7	6.0	2.8	38

[*] For more details refer to Figs 1-4.

As Table 3 shows all BN isomers are polar except D5 and D6 (Fig. 4). Their electric dipole moments were about zero due to their symmetry as explained above. This makes D5 and D6 (Fig. 4) attractive for application in host-guest chemistry. They might dissolve in nonpolar solvents and hosts positive small ions as 12c4 does. Table 3 also shows that A1 isomer of $C_6BNH_{14}O_4$ category (4.4 D) (Fig. 1) and D2 isomer of $B_4N_4H_8O_4$ category (4.4 D)had the largest electric dipole moments(compare with Cyanogen Amide, 4.27D; Methyl thiocyanate, 4.0D; trans-cyanopropene, 4.50D) [50].

The natural bond orbital analysis of chemical bonding of BN isomers of 12-crown-4 ether showed there were no π-bonds in 12-crown-4 ether (Table 4). On the other side, all of BN isomers had double bonds which make the BN ethers unsaturated compounds.

Due to the structure of BN isomer, a lone pair of nitrogen atoms and/or oxygen atoms could make π-bonds with boron atoms. All isomers in$B_4N_4H_8O_4$ category (Fig. 4) had the maximum number of BN double bonds (five BN π-bonds) among BN isomers. The electronic structures of the double bonds (see supplementary data) showed that the nitrogen and oxygen atoms used their *p*-rich orbitals to construct π-bonds with boron atoms as boron atoms did. In some isomers (A2, A3 and, A4 of $C_6BNH_{14}O_4$ category (Fig. 1), and B1 of $C_4B_2N_2H_{12}O_4$ category (Fig. 2)) one lone pair of substituted nitrogen atom remained fully unengaged in π-bond. In B4 (Fig. 2), C3 (Fig. 3), D2 and D4 isomers (Fig. 4) the π-bonds were conjugated which might make some stabilization interactions.

Table 4. Chemical bonds, lone pairs of nitrogen and oxygen atom/atoms (if available) of crown ethers studied at B3LYP/6311++G(d,p) level of theory with tight convergence criterion*

Crown ether		
$C_8H_{16}O_4$	**(Type of bond: Bond label)**	**Lone pairs**
12c4	-	(O3, O6, O9, O12)
	$C_6BNH_{14}O_4$	
A1	($\boldsymbol{\sigma}$:N24B26) ($\boldsymbol{\pi}$: N24B26)	(O3, O6, O7, O10)
A2	($\boldsymbol{\sigma}$:O8B26) ($\boldsymbol{\pi}$:O8B26)	(O3, O6, O8, O10, N24)
A3	($\boldsymbol{\sigma}$:O8B26) ($\boldsymbol{\pi}$:O8B26)	(O3, O6, O8, O10, N24)
A4	($\boldsymbol{\sigma}$:O10B26) ($\boldsymbol{\pi}$:O10B26)	(O2, O5, O7, O10, N24)
	$C_4B_2N_2H_{12}O_4$	
B1	($\boldsymbol{\sigma}$:O8B23, N17B21) ($\boldsymbol{\pi}$:O8B23, N17B21)	(O2, O5, O6, O8, N19)
B2	($\boldsymbol{\sigma}$:N17B23, N19B21) ($\boldsymbol{\pi}$:N17B23, N19B21)	(O3, O6, O7, O8)
B3	($\boldsymbol{\sigma}$:N17B23, N19B21) ($\boldsymbol{\pi}$:N17B23, N19B21)	(O3, O6, O7, O8)
B4	($\boldsymbol{\sigma}$:O7B21, N17B23, N19B21) ($\boldsymbol{\pi}$:O7B211, N17B23, N19B21)	(O3, O6, O7, O8)
B5	($\boldsymbol{\sigma}$:N17B23, N19B21) ($\boldsymbol{\pi}$:N17B23, N19B21)	(O3, O6, O7, O8)
	$C_2B_3N_3H_{10}O_4$	
C1	($\boldsymbol{\sigma}$:N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
C2	($\boldsymbol{\sigma}$:O3B21, N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:O3B21, N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
C3	($\boldsymbol{\sigma}$:O4B21, N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:O4B21, N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
C4	($\boldsymbol{\sigma}$:N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
C5	($\boldsymbol{\sigma}$:N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
C6	($\boldsymbol{\sigma}$:N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
C7	($\boldsymbol{\sigma}$:O3B21, N11B21, N13B19, N15B17) ($\boldsymbol{\pi}$:O3B21, N11B21, N13B19, N15B17)	(O3, O4, O5, O6)
	$B_4N_4H_8O_4$	
D1	($\boldsymbol{\sigma}$:N5B15, N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)
D2	($\boldsymbol{\sigma}$:O1B13, N5B15, N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:O1B13, N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)
D3	($\boldsymbol{\sigma}$:O3B17, N5B15, N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:O3B17, N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)
D4	($\boldsymbol{\sigma}$:N5B15,N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)
D5	($\boldsymbol{\sigma}$:N5B15, N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)
D6	($\boldsymbol{\sigma}$:N5B15, N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)
D7	($\boldsymbol{\sigma}$:N5B15, N7B13, N9B19, N11B17) ($\boldsymbol{\pi}$:N5B15, N7B13, N9B19, N11B17)	(O1, O2, O3, O4)

