

M \cdots π -conjugated complexes: simple materials with dramatic NLO features (M = Li, Na, K, and π = butadiene, cyclobutadiene, hexatriene, benzene)

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Abstract Theoretical investigation of linear and nonlinear optical (NLO) properties in simple complexes consist of alkali metals and π -conjugated systems have been studied at MP2/6-311++G(2d,2p) computational level. Lithium, sodium, and potassium as alkali metals were chosen for interaction with some non-aromatic, aromatic and anti-aromatic systems. For better comparison of results, the π -systems were chosen with the same carbon number: butadiene as a non-aromatic in comparison with cyclobutadiene as an anti-aromatic and hexatriene as a non-aromatic in comparison with benzene as an aromatic system. Results revealed that gap energy of studied π -systems was decreased under the interacting with alkali metals. Furthermore all designed complexes were shown very good results in average polarizability (α) and first hyperpolarizability (β_0) parameters. So these very simple dimer complexes could be introduced as promising innovative nonlinear optical materials.

Keywords Nonlinear optical (NLO) properties · π -conjugated systems · Alkali metals · Average polarizability (α) · Hyperpolarizability (β_0)

Introduction

The nonlinear optic (NLO) research field has been focused on attention since its beginning in 1961 [1]. The wide application of nonlinear optic materials in optical devices and other useful

applications such as medical imaging and cancer therapies is the reason for the rapid process of their expansion [2–4]. So, it is very interesting to design and introduce new material with the high efficiency of NLO feature.

Recently, organic materials with delocalized electrons introduce potential novel NLO materials [5, 6]. On the other hand, the compounds, atoms or molecules, with excess electron such as alkali metals have presented high performance. Hence, the conjugated organic molecules in interaction with alkali metals lead to an essential charge transfer and enhancing polarizability (α) and or hyperpolarizability (β_0).

Difficulties and the high cost of experimental methods have made clear the importance of computational methods in quantum mechanics as well [7–11]. Due to the essentiality of the decreasing of synthesis cost, the design of simple systems is very important. According to this importance, we motivated to focus on simple π -systems with delocalized electrons in interaction with alkali metals. The other interesting point in the present study is the design and comparison of NLO properties in complexes with diverse π -systems in terms of aromaticity nature for the first time.

Computational methods

Calculations were performed using the Gaussian 09 system of codes [12]. All optimizations, electronic properties, polarizability, and hyperpolarizability were done at the second-order Møller–Plesset perturbation theory (MP2) as one of quantum chemistry post-Hartree–Fock ab initio methods and 6-311++G(2d,2p) basis set. The MP2 method is known as a good method due to rather accurate estimates of geometries and energies for complexes with non-covalent interactions and intermediate computational cost [13–16]. Frequency calculations were performed at the same computational level in order

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to confirm that the structures obtained correspond to energy minima. The time-dependent density functional theory (TDDFT) [17] calculations were carried out using CAM-B3LYP/6-311++G(2d,2p) to gain the crucial excited states of all studied systems and optical absorption spectra. It has been shown that TDDFT method and more specifically, CAM-B3LYP is appropriate for calculating the signatures of electronically excited states, and optical (absorption) spectra of molecules [18–21]. The counterpoise approach of Boys and Bernardi [22] was used to correct the stabilization energy for basis set superposition error (BSSE). The natural bond orbital (NBO) charges analysis was done using NBO [23] program as implemented in the Gaussian program package.

