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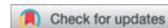


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RESEARCH ARTICLE



Organic superalkalis with closed-shell structure and aromaticity

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ABSTRACT

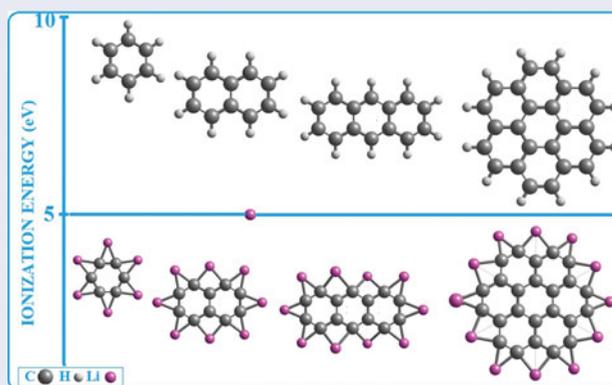
Benzene (C_6H_6) and polycyclic hydrocarbons such as naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$) and coronene ($C_{24}H_{12}$) are well known aromatic organic compounds. We study the substitution of Li replacing all H-atoms in these hydrocarbons using density functional method. The vertical ionisation energy of such lithiated species, i.e. C_6Li_6 , $C_{10}Li_8$, $C_{14}Li_{10}$ and $C_{24}Li_{12}$ ranges 4.24–4.50 eV, which is lower than the ionisation energy (IE) of Li atom. Thus, these species may behave as superalkalis due to their lower IE than alkali metal. However, these lithiated species possess planar and closed-shell structure, unlike typical superalkalis. Furthermore, all Li-substituted species are aromatic although their degree of aromaticity is reduced as compared to corresponding hydrocarbon analogues. We have further explored the structure of C_6Li_6 as star-like, unlike its inorganic analogue $B_3N_3Li_6$, which appears as fan-like structure. We have also demonstrated that the interaction of C_6Li_6 with a superhalogen (such as BF_4) is similar to that of a typical superalkali (such as OLi_3). This may further suggest that the proposed lithiated species may form a new class of closed-shell organic superalkalis with aromaticity.

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1. Introduction

Benzene (C_6H_6), a prototype six-membered ring, is the building block of aromatic organic species. Aromaticity is a distinguished feature of species, which leads to energy reduction and a variety of unusual chemical and physical properties [1] such as bond-length equalisation, unusual reactivity, characteristic spectroscopic features, etc. Aromatic rings are significantly stabilised due to complete delocalisation of π -electrons, which reduces their reactivity toward addition reactions. For instance, benzene possesses very large ionisation energy (IE) and no positive electron affinity. This is why the whole chemistry of benzene is based on substitution reactions in which an atom or group usually replaces hydrogen attached to the ring. The substitution causes to significantly affect

the chemical reactivity of the ring as noticed in many studies [2–4]. This may result in reducing the IE or increasing the electron affinity of the substituted rings. The increase in electron affinity by substitution at H-atoms (ligands) as well as C-atoms (core) in benzene has already been reported by Jena and co-workers [5–7]. Here, we study the substitution of lithium (Li) on benzene and its higher analogues such as naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$) and coronene ($C_{24}H_{12}$) replacing all H-atoms. Few polyolithium organic compounds have already been synthesised experimentally including C_6Li_6 [8,9].

The species with lower IE than alkali atoms are referred to as superalkalis. According to Gutsev and Boldyrev [10], and confirmed by Wu et al. [11], such species can be designed by central electronegative atom

with excess electropositive ligands. FLi_2 , OLi_3 , NLi_4 , etc. are typical examples of superalkalis. These are hyper-valent clusters possessing an excess electron and hence, open-shell structure. Therefore, they possess strong reducing capability and can be employed in the formation of a variety of charge transfer species with unusual properties. For instance, the use of superalkalis in the design of superbases with strong basicity [12–14] and super-salts with tailored properties [15–19] has been extensively studied. Owing to interesting properties of superalkalis and their compounds, such species have been continuously explored [20–25]. In this paper, we show that the vertical ionisation energies (VIEs) of lithiated benzene (C_6Li_6) and its higher analogues such as C_{10}Li_8 , $\text{C}_{14}\text{Li}_{10}$ and $\text{C}_{24}\text{Li}_{12}$ are lower than that of Li atom. Although the aromaticity of the rings is affected by substitution of Li-atoms, their planarity is retained. We have also studied the interaction of C_6Li_6 with BF_4 superhalogen and compared that with that of OLi_3 superalkali with BF_4 . Note that C_6Li_6 has been previously studied by several groups [26–29]. The application of C_6Li_6 in the hydrogen storage has also been reported [30,31]. We still believe that the low ionisation energy feature of C_6Li_6 is probably studied here for the first time.

