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Shedding light on static and dynamic hyperpolarizabilities of thia[7&8]circulenes, toward their NLO applications

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Abstract

Herein, we examined optoelectronic properties of thia[7&8]circulenes (**1-18**). Although Circulenes are the elemental building blocks of well-known nanomaterials such as graphene, nanotubes, and fullerenes. Organic chemists have given attention to circulenes during their studies for the improvement and development of aromaticity concept, but NLO properties of these structure-forming circulene subunits are not properly studied. The considered compounds (**1-18**) are thermodynamically, kinetically and chemically stable. Nonlinear optical (NLO) response is evaluated through static and frequency dependent first and second hyperpolarizabilities analyses. The static first hyperpolarizability (θ_0) of these compounds ranges between 0.00 – 496.54 au. The frequency dependent coefficients for all thia[7 & 8]circulenes show remarkable enhancement at 532 and 1064 nm, respectively. The nonlinear refractive index is increased up to 1.13×10⁻¹⁴ au for circulene **9** among all thia[7 & 8]circulenes at 532 nm. These findings successfully demonstrated that thia[7&8]circulenes nonlinear optical response can be increased by decorating multiple sulfur atoms. The unsymmetrical distribution of sulfur atoms is more effective as compared to symmetrical distribution.

Keywords: Circulene; Nonlinear optical response; Refractive index; Frequency dependent hyperpolarizability

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Introduction

Distinguished nonlinear optical materials are highly demanded in the field of optics since last decade. These have several applications in signal processing communication, data storage and data processing [1–10]. Many strategies have been adopted by scientists for improving the NLO response of different nanomaterials. These strategies include bond length alternation mechanism, metal-ligand frameworks, electron push-pull mechanism, octopolar complexes, and introduction of excess electron in desire system [11–19]. All these strategies need a surface consisting of homo or heteroatoms that can facilitated further optical processing. Organic chemists have given attention to circulenes during their studies for the improvement and development of aromaticity concept. Firstly, hydrocarbon-based circulenes were synthesized and designed which consist of fused benzene rings to form an annulene macrocycle. Most popular hydrocarbon-based circulenes are quadrannulene ([4]circulene, corannulene ([5]circulene), coronene ([6]circulene), and tetrabenzo[8]circulenes etc [20]. Although circulenes are the elemental building blocks of well-known nanomaterials such as graphene, nanotubes, and fullerenes but all the properties of these structure-forming circulene subunits are not properly studied. The study of circulenes provides detail information about the development of geometric, electronic and spectroscopic properties of sp^2 -hybridized carbon which are not nano-associated. Wynberg and Dopper synthesized heterocyclic analogues of hydrocarbon-based circulenes in 1972 and give them the name of heterocirculenes. These heterocirculenes comprises of two centralized annulene rings. The outer ring consists of heteroatoms and the inner ring consist of carbon without any hydrogen atom. The heteroatoms are oxygen, nitrogen, sulfur and selenium atoms and their respective heterocirculenes are named as oxacirculenes, azacirculenes, thiacirculenes and selenacirculenes. Most popular examples of heterocirculenes based on the number of outer heteroatom rings are octathia[8]circulene (OTC) and tetraoxa[8]circulenes (TOC) etc.[21].

Among these heterocirculenes, selena- and aza- derivatives have unusual inner skeleton (with high symmetry) which consist of the planar eight-membered aromatic nanosheets. From last few decades, scientist become interested in the synthesis of sulfur-rich polycyclic aromatic hydrocarbons [22–26]. The first generation of octathio[8]circulene ($C_{16}S_8$) is synthesized by Nenajdenko *et al.* in 2006 and reported it as sulflower [27]. The sulflower comprises of octagonal ring fused with thiophene rings and overall symmetry is *D*8h. Datta and Pati computationally analyzed the high hydrogen adsorption efficiency of C16S8 sulflower [28]. Second-generation of sulflower is actually a persulfurated coronene structure with an all-sulfur terminated edges ($C_{24}S_{12}$) [29]. These thia[8]and oxo[8] circulenes are thermally and chemically highly stable. It is suggested that their semiconducting properties may be use for the synthesis and designing of optics and photonic devices, light-emitting diodes and organic field-effect transistors.