*For more details refer to Figs 1-4.

A1, A2, A3, and A4 from $C_6BNH_{14}O_4$ category and B1 from $C_4B_2N_2H_{12}O_4$ category had one nitrogen atom with an electron lone pair (Table 4). The lone pairs of oxygen atoms of 12-crown-4 ether had similar electronic configurations (see supplementary data). Substituting B and N atoms changed the electronic configurations of oxygen atoms. The significant change observed for lone pairs with $p^{1.00}$ electronic. The main exception wasD5 isomer whose lone pairs of oxygen atoms were almost similar with those of 12-crown-4 ether. The characters of lone pairs turned to *p*-rich hybrid orbitals. This phenomenon is important due to the dramatic role of lone pairs in host-guest chemistry of crown ethers. In nonpolar D5 and D6 isomers all of four oxygen atoms had lone pairs free to interact with host species while lone pairs of nitrogen atoms all were engaged in BN double bonds (Table 4).

The stabilization energy, *E(2)* associated with delocalization of NBOs is another important feature of the natural bond orbitals. A selection of interactions is presented in Table5. One of the most interesting interaction observed in 12-crown-4 ether was hyperconjugation of lone pair of oxygen atom with non-lewis orbital of C-H bond ($n_O \rightarrow \sigma^*_{CH}$).

The interaction clearly implies internal hydrogen bonding inside 12-crown-4 ether structure. The stabilization energy of the H-bonding was7.9 kcal/mol (Table 5). (The H-bonding of two molecules of water at the same level of theory is 6.0 kcal/mol). This suggests a considerable internal H-bonding within 12-crown-4 structure. There were sixteen $n_O \rightarrow \sigma^*_{CH}$ interactions in 12-crown-4 ether but eight of them showed strong H-bonding. The oxygen atoms used their $p^{1.00}$lone pairs to interact with neighbor hydrogen atoms. The stabilization energies of the rest H-bondingswere2.4 kcal/mol. The internal H-bondings observed also in BN isomers but they have not been shown in Table 5 for summarization.

For each isomer we only picked out the largest stabilization energy and those with *E(2)* larger than 20.0 kcal/mol (based on the calculated stabilization energies of $\pi_{CC} \rightarrow \pi^*_{CC}$ in benzene, and $\pi_{BN} \rightarrow \pi^*_{BN}$ in borazine which are 20.5 kcal/mol and 36.7 kcal/mol at the same level of theory, respectively) (Table 5). One of the most significant interactions of NBOs was$\sigma_{O1B13} \rightarrow \sigma^*_{N7B13}$ in D2 isomer with 914.27 kcal/mol. The others were$\pi^*_{O3B21} \rightarrow \sigma^*_{N11B21}$ in C7 (268.78 kcal/mol) and $\pi^*_{N13B19} \rightarrow \sigma^*_{N13B19}$ in C5 (268.78 kcal/mol). (See category $C_2B_3N_3H_{10}O_4$ in Table 5).