2. Computational methods

All ring structures considered in this study were fully optimised at B3LYP method [32,33] using 6-311++G(d,p) basis set in Gaussian 09 program [34]. The geometry optimisation was performed without any symmetry constraints and followed by frequency calculations to ensure that the optimised structures correspond to true minima in the potential energy surface. There exists a variety of density functionals, which have been recently reviewed by Goerigk et al. [35] as well as Mardirossian and Head-Gordon [36], especially for thermochemistry and non-covalent interactions. However, our B3LYP computed C–C bond lengths (1.395 Å) and VIE (9.28 eV) of benzene are in good agreement with the experimental bond lengths of 1.399 Å measured by infrared spectroscopy [37] and ionisation energy of 9.24 eV [38], respectively. On the contrary, the computed VIE of benzene at MP2 level is found to be 9.62 eV, which is overestimated as compared to B3LYP as well as experimental values. Therefore, we have adopted the present computational scheme. The results obtained by B3LYP scheme are easily reproducible at reduced computational cost, especially for larger systems such as $\text{C}_{24}\text{H}_{12}$, $\text{C}_{24}\text{Li}_{12}$, etc. where MP2 calculations become quite expensive.

The aromaticity of the ring structures are evaluated using various criteria such as nucleus independent chemical shifts (NICS and NICS_{zz}), harmonic oscillator model

of aromaticity (HOMA) as well as para-delocalisation index (PDI). NICS is the most popular magnetic criteria of aromaticity [39,40], which has been calculated at the geometrical centre of the rings. HOMA index [41,42] is a structural criteria, which quantifies the bond-length equalisation of the rings. PDI [43], an electronic criteria, is applicable to six-membered ring systems only, which measures the delocalisation of electrons within the ring.

3. Results and discussion

We start our discussion by considering benzene (C_6H_6), naphthalene (C_{10}H_8), anthracene ($\text{C}_{14}\text{H}_{10}$) and coronene ($\text{C}_{24}\text{H}_{12}$) as displayed in Figure 1. Benzene is a six-membered ring system with the C–C bond lengths of 1.395 Å. Naphthalene and anthracene consist of two and three fused benzene rings along an axis with the C–C bond lengths of 1.374–1.420 Å and 1.367–1.443 Å, respectively. Coronene, on the contrary, contains seven fused rings in a plane such that the C–C bond lengths become 1.370–1.426 Å, ranging between those of naphthalene and anthracene. All these ring structures are planar with C–H bond length of 1.085 Å. Next, the H-atoms of all these rings are substituted with Li-atoms. The resulting optimised structures are also displayed in Figure 1 and corresponding parameters are listed in Table 1. Although all substituted ring structures retain their planarity like their hydrocarbon analogues, substituted Li-atoms bind with two carbons forming planar star-like structures. The tendency of Li atoms to bind with two C atoms has already been noticed in the case of C_6Li_6 [26,27].

The VIE of systems has been calculated by difference of total energy of equilibrium neutral structure and single-point energy of corresponding cation at the optimised geometry of neutral structure:

$$\text{VIE} = E_{\text{cation}} - E_{\text{neutral}}$$

The VIE of hydrocarbons considered ranges from 9.28 eV for C_6H_6 to 7.16 eV for $\text{C}_{14}\text{H}_{10}$ and 7.43 eV for $\text{C}_{24}\text{H}_{12}$. Note that these values are much large as compared to the IE of alkali metal, whose maximal value is limited to 5.39 eV for Li [44]. With the substitution of Li atoms in C_6H_6 , the VIE of C_6Li_6 is reduced to 4.48 eV, which is lower than the IE of Na (5.14 eV) [44]. Furthermore, the VIEs of C_{10}Li_8 and $\text{C}_{14}\text{Li}_{10}$ are even lower than the IE of K (4.34 eV) [44]. Although the VIE of $\text{C}_{24}\text{Li}_{12}$ tends to be increased as compared to those of C_{10}Li_8 and $\text{C}_{14}\text{Li}_{10}$, it is small enough as compared to those of Li and Na. Therefore, the VIEs of all lithiated analogues, being lower than those of alkali metals, suggest their superalkali behaviour. In order to explain the trend of VIE values, we have computed and listed the sum of natural bond orbital (NBO)