To the best of our knowledge, there is no such investigation on the potential of optical and nonlinear optical response of multiple thia[7&8]circulenes. Under these circumstances, in the present report we have investigated thia[7&8]circulenes for their thermodynamic stability, electronic and optical and nonlinear optical properties via density functional theory calculations.

2 Methodology

B3LYP/6-31+G(d) method is implemented for optimization of thia[7&8]circulenes geometries at equilibrium state. B3LYP/6-31+G(d) is a consider as golden charm for geometry optimization calculations because of minimization errors in describing geometrical and energetic parameters [30–36]. This structural optimization is followed by frequency analysis. The former study confirmed energy minimization on the potential energy surface for all structures and latter one justified them as true minimum energy structures on potential energy surface because of the absence of any imaginary frequency. Thermal and electronic properties including binding energies energies per atom (Eb/N), vertical ionization energies (VIEs), natural bond orbital (NBO) charges, molecular orbitals and energy gaps

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have been analyzed at the same level of theory (B3LYP/6-31+G(d)). The highest occupied molecular orbital and the lowest unoccupied molecular orbital energy gaps (G_{H-L}) of all thia[7&8]circulenes are obtained as:

$$G_{L-H} = E_L - E_H \tag{1}$$

Where E_L is the energy of the lowest unoccupied molecular orbital and E_H is the energy of highest occupied molecular orbital. Optical parameters including polarizability (α_o), the static first hyperpolarizability (β_o) and second hyperpolarizability (γ_{tot}) are calculated at CAM-B3LYP with 6-31+G(d) basis set to find out linear and nonlinear responses (NLO) of the respective systems. Range separated interactions play important role in accurate calculations of hyperpolarizability for description of NLO system. For this reason, CAM-B3LYP is selected in current study. CAM-B3LYP is a density functional of DFT which has 0.65 fraction of nonlocal exchange at asymptotic distance [31]. This functional also provide excellent balance between computational cost and accuracy[37], and used in current study for analyzing linear and nonlinear optical response. Literature reveals that Pople's 6-31+G(d) basis set is widely used in recent works for calculation of basis functions when nonlinear optical response of a complex is estimated [38]. Following equations are used to calculate optical parameter both for linear and nonlinear response:

Static polarizability $(\alpha_o) = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ (2)

Static first hyperpolarizability
$$(\beta_o) = \left[\beta_{x^2} + \beta_{y^2} + \beta_{z^2}\right]^{1/2}$$
 (3)

Where $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx}$ and $\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$

Static fsecond hyperpolarizability
$$(\gamma_{tot}) = \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2}$$
 (4)

Furthermore, coefficients for describing frequency dependent NLO response are investigated at routinely used two (532 nm and 1064 nm) laser wavelengths. These coefficients are the electro-optical

Pockels effect ($\beta(-\omega,\omega,0)$), second harmonic generation ($\beta(-2\omega,\omega,\omega)$), SHG form ($\gamma(-2\omega;\omega,\omega,0)$) and Electro-optic Kerr effect form ($\gamma(-\omega;\omega,0,0)$) are calculated using CAM-B3LYP/6-31+G(d). The results of these coefficients provide guidelines for the experimentalists those working in the field of nonlinear optics. The dynamic first hyperpolarizability can be measured through Equation 5.

$$\beta(\omega) = \left[\beta_{x^2}(\omega) + \beta_{y^2}(\omega) + \beta_{z^2}(\omega)\right]^{1/2}$$
(5)

For SHG values

$$\beta_{iii} = \beta_{iii}(-2\omega, \omega, \omega) + \beta_{ijj}(-2\omega, \omega, \omega) + \beta_{ikk}(-2\omega, \omega, \omega) \text{and}$$
(6)

and equation for EOPE values

$$\beta_i = \beta_{iii}(-\omega, \omega, 0) + \beta_{ijj}(-\omega, \omega, 0) + \beta_{ikk}(-\omega, \omega, 0)$$
(7)

All simulations are performed using Gaussian 09 package [39] and outcomes are analyzed through GaussView 5.0 code [40].