3. Ionizations, electron affinities

Calculated changes of enthalpies of ionization and electron affinity of all BN isomers at 298.15 K and 1 atm are listed in Table6. For 12-crown-4 ether the calculated value for change of enthalpy of ionization was 8.3 eV with a good agreement with experimental one, 8.8 eV [51]. All enthalpies of ionizations of BN isomers values were large positive quantities reflecting their trend against ionizations. Moreover all enthalpies of ionizations of BN isomers were smaller than that of 12c4 except D4 and D5. Between these two structures D5 is chemically more attractive due to its nonpolar structure like 12c4. Moreover this isomer showed stronger tendency toward ionization which might make D5 a more favorable structure than 12c4 in host-guest chemistry. The isomer with the largest change of enthalpy of ionization wasD4 (834.64 kJ/mol) (Fig. 4) while A4 (Fig. 1) was the isomer with the smallest one (694.81 kJ/mol).

The change of enthalpy of electron affinity for 12-crown-4 ether at 298.15 K and 1 atm was 0.55 eV (53.47 kJ/mol, Table 6). There is no experimental value for the electron affinity of 12-crown-4 in the literature. Among the BN isomers, D7 (Fig. 4) with change of enthalpy of electron affinity about 28.73 kJ/mol was the most suitable isomer to gain an electron (Table 6). 12-crown-4 with the largest change of enthalpy of electron affinity was the most inappropriate structure to capture electron.

Table 5. Interaction Energies, *E(2)* (kcal/mol) between Lewis–non-Lewis NBOs of BN 12-crown-4 ethers studied at B3LYP/6311++G(d,p) level of theory with tight convergence criteria*.