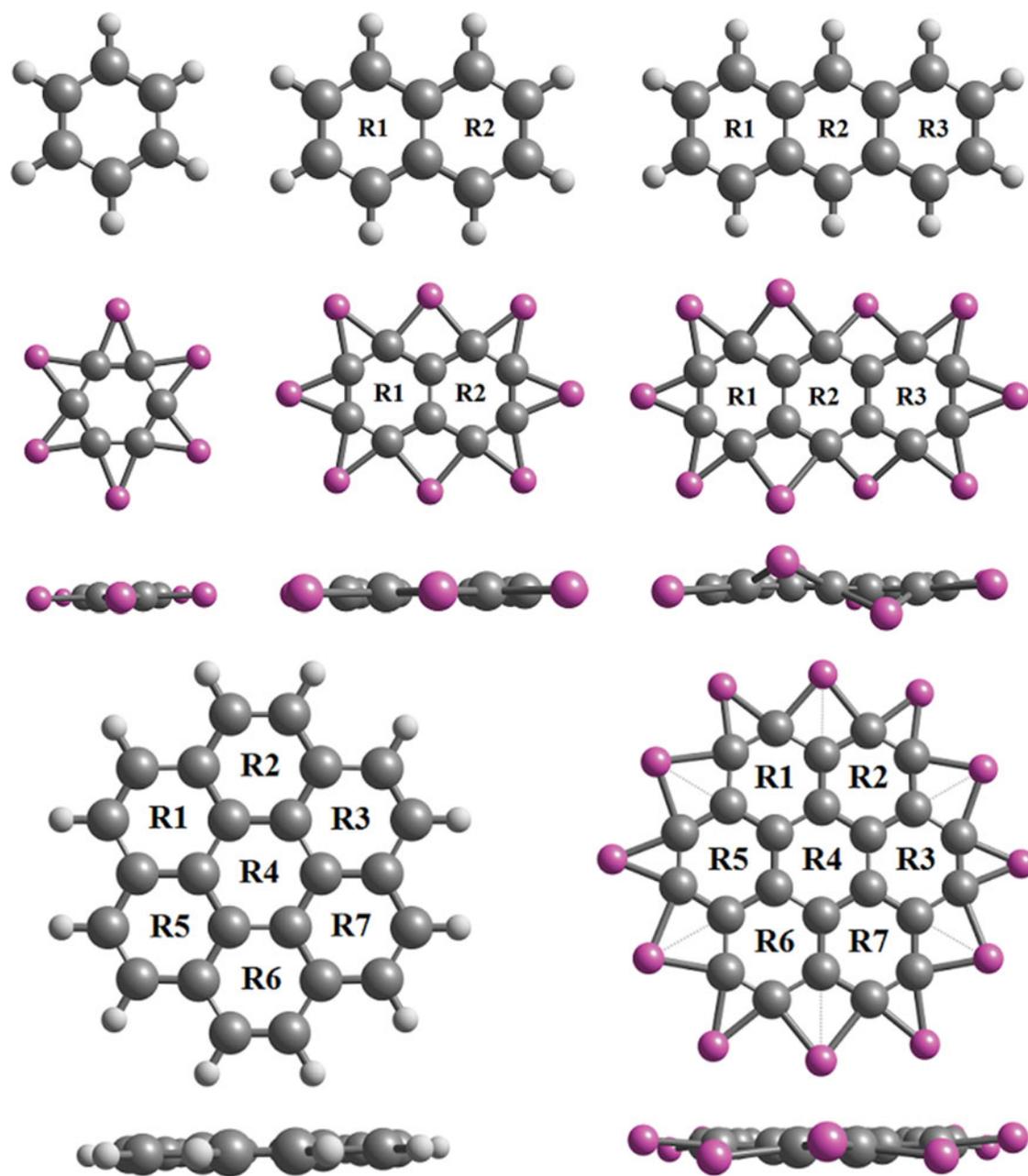


Figure 1. (Colour online) Equilibrium structures of benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$) and coronene ($C_{24}H_{12}$) along with their lithiated analogues obtained at B3LYP level.

Table 1. Calculated bond lengths and vertical ionisation energy of lithiated species along with their hydrocarbon analogues. NBO charges and HOMO composition are also listed.

Systems (Sym.)	d(C–C) (Å)	d(C–Li) (Å)	VIE (eV)	NBO charge on Li	Composition of HOMO	Hydrocarbon analogues		
						Systems	d(C–C) (Å)	VIE (eV)
C_6Li_6 (C_{2v})	1.420	1.914	4.48	$Q = 3.72$ $q = 0.62$	C = 52% Li = 48%	C_6H_6	1.395	9.28
$C_{10}Li_8$ (D_{2h})	1.390–1.463	1.896–1.962	4.29	$Q = 4.80$ $q = 0.60$	C = 34% Li = 48%	$C_{10}H_8$	1.374–1.420	7.97
$C_{14}Li_{10}$ (C_{2h})	1.382–1.468	1.919–1.963	4.24	$Q = 6.10$ $q = 0.61$	C = 16% Li = 36%	$C_{14}H_{10}$	1.367–1.443	7.16
$C_{24}Li_{12}$ (C_6)	1.383–1.450	1.904–1.953	4.50	$Q = 5.88$ $q = 0.49$	C = 74% Li = 0%	$C_{24}H_{12}$	1.370–1.426	7.43