3 Results and discussion

3.1 Geometries and thermodynamic parameters

Compounds **1-17** consist of 7 membered benzene rings in surrounding with central heptagon. Addition of an extra benzene ring in peripheral aromatic rings convert central heptagon to octagon (compound **18**). The structure of these pure hydrocarbon-based circulenes is substituted with multiple Sulfur atoms and optimized structures of the designed compounds (**1-18**) are given in Fig. 2. All the compounds (**1-18**) have planer geometries with 1.40 Å and 1.09 Å of C-C (B_{C-C}) and C–H (B_{C-H}) bond lengths in peripheral rings, respectively. The average C-C bond length calculated for central heptagon and octagon is also 1.40 Å. Exceptionally, bowel shaped geometry is obtained for compound **16** and **17**. The geometric parameters are comparable to the already reported works [41,42] which justified our computational method. The compounds 1-15 have same point group named as C_1 which represent their centrosymmetric behavior.

Compounds 6, 7 and 8 have quite different point groups *i.e.* C_{2V}, C_{7V} and D_{8h}, respectively. Xiao *et al.* also

obtained *D*_{8h} point group for thia[7 & 8]circulenes [43].

Table 1. Selected geometric parameters including Symmetry (*S*), average C-C and C–S bond distances (B_{C-c} and B_{C-s}) in Å, average NBO charges in |e| on C, H and S (Q_c, Q_H and Q_s), binding energy per atom energies in kcal mol⁻¹, vertical ionization energies (E_{VIE}) in eV, and dipole moment in Debye of thia[7 & 8]circulenes.

Compounds	S	B _{C-C}	B _{C-H}	B _{C-S}	Qc	Q _H	Qs	Eb/N	E _{VIE}	μ
1	<i>C</i> ₁				-3.36	2.90	0.46	0.244	5.48	0.75
2	<i>C</i> ₁				-3.14	2.40	0.81	0.246	5.49	1.40
3	<i>C</i> ₁				-3.28	2.40	0.91	0.247	5.52	0.34
4	<i>C</i> ₁				-3.31	2.45	0.89	0.246	5.51	1.14
5	<i>C</i> ₁				-3.38	2.49	0.45	0.252	5.48	0.76
6	<i>C</i> ₁				-3.25	1.94	1.40	0.248	5.58	0.68
7	<i>C</i> ₁				-3.07	1.94	1.26	0.248	5.55	1.30
8	<i>C</i> ₁	1			-3.29	2.00	1.31	0.249	5.57	0.68
9	<i>C</i> ₁	1 40	1 09	1 74	-3.35	1.50	1.85	0.250	5.63	0.85
10	<i>C</i> ₁		1.09	1.74	-3.36	1.48	1.89	0.249	5.69	2.21
11	<i>C</i> ₁				-3.33	1.50	1.82	0.250	5.68	1.41
12	<i>C</i> ₁				$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.250	5.38	0.62		
13	<i>C</i> ₁				-3.33	1.00	2.34	0.251	5.82	1.98
14	<i>C</i> ₁				-3.29	1.02	2.28	0.251	5.74	0.50
15	<i>C</i> ₁				-2.55	1.02	1.60	0.251	5.76	1.21
16	<i>C</i> _{2v}				-3.30	0.51	3.96	0.252	5.90	1.36
17	C _{7v}				-3.32		3.32	0.254	6.06	1.24
18	D _{8h}				-3.99		4.00	0.257	5.90	0.00

Thermodynamic stability of the compounds **1-18** are compared with each other through their binding energy per particle analysis. Binding energy of nanoclusters is defined as the total energy of a nanocluster subtracted from the total energy of all the isolated atoms in the nanocluster. This change in energy is

further divided by total number of individual atoms in the nanocluster. The energy per atom is called as binding energy per atom (Eb/N) [44]. The calculated Eb/N of all single and multiple thia[7&8]circulenes are between 0.244 to 0.257 kcal mol⁻¹ which indicate the high stability of these circulenes (see in Table 1). The Eb/N of these compounds reveals that thia[8]circulenes (**18**) is most stable than thia[7]circulene (**1**-**17**) (Fig. 1). The increasing trend of stability based on Eb/N is as **18** > **17** > **16** > **14** > **15** > **13** > **12** > **5** > **11** > **9** > **10**> **8** > **7** > **6** > **3** > **4** > **2** > **1**. Increasing number of sulfur atoms gives more stability to the nanosheet. Sulfur in thiol ring act as electron donor atom and involves its lone pair of electrons in conjugation with π electronic system of the C=C bonds found in circulene. The donor acceptor interactions results in intramolecular charge transfer (ICT) that causes stability of the compounds, such type of ICT is reported by Bharanidharani and Myvizhi for 2-(4-chlorophenyl)-1-((furan-2- yl)methyl)-4,5-dimethyl-1H-imidazole [45]. Arab and Habibzadeh reported that subtituion of another atom in cluster increase their stability which enhance cluster properties as we observed in our results [46]. The vertical ionization energies of all compounds are helpful to describe the electrochemical behavior and stability of these compounds. The designed compounds **1-18** express sufficiently high vertical ionization energies, those are ranged from 5.48 to 6.06 eV that suggest enough electronic stability of these compounds.