CrowNether	**(Donor NMO→Acceptor NMO; *E(2)*)**
	$C_8H_{16}O_4$
12c4	$(n_{O3}\rightarrow\sigma^*_{C4H17}; 7.89)$, $(n_{O3}\rightarrow\sigma^*_{C2H15}; 7.87)$, $(n_{O6}\rightarrow\sigma^*_{C7H22}; 7.88)$, $(n_{O6}\rightarrow\sigma^*_{C5H20}; 7.87)$, $(n_{O9}\rightarrow\sigma^*_{C10H25}; 7.89)$, $(n_{O9}\rightarrow\sigma^*_{C8H23}; 7.87)$
	$C_6BNH_{14}O_4$
A1	$(n_{O7}\rightarrow\pi^*_{N24B26}; 33.05)$
A2	$(n_{N24}\rightarrow\sigma^*_{C9O10}; 10.02)$
A3	$(\sigma_{C1C2}\rightarrow\sigma^*_{O8C9}; 14.96)$
A4	$(n_{N23}\rightarrow\sigma^*_{O5C6}; 9.49)$
	$C_4B_2N_2H_{12}O_4$
B1	$(n_{O5}\rightarrow\pi^*_{N17B21}; 30.07)$
B2	$(\pi^*_{N19B21}\rightarrow\sigma^*_{N19B21}; 45.60)$
B3	$(n_{O8}\rightarrow\pi^*_{N19B21}; 40.79)$
	$(n_{O6}\rightarrow\pi^*_{N17B23}; 29.28)$
B4	$(\sigma_{N19B21}\rightarrow\pi^*_{O7B21}; 59.52)$, $(\sigma_{N19B21}\rightarrow\pi^*_{N19B21}; 49.42)$, $(\pi_{N19B21}\rightarrow\pi^*_{O7B21}; 47.46)$, $(\sigma_{B21H22}\rightarrow\pi^*_{O7B21}; 33.71)$, $(\pi_{N19B21}\rightarrow\sigma^*_{N19B21}; 23.03)$, $(\pi_{O7B21}\rightarrow\pi^*_{N19B21}; 21.48)$
B5	$(\sigma_{N17B23}\rightarrow\pi^*_{N17B23}; 122.89)$, $(n_{O7}\rightarrow\pi^*_{N19B21}; 27.95)$
	$C_2B_3N_3H_{10}O_4$
C1	$(n_{O4}\rightarrow\pi^*_{N11B21}; 30.75)$, $(n_{O5}\rightarrow\pi^*_{N15B17}; 23.21)$
C2	$(\pi_{N11B21}\rightarrow\pi^*_{O3B21}; 54.80)$, $(\sigma_{N11B21}\rightarrow\pi^*_{N11B21}; 41.55)$, $(\pi_{O3B21}\rightarrow\pi^*_{N11B21}; 35.55)$, $(n_{O5}\rightarrow\pi^*_{N13B19}; 35.13)$, $(\sigma_{N11B21}\rightarrow\pi^*_{O3B21}; 30.19)$, $(n_{O5}\rightarrow\pi^*_{N15B17}; 28.97)$, $(\pi_{N11B21}\rightarrow\sigma^*_{N11B21}; 24.68)$
C3	$(\pi_{N11B21}\rightarrow\pi^*_{O4B21}; 59.70)$, $(\sigma_{N11B21}\rightarrow\pi^*_{N11B21}; 43.37)$, $(\pi_{O4B21}\rightarrow\pi^*_{N13B19}; 34.86)$, $(n_{O6}\rightarrow\pi^*_{N15B17}; 34.69)$, $(\sigma_{N11B21}\rightarrow\pi^*_{O4B21}; 31.52)$, $(\pi_{O4B21}\rightarrow\pi^*_{N11B21}; 27.42)$, $(\pi_{N11B21}\rightarrow\sigma^*_{N11B21}; 25.99)$
C4	$(\pi^*_{N15B17}\rightarrow\sigma^*_{N15B17}; 15.83)$
C5	$(\pi^*_{N13B19}\rightarrow\sigma^*_{N13B19}; 208.31)$, $(\pi^*_{N11B21}\rightarrow\sigma^*_{N11B21}; 55.84)$
C6	$(\sigma^*_{N11B21}\rightarrow\pi^*_{N11B21}; 39.36)$, $(n_{O4}\rightarrow\pi^*_{N13B19}; 27.42)$, $(n_{O6}\rightarrow\pi^*_{N15B17}; 27.04)$
C7	$(\pi^*_{O3B21}\rightarrow\sigma^*_{N11B21}; 268.78)$, $(\sigma_{N11B21}\rightarrow\pi^*_{N11B21}; 56.73)$, $(\pi_{N11B21}\rightarrow\pi^*_{O3B21}; 52.94)$, $(\sigma_{N11B21}\rightarrow\pi^*_{O3B21}; 39.51)$, $(\pi_{N11B21}\rightarrow\sigma^*_{N11B21}; 35.96)$, $(n_{O5}\rightarrow\pi^*_{N13B19}; 35.43)$, $(\pi_{O3B21}\rightarrow\pi^*_{N11B21}; 29.62)$
	$B_4N_4H_8O_4$
D1	$(n_{O1}\rightarrow\pi^*_{N7B13}; 39.11)$, $(n_{O3}\rightarrow\pi^*_{N9B19}; 23.76)$, $(n_{O4}\rightarrow\pi^*_{N11B17}; 22.42)$, $(n_{O1}\rightarrow\pi^*_{N5B15}; 21.47)$
D2	$(\sigma_{O1B13}\rightarrow\sigma^*_{N7B13}; 914.27)$, $(\sigma_{O1B13}\rightarrow\sigma^*_{N7B13}; 56.8)$, $(\sigma_{O1B13}\rightarrow\pi^*_{O1B13}; 52.07)$, $(\sigma_{O1B13}\rightarrow\pi^*_{N7B13}; 50.52)$, $(\sigma_{O1B13}\rightarrow\pi^*_{N9B19}; 39.94)$, $(\sigma_{01B13}\rightarrow\pi^*_{O1B13}; 37.03)$, $(\sigma_{O1B13}\rightarrow\pi^*_{N11B17}; 35.77)$, $(\pi_{O1B13}\rightarrow\sigma^*_{N7B13}; 24.81)$
D3	$(\sigma_{O1N5}\rightarrow\pi^*_{O3B17}; 88.55)$, $(\sigma_{O1N5}\rightarrow\pi^*_{N11B17}; 70.09)$, $(\sigma_{O1N5}\rightarrow\sigma^*_{N11B17}; 48.38)$, $(\sigma_{O1N5}\rightarrow\pi^*_{O3B17}; 32.12)$, $(\sigma_{O1B13}\rightarrow\pi^*_{N9B19}; 29.97)$, $(\sigma_{O1B13}\rightarrow\pi^*_{N5B15}; 28.09)$, $(\sigma_{O1B13}\rightarrow\pi^*_{O3B17}; 27.29)$, $(\sigma_{O1B13}\rightarrow\pi^*_{N7B13}; 24.84)$, $(\sigma_{O2N7}\rightarrow\sigma^*_{N11B17}; 21.08)$
D4	$(\sigma_{O1N5}\rightarrow\pi^*_{N9B19}; 31.89)$, $(\sigma_{O1N5}\rightarrow\pi^*_{N7B13}; 31.84)$, $(\sigma_{O1N5}\rightarrow\pi^*_{N5B15}; 31.81)$, $(\sigma_{O1N7}\rightarrow\pi^*_{N11B17}; 31.8)$
D5	$(\sigma_{O1N7}\rightarrow\pi^*_{N11B17}; 37.47)$, $(\sigma_{O1N7}\rightarrow\pi^*_{N7B13}; 37.42)$, $(\sigma_{O1N7}\rightarrow\pi^*_{N5B15}; 37.24)$, $(\sigma_{O1B15}\rightarrow\pi^*_{N9B19}; 37.24)$
D6	$(\sigma_{O1N5}\rightarrow\pi^*_{N7B13}; 27.58)$, $(\sigma_{O1N5}\rightarrow\pi^*_{N9B19}; 27.5)$, $(\sigma_{O1N5}\rightarrow\pi^*_{N5B15}; 27.49)$, $(\sigma_{O1N5}\rightarrow\pi^*_{N11B17}; 27.48)$
D7	$(\sigma_{O1N7}\rightarrow\pi^*_{N9B19}; 39.12)$, $(\sigma_{O1N7}\rightarrow\pi^*_{N11B17}; 23.76)$, $(\sigma_{O1N7}\rightarrow\pi^*_{N5B15}; 22.54)$, $(\sigma_{O1B15}\rightarrow\pi^*_{N7B13}; 21.76)$

