

# Theoretical investigation of Structural, Electronical, and Optical properties of [18] DBA annulene and its derivatives

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## Abstract:

The structure geometry, vibrational frequencies, electronic and optical properties of a series of donor-acceptor substituted dodecahydrotribenzo [18] annulenes ([18] DBA) were investigated using the B3LYP method at a 6-31+G (d, p) basis set. After optimization of the structures, HOMO and LUMO energies, gap energy ( $E_g$ ), global hardness ( $\eta$ ), chemical potential ( $\mu$ ), electrophilicity index ( $\omega$ ), maximum charge transfer ( $\Delta N_{max}$ ), electronegativity ( $\chi$ ), Fermi level ( $E_{FL}$ ), wavelength ( $\lambda$ ), oscillator power ( $f_0$ ), and participation percentage (% Con) for [18] DBA derivatives. A significant increase in the first hyperpolarizability was observed by substitution on [18] DBA. The results of this study may be used to design and construct materials with adjustable electrical properties. The results indicate that the NLO response of [18] DBA could be enhanced by functionalizing different substitutions. In general, the NLO response and electronic properties of the S1-10 are more excellent than others.

**Keywords:** Annulene; Nonlinear optical property; Electronic property; Hyperpolarizability

## 1. Introduction

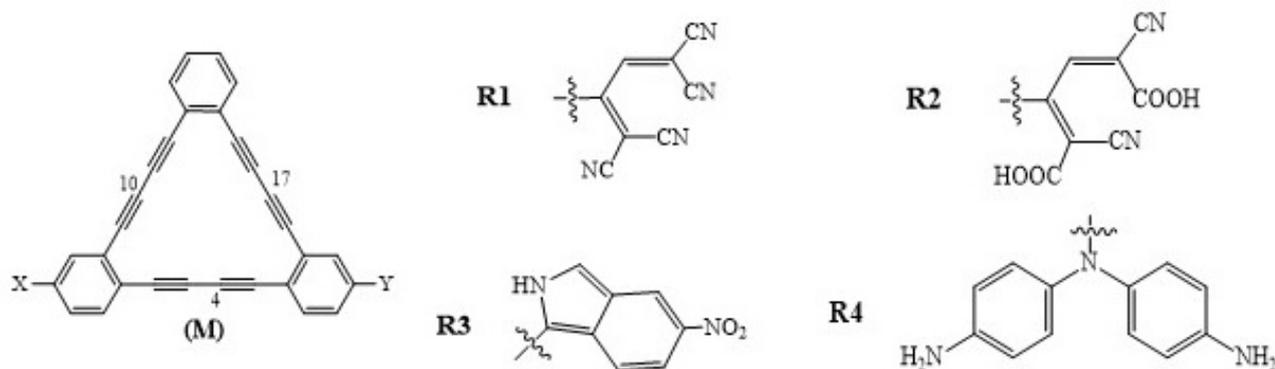
One of the important properties of annulene compounds is nonlinear optical properties (NLO). This property causes information storage, optical communications, optical switching devices, and the design of high-performance materials [1–5]. Since extra electrons play an essential role in increasing the first ultra-polarizability ( $\beta_0$ ), species such as the aromatic derivatives of annulene, which have excess electrons, can exhibit nonlinear optical properties [6–9].

Because of the potential of organic compounds to use as important nonlinear optical (NLO) responses due to fast nonlinear response times, better off-resonance susceptibilities, and small relative permittivity, in the past decade, many studies have focused on the properties of organic compounds for NLO applications [10–14]. Dehydrobenzo [n] annulenes (DBA) are important compounds among the comprehensive conjugated organic molecules. They have been recognized as an exciting class of carbon-rich materials, such as grapevines, which can be applied in various new electronic and optical materials [15]. Because of  $\pi$ -orbital overlap,

intermolecular  $\pi$ -stacking, and highly tunable dipoles and symmetries found for several derivatives, the use of dehydrobenzo [n] annulenes has been explored in numerous applications [15–17]. The main focus of the present study is to analyze the simplest substructure of graphiticness, dehydrobenzo [18] annulenes, for use in nonlinear optics due to the ease in placement of various groups on the benzene rings. Therefore, the series of one-dimensional molecules of dehydrobenzo [18] annulenes with systematic donor-acceptor substitutions have been investigated. The B3LYP/6-31+G (d, p) has been employed to determine the geometry optimization, vibrational frequencies, and electronic and optical properties of the considered structures.

## 2. Computational details

Calculations were performed using the Gaussian 09 and Gauss Sum 03 package [18, 19]. The geometries of the pristine dodecahydrotribenzo [18] annulene and their derivatives were fully optimized at the B3LYP/6-31+G (d, p) computational level [20–22]. In order to evaluate the [18] DBA



compound	X	Y	compound	X	Y
S1	NH <sub>2</sub>	R1	S10	R4	R3
S2	NH <sub>2</sub>	R2	M1	NH <sub>2</sub>	H
S3	NH <sub>2</sub>	R3	M2	OH	H
S4	OH	R1	M3	Ph <sub>2</sub> N	H
S5	OH	R2	M4	R1	H
S6	OH	R3	M5	R2	H
S7	Ph <sub>2</sub> N	R1	M6	R3	H
S8	Ph <sub>2</sub> N	R2	M7	R4	H
S9	R4	R2	M	H	H

Figure 1. Molecular structures of [18] DBA and their derivatives.

and their derivatives reactivity, quantum descriptors such as HOMO and LUMO energies, gap energy ( $E_g$ ), global hardness ( $\eta$ ), chemical potential ( $\mu$ ), electrophilicity index ( $\omega$ ), maximum charge transfer ( $\Delta N_{max}$ ), electronegativity ( $\chi$ ) and Fermi level ( $E_{FL}$ ) were calculated. These indexes were estimated through the following equations [23–27]:

$$E_g = E_{LUMO} - E_{HOMO} \quad (1)$$

$$\mu = -\frac{IP + EA}{2} \quad (2)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

$$\Delta N_{max} = -\frac{\mu}{\eta} \quad (5)$$

$$\chi = -\mu \quad (6)$$

$$E_{FL} = \frac{E_{LUMO} + E_{HOMO}}{2} \quad (7)$$

In these equations,  $E_{HOMO}$  and  $E_{LUMO}$  refer to the energies of HOMO and LUMO, respectively.  $IP$  and  $EA$  show the ionization and electron affinity energies.

Harmonic vibrational frequency calculations at the same level confirmed the structures as minima and enabled the evaluation of zero-point vibrational energies (ZPVE). Time-dependent density functional theory has been employed here to calculate the absorption wavelength and oscillator strength on the ground-state optimized geometries at the

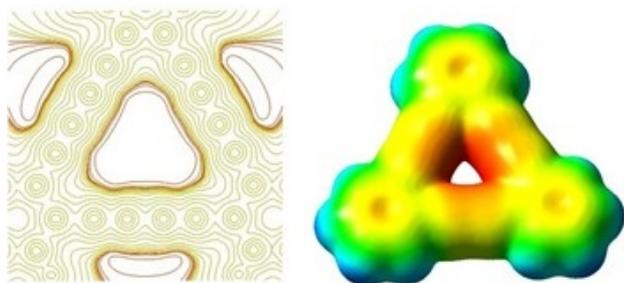


Figure 2. Contour maps and molecular electrostatic potential of [18] DBA compound.