Based on Taylor series expansion, the energy of a system in the weak and homogeneous electric field is described as [24, 25]:

$$E = E^0 - \mu_i F_i - 1/2 \alpha_{ij} F_i F_j - 1/6 \beta_{ijk} F_i F_j F_k - \dots$$

where E^0 , F_i , μ_i , α_{ij} , and β_{ijk} are the molecular total energy in the absence of the electric field, the electric field component along the i direction, the dipole moment, polarizability, and the first hyperpolarizability, respectively. The average polarizability (α), first hyperpolarizability (β_0), and the electric dipole moments μ_0 values are defined as [26]:

$$\alpha = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

in which

$$\beta_i = 3/5 (\beta_{iii} + \beta_{ijj} + \beta_{ikk}) \quad i, j, k = x, y, z$$

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

Results and discussion

Geometries and energy analysis

The optimized geometries of all structures have been depicted in Fig. 1. The binding distances between alkali metals and carbons are presented in Table 1. As can be seen, the metal stands in the central location of the carbon chain or carbon cycle expect in Li···hexatriene complex. In Li···hexatriene, lithium leads to the middle position of the carbon number 1 and 2. It is worth mentioning that a lot of conformers of each complex were generated and optimized in several directions, but many of these configurations were abandoned due to three reasons: (1) The metal atom was displaced to the same structure as reported, (2) some structures had negative frequencies so they were not related to the real structures and not considered for more analysis, and (3) some structures have lower stability. So all presented structures are related to the global minimum in the potential energy surface of the studied complexes.

All stabilization energies of studied complexes are negative, so the $M \cdots \pi$ complexes are more stable than separate isolated alkali metals and studied π -systems. As can be seen in Table 2, the stability of complexes with cyclic π -systems are more than chain and in order to $M \cdots$ Cyclobutadiene > $M \cdots$ Butadiene and $M \cdots$ Benzene > $M \cdots$ Hexatriene. The second comparison is in terms of the type of π -conjugated system. The values reveal that $M \cdots$ Cyclobutadiene are more stable than $M \cdots$ Benzene. The reason for this observation lies in Hückel's rule. Based on this rule, a cyclic ring molecule with its π -electrons equal to $4n + 2$ and $4n$ where " n " is zero or any positive integer is aromatic and anti-aromatic, respectively

Fig. 1 The optimized geometries of studied complexes. **a**

Li···Butadiene. **b**
Li···Cyclobutadiene. **c**
Li···Hexatriene. **d** Li···Benzene. **e**
Na···Butadiene. **f**
Na···Cyclobutadiene. **g**
Na···Hexatriene. **h** Na···Benzene.
i K···Butadiene. **j**
K···Cyclobutadiene. **k**
K···Hexatriene. **l** K···Benzene

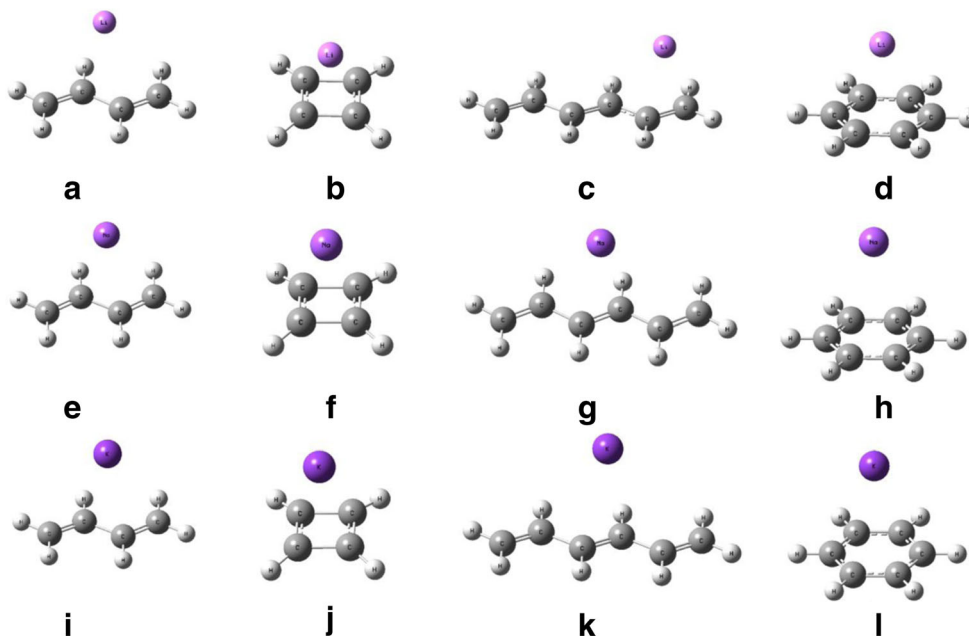


Table 1 The obtained interaction distances (metal-carbon) for the obtained structures (all values in Å)