*For more details refer to Figs 1-4.

Table 6. Changes of standard enthalpies (in kJ/mol) for ionization reactions, electron affinity reactions (in kJ/mol) of crown ethers at 1 atm and 298.15 K, ionization potentials (in eV) and electron affinities (in eV) based on single point calculations calculated by B3LYP/6-311++G(d,p) model chemistry*

Crown ether	Δ_rH^0(ionization)	Δ_rH^0(electron affinity)	IP(SP)	EA(SP)
$C_8H_{16}O_4$				
12c4	806.81	53.47	8.44	-0.616
$C_6BNH_{14}O_4$				
A1	749.41	38.99	7.74	-0.43
A2	728.23	35.29	7.53	-0.375
A3	707.72	28.54	7.34	-0.385
A4	694.81	30.00	7.24	-0.404
$C_4B_2N_2H_{12}O_4$				
B1	795.23	45.24	8.29	-0.506
B2	750.63	48.69	7.78	-0.531
B3	769.89	46.36	7.97	-0.514
B4	769.91	37.46	7.97	-0.418
B5	772.79	35.52	8.01	-0.396
$C_2B_3N_3H_{10}O_4$				
C1	794.15	31.64	8.24	-0.354
C2	776.23	39.84	8.03	-0.449
C3	772.23	38.98	7.99	-0.441
C4	761.90	37.66	7.90	-0.421
C5	766.55	39.49	7.95	-0.444
C6	785.78	43.28	8.15	-0.49
C7	769.82	36.73	7.97	-0.415
$B_4N_4H_8O_4$				
D1	785.88	28.72	8.17	-0.337
D2	791.98	26.31	8.23	-0.305
D3	775.08	44.07	8.04	-0.498
D4	834.64	35.37	8.74	-0.401
D5	823.35	34.34	8.61	-0.422
D6	785.39	50.64	8.22	-0.567
D7	785.90	28.73	8.17	-0.337

*For more details refer to Figs 1-4.