Figure 1. Binding energy per atom (Eb/N) energies of thia[7 & 8]circulenes (1-18).

NBO charge analysis is carried out for designed compounds (**1-18**). The obtained average charges revealed that the sulfur and hydrogen atoms have positive charge and carbon atoms have negative charge. The reason for such type of charge distribution is due to fact that the charge transfer is occurred from the sulfur atom to the unoccupied *p* orbitals of the carbon atoms in multiple thia[**7**&**8**]circulenes. The average charges on sulfur ranges from -2.39 to -3.99 and charges on carbon atoms are between 0.46 |e| to 4.00 |e|. The highest charge transfer is seen in thia[**8**]circulenes (where carbon and sulfur atoms have -3.99 |e| and 4.00 |e|, respectively), then followed by thia[**7**]circulenes (Table 1). The dipole moment (μ_o) of compound **18** (thia[8]circulenes) is zero Debye due to its planar symmetry, the same result is reported in literature [47]. However, the dipole moment of compounds **1-17** ranges from 0.34 D to 6.76 D due to broken symmetry after multiple sulfur atoms substitution.

Compounds	αo	Bo	Ytot	НОМО	LUMO	Е	VIE
1	333	142.32	219.25	-5.48	-1.73	3.75	5.48
2	323	195.42	273.48	-5.49	-1.73	3.75	5.49
3	296	193.42	73.54	-5.52	-1.76	3.76	5.52
4	323	241.44	315.82	-5.51	-1.80	3.72	5.51
5	332	142.32	217.25	-5.48	-1.73	3.75	5.48
6	315	103.24	30.41	-5.58	-1.75	3.83	5.58
7	314	265.85	268.34	-5.55	-1.82	3.73	5.55
8	305	284.52	386.82	-5.57	-1.85	3.72	5.57
9	287	82.87	196.68	-5.63	-1.65	3.98	5.63
10	315	496.54	287.04	-5.69	-1.76	3.93	5.69
11	305	284.52	385.60	-5.68	-1.83	3.85	5.68
12	314	265.87	266.82	-5.63	-1.95	3.68	5.63
13	290	68.87	504.67	-5.82	-1.77	4.05	5.82
14	296	33.67	104.28	-5.74	-1.54	4.20	5.74
15	296	104.62	104.31	-5.76	-1.86	3.91	5.76
16	285	207.02	207.25	-5.90	-2.05	3.84	5.90
17	273	231.83	209.86	-6.06	-2.64	3.42	6.06
18	326	0.00	25.01	-5.90	-1.48	4.42	5.90

Table 2. Polarizability (α_o), the static first (β_o) and second hyperpolarizability (γ_{tot}) are in au, energies of the highest occupied molecular orbitals, the energies of the lowest unoocpied molecular orbitals, HOMO& LUMO energy gaps (E_{L-H}) and vertical ionization energy (VIE) in eV of thia[7 & 8]circulenes (**1-18**).





Figure 2. Optimized geometries of thia[7 & 8]circulenes (1-18).