Complex	Distance (metal-carbon)	Complex	Distance (metal-carbon)
Li···Butadiene		Na···Hexatriene	
Li···C _{2,3}	3.87	Na···C _{3,4}	4.01
Li···C _{1,4}	4.20	Na···C _{2,5}	4.39
		Na···C _{1,6}	5.00
Li···Cyclobutadiene		Na···Benzene	
Li···C	2.11	Na···C	3.54
Li···Hexatriene		K···Butadiene	
Li···C _{1,2}	2.70	K···C _{2,3}	3.67
Li···C ₃	3.23	K···C _{1,4}	4.00
Li···Benzene		K···Cyclobutadiene	
Li···C	2.68	K···C	2.81
Na···Butadiene		K···Hexatriene	
		K···C _{3,4}	3.85
Na···C _{2,3}	4.11	K···C _{2,5}	4.25
Na···C _{1,4}	4.43	K···C _{1,6}	4.87
Na···Cyclobutadiene		K···Benzene	
Na-C	2.52	K···C	3.52

[27]. As is well-known, aromatic molecules are more stable than anti-aromatic ones. So, it is expected that benzene as an aromatic system is more stable than cyclobutadiene as an anti-aromatic system. As will be discussed in the next section, during complex formation, substantial charge transfer from alkali metal to cyclobutadiene happens. Indeed, this charge transfer happens for approximately the number of π -electrons to aromatic π -electron ($4n + 2$) number, and so the

Table 2 Values of the uncorrected stabilization energy (kJ mol^{-1}) as well as the corrected ones (SE_{corr}) with inclusion of the BSSE amounts

Complex	SE_{uncorr}	BSSE	SE_{corr}
Li···Butadiene	-3.06	0.69	-2.37
Li···Cyclobutadiene	-170.77	7.14	-163.63
Li···Hexatriene	-5.34	2.06	-3.27
Li···Benzene	-16.59	4.49	-12.10
Na···Butadiene	-3.05	0.90	-2.15
Na···Cyclobutadiene	-77.78	5.94	-71.84
Na···Hexatriene	-4.12	1.25	-2.87
Na···Benzene	-8.98	2.35	-6.63
K···Butadiene	-4.72	1.45	-3.27
K···Cyclobutadiene	-93.15	5.56	-87.59
K···Hexatriene	-5.45	1.58	-3.87
K···Benzene	-13.66	3.00	-10.66

SE_{uncorr} values were computed as follows: $SE_{\text{uncorr}} = E_{\text{complex}} - \sum E_{\text{monomers}}$. SE_{corr} values were computed as follows: $SE_{\text{corr}} = SE_{\text{uncorr}} + \text{BSSE}$

Table 3 NBO charge of alkali metal atoms in studied complexes (all values in a.u)

Complex	Li	Na	K
Li···Butadiene	-0.007	-	-
Li···Cyclobutadiene	0.704	-	-
Li···Hexatriene	-0.023	-	-
Li···Benzene	-0.086	-	-
Na···Butadiene	-	-0.019	-
Na···Cyclobutadiene	-	0.809	-
Na···Hexatriene	-	-0.033	-
Na···Benzene	-	-0.038	-
K···Butadiene	-	-	-0.052
K···Cyclobutadiene	-	-	0.838
K···Hexatriene	-	-	-0.051
K···Benzene	-	-	-0.055

amount of stability is increased. While the charge transfer in $M\cdots$ Benzene leads to the number of π -electrons getting distance from $4n + 2$, the amount of stability is decreased. So, it can be understood why the absolute charge transfer amount in benzene complexes are very low in comparison with the cyclobutadiene case. These two phenomena lead to the greater stability of $M\cdots$ cyclobutadiene complex than $M\cdots$ benzene complex under the same condition.

