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The linear, nonlinear optical properties and quantum chemical parameters of some sudan dyes

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Abstract

In this study, the polarizability (<α>), the anisotropy of the polarizability (<Δα>), ground-state dipole moment (μ) and the first-order hyperpolarizability (β) of the Sudan III (SIII) [1-({4-[(phenyl)diazenyl] phenyl}diazenyl) naphthalen-2-ol], Sudan Red G (SRG) [1-(2-Methoxyphenylazo)-2-naphthol] and Sudan Orange G (SOG) [4-(Phenylazo)resorcinol] are studied at the Hartree-Fock (HF) and Density Functional theory (DFT/B3LYP) levels of the theory with 3-21G, 6-31G, 6-31G(d), 6-31G(d,p), 6-31G+(d,p), 6-31G++(d,p), 6-311G, 6-311G(d), 6-311G(d,p), 6-311G++(d,p) basis sets. Also, E_{HOMO} *(the highest occupied molecular orbital energy),* E_{LUMO} *(the lowest unoccupied molecular orbital energy), HOMO-LUMO energy gap (ΔE), electron affinity (A), ionization potential (I), global hardness (η), softness (σ), electronegativity (χ), chemical potential (Pi), global electrophilicity index (ω) are investigated. All quantum chemical parameters, in general, are dependent on the choice of the basis sets, and are clearly influenced after the addition of polarization and diffusion functions.*

Keywords : *Sudan dyes, nonlinear optics, hyperpolarizability, polarizability, DFT, HF.*

Bazı sudan boyalarının lineer, lineer olmayan optik özellikleri ve kuantum kimyasal parametreleri

Özet

Bu çalışmada, Sudan III (SIII) [1-({4-[(fenil)diazenil] fenil}diazenil) naftalin-2-ol], Sudan Kırmızı G (SKG) [1-(2-Metoksifenilazo)-2-naftol] ve Sudan Turuncu G (STG) [4-(fenilazo)rezorsinol] moleküllerinin polarizabilite (<α>), anizotropi polarizabilite (<Δα>),

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taban-durum dipol moment (μ) ve birinci-derece hiperpolarizabilite (β) değerleri Hartree-Fock (HF) metodu ve Yoğunluk Fonksiyonel Teorisi (DFT/B3LYP) metodu ile 3-21G, 6-31G, 6-31G(d), 6-31G(d,p), 6-31G+(d,p), 6-31G++(d,p), 6-311G, 6-311G(d), 6-311G(d,p), 6-311G++(d,p) temel setleri kullanılarak incelendi. Ayrıca, E_{HOMO} *(en yüksek dolu moleküler orbital enerji),* E_{LUMO} *(en düşük boş moleküler orbital enerji), HOMO-LUMO enerji farkı (ΔE), elektron ilgisi (A), iyonizasyon potansiyeli (I), global sertlik (η), yumuşaklık (σ), elektronegatiflik (χ), kimyasal potansiyel (Pi), global elektrofilik indis (ω) değerleri araştırıldı. Tüm kuantum kimyasal parametreler, genelde, temel setlerin seçiminden bağımsızdır, ve açıkça polarizasyon ve difüz fonksiyonlarının eklenmesinden sonra etkilenmektedir.*

Anahtar kelimeler: *Sudan boyaları, lineer olmayan optik, hiperpolarizabilite, polarizabilite, DFT, HF.*

1. Introduction

Colorants are generally added into food to enhance its visual aesthetics, and to promote sales [1]. Although the allowable amount of synthetic colorants is reduced for consumer health reasons in recent years, many kinds of synthetic food dyes are still widely used all over the world due to their low price, high effectiveness, and excellent stability [2]. Azo-compounds are widely used as synthetic organic colorants. Generally, synthetic colorants can be classified as water-soluble or fat-soluble colorants based on their solubility. Most fat-soluble synthetic colorants present in the market are azo compounds, such as Sudan III (SIII) [3]. Belonging to the azo-dye class, sudan dyes are non-ionic fat-soluble dyes used in the gasoline, diesel, lubricating grease and polymer dye production, and as dye for food (chilli) and tattoos. SIII [1-({4-[(phenyl)diazenyl] phenyl}diazenyl) naphthalen-2-ol] is fat-soluble dye predominantly used for demonstrating the presence of triglycerides in frozen sections. In addition, SIII is commonly used for coloring waxes, oils and spirit varnishes [4]. Sudan Red G (SRG) [1-(2-Methoxyphenylazo)-2-naphthol] is a yellowish red lysochrome azo dye. It has the appearance of an odorless reddish-orange powder with melting point 225 °C. It is soluble in fats and used for coloring of fats, oils, and waxes, including the waxes used in turpentine-based polishes [5]. Sudan Orange G (SOG) [4-(Phenylazo)resorcinol] is useful for staining triglycerides in animal tissues (frozen sections) [6].

