

Aromaticity, response, and nonlinear optical properties of sumanene modified with boron and nitrogen atoms

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Abstract We investigated the effects of substitution on the sumanene benzylic CH₂ groups with BH and NH groups using density functional theory computations. Our study shows that various properties of sumanene could be finely tuned for the application in the areas closely related to the materials science. Structural properties are significantly altered with such modifications and other properties as well. Charge distributions were evaluated through natural population analysis (NPA), while stability of investigated structures was investigated using quantum molecular descriptors. Using molecular orbital analysis further insight into the effects of substitution was obtained. Potential of sumanene as a candidate for application in the field of organic electronics is assessed through calculations of exciton binding energy. Non-linear optical properties of investigated structures were investigated using the first hyperpolarizability tensor. Special attention was paid to the aromaticity of sumanene. This property was evaluated employing NICS parameter while for detailed study of obtained results we used NBO and NBOdel analysis.

Keywords Aromaticity · DFT · Exciton binding energy · NBO · NBOdel · NLO properties · Sumanene

Introduction

Sumanene is a typical representative of the bowl-shaped polyaromatic hydrocarbons (also known as buckybowls, π -bowls) which are considered to be another important class of materials in the science of non-planar π -conjugated carbon systems. Sumanene has a partial structure of fullerenes [1, 2], offering a lot of opportunities compared to these structures. Although the synthesis, structural characterization, and complexation of buckybowls have been studied for more than 15 years [1, 3–8] there is still a lot of space for theoretical research of potential application of these structures in the various fields of science. For instance, thanks to the significant charge separation, the sumanene dipole moment is relatively high and can induce a dipole moment in the molecules such as hydrogen, thus allowing the process of physisorption to happen [9]. The potential of sumanene is also seen in its structural features; it has three benzylic carbon atoms suitable for effective functionalization [10]. Another important structural feature is its bowl depth, which is significantly higher than in its “elder brother”—corannulene.

Until its successful, relatively recent synthesis by Sakurai et al. in 2003 [3] theoretical research had been done by Priyakumar and Sastry [11]. Recently, Purushotham and Sastry [12] have conducted a vast study of acene fused buckybowls, which electronic properties indicated potential for practical application. Experimental results of Amaya et al. [7] emphasize the great potential of sumanene also as an electronic material.

All these facts motivated us to investigate theoretically changes of essential properties of sumanene, the consequence of substitution of the benzylic CH₂ groups with BH and NH

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groups. We chose the DFT since this approach has proved to be a good solution when both accuracy and computational time are taken into account.

Typical bond lengths and their changes upon substitution were commented, together with characteristic vibrational modes. Charge separation was viewed in the terms of natural population analysis (NPA) charges, while with molecular orbital analysis we were able to understand further the effects of substitution.

Due to their specific properties, it is possible to apply sumanene in the field of electronics. Understanding the energy levels in organic semiconductors has been of great importance for the design of electronic devices and also for understanding their function and performance. Thus, we decided to calculate the exciton binding energy (E_b), in order to understand better the transport characteristics of modified sumanene. A special interest in the study of organic materials lies in the fact that nonlinear optical (NLO) response is basically microscopic in origin, thus provides the possibility of using theoretical modeling together with synthetic flexibility to design and produce novel materials [13–15]. Due to their large optical susceptibilities, inherent ultrafast response times and high optical thresholds for laser power, organic nonlinear optical materials have a great deal of attention. Optical properties (polarizability and first hyperpolarizability) were studied and the obtained results may have useful predictive values which can be of interest.

Using polarizability and first hyperpolarizabilities one is able to estimate how response properties of sumanene change with the substitution. Furthermore, once the polarizability is known it is possible to calculate the dielectric constants on the basis of Clausius-Mossotti model. Response properties are important as they determine the influence of external factors, such as electric field, and how much some material is prone to experimental investigation by certain methods.

Also, we were especially interested in the aromatic nature of sumanene rings and changes that occur after substitution. These changes were studied in more detail by calculating electron delocalization energy using the natural bond order (NBO) and NBOdel analysis. Within NBO analysis we located a certain NBO donor-acceptor interactions which might be related to the improvement of aromatic properties in the NH substituted sumanene. Further employing the NBOdel procedure (\$NBOdel keyword) certain interactions were deleted (actually certain elements of Fock matrix were deleted) and the energy was then recalculated. Such obtained energy differences finely correlate the improvement of aromatic properties.

Computational details

Gaussian 03 software [16] was employed for all DFT calculations with hybrid, non-local exchange, and correlation

functional of Becke-Lee, Parr, and Yang (B3LYP) [17, 18]. Two stages took place: first the ground state geometrical parameters have been determined using 6-31G(d) atomic basis set. Secondly, harmonic vibrational spectrum at the same level of theory has been checked in order to assure that the true minimum of potential energy is located. For the plot of IR spectra, IR peak half-width at half-height was taken at 4 cm^{-1} .

Polarizability and hyperpolarizability calculations were obtained after geometrical optimizations and frequency checks at the same level of theory but with 6-31++G(d,p) basis, tight convergence criteria, and ultrafine grid for computations of two-electron integrals for the purpose of more accurate results.

UV/Vis information were taken from our previous work [10] where simulations were done at the same level of theory with 6-31++G(d,p) basis set.

In this work we managed to successfully geometrically optimize and investigate six cases of substitution of benzylic CH_2 groups with BH and NH groups. Obtained structures upon geometrical optimizations are given in Fig. 2. Quantum molecular descriptors were calculated using the information on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, which we obtained after geometrical optimization, in order to check stability of obtained structures. According to Schleyer et al. [19], aromaticity was investigated by calculation of nucleus independent chemical shielding parameter in the centers of all rings NICS(0). Chemical shielding was calculated within gauge invariant atomic orbital method (GIAO) [20], employing Gaussian 03 software package. NBO analysis was performed with NBO 3 program written by Weighnold and coworkers [21], as implemented in Gaussian 03. Density of states (DOS) analysis was done using GaussSum2.2 [22].

Results and discussion

Structural changes, characteristic vibrational modes, and stability considerations

The changes that occurred as a consequence of the substitution of benzylic CH_2 are investigated through structural changes and changes of IR spectra. As for structural considerations, the geometries of investigated sumanene derivatives after geometrical optimizations are given in Fig. 1, together with specific bond lengths. For the purpose of easier comparison, the bond lengths of regular sumanene are underlined and given in red color.