The chemical stability of the compounds **1-18** is examined through frontier molecular orbital analysis. It is well known that a large energy gap reflects a high chemical stability [48]. Table 2 represents energies of the highest occupied molecular orbitals, energies of the lowest unoocpied molecular orbitals and their energy gaps (E_{L-H}) of compounds **1-18**. The highest E_{L-H} of compound **18** is 4.42 eV, which illustrate the chemical reactivity of thia[8]circulene. Increase in energy gap of compound **18** is due to decrease in the E_{HOMO} and increase in E_{LUMO} values compared to other compounds (**1-17**). The corresponding E_{HOMO} and E_{LUMO} are -5.90 eV and -1.48 eV, respectively. This energy gap is comparable to already reported thia[8]circulene used for lithiation to enhance their optical properties [47]. Energy gaps of thia[7]circulene (**1-17**) is in the range of 1.81 – 4.20 eV. Therefore, our designed thia[7 & 8]circulene have chemical stabilities close to already reported stable compounds. Previously, larger gaps are obtained for aza[n]circulenes (n = 6, 7, 8) studied by Poliak and coworkers [49]. Furthermore, discussing electronic density distribution on these compounds and pictorial representation is given in Fig. 3. HOMO densities are distributed on sulfur atoms and carbon atoms near these substituted sulfur atoms on circulenes sheet. While LUMOs reside on the carbon atoms far away from the substituted sulfur atoms and C=C bonds in the sheet. Here, occupied orbitals and unoccupied *p* orbitals are involved with each other which is cleared from the shape of *p* orbital in Fig. 3. Similar electronic density distribution is observed by Poliak and coworkers [49]. In compounds **17** and **18**, the electronic density of HOMO and LUMO reside on sulfur atoms substituted at peripheral of circulene rings because atomic size of sulfur size is large, and electrons are continuously delocalized on the whole ring.











Figure 1. HOMOs and LOUMOs of thia [7 & 8] circulenes (1-18) (isovalue: 0.05).

3.2 Linear and nonlinear optical response

Mean polarizabilities (α_0) and the static first hyperpolarizability (β_0) are calculated for all compounds (**1-18**) and results are summarized in Table 2. The α_0 of compounds **1-18** ranges from of 273 to 333 au. The β_0 value of thia[8]circulenes (**18**) is 0.00 au. The β_0 of all the remaining compounds **1-17** are in the range of 33.67 – 496.54 au. The largest β_0 (496.54 au) is observed for compound **10** whereas lowest β_{tot} (33.67 au) is computed for compound **14**. Symmetry of the respective compound effects the linear and nonlinear optical properties. These compounds can be used as efficient horses for better response of NLO, by using strategic planes as reported by Shakerzadeh[47]. Hyperpolarizability of a system is effected by two major factors: HOMO-LUMO gaps and dipole moment values of any compound [50]. For example, the (β_0) values increases with the decrease in HOMO-LUMO gaps of the compounds. The unsymmetrical distribution of charges causes higher dipole moment which results in higher β_0 value while symmetrical distribution decreases the dipole moment of the compounds. Compound **18** has zero dipole moment with largest gap (4.42 au) and show zero NLO response whereas, compound **10** has 2.21 Debye of dipole moment with lowest gap (3.93 au), consequently its NLO response is highest ($\beta_0 = 496.54$ au).

Routinely utilized laser wavelengths are used for estimation of frequency dependent first hyperpolarizability ($\beta(\omega)$) coefficients based NLO response. These coefficients are much more important for experimental investigations that provide insights of nonlinear optical materials. We also computed first hyperpolarizability coefficients *i.e.* second-harmonic generation of (SHG) with $\theta(-2\omega;\omega,\omega)$ and the electro-optic Pockel's effect (EOPE) with $\theta(-\omega;\omega,0)$. First hyperpolarizability ($\beta(\omega)$) coefficients of compounds **1-17** are more effected by variation in wavelengths but similar results are obtained for compound **18** (Table 3). Enhancement in the EOPE values of compounds **1-17** is seen compared to the θ_0 values. The EOPE values ranges from 2.48×10¹-6.30×10² au at 532 nm whereas the EOPE values are reduced to 3.45×10^{1} - 3.81×10^{2} au at 1064 nm wavelength. The SHG response for compound **14** is

enormously high (5.67×10⁴ au) at 532 nm but this value is decreased to 3.06×10¹ au at 1064 nm for the

same compound. Other compounds having SHG response values ranges 9.50×10¹ to 3.91×10⁴ au.