About 50% of the total world colorant production belongs to the so-called azo dyes compounds [7]. The main feature of this dye family is the presence of the azo group (-N=N-) which gives the possibility of providing a more extended electronic conjugation of π electrons, and consequently allowing for a strong light absorption in the visible region of the electromagnetic spectrum.

It is known that organic molecules formed by a donor–acceptor pair connected to a π-delocalized framework present attractive non-linear optics (NLO) characteristics, which can be estimated from their hyperpolarizabilities [8-11]. Recently, there has been a growing interest in the nonlinear optical (NLO) properties of azo materials with donor-acceptor groups for their large nonlinear refraction [12], which are interesting for the application in optical storage, optical-limiting and optical switching application [13, 14]. Their nonlinear optical response may result from electronic and/or nonelectronic process. Electronic nonlinearities occur as the result of the nonlinear response of bound electrons on an applied optical field. Furthermore, the usually good planarity of the azo bridge plays important role to larger π electron transmission effects [15-18]. The first hyperpolarizability, (β), gives information about the material capability to generate second order non-linear effects [11]. Also, the experimental and theoretical studies have been expanded to understand many aspects of molecular hyperpolarizabilities [15]. The use of quantum chemical methods as Hartree-Fock (HF) and density functional theory (DFT) for molecular hyperpolarizabilities is expected to supply a guidance and accelarate subsequent experimental studies [19,20]. Thus, in the present work, the molecular structures, E_{HOMO} (the highest occupied molecular orbital energy), E_{LUMO} (the lowest unoccupied molecular orbital energy), HOMO-LUMO energy gap (ΔE), dipole moments (μ), polarizabilities (<α>), the anisotropy of the polarizabilities (<Δα>) and first-order hyperpolarizabilities (β) are investigated using HF and B3LYP methods with different basis sets on some sudan azo dyes, such as SIII, SOG and SRG (Fig. 1).

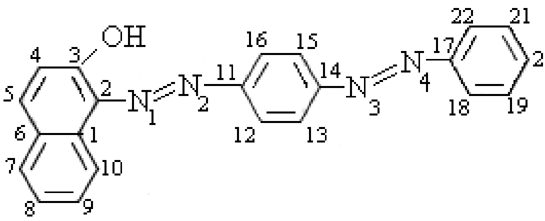
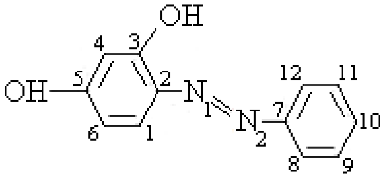
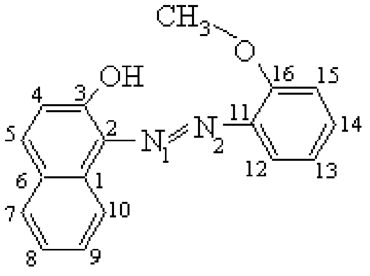
Dyes	**Chemical structures**	**Name of dyes**
SIII		[1-({4-[(phenyl)diazenyl] phenyl}diazenyl) naphthalen-2-ol]
SOG		[4-(Phenylazo)resorcinol]
SRG		[1-(2-Methoxyphenylazo)-2-naphthol]

Fig 1. Chemical structures of azo-dyes investigated.

Although the X-ray studies of SIII and SOG has not been reported till now, SIII has been calculated structural parameters by HF and DFT methods for investigation of the tautomerism in it [21]. Also, the nonlinear optical (NLO) parameters such as the polarizability (<α>), the anisotropy of the polarizability (<Δα>), ground-state dipole moment (μ) and the first-order hyperpolarizability (β) of SIII have been extensively studied density functional theory (DFT) calculation with 6-311G(d,p) basis set [22]. The experimental structure of SRG has been reported in the literature [23] and the molecular structural values of this molecule have been repoted in Cambridge Crystallographic Database (CSD code: JATJIX). In that study, SRG has analysed of the structure obtained for azo-form [23].