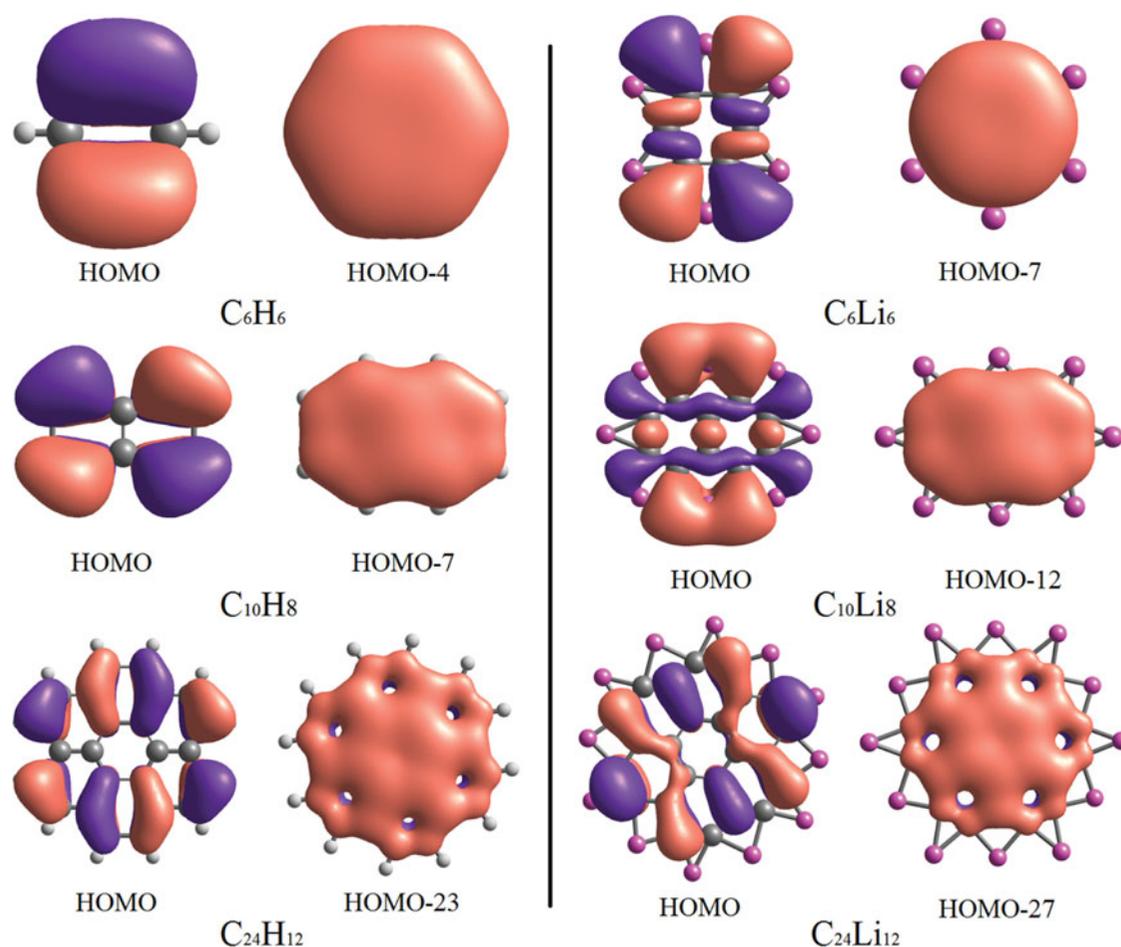


Figure 2. (Colour online) Selected molecular orbital surfaces including the highest occupied molecular orbital (HOMO) of the systems considered in this study with an isovalue of 0.02 a.u.

charge values of Li atoms (Q) and average charge on Li (q) in Table 1. As mentioned earlier, traditional superalkalis employ a central (electronegative) atom attached with electropositive metal ligands and their Lower IEs result due to increase in the charge delocalisation over electropositive ligands. Analogously, Li atoms can be treated as ligands attached to carbon ring system as centre in these organic superalkalis. In case of C_6Li_6 , net NBO charge on Li atoms is $3.72e$ with an average value of $0.62e$ per Li atom. For $C_{10}Li_8$ and $C_{14}Li_{10}$, Q increases to $4.80e$ and $6.10e$, respectively, although q does not change significantly. This causes to reduce VIE of these species relative to C_6Li_6 . On the contrary, Q value of $C_{24}Li_{12}$ is decreased to $5.88e$ resulting in the increase in its VIE (see Table 1).

These organic superalkalis possess closed-shell planar structures like their hydrocarbon analogues. It seems, therefore, interesting to compare the molecular orbitals of these superalkalis with those of parent hydrocarbons. In Figure 2, we have plotted the highest occupied molecular orbital (HOMO) and delocalised molecular orbital of C_6H_6 , $C_{10}H_8$, $C_{24}H_{12}$ and compared with those of

C_6Li_6 , $C_{10}Li_8$, $C_{24}Li_{12}$, respectively. The HOMO of C_6H_6 consists of delocalised electron cloud over C=C bond whereas HOMO-4 shows complete delocalisation of electron over the whole ring. In the HOMO of C_6Li_6 , the delocalisation of electron cloud over C=C bond is reduced due to substitution of Li atoms. Table 1 lists the percentage contribution of atomic orbitals in the HOMOs of C_6Li_6 , $C_{10}Li_8$, $C_{14}Li_{10}$ and $C_{24}Li_{12}$. One can note that the HOMO of C_6Li_6 is composed of 48% of Li and 52% of C atomic orbitals. However, HOMO-7 of C_6Li_6 is completely delocalised, like HOMO-4 of C_6H_6 . In case of $C_{10}Li_8$ and $C_{14}Li_{10}$, the contribution of Li atoms is 48% and 16%, respectively. On the contrary, the HOMO of $C_{24}Li_{12}$ is contributed by only C-atoms (see Table 1), which resembles to that of $C_{24}H_{12}$ (see Figure 2). Nevertheless, HOMO-12 of $C_{10}Li_8$ and HOMO-27 of $C_{24}Li_{12}$ possess delocalised π -electron cloud, corresponding to HOMO-7 of $C_{10}H_8$ and HOMO-23 of $C_{24}H_{12}$, respectively.