The results of single point calculations of ionization potentials were in excellent correlation with those based on thermochemistry (R^2=0.99) (Table 6, Fig. 6). In addition the results of electron affinities calculated on the basis of single point calculations correlated well with thermochemistry ones (R^2=0.94) (Table 6, Fig. 7). So one can achieve ionization potentials and electron affinities of the BN crown ethers based on single point energy calculations with a considerable lower cost of computations.

4. Polarizabilities and Nonlinear optical responses

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field. They specify properties of structure like the long-range intermolecular induction, dispersion forces, cross sections of different scattering and collision processes, etc. They also determine the nonlinear optical properties of the system [46]. Table 7 lists the values of the calculated isotropic polarizability, polarizability anisotropy invariant and hyperpolarizability of 12c4 and its BN substituted derivatives.

Table 7. Isotropic polarizabilities $\boldsymbol{\alpha}$, polarizability anisotropy invariant $\Delta\boldsymbol{\alpha}$, and average hyperpolarizabilities $\boldsymbol{\beta}_{||}$ of BN-derivatives of 12-crown-4 ether calculated at B3LYP/6-311++G (d,p) level of theory

Crown ether	α (a.u.)	$\Delta\alpha$ (a.u.)	$\beta_{\|\|}$ (a.u.)
	$C_8H_{16}O_4$		
12-crown-4	117.0	24.30	-8.26×10^{-02}
	$C_6BNH_{14}O_4$		
A1	63.60	125.0	5.08
A2	110.0	14.70	-52.1
A3	112.0	19.40	25.6
A4	111.0	16.30	73.3
	$C_4B_2N_2H_{12}O_4$		
B1	109.0	23.20	90.7
B2	109.0	19.20	43.8
B3	110.0	24.50	72.4
B4	108.0	15.70	-89.2
B5	108.0	13.80	-66.6
	$C_2B_3N_3H_{10}O_4$		
C1	105.0	11.50	27.7
C2	108.0	31.20	228
C3	107.0	30.80	-107
C4	106.0	24.10	-22.7
C5	105.0	30.80	26.4
C6	106.0	25.80	59.7
C7	107.0	32.9	138
	$B_4N_4H_8O_4$		
D1	102.0	11.60	73.8
D2	103.0	14.10	-17.4
D3	104.0	16.90	58.8
D4	106.0	36.40	-205
D5	99.10	11.10	2.68×10^{-02}
D6	104.0	18.10	1.96×10^{-03}
D7	102.0	11.60	73.9

* [*]For more details refer to Figs 1-4.

All BN substituted derivatives of 12c4 crown ethers had isotropic polarizabilities smaller than that of 12c4 with α about 117.0 au (Table 7). The larger isotropic polarizability of 12c4 crown ether results in the stronger response of external field. The nonpolar BN derivatives of 12c4, D5 and D6 (from $B_4N_4H_8O_4$ category) had isotropic polarizabilities of 99.1 and 104 au, respectively. The nonlinear optical response of a molecule to applied electric fields is described in terms of the hyperpolarizabilities of the molecule [46].

In the case that all applied fields have parallel polarization, the measurable quantities are the vector component of the tensor $\beta_{||}$ in the direction of the permanent dipole moment μ which defines the molecular z axis (Eq. 3) [46]. As it comes from the average hyperpolarizabilities $\beta_{||}$ (Table 7), C2 from $C_2B_3N_3H_{10}O_4$ category with $\beta_{||}$ of 228.0 au had the strongest nonlinear optical response. D5, D6 isomers, and 12c4 with molecular dipole moment of about zero (like 12c4) showed a very weak nonlinear optical response (Table 7). These structures seem not suitable for the construction of practical devices for optical harmonic generation and signal processing.

CONCLUDING REMARKS

We constructed 531 boron nitride substituted 12-crown-4 ethers with the same number of B and N atoms. The stable structures of the BN isomers verified at B3LYP/6-31+G(d,p) level of theory. We selected 23 BN isomers from the viable structures. Hybrid functional of DFT, B3LYP with large basis set 6-311++G(d,p) applied for computations. None of energetically favorable BN isomers had a full alternative array of B and N atoms. The energy gaps of the BN substituted crown ethers were in the range of 6.8-7.3 eV. All BN isomers were polar compounds except D5 and D6 which were non-polar like 12-crown-4. All BN isomers of 12-crown-4 ether had double bond/bonds. Substituting nitrogen atoms for carbon atoms of 12-crown-4 ether might develop their capacity to interact with host cations as well.