The other objective of this paper is to find effective quantum chemical methods (HF and DFT methods) that would offer a certainty of finding molecular parameters. The HF and DFT studies were initiated with the minimal basis set 3-21G and moved to higher basis sets for checking both (d), (p), (d,p) polarization function and +, ++ diffuse function effects. The basis sets incorporated in this study include 3-21G, 6-31G, 6-311G, 6-31G(d), 6-311G(d), 6-31G(d,p), 6-311G(d,p), 6-31G+(d,p), 6-31G++(d,p), 6-311G++(d,p) [24-30]. Also, the molecular hardness (η), global softness (σ) electronegativity (χ), chemical potential (Pi) and global electrophilicty index (ω) have been obtained from molecular frontier orbital energies using ab initio methods at different basis sets.

2. Computational Details

All calculations were performed using the GAUSSIAN-09W [31] software package and GaussView, Rev 5.0.9 [32] molecular visualization programs. The molecular geometries of SIII, SOG and SRG are restricted. The DFT calculations were performed using Becke's three-parameter hybrid functional [33] with the Lee-Yang-Parr correlation functional [34], a combination that gives rise to the well-known B3LYP method. In addition, the HF method was also used to obtain the NLO properties and energies (E_{HOMO}, E_{LUMO}, $\Delta E = E_{LUMO} - E_{HOMO}$) of SIII, SOG and SRG for comparison with B3LYP results. The effects of basis sets on calculations are studied at HF and B3LYP levels with 3-21G, 6-31G, 6-311G, 6-31G(d), 6-311G(d), 6-31G(d,p), 6-311G(d,p), 6-31G+(d,p), 6-31G++(d,p), 6-311G++(d,p) basis sets.

In the context of the HF theorem, the E_{HOMO} and E_{LUMO} is used to approximate the ionization potential (I) and electron affinity (A) given by Koopmans' theorem [35], respectively. Although no formal proof of this theorem exists within DFT, its validity is generally accepted. I and A are related to

$$I = -E_{HOMO} \qquad A = -E_{LUMO} \tag{1}$$

If we assume that these relations are valid within the DFT frame, the chemical potential (Pi) known as the negative of electronegativity (χ) , and hardness (η) can be estimated with

$$Pi = -\left(\frac{I + A}{2}\right); \quad \chi = \left(\frac{I + A}{2}\right); \quad \eta = \left(\frac{I - A}{2}\right) \quad . \tag{2}$$

Recently, several researches [36-39] have introduced an global electrophilicity index (ω) defined as

$$\omega = (Pi)^2 / 2\eta \quad . \tag{3}$$

This was proposed as a measure of the electrophilic power of a molecule and global softness (σ) is given by [40]

$$\sigma = 1/\eta \tag{4}$$

Polarizabilities were calculated at the same level of theory using the standard GAUSSIAN-09W keyword 'Polar' [41]. This keyword means that the polarizabilities were obtained analytically rather than by numerical differentiation.

The energy of an uncharged molecule under a weak, general electric field can be expressed by Buckingham type expansion [42-44]

$$E = E_0 - \mu_i F_i - (1/2)\alpha_{ij} F_i F_j - (1/6)\beta_{ijk} F_i F_j F_k + \ldots.. \quad (5)$$

where E is the energy of a molecule under the electric field F, E_0 is the unperturbed energy of a free molecule, F_i is the vector component of the electric field in the i direction, and $\mu_i, \alpha_{ij}, \beta_{ijk}$ are the dipole moment, linear polarizability and first-order hyperpolarizability, respectively. Here, each subscript of i, j and k denotes the indices of the Cartesian axes x, y, z, and a repeated subscript means a summation over the Cartesian indices x, y, z. The ground state dipole moment μ, the polarizability $<\alpha>$, the anisotropy of the polarizability $<\Delta\alpha>$ and the first-order hyperpolarizability β, using the x, y, z components they are defined as [45, 46]

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \quad (6)$$

$$\langle\alpha\rangle = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (7)$$

$$\langle\Delta\alpha\rangle = \left[\frac{\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\left(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2\right)}{2}\right]^{1/2} \quad (8)$$

$$\beta = \sqrt{\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2}\,. \quad (9)$$

Since the values of the polarizabilities (α) and first-order hyperpolarizability (β) of GAUSSIAN-09W output [30] are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) (α: 1 a.u. = 0.1482×10^{-24} esu; β: 1 a.u.= 8.6393×10^{-33} esu) [47].