Bond lengths changed significantly in the near vicinity of introduced boron and nitrogen atoms. The introduction of BH/NH groups increased/decreased bond lengths between atom at benzylic position and near carbon atoms. These structural changes are related to the changes of bowl depth [10] which is dictated by the size of substituent, as stated by Priyakumar

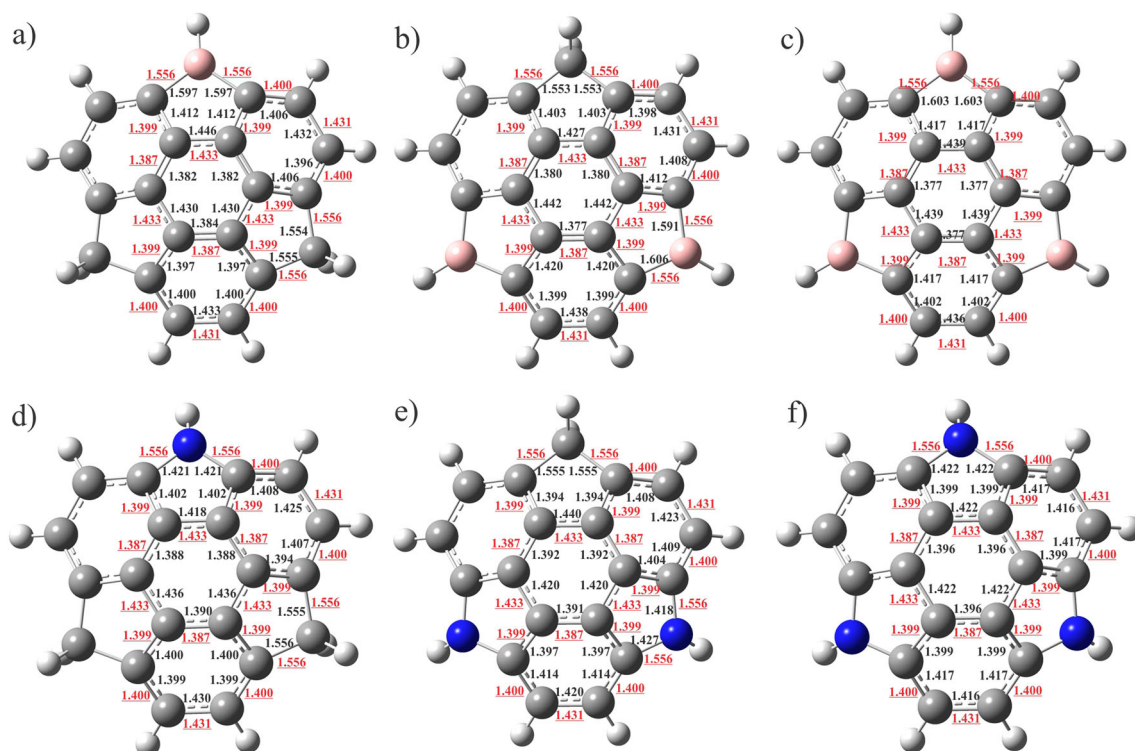


Fig. 1 Typical bond lengths and their changes upon substitution. Sumanene substituted with a) one, b) two, and c) three BH groups and with d) one, e) two, and f) three NH groups

et al. [11]. Larger substituent tends to flatten the structure and vice versa. As presented in Fig. 2, IR spectra changed significantly and specifically.

All the IR spectra were scaled by factor 0.9613 as proposed by Merrick et al. [23]. The theoretically predicted IR spectrum of sumanene indicates the intense vibrational modes above 3000 cm^{-1} , corresponding to the C-H stretching. There are no vibrational modes in the area between 1436 and 2923 cm^{-1} .

Specific vibrational modes corresponding to the B-H stretching are obtained at frequencies of around 2550 cm^{-1} , after substitution with BH groups. The number of additional vibrational modes around 2550 cm^{-1} corresponds to the number of introduced BH groups. The intensity of vibrational modes around 500 cm^{-1} and around 3000 cm^{-1} , specific for regular sumanene, are significantly decreased when BH groups are introduced. Maximal IR intensities significantly increased subsequently with the increase of introduced boron atoms.

Vibrational modes corresponding to the N-H stretching are obtained at around 3500 cm^{-1} , after the introduction of NH groups. The number of these specific vibrational modes again corresponds to the number of introduced NH groups. The intensity of the vibrational modes around 500 cm^{-1} increased, while the intensity of vibrational modes around 3000 cm^{-1} decreased. Maximal IR intensities significantly increased subsequently with the increase of introduced NH groups, however this increase is significantly lower than in the case when BH groups are introduced.

The cohesive energy or binding energy per atom is calculated, Fig. 3, in order to evaluate the structural stability of model systems presented here. This quantity is defined as the energy required for breaking the system into the isolated atomic species, and is given in the usual form [24–26]:

$$E_b = \frac{(aE(C) + bE(X) + cE(H) - E(\text{sumanene} + bX))}{a + b + c}, \quad (1)$$

where a and c correspond to the number of carbon and hydrogen atoms, while b corresponds to the number of introduced boron or nitrogen atoms. $E(C)$, $E(H)$ are the ground state total energies of carbon and hydrogen atoms while $E(X)$ corresponds to the ground state total energies of introduced boron or nitrogen atoms. $E(\text{Sumanene} + bX)$ stands for the ground state total energy of corresponding sumanene derivative.

Sum/ n BH denotes sumanene substituted with n number of BH or NH groups. Binding energy per atom increased subsequently with the introduction of boron and nitrogen atoms in all cases. Derivatives with nitrogen atoms have higher binding energies per atoms than those with boron atoms. It can be concluded, according to E_b , that substitution of CH_2 groups with BH and NH groups yields a stabilizing effect to the molecule.