Table 3. Coefficients of frequency dependent hyperpolarizability ($\beta(\omega)$) *i.e.* second-harmonic generation with $\beta(-2\omega;\omega,\omega)$ term, the electro-optic Pockel's effect (EOPE) with $\beta(-\omega;\omega,0)$ term, coefficients of frequency dependent second hyperpolarizability *i.e.* electric field induced second-harmonic generation of (SHG) with $\beta(-2\omega;\omega,\omega,0)$ term, the electro-optical Karr effect (EOKE) with $\beta(-\omega;\omega,0,0)$) term and nonlinear refractive index of thia[7 & 8]circulenes (**1-18**).

Compou	β(-ω,ω,0)		β(-2ω,ω,ω)						······································	
nds					γ(- <i>ω;ω</i> ,0,0)		γ(-2ω;ω,ω,υ)		//₂ (Cm⁻/ W)	
ω	532	1064	532	1064	532	1064	532	1064	532	1064
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1	1.94×	1.52×	1.43×	1.79×	1.10×	7.61×	5.73×1	9.62×	1.89×	4.76×
	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	0 ⁵	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
2	2.38×	2.04×	3.39×	2.27×	1.11×	7.53×	2.49×	9.60×	7.19×	4.73×
2	10 ²	10 ²	10 ³	10 ²	10 ⁵	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
2	1.81×	2.73×	2.64×	1.05×	1.12×	7.56×	2.59×	9.69×	7.47×	4.77×
3	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
4	6.30×	3.64×	3.91×	5.14×	1.06×	7.31×	4.36×	9.24×	1.23×	4.58×
	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁶	10 ⁻¹⁸
5	1.95×	1.50×	1.43×	1.77×	1.12×	7.73×	5.63×	9.52×	1.80×	4.60×
	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	10 ⁵	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
6	1.96×	1.15×	6.73×	1.58×	1.16×	7.59×	7.96×	9.86×	2.52×	4.82×
	10 ²	10 ²	10 ³	10 ²	10 ⁵	10 ⁴	10 ⁵	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
7	4.77×	3.00×	5.53×	4.02×	1.06×	7.28×	9.83×	9.23×	3.01×	4.56×
/	10 ²	10 ²	10 ³	10 ²	10 ⁵	10 ⁴	10 ⁵	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
0	8.16×	3.81×	3.07×	6.18×	1.05×	7.17×	5.00×	9.10×	1.67×	4.50×
8	10 ²	10 ²	10 ³	10 ²	10 ⁵	10 ⁴	10 ⁵	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
9	6.17×	3.23×	2.28×	4.87×	1.06×	7.24×	4.09×	9.22×	1.13×	4.55×
	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	10 ⁸	10 ⁴	10 ⁻¹⁴	10 ⁻¹⁸
10	6.01×	3.31×	3.15×	4.81×	9.56×	8.64×	6.19×	1.32×	5.82×	6.91×
10	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	10 ⁸	10 ⁵	10 ⁻¹⁷	10 ⁻¹⁷

11	5.31×	2.31×	2.13×	5.92×	1.06×	7.14×	5.41×	9.13×	1.52×	4.49×
	10 ²	10 ²	10 ⁴	10 ²	10 ⁵	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁶	10 ⁻¹⁸
12	2.80×	1.07×	7.18×	2.04×	1.01×	6.52×	1.12×	8.49×	3.38×	4.14×
	10 ²	10 ²	10 ³	10 ²	10 ⁵	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
12	8.57×	4.99×	1.31×	7.03×	9.76×	6.78×	3.68×	8.53×	1.04×	4.24×
15	10 ²	10 ²	10 ⁴	10 ²	10 ⁴	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁶	10 ⁻¹⁸
14	2.48×	3.45×	5.67×	3.06×	9.53×	6.75×	2.91×	8.40×	8.05×	4.19×
	10 ¹	10 ¹	10 ⁴	10 ¹	10 ⁴	104	10 ⁷	10 ⁴	10 ⁻¹⁶	10 ⁻¹⁸
45	8.41×	1.03×	7.72×	9.50×	9.56×	6.68×	1.85×	8.37×	5.36×	4.15×
15	10 ¹	10 ²	10 ³	10 ¹	10 ¹	10 ⁴	10 ⁶	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
16	2.74×	2.21×	5.85×	2.55×	8.84×	6.35×	5.63×	7.83×	1.80×	3.92×
	10 ²	10 ²	10 ³	10 ²	10 ¹	10 ⁴	10 ⁵	10 ⁴	10 ⁻¹⁷	10 ⁻¹⁸
17	2.72×1	2.40×1	9.83×1	2.61×1	8.24×1	5.92×1	2.45×1	7.29×1	9.05×	3.65×
	0 ²	0 ²	0 ³	0 ²	01	04	05	04	10 ⁻¹⁸	10 ⁻¹⁸
10	0	0	0	0	8.45×1	6.50×1	3.94×1	7.70×1	1.32×	3.92×
10				0	01	04	05	04	10 ⁻¹⁷	10 ⁻¹⁸