Table 1. The optimized structural parameters, namely bond lengths, bond angles, and frequency of [18] DBA at B3LYP/6-31G + (d, p).

Bond angle (°)	Frequency (cm <sup>-1</sup> )	Bond length (Å)	Bond length (Å)
120.83 ( $\theta_{1-2-3}$ )	3218 ( $\nu_{C-H}$ )	1.222 ( $r_{5-6}$ )	1.429 ( $r_{1-2}$ )
179.96 ( $\theta_{2-3-4}$ )	2240 ( $\nu_{3-4}$ )	1.415 ( $r_{6-7}$ )	1.416 ( $r_{2-3}$ )
179.21 ( $\theta_{3-4-5}$ )	1520 ( $\nu_{1-2}$ )	1.429 ( $r_{7-8}$ )	1.222 ( $r_{3-4}$ )
179.96 ( $\theta_{4-5-6}$ )	990 ( $\nu_{ring}$ )	1.389 ( $r_{a-b}$ )	1.356 ( $r_{4-5}$ )

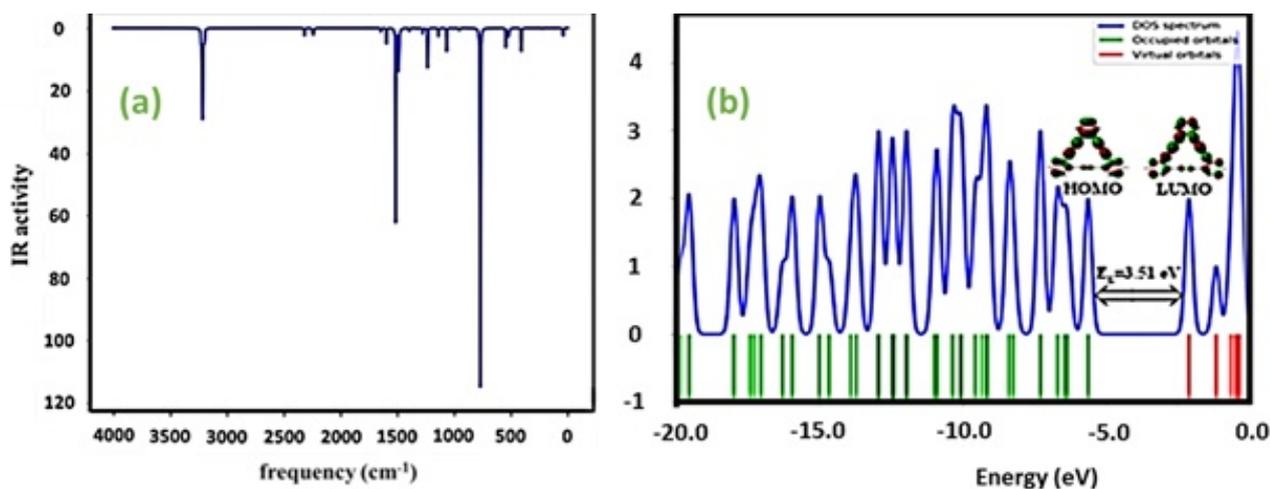


Figure 3. Vibrational spectra (a) and DOS spectra (b) of [18] DBA.

6-31+G (d, p) level. Also, we calculated the wavelength ( $\lambda$ ), oscillator power ( $f_0$ ), participation percentage (% Con), polarizability ( $\alpha$ ), and first hyperpolarizability ( $\beta_0$ ) for [18] DBA derivatives.

The average polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta_0$ ) were estimated through the following equations [28–30]:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (8)$$

$$\beta_x = \frac{1}{3}(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}) \quad (9)$$

$$\beta_y = \frac{1}{3}(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}) \quad (10)$$

$$\beta_z = \frac{1}{3}(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}) \quad (11)$$

$$\beta_0 = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (12)$$

### 3. Results and discussion

Results of geometry optimizations for the [18] DBA and its derivatives with different substations are classified into two categories. In the first type, denoted as M1-M7, we

have one donor/acceptor substituent in predetermined positions, while the second type (S1-10) possesses two different donor and acceptor substituents on the phenyl rings. The optimized structures of these functionalized DBA are represented in Figures 1 and S1. The electronic and optical properties, as well as to incorporate easily polarizable functionalities of DBA have been shown to be strongly influenced by the nature of substituents. It would be interpretable in terms of charge transfer in conjugated  $\pi$ -systems with donor (D) and acceptor (A) moieties as terminal substituents. The electronic and optical responses of S1-10 construction, which are substituted at various positions with donor and acceptor groups, are often longer wavelengths. This corresponds to the transition of the excess electron. It has been proposed as a suitable approach to increase the NLO response. The selection bond lengths and bond angles of [18] DBA in optimized geometries indicate that all structure is planar conformation.

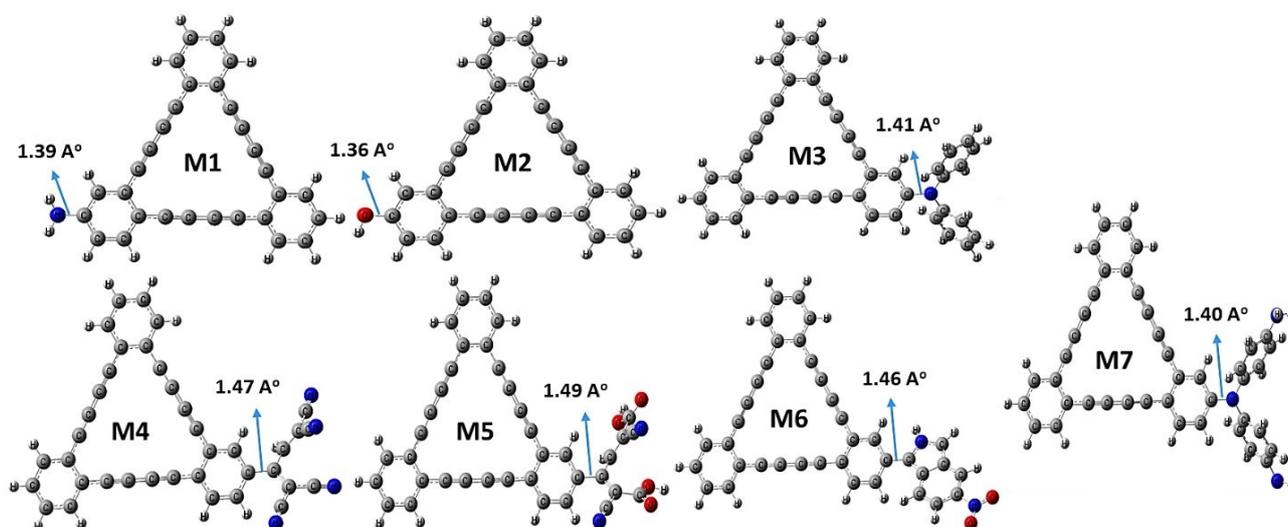


Figure 4. Optimized structures of M1-M7 compounds at the level of B3LYP/6-31+G (d, p).