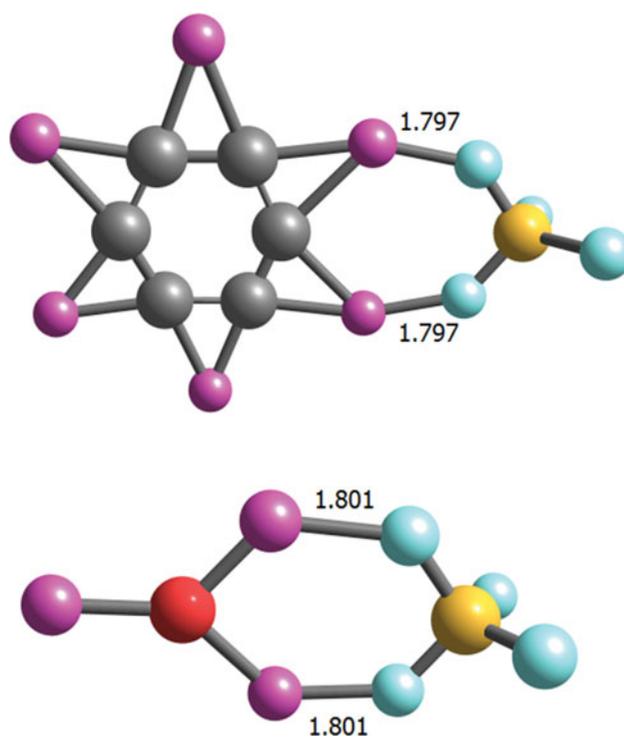
The complete delocalisation of electrons is a distinct feature of aromatic ring systems. Therefore, we have quantified and analysed the aromaticity of lithiated

Table 2. Various aromaticity descriptors of lithiated species along with their hydrocarbon analogues. Please refer to Figure 1 for labelling of rings.

Para-meter	X	C_6X_6	$C_{10}X_8$		$C_{14}X_{10}$			$C_{24}X_{12}$						
			R1	R2	R1	R2	R3	R1	R2	R3	R4	R5	R6	R7
NICS (ppm)	H	-8.05	-8.39	-8.39	-7.28	-11.05	-7.28	-9.60	-9.72	-9.72	-0.22	-9.72	-9.72	-9.60
	Li	-3.38	-7.74	-7.74	-5.21	-11.59	-5.21	-7.84	-7.84	-7.69	0.35	-7.69	-7.84	-7.84
NICS _{zz} (ppm)	H	-14.49	-13.29	-13.29	-9.68	-19.02	-9.68	-13.41	-13.68	-13.68	16.94	-13.68	-13.68	-13.41
	Li	-25.11	-25.22	-25.22	-18.92	-23.79	-18.92	-15.59	-15.59	-15.11	-19.31	-15.11	-15.59	-15.59
HOMA	H	0.987	0.783	0.783	0.629	0.720	0.629	0.736	0.736	0.736	0.627	0.736	0.736	0.736
	Li	0.730	0.295	0.295	0.016	0.294	0.016	0.402	0.402	0.402	0.378	0.402	0.402	0.402
PDI	H	0.104	0.076	0.076	0.067	0.066	0.067	0.054	0.054	0.054	0.033	0.054	0.054	0.054
	Li	0.091	0.068	0.068	0.060	0.061	0.060	0.051	0.051	0.051	0.031	0.051	0.051	0.051

analogues and compared with corresponding hydrocarbons. In Table 2, we have listed NICS and NICS_{zz} at the ring centre as well as HOMA and PDI values. NICS_{zz}, a tensor component of NICS along the direction perpendicular to the plane of ring, measures the contribution of π -electrons in the ring current. The positive value of NICS indicates anti-aromaticity whereas negative values confirm aromaticity. For instance, NICS and NICS_{zz} values of C_6H_6 are -8.05 ppm and -14.49 ppm, which indicate its aromatic nature. This is further supported by its HOMA index (0.987) and PDI value (0.104). Although NICS_{zz} value of C_6Li_6 is -25.11 ppm, its NICS value is only -3.38 ppm. This is due to contribution of σ -electrons from substituted Li atoms, which supports paratropic ring currents and reduces the aromaticity significantly. This is also supported by smaller HOMA index (0.730) and PDI (0.091) of C_6Li_6 . $C_{10}H_8$ contains two fused rings R1 and R2, which are as aromatic as C_6H_6 due to approximately similar NICS and NICS_{zz} values, although HOMA and PDI values suggest the lower degree of aromaticity of $C_{10}H_8$ as compared to C_6H_6 . The aromaticity of $C_{10}Li_8$ is slightly lower than that of its hydrocarbon analogue as suggested by NICS, NICS_{zz}, as well as PDI values, but not by HOMA index, which suggests very poor aromaticity. The aromaticity of central ring of $C_{14}H_{10}$ (R2) is larger than those of accompanying rings (R1 and R3), but $C_{24}H_{12}$ (R4) is very less aromatic or not aromatic at all. This is supported by all aromaticity measures listed in Table 2. Likewise, the aromaticity of $C_{14}Li_{10}$ and $C_{24}Li_{12}$ is smaller than their hydrocarbon analogues as reflected by NICS and PDI values. The decrease in aromaticity can be expected due to Li-substitution. This feature has already been seen in some mono-substituted benzene [3,4]. Therefore, our calculated NICS and PDI values clearly suggest that all lithiated analogues are indeed aromatic; however, their degree of aromaticity is lower than corresponding hydrocarbons.