The third evaluation is in terms of the type of alkali metal. The values show that the lithium complexes are more stable among the other ones.

Natural bond orbital (NBO) analysis

The aim of NBO analysis in this work is the investigation of charge direction between metal and π -conjugated hydrocarbons in different categories. From the results in Table 3, the absolute charge of alkali metals increases in order to “Li < Na < K, excepting the complex M-benzene.”

The obtained results show that the alkali metal atoms (Li, Na, and K) have negative charge in interaction with chain π -conjugated hydrocarbons (butadiene and hexatriene) and benzene systems that it exhibits the charge transfer from π -conjugated hydrocarbons to alkali metal. Alkali metals display positive charge in interaction with cyclobutadiene. This means charge transfer from the alkali metal atom to the π -conjugated hydrocarbons. The amount of charge transfer in $M\cdots$ Cyclobutadiene is rather large and about 0.70, 0.81 and 0.84 a.u. for Li, Na, and K, respectively. This could be indicative of the effort of the system to increase the number of π -electrons to aromatic π -electron ($4n + 2$) number for an achievement to more stability. The values show that the amount of charge transfer depends on the type of π -system and changes in the following order: Cyclobutadiene \gg Benzene > Hexatriene > Butadiene. So, the nature of π -

Table 4 The electronic properties of different π -systems and studied complexes

	HOMO (eV)	LUMO (eV)	E_g	μ	η	ω
Butadiene	-0.320	0.042	0.36	-0.14	0.18	0.05
Cyclobutadiene	-0.276	0.044	0.320	-0.12	0.16	0.04
Hexatriene	-0.293	0.041	0.334	-0.13	0.17	0.05
Benzene	-0.340	0.042	0.380	-0.15	0.19	0.06
Li \cdots Butadiene	-0.177	0.013	0.190	-0.08	0.09	0.04
Li \cdots Cyclobutadiene	-0.237	0.002	0.239	-0.07	0.12	0.02
Li \cdots Hexatriene	-0.163	0.013	0.176	-0.07	0.09	0.03
Li \cdots Benzene	-0.149	0.010	0.158	-0.07	0.08	0.03
Na \cdots Butadiene	-0.172	0.012	0.184	-0.08	0.09	0.03
Na \cdots Cyclobutadiene	-0.206	-0.008	0.198	-0.11	0.10	0.06
Na \cdots Hexatriene	-0.236	0.011	0.248	-0.11	0.12	0.05
Na \cdots Benzene	-0.159	0.014	0.173	-0.07	0.09	0.03
K \cdots Butadiene	-0.133	0.007	0.140	-0.06	0.07	0.03
K \cdots Cyclobutadiene	-0.192	-0.007	0.186	-0.10	0.09	0.05
K \cdots Hexatriene	-0.134	0.007	0.141	-0.06	0.07	0.03
K \cdots Benzene	-0.126	0.007	0.133	-0.06	0.07	0.03

system is the determinant factor, too. The dual role of metal, charge donor, or acceptor could greatly increase the NLO properties [28–32].