**Table 2.** Calculated values of stability energy ( $E_S$ ), bipolar moment ( $\mu$ ), polarizability ( $\alpha$ ), hyperpolarizability ( $\beta_0$ ), and anisotropy ( $IP$ ) of M1-M7 compounds at B3LYP/6-31+G (d, p) level.

	$E_S$ (kcal/mol)	$\mu$	$\alpha$	$\beta_0$	$IP$
M		0.000	448.638	1141.508	244.92
M1	-752.373	3.091	471.857	3290.084	294.629
M2	-752.373	1.535	459.444	1012.682	270.043
M3	-758.138	2.099	645.903	7313.819	409.018
M4	-748.608	11.068	635.705	19174.243	432.279
M5	-753.628	9.676	615.958	10217.966	385.673
M6	-746.725	7.781	650.394	10201.764	342.341
M7	-752.373	7.027	683.979	12605.476	430.068

### 3.1 Structure of dodecahydrotribenzo[18] annulenes

The geometrical parameters, as well as vibrational spectra of the [18] DBA, are given in Figures 2, 3, and Table 1. The optimized geometry indicates that [18] DBA has planar conformation with D3h symmetry which is in favor of the intermolecular conjugated  $\pi$ -systems (Fig. 2). The symmetry MEP map indicates that the harmful potential sites are on the annulene ring, and the positive potential sites are around the hydrogen atoms.

The nonlinear optical properties of the [18] DBA were evaluated. The reasonable first hyperpolarizability of DBA (1141.5 a.u.) implies a proper NLO response. The energy gap ( $E_g$ ) value of DBA is 3.51 eV. Which is presented in the DOS spectrum (Fig. 3). The UV-Vis absorption spectra of [18] DBA display mainly three bands with proper oscillator strengths at 360, 419, and 439 nm.

### 3.2 M1-M7 compounds (derivatives of [18] DBA)

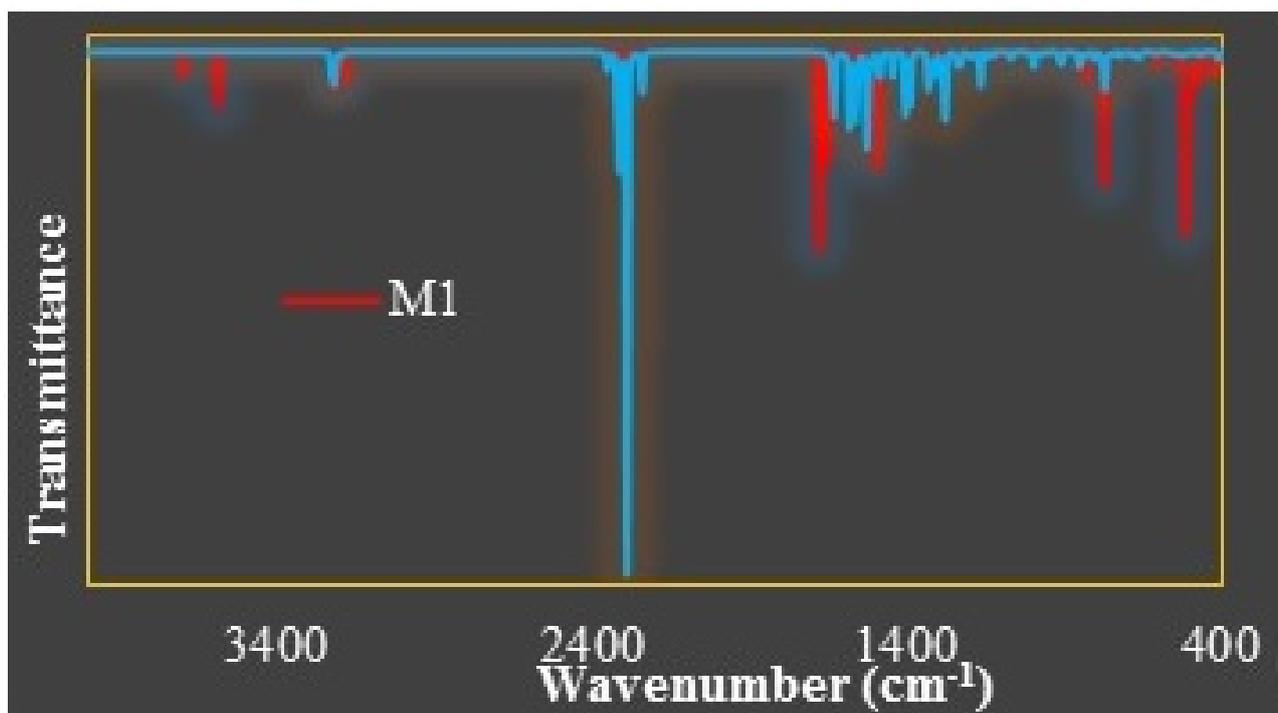
To investigate the effect of donor-acceptor substitutions on annulene molecule (M) from (H, NH<sub>2</sub>), (H, OH), (H, Ph<sub>2</sub>N), (H, R1), (H, R2), (H, R3) and (H, R4) are used with the letters M1, M2, M3, M4, M5, M6, and M7, respectively (Fig. 4). The parameters of stability energy ( $E_S$ ), bipolar moment ( $\mu$ ), polarizability ( $\alpha$ ), hyperpolarizability ( $\beta_0$ ), and anisotropy ( $IP$ ) were investigated (Table 2). The

results show that all substitutions lead to the stability of the annulene molecule. Among them, M3 has the highest stability ( $E_S = -758.138$  kcal/mol) and M6 has the lowest stability ( $E_S = -746.1725$  kcal/mol). Also, calculations show that the M4 has the highest and the M2 molecule has the lowest bipolar moment. Another parameter whose changes were evaluated by the mentioned substitutions is polarization ( $\alpha$ ). Polarity is the relative tendency of an electron charge distribution function to deviate from its standard shape by an external electric field. Accordingly, the M2 and M7 molecules have the lowest and highest polarizations, respectively. Also, based on the obtained results, it was observed that M1 and M4 molecules have the lowest and highest hyperpolarizability, respectively. Therefore, M1 with the electron donor group NH<sub>2</sub> has more negligible effect on amplifying the properties of NLO. On the other hand, M4 with tetracyano electron acceptor ( $\beta_0 \sim 19174$ ) is the most suitable substitution to improve the nonlinear optical properties of annulene. Finally, the amount of anisotropy in M2 and M4 molecules has the lowest and highest values, respectively.