We have already established that the IEs of C_6Li_6 and other lithiated analogues of higher hydrocarbons become lower than that of Li atom, just as those of

**Figure 3.** (Colour online) Equilibrium structure of $C_6Li_6-BF_4$ and OLi_3-BF_4 complexes obtained at B3LYP/6-311+G(d) level. The inter-action bond lengths (in Å) are also displayed.

superalkalis. For instance, the VIE of C_6Li_6 4.48 eV is comparable to the IE of FLi_2 (4.20 eV), but smaller than that of OLi_3 (3.85 eV) superalkalis computed at the same level. Therefore, it seems interesting to study the interaction of C_6Li_6 with a superhalogen [45]. It has already been shown [15–19] that superalkalis interact with superhalogens and form ionic complexes known as supersalts. We have studied the interaction of C_6Li_6 with BF_4 superhalogen and compared it with that of OLi_3 superalkali [11]. This interaction leads to formation of $C_6Li_6-BF_4$ and OLi_3-BF_4 complexes as displayed in Figure 3. In both complexes, bonding between two units takes place via two Li atoms as shown. The binding energy of OLi_3-BF_4 is 8.55 eV in which the charge $-0.91e$ is transferred

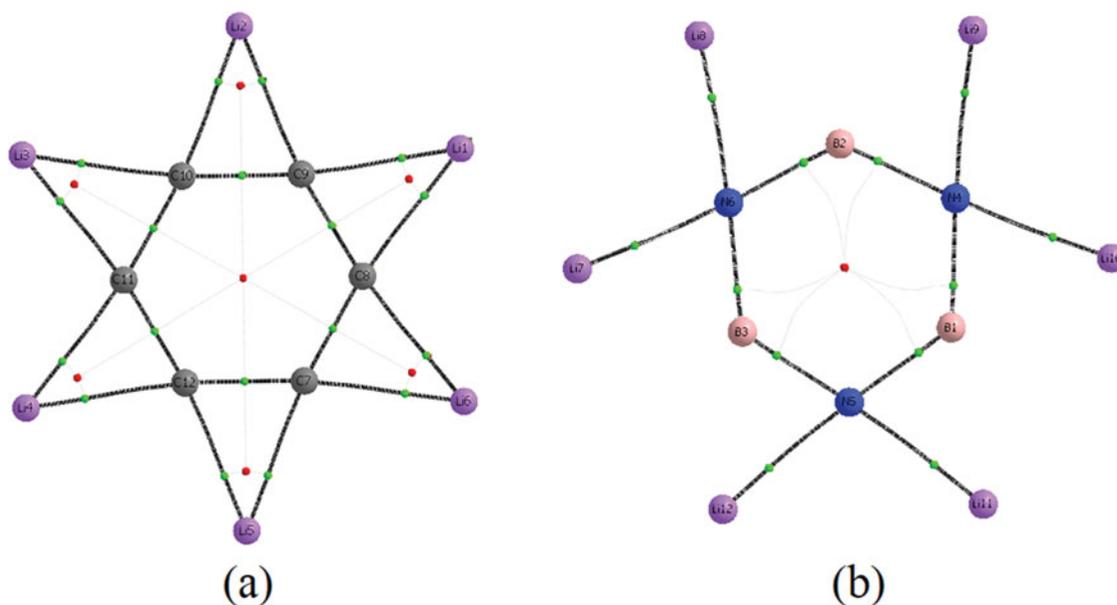


Figure 4. (Colour online) Molecular graphs of C_6Li_6 (a) and $B_3N_3Li_6$ (b) computed by QTAIM method. BCPs are shown by green points on the bonds connecting two atoms.

from OLi_3 to BF_4 . Therefore, OLi_3-BF_4 is an ionic complex, which can be written as $(OLi_3)^+(BF_4)^-$. Likewise, the charge transfer from C_6Li_6 to BF_4 is $-0.87e$ such that the binding energy of $C_6Li_6-BF_4$ is reduced only slightly (7.80 eV). Nevertheless, this complex can also be considered as $(C_6Li_6)^+(BF_4)^-$. Thus, C_6Li_6 interacts with superhalogen more or less similarly as a typical superalkali does.

Borazine ($B_3N_3H_6$) is an inorganic analogue of C_6H_6 . Lithiated borazine ($B_3N_3Li_6$) has also been reported to be star-like structure [46]. Our recent study [47] shows that the VIE of $B_3N_3Li_6$ is 4.25 eV, which is comparable to that of C_6Li_6 . Therefore, it seems interesting to compare the bonding feature of C_6Li_6 and $B_3N_3Li_6$. We have calculated the molecular graph of both C_6Li_6 and $B_3N_3Li_6$ using quantum theory of atoms in molecule (QTAIM) method [48,49] as displayed in Figure 4. In the framework of QTAIM, the bonding between two atoms is characterised by a bond critical point (BCP), shown by green points in Figure 4. In the molecular graph of C_6Li_6 , we obtain two BCPs for each Li atom, which correspond to C–Li bonds. Therefore, C_6Li_6 is indeed a star-like structure in which Li atoms interact with two neighbouring C atoms of the ring. Likewise, we find two BCPs for each Li atoms in $B_3N_3Li_6$. In contrast to C_6Li_6 , both BCPs in $B_3N_3Li_6$ correspond to N–Li bonds, not to B–Li bonds. Thus, there exists no B–Li bond in $B_3N_3Li_6$ according to QTAIM analysis. Consequently, $B_3N_3Li_6$ is not strictly star-like; rather it appears as a fan-like structure. This is evidently due to large electronegativity difference between B and N atoms in $B_3N_3Li_6$, which is not the case for C_6Li_6 .