Strong internal hydrogen bonds observed in 12-crown-4 ether between oxygen and hydrogen atoms. Such internal H-bondings observed in BN isomers were weaker than that of 12c4. The ionization potentials and electron affinities based on single point calculations were in a good agreement with those based on thermochemistry computations. The single point calculations might be a more economical way of achieving ionization potentials and electron affinities of the mentioned crown ethers. Some BN substituted isomers of 12c4 like C2 and C7 showed strong nonlinear optical response making them candidates for construction of practical optical devices.

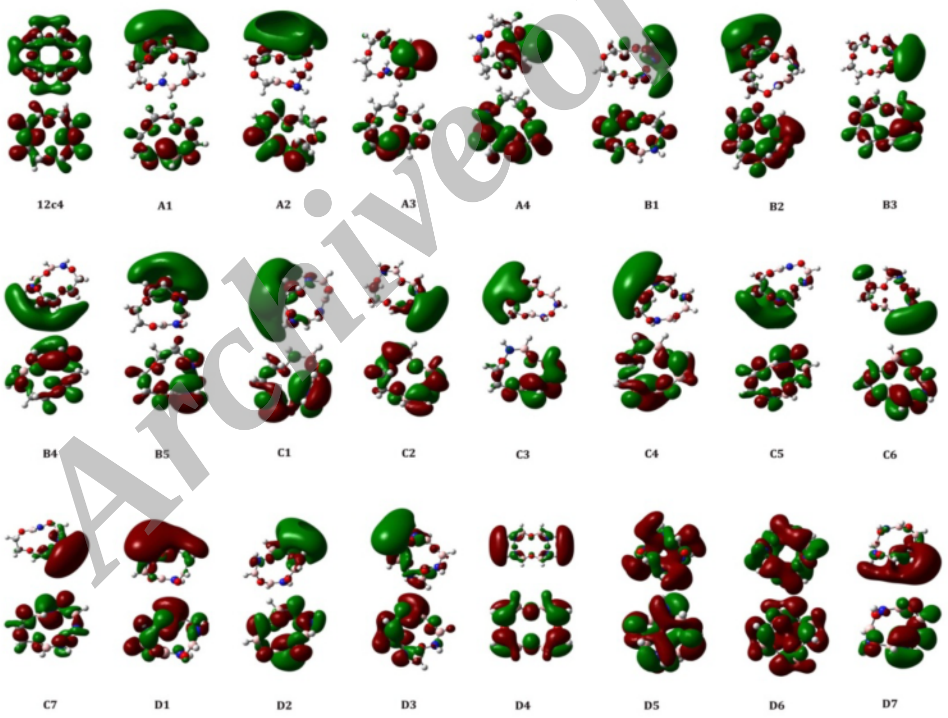

Fig. 5. Spatial representations of HOMO (up) and LUMO (down) BN isomers of 12c4 ether.