In Table 3, *HOMO* and *LUMO* energies, gap energy ( $E_g$ ), wavelength ( $\lambda$ ), global hardness ( $\eta$ ), chemical potential ( $\mu$ ), electrophilicity index ( $\omega$ ), maximum charge transfer ( $\Delta N_{max}$ ), electronegativity ( $\chi$ ) and Fermi level ( $E_{FL}$ ) and in Table 4, oscillator power ( $f_0$ ), and participation percentage (% Con) for M1-M7 were shown. The results indicate

**Table 3.** Molecular orbitals energy and quantum descriptors (eV) M1-M7 compounds.

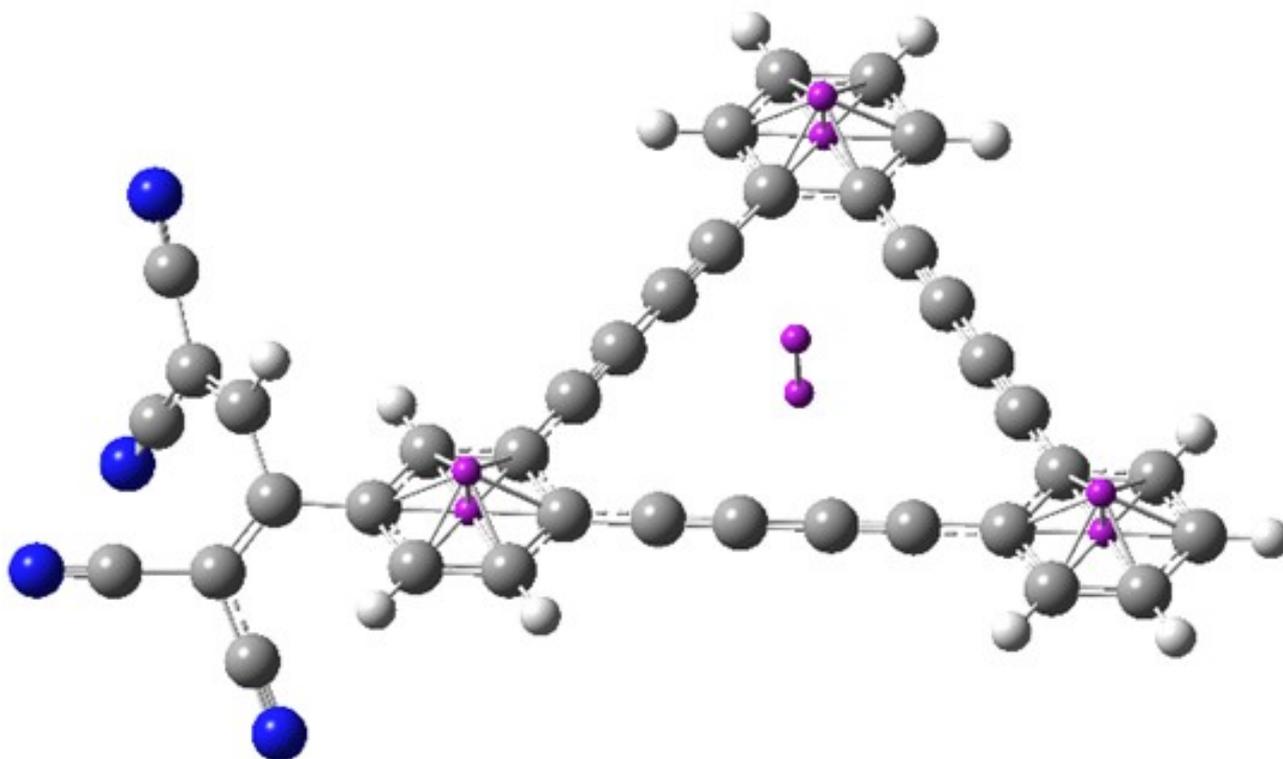
	$E_{HOMO}$	$E_{LUMO}$	$E_g$	$\eta$	$\mu$	$\omega$	$\Delta N_{max}$	$\chi$	$E_{FL}$
M	-5.60	-2.09	3.51	1.75	-3.84	4.21	2.19	3.84	-3.84
M1	-5.21	-1.99	3.22	1.61	-3.60	4.02	2.24	3.60	-3.60
M2	-5.43	-2.07	3.36	1.68	-3.75	4.19	2.23	3.75	-3.75
M3	-5.06	-2.01	3.05	1.52	-3.53	4.10	2.32	3.53	-3.53
M4	-6.01	-3.95	2.06	1.03	-4.98	12.04	4.83	4.98	-4.98
M5	-5.87	-3.45	2.42	1.21	-4.66	8.97	3.85	4.66	-4.66
M6	-5.39	-2.34	3.05	1.52	-3.86	4.90	2.54	3.86	-3.68
M7	-4.60	-1.87	2.73	1.36	-3.23	3.84	2.37	3.23	-3.23



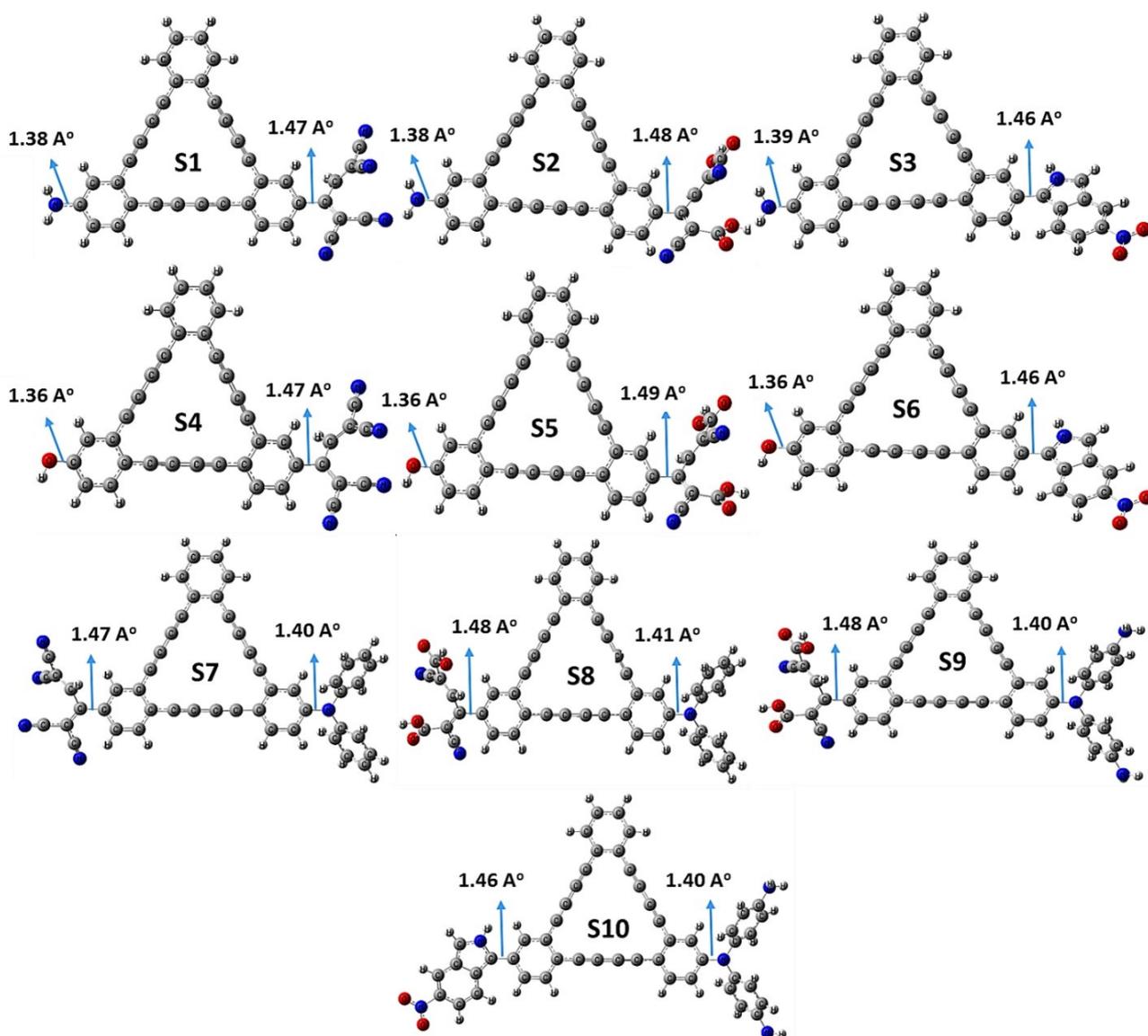
**Figure 5.** Comparison of infrared spectra of M1 and M4 compounds.