4. Conclusions

We have performed density functional investigations on Li-substituted at all H-atoms of aromatic hydrocarbons such as benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$) and coronene ($C_{24}H_{12}$). Our study leads to conclude the following:

- (1) Unlike corresponding hydrocarbons, the VIEs of all lithiated species are lower than the IE of Li atom, just like those of superalkalis. However, they all possess closed-shell structures, unlike superalkalis.
- (2) Like corresponding hydrocarbons, all lithiated species are planar and aromatic. However, their aromaticity is reduced due to Li-substitution as compared to hydrocarbons.
- (3) The interaction of C_6Li_6 with BF_4 superhalogen is similar to that of OLi_3 superalkali. This may suggest that these lithiated species behave as superalkalis.
- (4) C_6Li_6 possesses star-like structure, unlike its inorganic analogue $B_3N_3Li_6$, which is found to be fan-like structure rather than star-like as proposed earlier.

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Disclosure statement

No potential conflict of interest was reported by the author.

References

- [1] K.B. Wiberg, *Tetrahedron* **24**, 1083 (1968). doi:10.1016/0040-4020(68)88057-3.
- [2] T.M. Krygowski, K. Ejsmont, B.T. Stepien, M.K. Cyranowski, J. Poater, and M. Sola, *J. Org. Chem.* **69**, 6634 (2004). doi:10.1021/jo0492113.
- [3] A.K. Srivastava, S.K. Pandey, and N. Misra, *Theor. Chem. Acc.* **135**, 158 (2016). doi:10.1007/s00214-016-1918-5.
- [4] A.K. Srivastava, S.K. Pandey, and N. Misra, *Mol. Phys.* **114**, 1763 (2016). doi:10.1080/00268976.2016.1145749.
- [5] B.Z. Child, S. Giri, S. Gronert, and P. Jena, *Chem. Eur. J.* **20**, 4736 (2014). doi:10.1002/chem.201305057.
- [6] S. Giri, B.Z. Child, and P. Jena, *ChemPhysChem*. **15**, 2903 (2014). doi:10.1002/cphc.201402472.
- [7] N. Driver and P. Jena, *Int. J. Quantum Chem.* **118**, e25504 (2017). doi:10.1002/qua.25504.
- [8] L.A. Shimp, J.A. Morrison, J.A. Gurak, J.W. Chinn Jr., and R.J. Lagow, *J. Am. Chem. Soc.* **103**, 5951 (1981). doi:10.1021/ja00409a074.
- [9] J.R. Baran Jr. and R.J. Lagow, *J. Am. Chem. Soc.* **112**, 9415 (1990). doi:10.1021/ja00181a066.
- [10] G.L. Gutsev and A.I. Boldyrev, *Chem. Phys. Lett.* **92**, 262 (1982). doi:10.1016/0009-2614(82)80272-8.
- [11] C.H. Wu, H. Kudo, and H.R. Ihle, *J. Chem. Phys.* **70**, 1815 (1979). doi:10.1063/1.437656.
- [12] A.K. Srivastava and N. Misra, *New J. Chem.* **39**, 6787 (2015). doi:10.1039/C5NJ01259G.
- [13] A.K. Srivastava and N. Misra, *RSC Adv.* **5**, 74206 (2015). doi:10.1039/C5RA14735B.
- [14] A.K. Srivastava and N. Misra, *Chem. Phys. Lett.* **648**, 152 (2016). doi:10.1016/j.cplett.2016.02.010.
- [15] Y. Li, D. Wu and Z.-R. Li, *Inorg. Chem.* **47**, 9773 (2008). doi:10.1021/ic800184z.
- [16] H. Yang, Y. Li, D. Wu, and Z.-R. Li, *Int. J. Quantum Chem.* **112**, 770 (2012). doi:10.1002/qua.23053.
- [17] A.K. Srivastava and N. Misra, *Mol. Phys.* **112**, 2621 (2014). doi:10.1080/00268976.2014.900198.
- [18] Y.-Q. Jing, Z.-R. Li, D. Wu, Y. Li, B.-Q. Wang, F.L. Gu, and Y. Aoki, *ChemPhysChem*. **7**, 1759 (2006). doi:10.1002/cphc.200600157.
- [19] S. Giri, S. Bahera, and P. Jena, *J. Phys. Chem. A* **118**, 638 (2014). doi:10.1021/jp4115095.
- [20] E. Rehm, A.I. Boldyrev, and P.v.R. Schleyer, *Inorg. Chem.* **31**, 4834 (1992). doi:10.1021/ic00049a022.
- [21] N. Hou, Y. Li, D. Wu, and Z.-R. Li, *Chem. Phys. Lett.* **575**, 32 (2013). doi:10.1016/j.cplett.2013.05.014.