Chemical reactivity or electronic properties

Electronic properties of the studied complexes were investigated in terms of the energy gap (E_g) [33], the chemical

Table 5 The average polarizability α (a.u.), hyperpolarizability β_0 (a.u.), and the molecular electric dipole moment μ_0 (Debye) values for urea as the standard molecule, π -systems, and studied complexes

	α	β_0	μ_0
Urea	34.73	22.34	1.67
Butadiene	52.55	0.11	0.00
Cyclobutadiene	42.10	0.01	0.00
Hexatriene	86.56	0.66	0.00
Benzene	67.19	0.14	0.00
Li \cdots Butadiene	212.58	563.20	0.60
Li \cdots Cyclobutadiene	60.94	1298.47	1.49
Li \cdots Hexatriene	257.72	4631.72	1.76
Li \cdots Benzene	223.22	1411.06	2.21
Na \cdots Butadiene	234.43	2899.19	0.52
Na \cdots Cyclobutadiene	63.74	2715.95	2.56
Na \cdots Hexatriene	323.39	33,199.24	0.19
Na \cdots Benzene	247.00	3443.05	1.15
K \cdots Butadiene	349.94	12,420.26	1.07
K \cdots Cyclobutadiene	62.10	2122.87	3.18
K \cdots Hexatriene	366.76	15,907.57	0.94
K \cdots Benzene	373.86	12,733.60	1.49

potential (μ) [34] and the global hardness (η) [34]. The values are measured and gathered in Table 4. The E_g values are measured by using the following equation:

$$E_g = E_{LUMO} - E_{HOMO}$$

Which E_{HOMO} and E_{LUMO} are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

According to atomic physics, the chemical potential (μ) of the electrons in a molecule could be defined as the negative of the atom's electronegativity and can be obtained with Mulliken equation as follow:

$$\mu = -\chi_{Mulliken} = -(I + A)/2$$

where I and A are the ionization potential and electron affinity of the atom, respectively.

On the other hand, based on the Koopman's theorem [35], (HOMO) and (LUMO) energies are related to the ionization potential (I) and the electron affinity (A), respectively, and can be stated as $I = -E_{HOMO}$ and $A = -E_{LUMO}$. By combining Mulliken equation and Koopman's theorem, chemical potential can be calculated using the following equation:

$$\mu = (E_{HOMO} + E_{LUMO})/2$$

Chemical hardness (η) is one of the important properties of atoms, ions, or molecules and described as the resistance towards the deformation or polarization of electron cloud [36, 37]. Chemical hardness is formulated as [34]:

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

Table 6 Selected excitation energies (ΔE), wavelength (λ), oscillator strength (f_0), and the most strongly contributing transitions between single-electron states and providing their percentages