that the M4 molecule with tetracyanone substitution and M7 molecule with diamine substitution have the lowest and highest energy boundary orbitals, respectively. Based on  $E_g$ , the electrical conductivity of the substations can be explained. As we know, a low value of  $E_g$  indicates a

higher electrical conductivity. Accordingly to the data in Table 3, the M4 compound has the lowest  $E_g$  (2.06 eV) and the highest electrical conductivity compared to other substitutions. The process of increasing the electrical conductivity of other substations is as follows.



**Figure 6.** The image of the M4 compound from NICS calculations at B3LYP/6-31+G (d, p) level.



**Figure 7.** Optimized structures of S1-S10 compounds at the level of B3LYP/6-31+G (d, p).

$$M4 > M5 > M7 > M3 = M6 > M1 > M2$$

Physically, chemical potential ( $\mu$ ) describes the tendency of an electron to escape an equilibrium system. Negative values of chemical potential show that charge transfer between two particles is easy. In present work, the chemical potential electron ( $\mu$ ) for all compounds (M1-M7) is negative in the range of -3.23 to -4.98 eV. In a molecule, chemical hardness expresses resistance to changes in electron distribution or electron transfer or charge transfer. There is a direct relationship between chemical hardness and energy gap. Higher chemical hardness and energy gap means the reduced reactivity. Therefore, the M4 molecule with the highest chemical potential (-4.98 eV) and the lowest chemical hardness (1.03eV) and energy gap (2.06 eV) has the highest reactivity.

Electrophilicity ( $\omega$ ) is a parameter related to chemical potential and chemical hardness. In this research,  $\omega$  for all of the molecules is high. Also, this parameter for M4

(12.04 eV) is higher than that for other molecules.

Maximum charge transfer ( $\Delta N_{max}$ ) shows the charge capacity of the particle. According to the  $\Delta N_{max}$  equation (Eq. 5), when the chemical potential increases, the chemical hardness decreases and the electrophilicity increases. The results showed that (Table 3) the level of this parameter in M4 is higher than that in other molecules.

The results show that M1 to M7 compounds have different UV-Vis spectra (S1). As expected, the M4 combination with the highest conductivity has the highest shift wavelength (667 nm), and the M2 showed the shortest shift wavelength (375 nm) relative to the annulene. Also, two different peaks appear for the M1 has a wavelength of 357.11 nm with an absorption intensity of 0.733, which is the highest peak. Similarly, for M3 in the region of 403.353 nm with an intensity of 0.758, M5 with a wavelength of 567.03 nm with an intensity of 0.119, M6 in the region of 467.31 nm with an intensity of 0.359, and the molecule M7 in the region of wavelength 497.53 nm with an intensity of 0.393 have the highest peak and the highest absorption

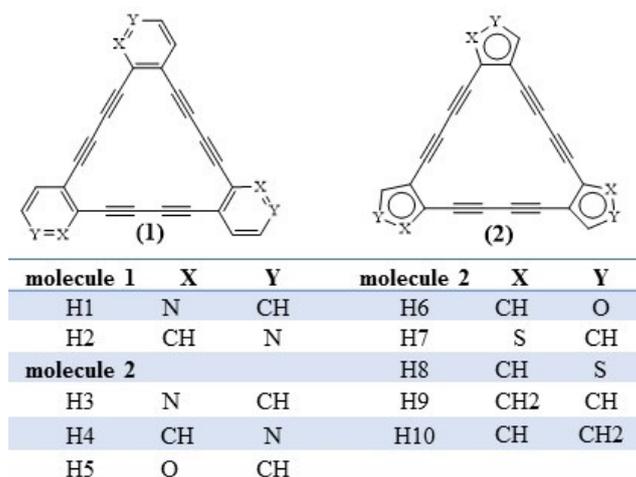


Figure 8. Structure of heterocyclic [18] annulene.

intensity.

DOS analysis was performed based on B3LYP/6-31G+(d, p) for compounds M1 to M7 similar to the annulene molecule. According to the results (S2), M2 and M4 molecules with values of 3.36 and 2.06 eV have the highest and lowest energy gap, respectively. The diversity and variety of electronic states in all forms is another reason for the optical properties of annulene derivatives.

Calculations of structural parameters were measured by determining the bond length, bond angle, and vibration

Table 4. Wavelength ( $\lambda$ ), oscillator power ( $f_0$ ), participation percentage (% Con) for M1-M7 compounds.