- [22] J. Tong, Y. Li, D. Wu, Z.-R. Li, and X.-R. Huang, *J. Phys. Chem. A* **115**, 2041 (2011). doi:10.1021/jp110417z.
- [23] J. Tong, Y. Li, D. Wu, and Z.-J. Wu, *Inorg. Chem.* **51**, 6081 (2012). doi:10.1021/ic202675j.
- [24] J. Tong, Z. Wu, Y. Li, and D. Wu, *Dalton Trans.* **42**, 577 (2013). doi:10.1039/C2DT31429K.
- [25] W.-M. Sun, Y. Li, D. Wu, and Z.-R. Li, *J. Phys. Chem. C* **117**, 24618 (2013). doi:10.1021/jp408810e.
- [26] Y. Xie and H.F. Schaefer III, *Chem. Phys. Lett.* **179**, 563 (1991). doi:10.1016/0009-2614(91)87104-J.
- [27] B.J. Smith, *Chem. Phys. Lett.* **207**, 403 (1993). doi:10.1016/0009-2614(93)89021-9.
- [28] S.M. Bachrach and J.V. Miller Jr., *J. Org. Chem.* **67**, 7389 (2002). doi:10.1021/jo025920+.
- [29] Y.-B. Wu, J.-L. Jiang, R.-W. Zhang, and Z.-X. Wang, *Chem. Eur. J.* **16**, 1271 (2010). doi:10.1002/chem.200901983.
- [30] A. Vasquez-Espinal, R. Pino-Rios, P. Fuentealba, W. Orellana, and W. Tiznado, *Int. J. Hydrog. Energy* **41**, 5709 (2016). doi:10.1016/j.ijhydene.2016.02.018.
- [31] S. Giri, F. Lund, A.S. Núñez, and A. Toro-Labbé, *J. Phys. Chem. C* **117**, 5544 (2013). doi:10.1021/jp3095819.
- [32] A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988). doi:10.1103/PhysRevA.38.3098.
- [33] C. Lee, W. Yang, and R.G. Parr, *Phys. Rev. B* **37**, 785 (1988). doi:10.1103/PhysRevB.37.785.
- [34] M.J. Frisch, G.W. Trucks, and H.B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 09, Revision C02* (Gaussian Inc., Wallingford, CT, 2009).
- [35] L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibia, and S. Grimme, *Phys. Chem. Chem. Phys.* **19**, 32184 (2017). doi:10.1039/C7CP04913G.
- [36] N. Mardirossian and M. Head-Gordon, *Mol. Phys.* **115**, 2315 (2017). doi:10.1080/00268976.2017.1333644.
- [37] M.D. Harmony, V.W. Laurie, R.L. Kuczkowski, R.H. Schwendeman, D.A. Ramsay, F.J. Lovas, W.J. Lafferty, and A.G. Maki, *J. Phys. Chem. Ref. Data* **8**, 619 (1979). doi:10.1063/1.555605.
- [38] G.I. Nemeth, H.L. Selzle, and E.W. Schlag, *Chem. Phys. Lett.* **215**, 151 (1993). doi:10.1016/0009-2614(93)89279-Q.
- [39] P.v.R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N.J.v.E. Hommes, *J. Am. Chem. Soc.* **118**, 6317 (1996). doi:10.1021/ja960582d.
- [40] P.v.R. Schleyer and H. Jiao, *Pure Appl. Chem.* **68**, 209 (1996).
- [41] I.D. Madura, T.M. Krygowski, and M. Cyranowski, *Tetrahedron* **54**, 14913 (1998). doi:10.1016/S0040-4020(98)00933-8.
- [42] T.M. Krygowski and M. Cyranowski, *Tetrahedron* **52**, 10255 (1996). doi:10.1016/0040-4020(96)00560-1.
- [43] J. Poater, M. Duran, M. Sola, and B. Silvi, *Chem. Rev.* **105**, 3911 (2005). doi:10.1021/cr030085x.

- [44] J.E. Sansonetti, W.C. Martin, and S.L. Young, *J. Phys. Chem. Ref. Data* **34**, 1559 (2005). doi:[10.1063/1.1800011](https://doi.org/10.1063/1.1800011).
- [45] G.L. Gutsev and A.I. Boldyrev, *Chem. Phys.* **56**, 277 (1981). doi:[10.1016/0301-0104\(81\)80150-4](https://doi.org/10.1016/0301-0104(81)80150-4).
- [46] A. Chakraborty, S. Bandaru, R. Das, S. Duley, S. Giri, K. Goswami, S. Mondal, and S. Pan, *Phys. Chem. Chem. Phys.* **14**, 14784 (2012). doi:[10.1039/c2cp41424d](https://doi.org/10.1039/c2cp41424d).
- [47] A.K. Srivastava, S.N. Tiwari, and N. Misra, *Int. J. Quantum Chem.* **119**, e25507 (2018). doi:[10.1002/qua.25507](https://doi.org/10.1002/qua.25507).
- [48] R.F.W. Bader, *Atoms in Molecules: A Quantum Theory* (Clarendon Press, Oxford, 1990).
- [49] T.A. Keith, *AIMAll (Version 12.09.23)* (TK Gristmill Software, Overland Park, KS, 2012).