Complex	Excited state	ΔE (eV)	λ (nm)	f_0	Assignment
Li···Butadiene	25	5.74	215.8	0.4110	HOMO-1 \rightarrow LUMO (29.45%)
	26	5.87	211.1	0.2617	HOMO \rightarrow LUMO + 2 (47.03%)
	4	2.13	583.2	0.2172	HOMO \rightarrow LUMO + 3 (30.13%)
	12	4.47	277.3	0.1006	HOMO \rightarrow LUMO + 12 (91.47%)
Li···Cyclobutadiene	9	4.24	292.1	0.0404	HOMO-1 \rightarrow LUMO + 1 (59.46%)
	33	5.72	216.8	0.0371	HOMO-1 \rightarrow LUMO + 11 (43.47%)
	24	4.78	259.5	0.8692	HOMO-1 \rightarrow LUMO (42.26%)
Li···Hexatriene	3	1.80	687.8	0.1948	HOMO \rightarrow LUMO + 3 (39.62%)
	5	2.31	537.1	0.1886	HOMO \rightarrow LUMO + 2 (44.99%)
	3	1.57	791.7	0.1716	HOMO \rightarrow LUMO + 4 (65.06%)
Li···Benzene	4	1.57	791.6	0.1716	HOMO \rightarrow LUMO + 3 (65.07%)
	6	2.33	532.2	0.1174	HOMO \rightarrow LUMO + 5 (89.25%)
	26	5.81	213.4	0.6417	HOMO-1 \rightarrow LUMO (45.51%)
Na···Butadiene	4	2.36	524.3	0.3428	HOMO \rightarrow LUMO + 3 (41.18%)
	1	2.04	608.0	0.2536	HOMO \rightarrow LUMO + 1 (76.24%)
	16	4.02	308.1	0.0997	HOMO \rightarrow LUMO + 13 (69.16%)
Na···Cyclobutadiene	44	5.39	229.8	0.0559	HOMO-1 \rightarrow LUMO + 1 (61.50%)
	8	3.39	365.6	0.0495	HOMO-1 \rightarrow LUMO + 1 (60.94%)
	5	2.36	524.3	0.3515	HOMO \rightarrow LUMO + 7 (44.71%)
Na···Hexatriene	3	2.00	619.3	0.2365	HOMO \rightarrow LUMO + 1 (75.95%)
	4	2.14	579.3	0.2211	HOMO \rightarrow LUMO + 2 (64.75%)
	5	2.34	530.6	0.2559	HOMO \rightarrow LUMO (55.66%)
Na···Benzene	3	1.95	634.7	0.2289	HOMO \rightarrow LUMO + 1 (67.80%)
	4	1.95	634.6	0.2289	HOMO \rightarrow LUMO + 2 (67.78%)
	32	5.85	211.8	0.5384	HOMO-1 \rightarrow LUMO (50.94%)
K···Butadiene	3	1.43	866.8	0.2661	HOMO \rightarrow LUMO + 2 (74.31%)
	4	1.73	716.0	0.2632	HOMO \rightarrow LUMO + 3 (44.02%)
	13	3.59	345.7	0.0716	HOMO \rightarrow LUMO + 13 (57.09%)
K···Cyclobutadiene	38	4.73	261.9	0.0403	HOMO-1 \rightarrow LUMO + 8 (52.06%)
	27	4.17	297.1	0.0194	HOMO-1 \rightarrow LUMO + 8 (85.85%)
	4	1.74	713.0	0.3144	HOMO \rightarrow LUMO + 3 (49.55%)
K···Hexatriene	3	1.48	837.5	0.2415	HOMO \rightarrow LUMO + 2 (66.69%)
	2	1.31	950.0	0.2334	HOMO \rightarrow LUMO + 1 (81.71%)
	3	1.31	944.4	0.2590	HOMO \rightarrow LUMO + 1 (73.43%)
K···Benzene	4	1.31	944.3	0.2589	HOMO \rightarrow LUMO + 2 (73.39%)
	5	1.61	771.9	0.2202	HOMO \rightarrow LUMO (60.03%)

The global electrophilic index (ω) was established by Parr et al. stated formula [33]:

$$\omega = \mu^2/2\eta.$$

From the values in Table 4, following results were obtained in studied complexes in comparison with π -conjugated systems. In all cases, the energy gap (E_g) has decreased. The obtained chemical potential (μ) was negative in the all-designed complexes. Due to the fact that the escaping tendency of electrons from a stable system can be described by μ ; negative values demonstrate stable systems [38]. So, all

systems are stable in our work. The chemical hardness (η) was decreased at least 25 and up to 63%, so the chemical softness was increased. The electrophilic index (ω) values are relatively small and have not changed much upon complex formation.

NLO response and optical absorption spectra

The characteristics of optical properties are reported in Table 5. The resulted data illustrate that the average polarizability (α), hyperpolarizability (β_0), and the electric dipole