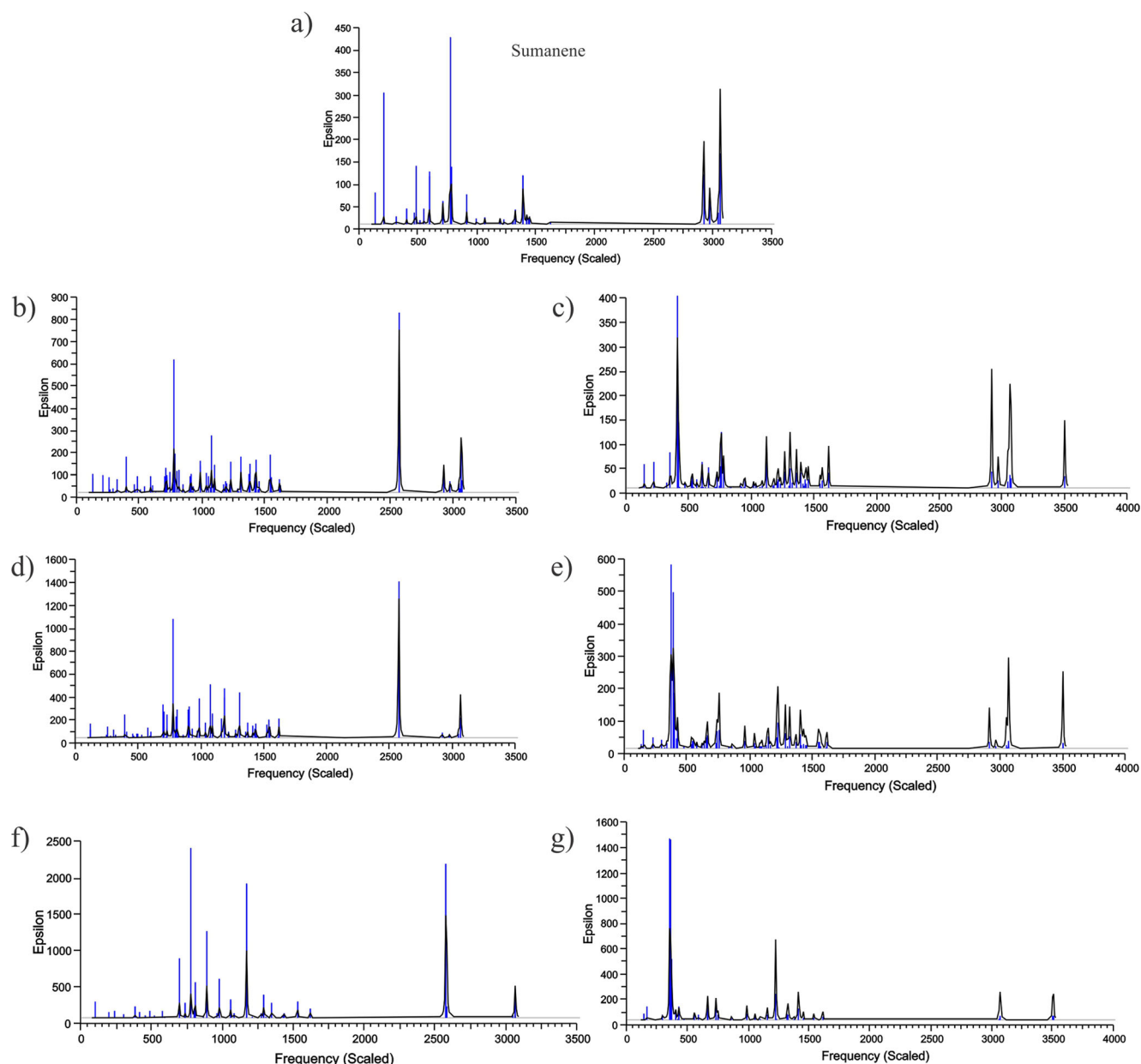


Fig. 2 IR spectra of sumanene and sumanene derivatives: a) sumanene and sumanene substituted with b) one, d) two, and f) three BH groups and with c) one, e) two, and g) three NH groups

NPA charges and dipole moments

The practical application of some molecule in the field of electronics is much more prominent if its charge distribution is known. Besides that, it is also useful to know the possibilities of manipulation of its charge distribution. Adsorption properties are also highly influenced by this factor. Thus, the NPA charges of atoms are provided in Table S1 of supplementary materials together with numbering schemes for all investigated structures in this work. To study the charge distribution of some molecule it is better to use the NPA than Mulliken one, since the NPA does not exhibit dependence on basis set [27].

The specific feature of molecular bowls related to the charge distribution is that they are polar, in contrast to the planar aromatic hydrocarbons. This is due to the anisotropic distribution of π -electrons and the C–H bonds, which is the trigger for separation of charges [11]. According to the NPA charges, a significant negative charge is located at the benzylic carbon atoms of regular sumanene. The NPA charge values are changed after substitution with both BH and NH groups due to the significant charge transfer in all cases.

The atom charges of benzylic positions practically inverted, after substitution with BH groups. Charges remain of the same sign but with higher/lower values, when substituted with NH groups. The difference between maximal and

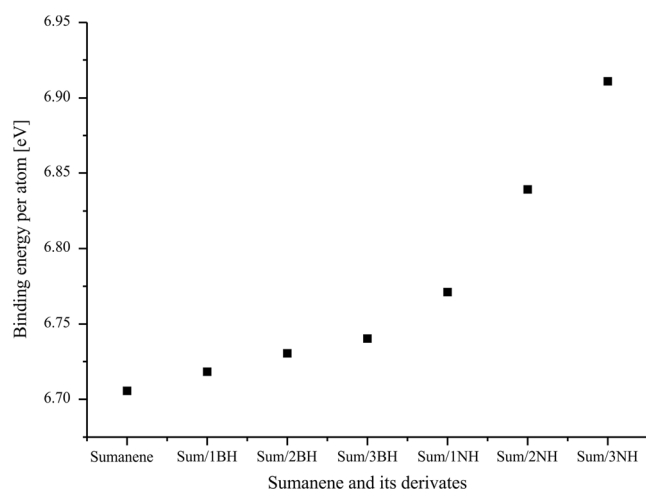


Fig. 3 Binding energies per atom of sumanene and its derivatives

minimal value of atom charge changed in both cases, which indicates a stronger charge separation. This results in the higher dipole moment than of regular sumanene. The dipole moments changed significantly after modification of sumanene, Fig. 4.