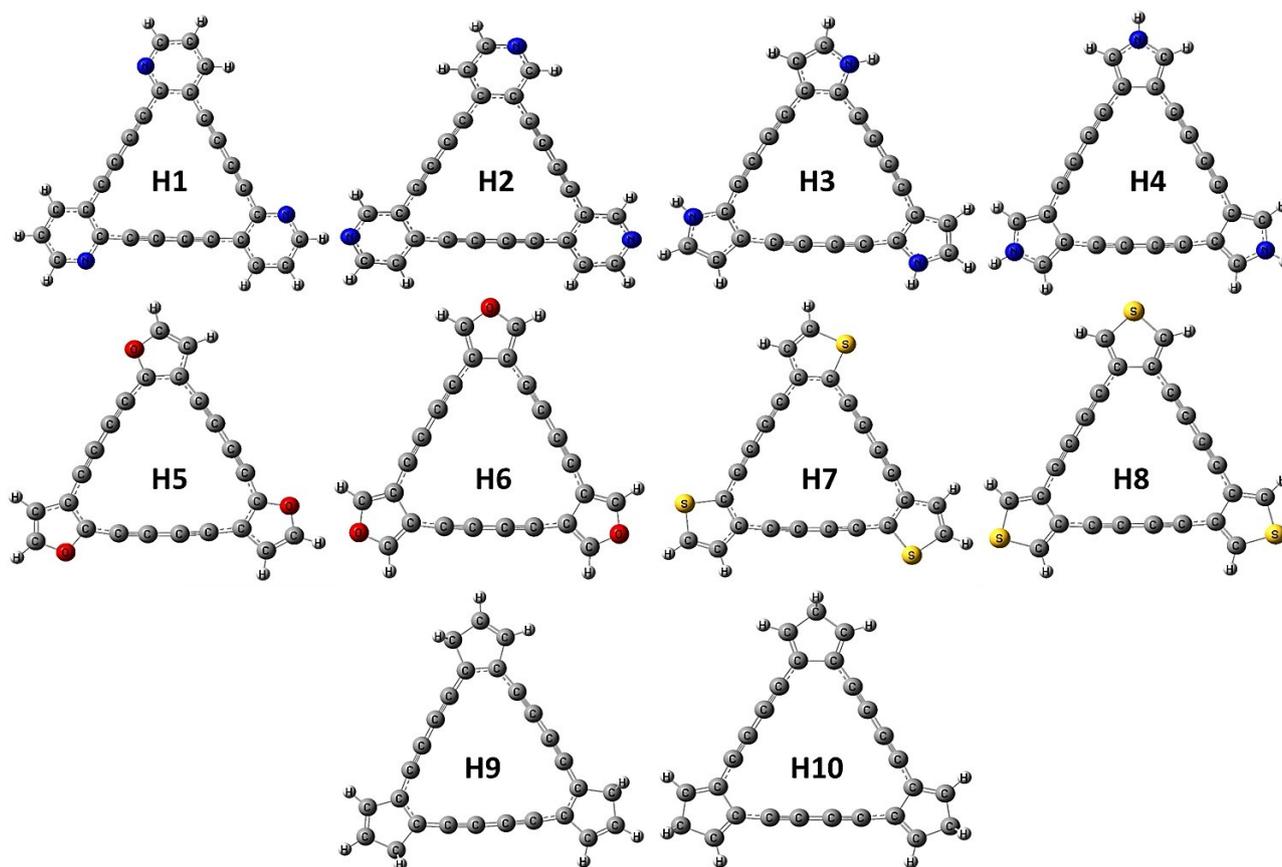
	$\Delta E(\text{cm}^{-1})$	$\lambda(\text{nm})$	$f_0$	% Con
M	22746	360.45	0.010	H-3->L (74%)
	22861	419.08	0.010	H->L+ (50%)
	27743	439.63	0.010	H->L (49%)
M1	26302	380.19	0.760	H->L (56%)
	22601	443.45	0.060	H->L (82%)
M2	26659	375.11	0.733	H-1->L (49%)
M3	24792	403.35	0.758	H-1->L (58%)
	21371	467.92	0.241	H->L+ (76%)
M4	19993	500.20	0.043	H-2->L (97%)
	14989	667.12	0.153	H-1->L (87%)
M5	22097	452.55	0.033	H-1->L+ (64%)
	17360	573.03	0.119	H-1->L (66%)
M6	21398	467.31	0.359	H-1->L+1 (15%)
M7	23894	418.51	0.287	H-2->L+1 (30%)
	20099	497.53	0.393	H->L+1 (89%)

spectroscopic properties to investigate the effect of substitution on annulene in compounds M1 to M7 compounds (S2). Observation of the values of lengths, angles, and bonding frequencies calculated for the M1 to M7 compounds in the range of 1.383-1.430 Å, 179.06-179.91, and 3219-994  $\text{cm}^{-1}$ , respectively, and its comparison with annulene (M) indicate stabilization of annulene molecular skeleton has a flat structure. Also, Fig. 5 shows the infrared spectra of the M1 (electron donor) and M4 (electron acceptor) compounds. A comparison of these two spectra, in particular the observed absorption and displacement, clearly indicates the substitution effect.

To compare the aromatic properties of the rings due to the presence of substitution, the NICS index was calculated at the level of B3LYP/6-31+G (d, p) (Fig. 6). NICS calculations were performed at distances of 0 and 1.5 from the centers of the rings to the M4 compound. The results in the 10.12-22.32 show that the ring scope has the highest value in the 0.5 Å. The results also showed that the coverage of the ring involved with substitution is more than the ring without substitution.

Table 5. Calculated values of stability energy ( $E_S$ ), bipolar moment ( $\mu$ ), polarizability ( $\alpha$ ), hyperpolarizability ( $\beta_0$ ), and anisotropy ( $IP$ ) of S1-S10 compounds at B3LYP/6-31+G (d, p) level.

	$E_S$ (kcal/mol)	$\mu$	$\alpha$	$\beta_0$	$IP$
S1	-1500.353	14.766	689.666	28247.752	523.509
S2	-1506.000	11.363	656.418	18583.536	460.661
S3	-1499.098	9.978	677.062	1305.051	592.155
S4	-1501.608	12.109	659.090	19734.694	473.765
S5	-1506.628	10.162	634.077	13475.441	420.656
S6	-1499.098	7.773	662.159	3294.193	564.804
S7	-1504.745	14.864	900.711	45547.212	662.638
S8	-1509.765	11.980	849.223	28925.191	591.754
S9	-1505.373	16.418	916.149	43524.812	633.592
S10	-1499.098	14.089	908.517	15289.892	728.512



**Figure 9.** Optimized structures of H1-H10 compounds at the level of B3LYP/6-31+G (d, p).

### 3.3 S1-S10 compounds (derivatives of [18] DBA)

After examining the effect of one substitution on the properties of annulene, an important question that arises in mind is the effect of subsequent substitutions. For this purpose, the effect of two different substitutions on annulene was investigated (Fig. 7).

The results showed that annulene with two substitutions has a more stable structure than a single substitution. On the other hand, S8 has the most stability ( $E_s \sim -1509$  eV).