3. Results and Discussion

In general, sudan dyes display two possible tautomeric forms, the azo (O-H) and hydrazo (N-H) forms, as shown in Fig. 2 for SRG [22, 23]. Depending on the tautomers, two types of intermolecular hydrogen bonds are observed in sudan dyes: O-H···N in azo and N-H···O in hydrazo tautomer. Several researchers have studied the azo/hydrazo form of sudan dyes [21, 23, 48]. The position and nature of the equilibrium depends on the solvent utilized. In this study, we have not used any solvents to determine the molecular parameters of sudan dyes. Therefore, we decided to study only the azo (OH) form of the sudan dyes because of their molecular parameters and non-linear optical properties.

The molecular structures of SIII, SOG and SRG have been completely optimized at the HF and B3LYP levels with 3-21G, 6-31G, 6-31G(d), 6-31G(d,p), 6-31G+(d,p), 6-31G++(d,p), 6-311G, 6-311G(d), 6-311G(d,p), 6-311G++(d,p) basis sets. The optimized structures of the studied molecules at the DFT/B3LYP level using the 6-31G(d,p) basis set are shown in Fig. 3.

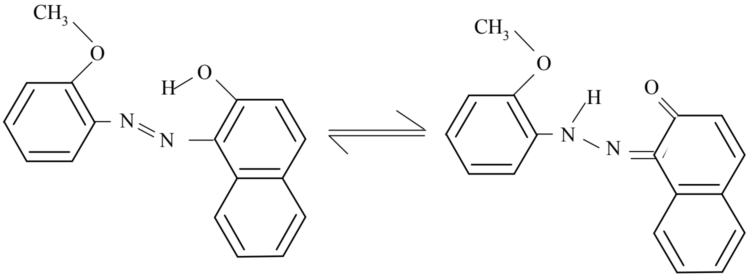


Fig 2. Tautomeric equilibrium for the SRG.

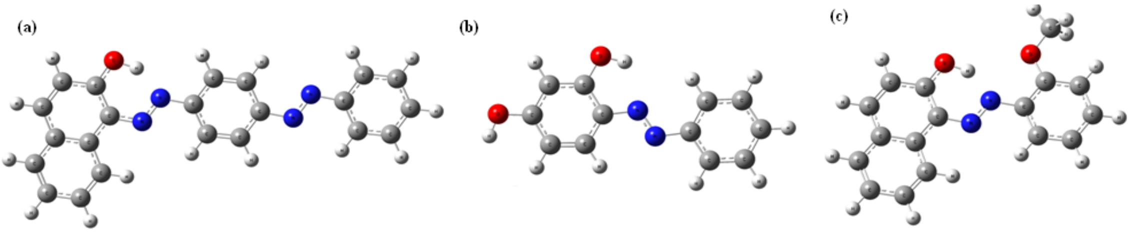


Fig. 3. The optimized structures obtained using B3LYP/6-31G(d,p) level of (a) SIII, (b) SOG and (c) SRG.

The calculated N-N and C-N lengths of the three compounds are presented in Table 1, and are compared with the experimental values of SRG values from X-ray diffraction data [23]. Also, the experimental structure of SIII has not been reported until now, therefore we have compared the calculated bond lengths of SIII with its experimentally available parent compound trans-azobenzene from the X-ray study [49]. From the crystalline structure described for trans-azobenzene, the N_1-N_2 bond length was 1.247 Å. In the present study, the calculated N-N bond distances for SIII was found to be between 1.222 and 1.250 Å by HF and between 1.274 and 1.344 Å by B3LYP level for N_1-N_2 and 6-31G basis set for OH isomer structure of SIII. In that study, the N_1-N_2 and N_3-N_4 bonds were found to be 0.02 Å shorter than our calculated values with same basis set. Due to the lack of experimental data in SOG, we compared the experimental N-N bond length of SRG with the theoretical value obtained with several basis sets of SOG. From the theoretical values, it can be stated that N-N bond lengths of SRG and SOG are lower than the experimental value of SRG [23]. The discrepancy between the experimental and calculated bond lengths of SRG might result from the different forms of SRG (experimentally in the hydrazo form and theoretically in the azo form). Going from 3-21G to 6-31G decreases the N-N bond lengths of the studied molecules, and using the 6-311G basis set shows little change in this bond length. This suggests that increasing the size of the orbitals does not improve the description of this bond length. The same conclusion can be arrived at with respect to the addition of polarization (d, (d,p)) and diffuse (+, ++) functions.