Physisorption is a very useful method for the storage of molecular hydrogen characterized with low adsorption/desorption energy and is related to the dipole moment. Hydrogen is more readily accessible within this mechanism at ambient conditions as opposed to the chemisorption, within which temperatures of the order of 600 K are typically required for desorption [28]. We have shown in our recent paper [9] that sumanene has suitable range of adsorption energies for the physisorption of hydrogen and this applicable result of sumanene is a consequence of its relatively high dipole moment, 1.96 D as calculated using B3LYP/6-31Gdp level of theory. With substitution of its benzylic positions with BH and NH groups the dipole moment significantly increases, Fig. 4, especially for the case when three NH groups are introduced. Calculated dipole moment in this case is calculated to be more than twice as high as the dipole moment of regular sumanene, 4.87 D. The only decrease of dipole moment was in the case when three BH groups are introduced. These changes of dipole moments are important because with the increase of dipole moments response to the external electromagnetic field is improved as well.

Molecular orbital analysis

Molecular orbitals provide an insight into the nature of reactivity, conjugation, aromaticity, lone pairs, and structural and physical properties of molecules [29]. Using energies of frontier molecular orbitals, HOMO and LUMO, one is able to obtain a series of useful quantum molecular descriptors important for understanding the properties of investigated molecules. Furthermore, employing DOS analysis it is possible to

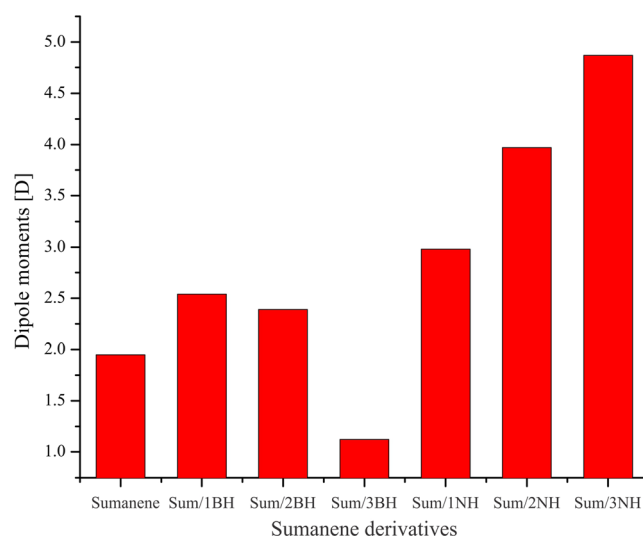


Fig. 4 Dipole moments of sumanene and its derivatives

gain an insight into the effects of substitution through observing molecular orbital contributions of substituted atoms to the HOMO and LUMO.

Using chemical hardness (η), in this work we investigated stability of obtained isomers. We used this quantity since η proved to be a useful index of reactivity in atoms, molecules, and solids [30–35].

The hardness, η , was calculated using Koopmans approximation [36], according to the following equation:

$$\eta = (E_{LUMO} - E_{HOMO})/2. \quad (2)$$

Pearson showed that the HOMO-LUMO gap represents η of the molecule [37]. The hardness represents the resistance toward the deformation of electron cloud of the observed system under small perturbation encountered during the interaction with other structures. Soft systems are large and highly polarizable, while hard systems are relatively small and much less polarizable [38].

We also calculated two more descriptors which also might be useful for understanding of investigated structures, chemical potential (μ) and electrophilicity (ω). They are calculated as follows:

$$\mu = -\chi = (E_{HOMO} + E_{LUMO})/2 \quad (3)$$

$$\omega = \mu^2/2\eta. \quad (4)$$

Chemical potential is equivalent to the negative electronegativity (χ) and describes the tendency of a system to attract electrons, while ω measures the deficiency in electron of the

element [39]. Global quantum molecular descriptors for all structures are summarized in Table 1.

Structures upon substitution still have significantly high values of quantum descriptor η . The highest value of chemical hardness was obtained for sumanene substituted with three BH groups and for sumanene substituted with one NH group. Chemical potential was increased for sumanene substituted with two BH groups comparing with regular sumanene. Electrophilicity, for the case of sumanene substituted with two BH groups, was three times higher than of regular sumanene, while for the case of substitution with NH groups this descriptor lowered. These mentioned changes of chemical potential and electrophilicity indicate that sumanene derivatives with BH groups are prone to a higher extent to interaction with other molecules through acceptance of electrons, than sumanene derivatives with NH groups.

Further insight into the changes of chemical potential and electrophilicity was gained through DOS analysis. While total density of states (TDOS) is useful for track of band gap change, a partial density of states (PDOS) is useful for determination of molecular orbital contributions; it mainly presents the composition of fragment orbitals contributing to the molecular orbitals. Analyzing PDOS we are able to conclude whether and how much substitute atoms contribute to the HOMO and LUMO orbitals.

The TDOS and PDOS of investigated isomers, Fig. 5, were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 eV using GaussSum2.2.

As can be seen in Fig. 5, when boron atoms are introduced they mainly contribute to the LUMO orbitals, while the nitrogen atoms mainly contribute to the HOMO orbitals. It is useful to remember at this step that LUMO represents the ability to obtain an electron, while HOMO represents the ability to donate an electron. Thus, the introduction of boron atoms tends to increase the ability of corresponding derivate to react with some other system by obtaining an electron, while the introduction of nitrogen atoms tends to increase the ability of corresponding isomer to react with some other system by donating electron.

The percentage contributions of substituting atoms to the HOMO and LUMO orbitals, Fig. 6, can be obtained by GaussSum2.2. These values are obtained by employing the orbital overlap information, information on the molecular orbital coefficients, and Mulliken analysis.

With increase of the number of substituting atoms their contribution to the frontier molecular orbitals rises. The contribution of boron atoms to the frontier orbitals is two times higher when the BH groups are introduced than in the case of nitrogen atoms when the NH groups are introduced. These results also explain the results related to the values of chemical potential and electrophilicity. Namely, for the case of derivatives with boron atoms it is clear from Fig. 6 that the higher values of chemical potential and electrophilicity index are due to the fact

that introduced boron atoms contribute to the LUMO. For the case of derivatives with nitrogen atoms, lower values of chemical potential and electrophilicity are related to the fact that introduced nitrogen atoms contribute to the HOMO.