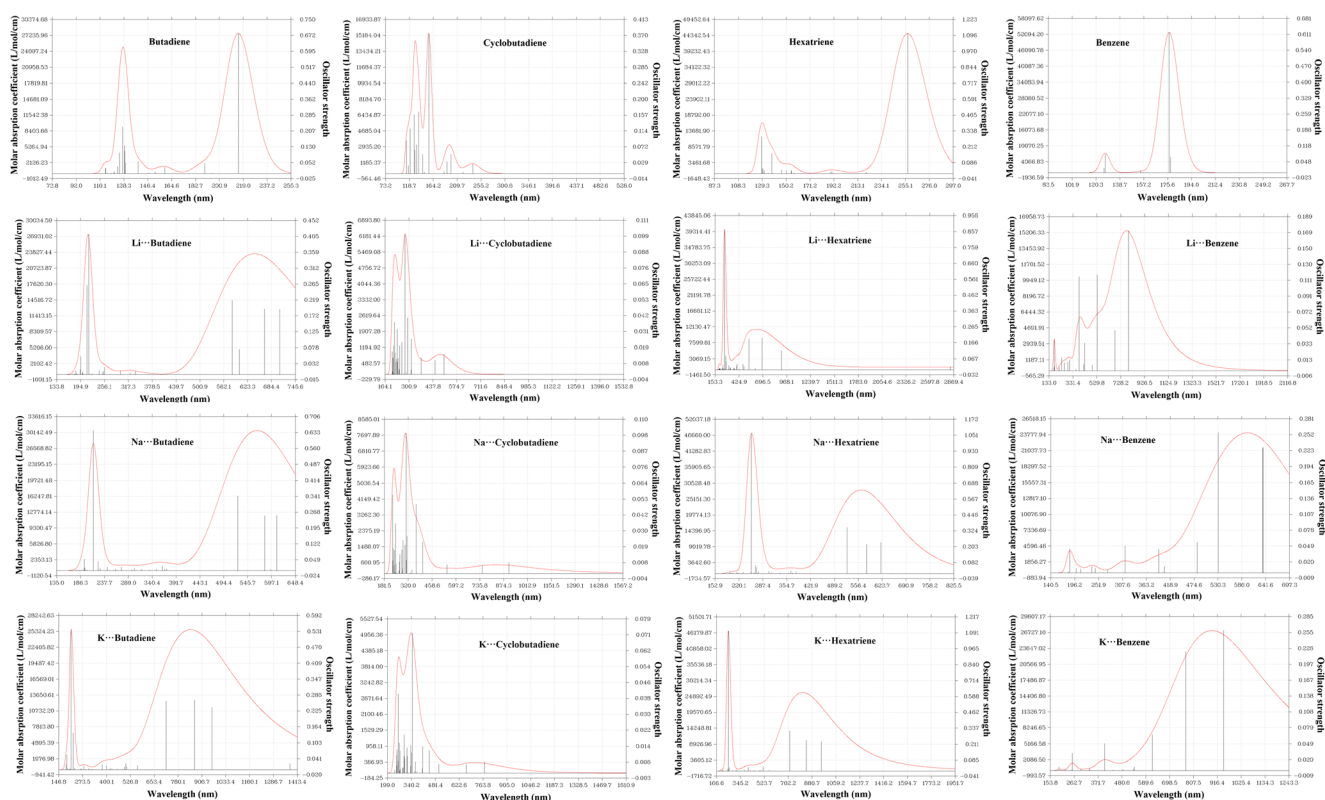


Fig. 2 UV-Vis spectrum

moment (μ_0) values have been larger for studied complexes in comparison with pure π -systems and urea. As we know, urea has been used as the standard reference for investigation of nonlinear optical (NLO) properties. The results reveal following trend in polarizability: Hexatriene > Benzene > Butadiene > Cyclobutadiene in interaction with the same metal. On the other hand, with the change of alkali metal, α value is increased in the following order: K > Na > Li. Also, a very satisfactory result was obtained from hyperpolarizability data. Interaction of π -systems with alkali metals results to about 5000–271,000 times enhancement of β_0 values in the $M \cdots \pi$ -molecule adducts. Cyclobutadiene, as an anti-aromatic system has maximum enhancement of β_0 after interaction with alkali metals among of the rest of the types of studied π -molecules. So, cyclobutadiene is obtained 129,847, 271,595, and 212,287 times enhancement of β_0 values in interaction with Li, Na, and K, respectively. Also, atomic number is one affective factor on the first hyperpolarizability so that increasing of atomic number induces greater β_0 [39]. Herein, heavier alkali metals lead to greater enhancement in β_0 . Therefore, the nature of π -system and metal is the determinant factor.