The calculated C-N bond lengths for sudan dyes compare with those corresponding to data reported in the literature [23, 49]. As shown in Table 1, the calculated values correspond well to those within the literature [21] (1.404 Å for HF/6-31G and 1.388 Å for B3LYP/6-31G) and for our study (between 1.400 and 1.404 Å for HF and between 1.334 and 1.388 Å for B3LYP) values of C_2-N_1 bonds for SIII, but there was a discrepancy in the experimental results regarding the structure of *trans*-azobenzene (1.428 Å) [49]. The deviations in the C_2-N_1 and N_2-C_{11} bond lengths for SIII are less than 0.028 and 0.010 Å for HF/6-31G and 0.044 and 0.017 Å for B3LYP/6-31G when compared to the *trans*-azobenzene, respectively. The differences of bond lengths between the experimental [23] and the calculated values for SRG are found in the C_2-N_1 and N_2-C_{11} bonds, with the different values being 0.074 and 0.004 Å for HF/6-31G and 0.059 and 0.001 Å for B3LYP/6-31G, respectively. For the optimized SOG structure, the difference of C_2-N_1 and N_2-C_{11} bond lengths are found to be 0.077 and 0.016 Å for HF/6-31G and 0.072 and 0.018 Å for B3LYP/6-31G, respectively, as compared to the observed value of 1.330 and 1.404 Å in the X-Ray data for SRG [23]. The use of several basis sets for sudan dyes has no effect on the value of these bond lengths.

Analyses of the conformation of individual rings for azo dyes have been important [50], thus the dihedral angles around N-N moiety of studied molecules have been investigated. The values of N_1-N_2-C_{11}-C_{12} and N_2-N_1-C_2-C_1 dihedral angles are given in Table 2. It can be seen that all the rings for sudan dyes were found planar (~180°). Also, the experimental values of N_1-N_2-C_{11}-C_{12} and N_2-N_1-C_2-C_1 for SRG [22] are 0.8º and 178º (X-ray) which are closer to the dihedral angles calculated using the HF and B3LYP levels. The O-H···N distances were 1.62, 2.07 and 1.61 Å (with B3LYP/6-31G(d,p)) for SIII, SOG and SRG, respectively. These distances are significantly smaller than the summation of the Van der Waals radii (~2.6 Å), by just confirming the presence of a very strong hydrogen interaction in these compounds [48,50].

The highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) orbitals are called frontier molecular orbitals as they lie at the outermost boundaries of the electrons of the molecules. The HOMO and LUMO are the main orbitals responsible for chemical stability. The HOMO-LUMO orbital pictures of SIII, SOG and SRG molecules are given in Fig. 4. The HOMO of SIII and SOG molecules are delocalized over the N-N bond and the HOMO of SRG is delocalized over the C-C and N-N bonds. In contrast, the LUMO of SIII, SOG and SRG molecules are located in all of the molecules.

Table 1. Selected bond lengths (in Å) calculated for SIII, SOG and SRG at HF and B3LYP levels and literature values for comparison.