Static and frequency dependent second hyperpolarizability is also computed for compounds **1-18**. The study includes calculations of third order hyperpolarizability coefficients at 0, 532 and 1064 nm, as discussed above for second order hyperpolarizability. From Table 3, it is noticed that all compounds show large electric field induced second harmonic generation (ESHG) γ with (-2 ω ; ω , ω ,0) and dc-Kerr effect with γ (- ω ; ω ,0,0). These results indicating remarkably enhanced ESHG and dc-Kerr effects for all these compounds at higher wavelength and can be detect in ESHG applications at the routinely used lasers. The dc-Kerr effect and ESHG effects are increases up to power of eight at higher wavelength. But the pronounced effect is observed at 532 nm. The highest ESHG and dc-Kerr effects is noticed for compound **10** are 9.56×10⁵ and 6.19×10⁸ au, respectively at 532 nm. The highest ESHG and dc-Kerr effects is noticed for compound **10** are 9.56×10⁵ and 6.19×10⁸ au, respectively at 532 nm. The highest ESHG and dc-Kerr effects is noticed for compound **10** are 9.56×10⁵ and 6.19×10⁸ au, respectively at 532 nm. The highest ESHG and dc-Kerr effects is noticed for compound **10** are 9.56×10⁵ and 6.19×10⁸ au, respectively at 532 nm. The highest ESHG and dc-Kerr effects is noticed for same compound **10** at 1064 nm which are 8.64×10⁴ and 1.32×10⁵ au, respectively.

Tarazkar *et al.* developed an equation for the degenerate four-wave mixing ($\gamma^{\text{DFWM}}(\omega)$) values in 2014.[51] This equation is based on product of the static, frequency dependent ESHG and dc-Kerr coefficients 52.

$$\gamma^{DFWM}(-\omega;\ \omega,-\omega,\omega)\approx(1/3)\gamma(-2\omega;\ \omega,\omega,0)+\gamma(-\omega;\ \omega,0,0)-(1/3)\gamma(0;\ 0,0,0)$$

Another important parameter of materials known as quadratic nonlinear refractive index (n_2) is easily estimated via γ^{DFWM} we also obtained the n_2 of these organometallic compounds from below given mathematical expression[52]:

$$n_2~({
m cm^2/W}) = 8.28 imes 10^{-23}~{
m \gamma^{DFWM}}$$
 (au)

At 1064 nm, the calculated n₂ values are between 9.05×10^{-18} to 1.13×10^{-14} au (see in Table 3). The largest n_2 (1.13×10^{-14} au) is noticed for compound **9** at 532 nm. All these results notify that the amplitude of the second order NLO response is highly dependent at variational wavelengths. The nonlinear response can be enhanced by doping different species on these surfaces as reported for thia[8]circulenes [47].

4 Conclusions

In this paper, we examined geometric, electronic and nonlinear optical (NLO) properties of multiple sulfur substituted circulenes (thia[7&8]circulenes). Thia[7 & 8]circulenes compounds **1-18** are thermodynamically stable. HOMO-LUMO energy gaps of these thia[7&8]circulenes ranges from 3.42 eV to 4.42 eV which indicate their electronic stability. NLO response is evaluated through static and frequency dependent the first and second hyperpolarizabilities. The static first hyperpolarizability β_0 of these compounds are increased up to 496.54 au. The frequency dependent coefficients show remarkable enhancement at 532 nm and 1064 nm for all thia[7&8]circulenes. Among all thia[7&8]circulenes, circulene **9** has the nonlinear refractive index of 1.13×10^{-14} au at 532 nm. These findings successfully demonstrated that nonlinear optical response of circulenes is enhanced by decorating sulfur atoms on these surfaces

which can be used for synthesis of NLO materials those have potential applications in the field of nonlinear optics.

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