The molecular electric dipole moment (μ_0) parameter indicates molecular charge distribution in three directions. All the studied molecular π -systems have no dipole moments while after interaction with the alkali metal; the resulted complexes were obtained as polar nature. It is clear that the decreasing of symmetry as the result of interaction with a moiety, for

example, an alkali metal in this work, is the main reason for increasing in μ_0 values.

Generally, every factor that can be affected on α , β_0 , and μ_0 parameters can change NLO properties.

Furthermore, the UV-visible absorption spectra of the all studied complexes are characterized in Table 6 and exhibited in Fig. 2. From the results, strong absorption peaks according to a rather high oscillator strength values in the $M \cdots \pi$ -complexes have occurred in the UV and visible regions. While, π -conjugated systems, show a few number of absorption peaks that located in the UV region. Therefore, appearance of much number of strong absorption peaks shifted to larger wavelengths after complex formation, and this can be attributed to the interaction between π -conjugated systems and alkali metals.

The interesting point inferred from the comparison of the transitions given in Table 6 is shift effect in the major peaks of optical spectrums and explained as follow:

In the optical spectrum of $Li \cdots Butadiene$, the peak with the largest oscillator strength is located in 215.8 nm and when Li atom is replaced with Na and K this peak is shifted to 213.4 and 211.8 nm, respectively, and shows blue shift about 2.4 and 1.6 nm. Hence, in the case of $M \cdots Butadiene$, excitation energies are increased in order to K > Na > Li. By comparing the same way, $Li \cdots Cyclobutadiene$ shows 30.8 and 68.4 nm red shift with replacing of Li atom with Na and K and so in case of $M \cdots Cyclobutadiene$, excitation energies are increased in order

to $\text{Li} > \text{Na} > \text{K}$. Similarly, $\text{Li}\cdots\text{Hexatriene}$ reveals red shift in $\text{Na}\cdots\text{Hexatriene}$ and $\text{K}\cdots\text{Hexatriene}$ and finally $\text{Li}\cdots\text{Benzene}$ shows blue and red shift after metal changing with Na and K, respectively.

Conclusion

The most important achievement of this research work is the introduction of simple molecules with high optical and nonlinear optical (NLO) properties. For the attainment of this aim, we have investigated the effect of interaction with alkali metals (Li, Na, and K) on the average polarizability (α), hyperpolarizability (β_0), and the molecular electric dipole moment (μ_0) of π -conjugated systems (π = butadiene, cyclobutadiene, hexatriene, and benzene). The $\text{M}\cdots\pi$ -conjugated interaction leads to about 5000–271,000 times enhancement of β_0 values in the π -systems and the nature of π -system and metal is the determinant factor in this enhancement.

The NBO analysis represents that the studied π -conjugated systems act as charge donors as well as acceptors in interaction with alkali metals and lead to charge transfer between the alkali metal and π -conjugated system.

The energy gap (E_g) of studied π -systems is decreased; α and β_0 are increased dramatically and μ_0 finds the notable values during complex formation. The UV-Vis spectra revealed strong absorption after complex formation that it is attributed to the interaction between π -conjugated systems and alkali metals. The major peak (the absorption peak with the largest oscillator strength) of $\text{Li}\cdots\text{Butadiene}$ reveals blue shift, while $\text{Li}\cdots\text{Cyclobutadiene}$ and $\text{Li}\cdots\text{Hexatriene}$ show red shift effects with the change of Li with Na and K, respectively. Interestingly, LiBenzene shows blue and red shift after metal replacing with Na and K, respectively.

Compliance with ethical standards This material has not been published in whole or in part elsewhere; the manuscript is not currently being considered for publication in another journal; all authors have been personally and actively involved in substantive work leading to the manuscript, and will hold themselves jointly and individually responsible for its content.

Conflict to interest The authors declare that they have no conflict of interest.

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