		SIII						SOG			SRG		
Basis Sets		C_2-N_1	N_1-N_2	N_2-C_{11}	C_{14}-N_3	N_3-N_4	N_4-C_{17}	C_2-N_1	N_1-N_2	N_2-C_7	C_2-N_1	N_1-N_2	N_2-C_{11}
3-21G	HF	1.401	1.250	1.422	1.425	1.240	1.426	1.411	1.241	1.426	1.407	1.246	1.410
	B3LYP	1.334	1.344	1.392	1.419	1.295	1.426	1.398	1.295	1.424	1.337	1.337	1.395
6-31G	HF	1.400	1.241	1.418	1.419	1.233	1.419	1.407	1.234	1.420	1.404	1.239	1.408
	B3LYP	1.384	1.302	1.411	1.419	1.281	1.422	1.402	1.282	1.422	1.389	1.298	1.405
6-31G(d)	HF	1.401	1.227	1.418	1.419	1.220	1.420	1.407	1.221	1.419	1.405	1.225	1.412
	B3LYP	1.380	1.280	1.406	1.413	1.263	1.416	1.395	1.266	1.415	1.386	1.277	1.403
6-31G(d,p)	HF	1.401	1.227	1.418	1.419	1.220	1.420	1.406	1.221	1.420	1.404	1.225	1.413
	B3LYP	1.379	1.281	1.406	1.413	1.263	1.416	1.396	1.266	1.414	1.384	1.278	1.403
6-31+G(d,p)	HF	1.401	1.226	1.420	1.420	1.218	1.421	1.408	1.220	1.420	1.405	1.224	1.413
	B3LYP	1.380	1.279	1.408	1.414	1.260	1.417	1.397	1.263	1.416	1.384	1.277	1.404
6-31++G(d,p)	HF	1.401	1.226	1.420	1.421	1.218	1.421	1.408	1.220	1.421	1.405	1.224	1.414
	B3LYP	1.380	1.279	1.408	1.414	1.260	1.417	1.397	1.263	1.415	1.384	1.277	1.404
6-311G	HF	1.404	1.243	1.421	1.422	1.235	1.422	1.410	1.236	1.422	1.408	1.241	1.412
	B3LYP	1.388	1.301	1.414	1.421	1.281	1.424	1.404	1.282	1.424	1.393	1.298	1.407
6-311G(d)	HF	1.402	1.222	1.419	1.420	1.215	1.420	1.407	1.216	1.420	1.406	1.220	1.413
	B3LYP	1.379	1.274	1.406	1.412	1.256	1.415	1.395	1.259	1.413	1.385	1.271	1.402
6-311G(d,p)	HF	1.402	1.222	1.419	1.420	1.215	1.421	1.408	1.216	1.420	1.405	1.221	1.414
	B3LYP	1.379	1.275	1.406	1.412	1.256	1.416	1.395	1.259	1.414	1.384	1.272	1.402
6-311++G(d,p)	HF	1.402	1.222	1.419	1.421	1.214	1.422	1.408	1.216	1.421	1.405	1.221	1.414
	B3LYP	1.380	1.274	1.407	1.414	1.255	1.417	1.396	1.258	1.415	1.384	1.272	1.403
6-31G[a]	HF	1.404	1.224	1.423	1.423	1.217	1.423	-	-	-	-	-	-
	B3LYP	1.388	1.275	1.414	1.420	1.259	1.422	-	-	-	-	-	-
X-ray[b]		1.428	1.247	1.428	1.428	1.247	1.428	-	-	-	-	-	-
X-ray[c]	- -	-	-	-	-		-	-		-	1.330	1.311	1.404

[a] Taken from Ref [23]

[b] Taken from Ref [51]

[c] Taken from Ref [24, 25]

Table 2. Selected calculated and experimental dihedral angles (^{o}) of SIII, SOG and SRG.