Polarizability and hyperpolarizability

The polarizability indirectly provides a measure of the extent of distortion in the electron density. This provides an insight into the response of system under the influence of an external static electric field. This parameter is also known to be sensitive to the nature of bonding and geometrical structure of the systems [40].

NLO response is related to the first hyperpolarizability. Computational approach allows determination of the molecular NLO properties as an inexpensive way to design molecules by analyzing their potential before synthesis [41]. The higher the NLO response the easier is its investigation and application.

The mean polarizability, α , and the mean first hyperpolarizability, β , are important and rather common quantities that can be readily calculated by computational methods. Therefore their definitions and concepts can be found in many papers [42–44]. It is important to note that these quantities can be expressed through x, y, z components as follows:

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3, \quad (5)$$

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2}. \quad (6)$$

The polarizability and hyperpolarizability tensors can be obtained by the frequency job output file of Gaussian. It has to be noted that α and β values of Gaussian output are in the atomic units (a.u.). They can be converted to the electronic units (esu) (for α 1 a.u.= 0.1482×10^{-24} esu and for β ; 1 a.u.= 8.6393×10^{-33} esu). Results are summarized in Table 2.

The highest polarizability was calculated for the structure of three boron atoms, 37.3×10^{-24} esu, compared to the value of 35.4×10^{-24} esu for regular sumanene. The lowest polarizability was calculated for the structure of two nitrogen atoms, 34.8×10^{-24} esu. Clearly, the introduction of boron atoms leads to increase, while the introduction of nitrogen atoms leads to decrease in the polarizability of sumanene.

Concerning the hyperpolarizability, it is a usual practice to compare obtained values to that of standard non-linear optical medium — urea molecule [45–47]. The calculated hyperpolarizability of sumanene is nine times higher than urea (0.13×10^{-30} esu) [42]. Sumanene derivate with one boron atom is 49 times higher than that of urea. All the other derivatives investigated in this paper have higher

Table 1 Quantum molecular descriptors of investigated structures

Property	Sumanene	Sum/1BH	Sum/2BH	Sum/3BH	Sum/1NH	Sum/2NH	Sum/3NH
η [eV]	2.380	1.688	1.522	2.100	2.138	1.996	2.022
μ [eV]	-3.096	-3.916	-4.330	-4.004	-2.901	-2.756	-2.699
ω [eV]	2.014	4.542	6.159	3.817	1.968	1.903	1.801

hyperpolarizability than urea, except the derivative with three boron atoms.

It is clear that NLO properties can be significantly manipulated by presented substitutions. In all cases, except for the case when three BH groups are introduced, NLO response is significantly improved. This improvement is especially high for the cases when one and two BH groups are introduced as for these cases NLO response increased six and five times, respectively. Again, introduction of BH groups had higher influence as in these cases the hyperpolarizability changed much more than for the cases when NH groups are introduced.

At this point it was interesting to test the statement about the relation of chemical hardness and polarizability, noted in

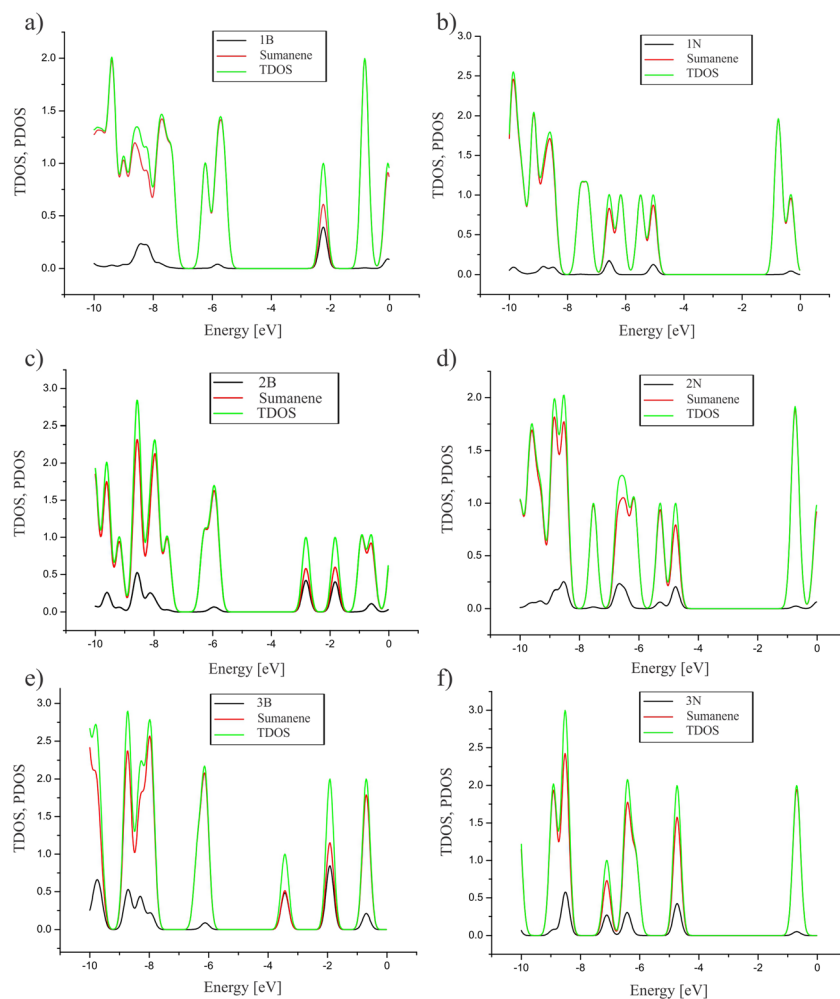
Molecular orbital analysis. Namely, to check if soft systems are more polarizable than hard systems, we correlated the data related to chemical hardness and polarizability, Fig. 7.

Obtained results in general and qualitatively indicate that softer systems investigated in this paper are indeed more polarizable opposed to the hard systems which are less polarizable. The only significant exception was the derivative where three BH groups are introduced.