In this group, S3, S6, and S10 have the highest amount of energy and the least amount of stability. Calculations to determine the amount of dipole moment showed that S9 with the highest value of  $\mu$  (16.418 D) had the lowest symmetry and S6 with the lowest value of  $\mu$  (7.773 D) had the most symmetric state. The results showed that S3 and S7 compounds have the lowest and highest  $\beta_0$  values (1305.051 and 45547.212), respectively. As expected, the highest anisotropy was observed for the S7 molecule. Also, the results showed that (Tables 6 and 7) the effect of two-exchange electron donor and lethal groups (S7) on the

**Table 6.** Molecular orbitals energy and quantum descriptors (eV) S1-S10 compounds.

	$E_{HOMO}$	$E_{LUMO}$	$E_g$	$\eta$	$\mu$	$\omega$	$\Delta N_{max}$	$\chi$	$E_{FL}$
S1	-5.68	-3.83	1.85	0.92	-4.75	12.26	5.16	4.75	-4.75
S2	-5.52	-3.35	2.17	1.08	-4.43	9.09	4.10	4.43	-4.43
S3	-5.16	-2.19	2.97	1.48	-3.67	4.55	2.48	3.67	-3.67
S4	-5.93	-3.90	2.03	1.01	-4.91	11.93	4.86	4.91	-4.91
S5	-5.76	-3.41	2.35	1.17	-4.58	8.96	3.91	4.58	-4.58
S6	-5.30	-2.26	3.04	1.52	-3.78	4.70	2.49	3.78	-3.78
S7	-5.43	-3.84	1.59	0.79	-4.63	13.57	5.86	4.63	-4.63
S8	-5.32	-3.37	1.95	0.97	-4.34	9.77	4.51	4.33	-4.33
S9	-4.83	-3.26	1.57	0.78	-4.04	10.46	5.18	4.04	-4.04
S10	-4.68	-2.10	2.58	1.29	-3.39	4.45	2.63	3.39	-3.39

**Table 7.** Wavelength ( $\lambda$ ), oscillator power ( $f_0$ ), participation percentage (% Con) for S1-S10 compounds.

	$\Delta E(\text{cm}^{-1})$	$\lambda(\text{nm})$	% Con
S1	12967	771.14	H->L (99%)
S2	20980	476.64	H-1->L+2 (14%)
	15201	657.85	H->L (98%)
S3	20863	479.29	H->L (78%)
S4	19563	511.15	H-2->L (97%)
	14190	704.69	H-1->L (15%)
S5	21727	460.24	H-1->L+2 (20%)
	16435	608.42	H-1->L (10%)
S6	21289	469.73	H-1->L+1 (10%)
S7	16774	596.13	H-2->L (95%)
	11194	893.32	H->L (99%)
S8	19299	518.15	H-2-> (94%)
	13662	731.95	H->L (99%)
S9	17338	576.75	H-2->L (65%)
	11048	905.06	H->L (99%)
S10	18945	527.82	H->L (18%)

single exchange (M4) shows the improvement of nonlinear optical properties of annulene.

The results of Table 6 show that molecules S4 and S10 have the lowest and highest amounts of *HOMO* and *LUMO* energy, respectively. Investigating electrical conductivity indicates that S6 and S7 molecules have the highest and lowest electrical conductivity, respectively. UV spectra show that the S7 compound has the highest wavelength. Other S compounds have different and, of course, different adsorp-

tions from M compounds (S3).

Also, the chemical potential electron ( $\mu$ ) for all compounds (S1-S10) is negative in the range of -3.39 to -4.91 eV. The S4 molecule with the highest chemical potential (-4.91 eV) has the highest reactivity. In this research,  $\omega$  for all of the molecules is high. Also, this parameter for S7 (13.57 eV) is higher than that for other molecules. Also, the results showed that (Table 6) the amount of  $\Delta N_{max}$  for S7 is higher than that in other molecules (5.86 eV).

**Table 8.** Calculated values of stability energy ( $E_S$ ), bipolar moment ( $\mu$ ), polarizability ( $\alpha$ ), hyperpolarizability ( $\beta_0$ ), and anisotropy ( $IP$ ) of H1-H10 compounds at B3LYP/6-31+G (d, p) level..

	E	$\mu$	$\alpha$	$\beta_0$	IP
H1	-1198.225	0.001	429.713	337.258	231.903
H2	-1198.229	2.590	424.672	335.808	245.269
H3	-1083.911	0.001	387.817	233.781	210.494
H4	-1083.899	0.004	357.521	78.478	192.378
H5	-1143.451	0.004	372.303	251.335	200.618
H6	-1143.439	0.003	329.475	120.328	175.153
H7	-2112.395	0.002	446.450	178.733	237.124
H8	-2112.385	0.001	409.895	298.569	215.586
H9	-1035.726	0.001	437.432	361.699	229.163
H10	-1035.702	0.001	380.991	80.087	194.683

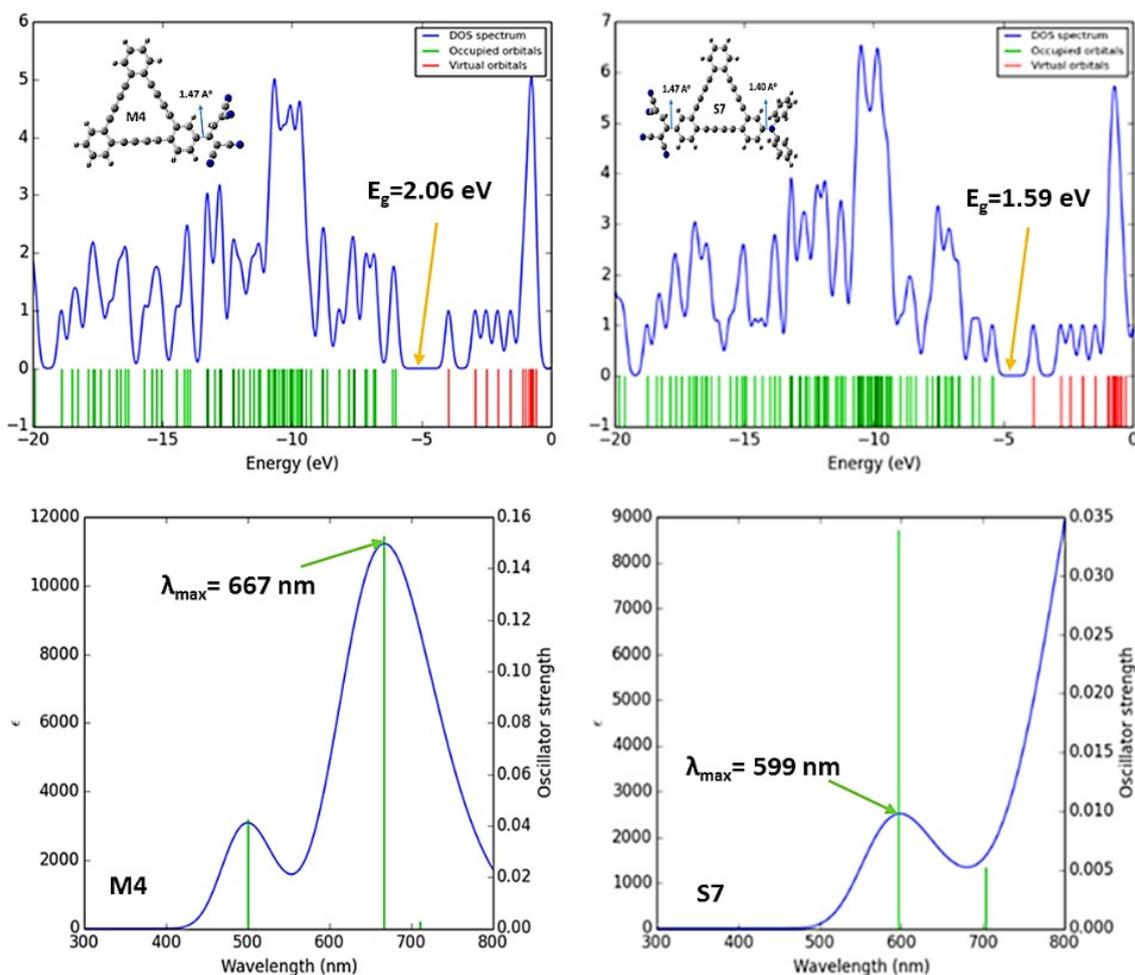


Figure 10. DOS and UV-Vis spectra of M4 and S7 compounds.