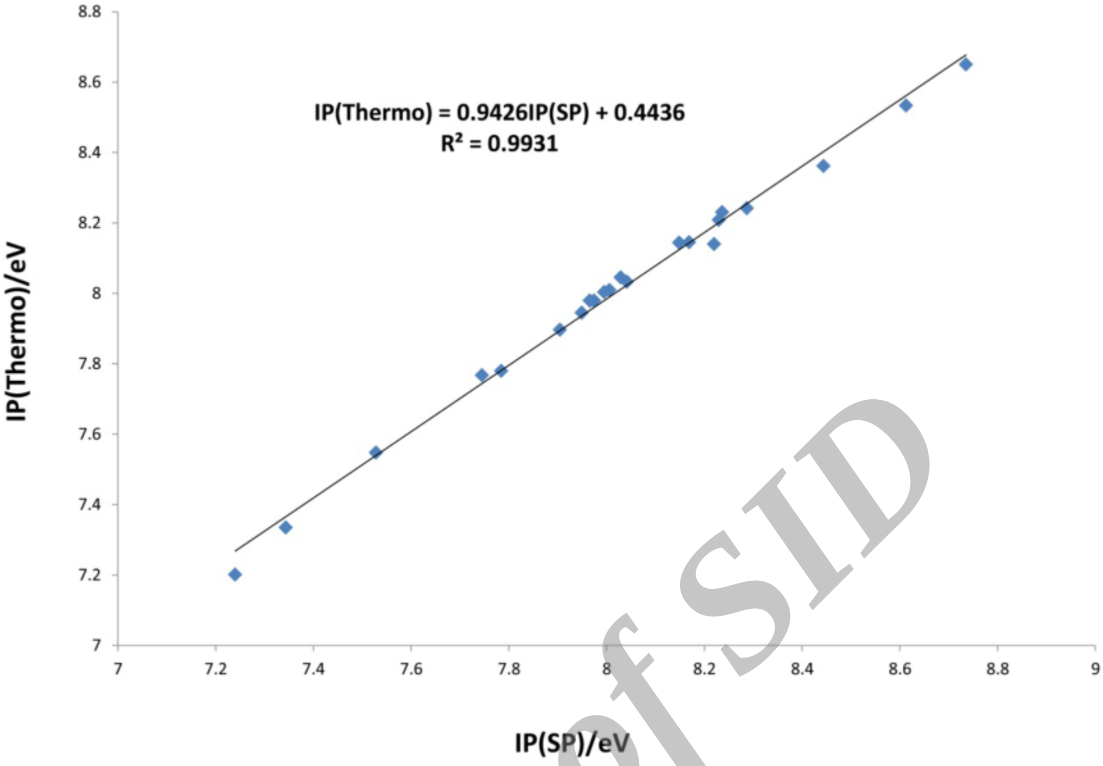

Fig.6. Plot of ionization potential calculated through thermochemistry versus single point calculated ionization potential.

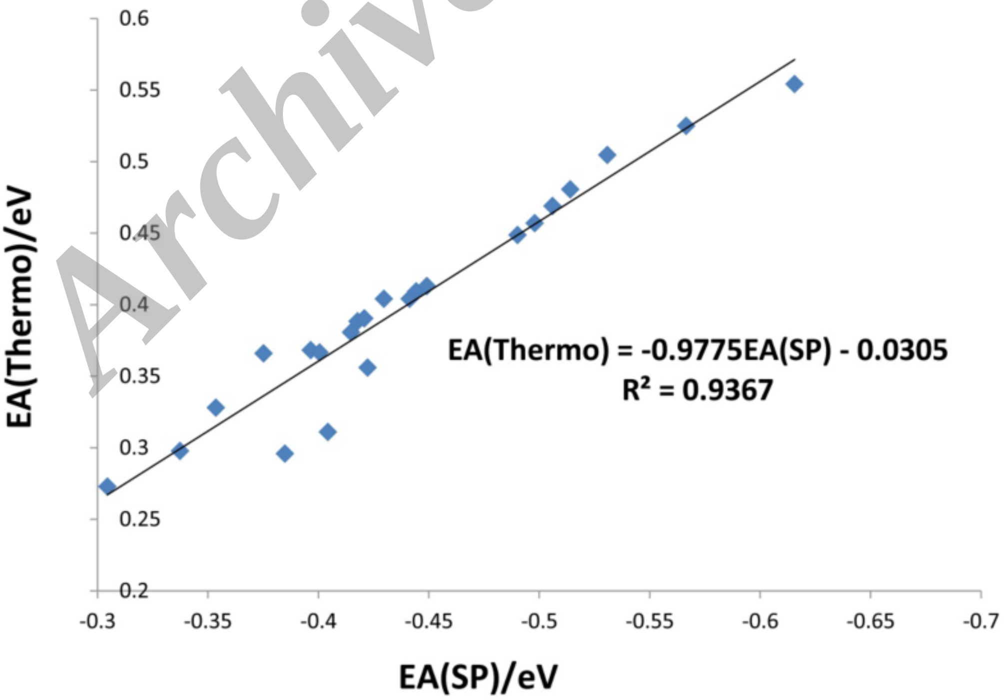

Fig.7. Plot of electron affinity calculated through thermochemistry versus single point calculated electron affinity.

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