Dielectric constant

The dielectric constant is calculated using a simple equation based on the Clausius-Mossotti model [39]. This model is frequently used and what is even more important it is used

Fig. 5 PDOS plots of investigated isomers. Left side corresponds to the case when BH groups are introduced while left side corresponds to the case when NH groups are introduced



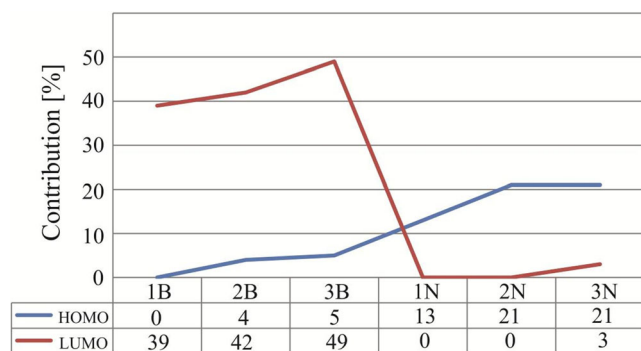


Fig. 6 Contribution of substituting atoms to HOMO and LUMO orbitals. Provided numbers represent percentage contribution of substituting atoms to the frontier molecular orbitals

for the evaluation of dielectric constant of C_{60} (to which sumanene is a model compound) and other conjugated organic molecules [48, 49]. Within the Clausius-Mossotti model, the dielectric constant, ϵ , can be expressed as:

$$\epsilon = \frac{1 + (8\pi\alpha)/3v}{1 - (4\pi\alpha)/3v}, \quad (7)$$

where α is the first order polarizability and v is the volume occupied by a single molecule. In order to obtain better accuracy tight option and ultrafine grid for calculation of integrals are used, while the volumes of optimized structures are calculated employing Vegazz [50]. Results are summarized in Table 3.

The calculated dielectric constant of sumanene is 6.11 and this quantity can be manipulated with substitution. The dielectric constant of investigated structures is in the range of 6.04 to 6.75, Table 3. Substitution with NH groups gradually increased dielectric constant to the value of 6.75, which represents an increase of about 10 %. Introduction of BH groups somewhat lowered dielectric constant, except in the case of substitution with just one BH group when dielectric constant increased to the value of 6.34. It may also be seen that the larger values of dielectric constant are related to the lower volumes of structures.

Table 2 Mean polarizability and the first hyperpolarizability of investigated structures

Structure	α [esu 10^{-24}]	β [e.s.u 10^{-30}]
Sumanene	35.4	1.17
Sumanene/1BH	36.2	6.43
Sumanene/1NH	35.2	1.40
Sumanene/2BH	36.9	5.23
Sumanene/2NH	34.8	1.43
Sumanene/3BH	37.3	0.51
Sumanene/3NH	34.5	1.25

It is useful to emphasize that the dielectric constant of pristine fullerene C_{60} ranges from 4.0 to 4.5 [51–53]. Numerous studies have shown that fullerenes are considered as promising candidates for design of low k dielectrics [54–57]. On the other hand the studies of dielectric properties of carbon nanotubes indicated the potential of these structures to be the basis for high k dielectrics. Namely, for the chemically modified multi wall carbon nanotubes (MWCNT) it is demonstrated to have the values of dielectric constant ranging from 0 to 10^4 , depending on the volume fraction of MWCNTs [58, 59]. Calculated values of dielectric constant for sumanene and its derivatives investigated in this paper are much closer to the values obtained for fullerene, thus implying the potential of sumanene to be used as a low k dielectric. This still needs to be investigated, both theoretically and experimentally.

Exciton binding energies

The exciton binding energy may be seen as the energy required to decompose an exciton into a free electron and hole in the solid and is defined using the following equation:

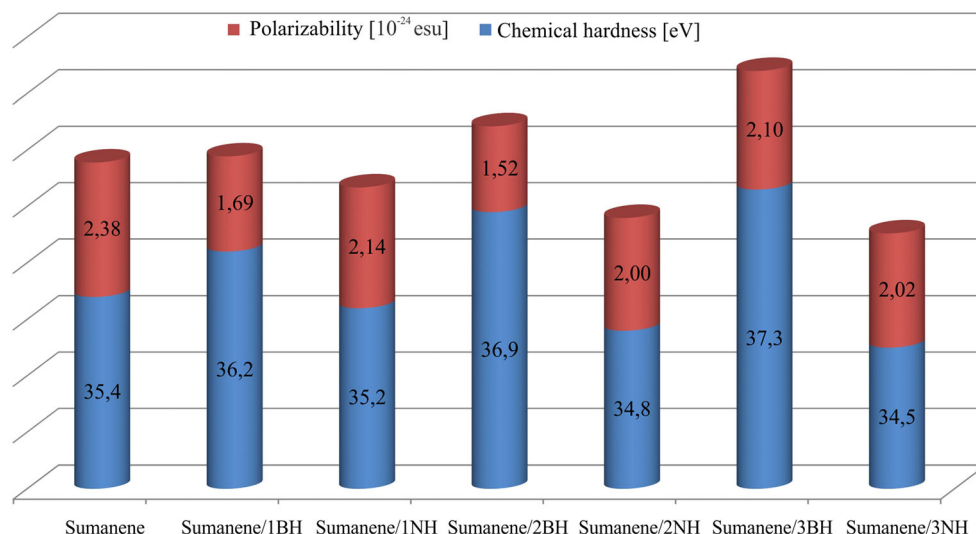
$$E_b = E_t - E_{opt}. \quad (8)$$

The difference between the two transport levels is referred to as the transport gap (E_t) which is different from the optical gap (E_{opt}) in organic semiconductors. This is due to the fact that optical excitations give rise to excitons rather than free electrons. These excitons, localized to the molecule, are Frenkel excitons and an extra amount of energy, exciton binding energy (E_b), is needed to produce free charge carriers [49, 57, 60, 61].

E_t can be interpreted as the orbital energy difference between the HOMO and LUMO [62], while E_{opt} can be calculated as the allowed lowest singlet optical transition energy with non-zero oscillator strength. We obtained E_{opt} in this paper after time-dependent DFT (TD-DFT) calculations at 6–31++Gdp basis, as the employment of diffuse functions significantly improve the UV/Vis calculations.

According to the obtained results, the exciton binding energy can be effectively manipulated by substitution of sumanene benzylic positions, Table 4.