DOS analysis based on B3LYP/6-31G+ (d, p) was performed for S1-S10 compounds similar to the annulene molecule (S4). According to the results, molecules S6 and S7, with values of 3.04 eV and 1.59 eV, respectively, have the highest and lowest energy gap, and as a result, the optical properties are desirable. Calculations were performed for S1-S10 compounds to determine the amount of

bond length in the range of 1.431-1.382 Å. The measured frequency values are in the range of 993-3233  $\text{cm}^{-1}$ . Also, the bonding angle for S1-S10 compounds was observed in the range of 121.13-179.30°, which all indicates that the structure of the all compounds are flat (S5).

Table 9. Molecular orbitals energy and quantum descriptors (eV) H1-H10 compounds.

	$E_{HOMO}$	$E_{LUMO}$	$E_g$	$\eta$	$\mu$	$\omega$	$\Delta N_{max}$	$\chi$	$E_{FL}$
H1	-5.98	-2.45	3.53	1.76	-4.21	5.04	2.39	4.21	-4.21
H2	-6.12	-2.83	3.29	1.64	-4.47	6.09	2.73	4.47	-4.47
H3	-4.89	-1.44	3.45	1.72	-3.16	2.90	1.84	3.16	-3.16
H4	-4.90	-0.88	4.02	2.01	-2.89	2.08	1.44	2.89	-2.89
H5	-5.49	-2.15	3.34	1.67	-3.82	4.37	2.29	3.82	-3.82
H6	-5.77	-1.60	4.17	2.08	-3.68	3.26	1.77	3.68	-3.68
H7	-5.49	-2.30	3.19	1.59	-3.89	4.76	2.45	3.89	-3.89
H8	-5.67	-1.71	3.96	1.98	-3.69	3.44	1.86	3.69	-3.69
H9	-5.17	-2.30	2.87	1.43	-3.73	2.42	2.61	3.73	-3.73
H10	-5.39	-1.91	3.48	1.74	-3.65	3.83	2.48	3.65	-3.65

**Table 10.** Wavelength ( $\lambda$ ), oscillator power ( $f_0$ ), participation percentage (% Con) for H1-H10 compounds.

	$\Delta E(\text{cm}^{-1})$	$\lambda(\text{nm})$	% Con
H1	22755	439.45	H-1->L (22%)
	23896	418.47	H->L (41%)
	26323	379.88	H-2->L (71%)
H2	22556	443.34	H>L+1 (22%)
	23116	432.60	H->L (79%)
	26216	381.44	H-2->L (56%)
H3	22205	450.34	H->L (49%)
	23190	431.21	H>L+1 (49%)
	27374	365.31	H>L+3 (39%)
H4	26212	381.49	H>L+1 (48%)
	28190	354.73	H->L (50%)
	30011	333.21	H-1>L+3 (37%)
H5	21656	461.76	H-1>L+1 (47%)
	22046	453.59	H>L+1 (47%)
	27831	359.31	H>L+1 (52%)
H6	27726	360.67	H-1>L+1 (38%)
	29342	340.80	H-1->L+1 (41%)
	30258	330.48	H-1>L+1 (31%)
H7	20661	483.99	H->L (31%)
	21115	473.58	H-1->L (31%)
	28028	356.77	H-1>L+2 (55%)
H8	26264	380.74	H-1->L (42%)
	27724	360.69	H-1>L+1 (44%)
	28791	347.32	H>L (14%)
H9	17974	556.35	H-1>L+1 (50%)
	19001	526.27	H->L (49%)
	25590	390.77	H-3>L (46%)
H10	25085	398.63	H>L (99%)
	26949	371.06	H-2>L (60%)

### 3.4 Effect of heterocyclic rings on the structure of [18] DBA (structures H1-H8)

To investigate the effect of heterocyclic rings on the properties of annulene, symmetric heterocyclic in [18] annulene were designed and optimized (Fig. 8 and 9).

The effect of heterocyclic rings on the properties of [18] DBA shows the following results (Table 8). The effect of dipole moment showed that the H2 molecule has the highest polarity (2.590 D), and other molecules have the lowest polarity and are similar to annulene (M). Also, the highest hyperpolarizability was observed for H9 (361.699) due to the lower transfer energy, but, generally it is much lower than M and S molecules.

The results in Table 9 show that the H9 molecule and H6 molecule have the lowest and highest energy levels in *HOMO* and *LUMO*, respectively. Hence, H9 has the highest wavelength at 559 nm. Of course, it is emphasized

that the  $E_g$  values of H compounds are insignificant compared to S and M. Investigation of the DOS diagram for H1 to H10 compounds showed that they are similar to the annulene molecule (S6). Also, calculations were performed for M1-M10 compounds to determine the amount of bond length, frequency values, and bonding angle (S8). The results showed that the flatness of annulene is similar to the previous cases.

According to the values of chemical potential, chemical hardness and energy gap, it can be concluded that molecule A has the highest reactivity.

Comparing the value of first hyperpolarizability ( $\beta_0$ ) which is an important parameter in nonlinear optical compounds shows that in single substitution and double substitution, the highest amount belongs to M4 ( $\beta_0=19174.243$ ) and S7 ( $\beta_0=45547.212$ ). Figure 10 shows the spectra of DOS and UV-Vis of M4 and S7 compounds.

## 4. Conclusion

We have investigated the effect of functionalizing on the static first hyperpolarizability of dodecahydrotribenzo[18] annulene ([18] DBA). The NBO analysis shows a meaningful charge transfer between functional groups and [18] DBA, leading to a considerable variation in the dipole moments and a notable decrease in the  $E_g$  value. The results showed that the [18] DBA has unique electrical and optical properties. Substitution on [18] DBA improved these properties. Comparing the stability energy values of M4 and S8 derivatives (each of which had the highest stability compared to the compounds in the same group), it was observed that the S8 compound is more stable than the M4, which confirms that S- derivatives are more stable than M- derivatives. Finally, the effect of substitution on the nonlinear optical properties of [18] DBA was investigated, and it was found that the S7 compound ( $\beta_0=45547.212$ ) has the best optical properties.

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### Conflict of interest statement

The authors declare that they have no conflict of interest.

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