Exciton binding energies decreased significantly with the introduction of BH and NH groups and in both cases the lowest exciton binding energy was obtained for isomers containing two BH or NH atoms. In these cases E_b decreased for 25 % and 32 % for substitution with BH and NH groups, respectively. An interesting situation happened in the case when three BH groups are introduced, namely the E_b then became negative. This result indicates that there is a very low possibility for exciton to be formed due to the much lower transport gap obtained for this case. Due to the low transport gap electron and hole are too close, thus recombination

Fig. 7 Comparison of polarizability and chemical hardness

occurs. Consequently, the increased recombination of electrons and holes in this derivative might lead to the decrease of optical properties related with exciton subsystem. In our previous work [10] it is shown that of all investigated derivatives precisely this derivative has the lowest absorption properties in the UV spectra.

Exciton binding energies of 0.8 nm carbon nanotubes are found to be around 0.4 eV, as reported in [63] while the exciton binding energies of conventional bulk semiconductors such as GaAs have values of around 0.01 eV, due to strong Coulombic interactions [64]. In general, the large binding energy of one dimensional excitons results in the large radiative lifetimes (up to 100 ns) [65] and fluorescence lifetimes (up to 100 ps) [66] at room temperature, thereby enabling the straightforward study of exciton dynamics at room temperature [67, 68].

Aromaticity and electron delocalization

π -stacking is the attractive interaction between aromatic rings. This is common phenomena for bowl-shaped π -aromatics which favor a stacking structure in a concave-convex fashion. Sakurai et al. [8, 69] observed such arrangement for sumanene with approximate stacking distance of 3.86 Å. Within conventional understanding aromaticity is crucial for π stacking

to occur. Schleyer introduced magnetic criterion, namely the nucleus independent chemical shielding (NICS), for the [19] the evaluation of aromaticity. According to Schleyer the NICS is calculated as a negative value of absolute magnetic shielding calculated at the aromatic ring center, NICS(0) or one angstrom above the molecular plane, NICS(1). NICS are very important parameters because they are closely related to the energetic, structural, and magnetic properties of molecules. In this paper we tracked changes of NICS(0) parameter, and results are summarized in Fig. 8.

According to the NICS(0) sumanene's six member rings have aromatic nature while five member rings have non-aromatic nature [70]. After introduction of BH and NH groups, aromatic nature of all rings changed significantly, especially for the cases when three boron/nitrogen atoms are introduced.

Aromatic nature of the central six member ring somewhat increased, the aromatic nature of outer six member rings decreased while aromatic nature of five member rings became anti-aromatic when BH groups are introduced. A much more interesting situation happened with the introduction of three NH groups. The aromatic nature of central six member ring became non-aromatic, but the aromatic nature of both six member and five member rings significantly increased. To

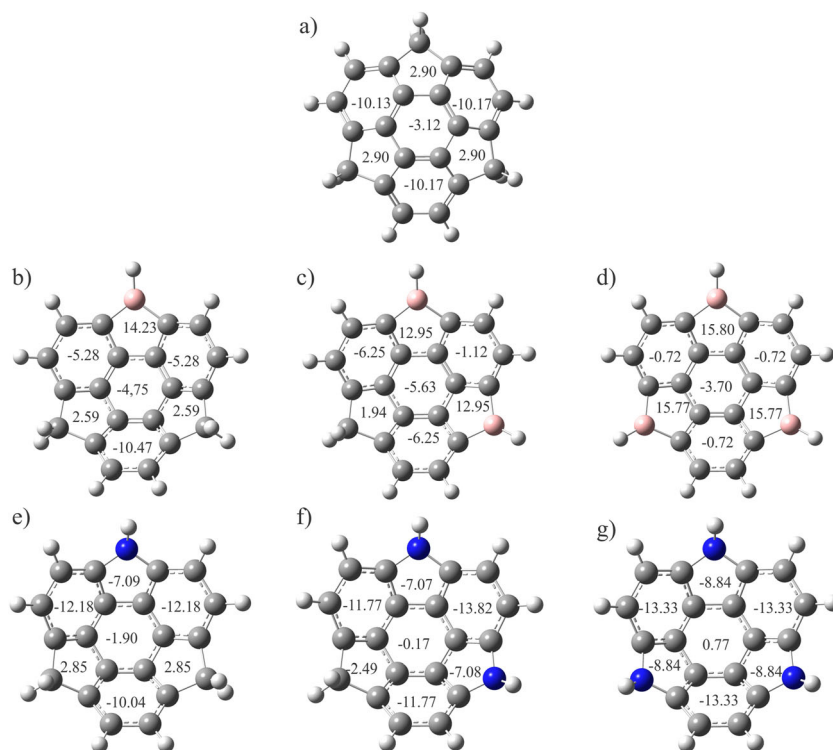
Table 3 Volumes and dielectric constants of investigated structures

Structure	Volume [\AA^3]	ϵ
Sumanene	234.9	6.11
Sum+1B	236.2	6.34
Sum+1 N	226.8	6.53
Sum+2B	246.3	6.04
Sum+2 N	223.6	6.61
Sum+3B	247.9	6.09
Sum+3 N	219.2	6.75

Table 4 Exciton binding energies of sumanene and its derivatives

System	E_t [eV]	E_{opt} [eV]	E_b [eV]
Sumanene	4.657	3.794	0.863
Sum/1BH	3.339	2.563	0.776
Sum/2BH	3.023	2.307	0.716
Sum/3BH	2.677	3.430	-0.753
Sum/1NH	4.171	3.545	0.626
Sum/2NH	3.892	3.359	0.533
Sum/3NH	3.948	3.302	0.646

Fig. 8 NICS(0) parameters of a) sumanene and sumanene substituted with b) one, c) two, and d) three BH groups and sumanene substituted with e) one, f) two, and g) three NH groups



explain better the aromatic properties of sumanene derivatives with NH groups we shall refer to NBO and NBOdel analysis.

The NBO analysis is carried out by the energetic examination of all possible interactions between ‘filled’ (donor) NBOs and ‘empty’ (acceptor) NBOs, and estimating their energetic importance by 2nd-order perturbation theory. In this manner we obtained the energies of delocalization of electrons from filled NBOs into empty NBOs, e.g., we obtained the stabilization energies gained by donation from the donor NBO to the acceptor NBO. In this way we are able to conclude which interactions among all possible interactions produce stability of certain molecule [71–73].

For each donor NBO (*i*) and acceptor NBO (*j*), the stabilization energy associated with *i*→*j* delocalization may be estimated on the basis of second order perturbation theory as:

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i \varepsilon_j}, \quad (9)$$

where q_i is the donor orbital occupancy, $\varepsilon_i, \varepsilon_j$ are diagonal elements (orbital energies) and $F(i,j)$ is the off-diagonal NBO Fock matrix element.

Using NBOdel analysis, precisely the \$NBOdel keyword, one is able to delete specific donor-acceptor interactions and

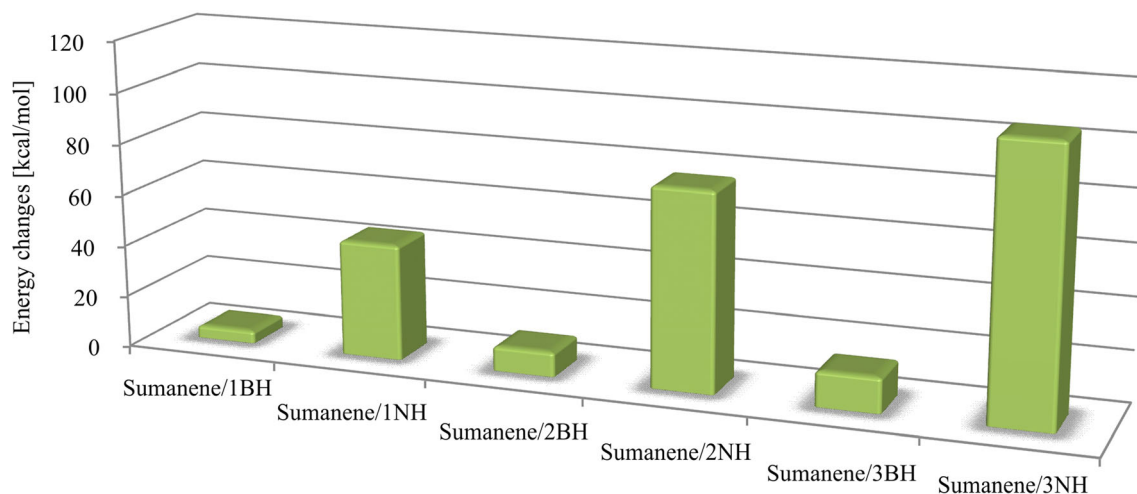


Fig. 9 Electron delocalization of sumanene substitution by BH and NH groups

to recalculate the energy. Obtained energy changes indicate the energetic contribution of specific interactions and can be used to isolate those interactions that are responsible for a particular feature of interest, in this case the aromaticity.

The idea in this work was to delete certain interactions, to track the energy changes due to the deletions of those interactions and finally to correlate successfully energy changes with aromatic properties of sumanene derivatives. Of course, the main issue was the selection of interactions for deletion. At first we decided to delete all of the NBO donor-acceptor interactions that included B or N atoms for which $E(2)$ energies are higher than some arbitrarily chosen value (5 kcal mol^{-1}). The second choice was to delete only the most significant donor-acceptor interactions that are including B or N atoms, namely those with $E(2)$ energies higher than 20 kcal mol^{-1} . These two choices did not yield values of energy changes that could be related with mentioned changes of aromaticity upon introduction of BH and NH groups.

However, after detailed inspection of the NBO output it was concluded in cases when NH groups are introduced that, according to $E(2)$ energies, there are no significant interactions where the acceptor NBO orbital is including nitrogen atoms. On the other hand, for cases when BH groups are introduced there is a certain number of significant interactions where the acceptor NBO orbitals are including boron atoms. This gave us an idea to focus specifically on significant interactions where donor NBO orbitals are including boron or nitrogen atoms. Namely, using the NBODEL keyword we deleted precisely these interactions, marked with yellow color in Tables S2-S7 of Supplementary materials, and we obtained energy changes which correspond to the changes of aromatic properties of investigated derivatives, Fig. 9.

Obtained changes in energy are presented in Fig. 8. NBODEL procedure is performed at Hartree-Fock level of theory with the same basis set, as within DFT code this procedure is known to produce some problems [74].

It can be seen that the energy changes in cases when BH groups are introduced are low and very similar. In the cases when NH groups are introduced the situation is quite opposite—the energy changes significantly increase with the increased number of introduced NH groups. As NH groups are introduced, the aromatic properties of corresponding derivatives are improving subsequently with the increase of NBODEL energy changes. Thus, it can be concluded that significant interactions where donor NBO orbitals are including nitrogen atoms are responsible for improved aromatic properties of sumanene derivatives with NH groups.

Qualitative explanation of better aromatic properties of derivatives with NH groups can be provided with regard to the molecular orbitals theory. Namely, contrary to NH group which has electron lone pair, BH has an empty p orbital.

Taking into account that the delocalization of p electrons can be related with aromaticity [75, 76], empty p orbital of BH group results in the lower delocalization of p electrons in derivatives with BH groups.

Conclusions

Properties of sumanene and its derivatives obtained by substitution of benzylic CH_2 groups with BH and NH groups were theoretically investigated. This study represents the contribution to overall theoretical characterization of buckybowls. Data presented here and in other studies could be useful for the creation of an expert system adequate to successfully emulate the decision making ability in the areas where buckybowls could be applied [77–80].

The structure of sumanene is significantly affected by substitution and specific vibrational modes occurred as well. The substitution further affected the charge separation in sumanene molecule. DOS analysis indicates that boron atoms contribute to the LUMO orbitals, while nitrogen atoms contribute to the HOMO orbitals. Contribution to the frontier orbitals is much higher for the case of boron atoms.

Response properties were investigated through calculations of polarizability, first hyperpolarizability, and dielectric constants; for these quantities it is shown that substitution with BH and NH groups leads to significant improvement. Exciton binding energy was also calculated and it can be concluded that this important parameter can also be improved and finely tuned through substitution.

Aromaticity study showed the improvement of aromatic nature of certain sumanene rings indicating that π stacking might be improved with substitution with boron and nitrogen atoms. Better aromatic properties of five member rings of derivatives with nitrogen atoms are related with higher energy difference as a consequence of deletion of the significant NBO donor-acceptor interactions where donor NBO orbitals include boron and nitrogen atoms, as shown by NBODEL analysis.

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