Basis Sets		SIII				SOG		SRG	
		N_1-N_2-C_{11}-C_{12}	N_2-N_1-C_2-C_1	N_3-N_4-C_{17}-C_{18}	N_4-N_3-C_{14}-C_{13}	N_1=N_2=C_7=C_8	N_2-N_1-C_2-C_1	N_1=N_2=C_{11}=C_{12}	N_2=N_1=C_2=C_1
3-21G	HF	-0.002	-179.994	-0.002	179.995	-179.893	0.028	0.003	-179.970
	B3LYP	-0.002	179.995	0.000	179.990	179.998	-0.028	-0.018	-179.988
6-31G	HF	0.007	-179.997	-0.004	-179.994	-179.955	-0.017	0.002	-179.995
	B3LYP	0.001	179.997	0.004	-179.994	-179.998	0.004	0.001	-179.985
6-31G(d)	HF	0.109	-179.976	-0.038	180.000	-179.932	0.016	0.009	-179.993
	B3LYP	-0.001	-179.980	-0.001	179.990	-179.987	-0.010	0.002	179.991
6-31G(d,p)	HF	0.146	-179.968	-0.040	179.999	-179.922	0.017	0.001	179.991
	B3LYP	-0.001	179.989	0.001	179.997	-179.616	0.107	0.000	-179.998
6-31+G(d,p)	HF	0.124	-179.977	-0.053	179.979	-179.880	0.040	0.030	-179.990
	B3LYP	-0.002	-179.998	0.002	179.999	-179.948	0.018	0.000	-179.984
6-31++G(d,p)	HF	0.024	-179.991	-0.055	179.979	-179.841	0.071	0.032	-179.992
	B3LYP	0.002	-180.000	0.001	-179.995	-179.922	0.025	-0.001	-179.962
6-311G	HF	0.008	179.998	-0.004	-179.990	-179.943	-0.002	-0.001	-179.994
	B3LYP	-0.001	179.997	0.004	-179.997	-179.987	0.007	-0.002	-179.995
6-311G(d)	HF	0.149	-179.955	-0.014	179.990	-179.894	0.020	0.009	-179.986
	B3LYP	0.004	179.998	-0.003	-179.992	-179.950	0.005	0.004	-179.994
6-311G(d,p)	HF	0.198	-179.956	-0.045	179.995	-179.891	0.022	0.009	-179.989
	B3LYP	0.000	179.992	0.000	-179.995	-179.941	0.015	-0.004	-179.996
6-311++G(d,p)	HF	0.079	-179.986	-0.030	179.982	-179.815	0.080	0.008	-179.990
	B3LYP	0.002	179.999	0.001	-179.999	-179.899	0.044	-0.003	-179.966
X-Ray[a]	-	-	-	-	-	-	-	0.800	178.000

[a] Taken from Ref [23]

The calculated values for the E_{HOMO} and E_{LUMO} and the frontier molecular orbital energy gap (ΔE) with several basis sets are given in Table 3. E_{HOMO} is often associated with the electron-donating ability of a molecule, whereas E_{LUMO} indicates its ability to accept electrons. The frontier orbital gap helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with a high chemical reactivity, low kinetic stability, and is also defined as a LUMO energy gaps with B3LYP/6-31G for SIII, SOG and SRG decrease in the order soft molecule [40]. The E_{HOMO} and E_{LUMO} energies for SIII were calculated using the DFT calculation with the B3LYP functional and the 6-31G basis set by Silva et al. [51]. The E_{HOMO} and E_{LUMO} energies for the SIII molecule obtained using B3LYP/6-31G level were found to be -5.67 and -2.70 eV, respectively [52]. In this study, these energies for SIII, SOG and SRG have been calculated to be -7.668 and -5.698 eV for SIII, -8.167 and -5.881 eV for SOG, -7.451 and -5.432 eV for SRG (E_{HOMO}) and 0.706 and -2.961 eV for SIII, 1.419 and -2.382 eV for SOG, 1.389 and -2.386 eV for SRG (E_{LUMO}) by HF/6-31-G and B3LYP/6-31G levels. According to these results obtained from the HF and DFT methods, the values of E_{HOMO} and E_{LUMO} show the decreasing trend of the properties: SOG < S3 < SRG and S3 < SRG < SOG, respectively. As can be seen from Table 3, the E_{HOMO} and E_{LUMO} values with 6-31G at HF and B3LYP levels follow the same trend as other theoretical basis sets. SOG has more E_{LUMO} than SRG for two basis sets results [6-31++G(d,p) and 6-311G]. Silva et al. [51] were calculated at the Fermi level (approximately -4.18 eV) located at the center of the E_{HOMO} and E_{LUMO} levels of the SIII, so the ΔE value from this energy was found to be 2.97 eV. In this study, the HOMO -3.50 (SOG) > 3.05 (SRG) > 2.74 (SIII) eV, which are consistent with the ability of the electron-donating of the group $N_2C_6H_{10} > CH_3O > H$. Concerning the value of the energy of the gap ΔE, larger values of the energy difference will also provide low reactivity to chemical types. As seen in Table 3, the addition of diffuse and polarization functions, and the calculated values of ΔE were found to be almost the same. Fig. 5(a)-(c) show the variation of the calculated energy levels of E_{HOMO}, E_{LUMO} and ΔE values at HF and B3LYP methods using different basis sets. It can be seen in Fig. 5(a)-(c) that there is an overlap between the different methods and the basis sets of E_{HOMO}, E_{LUMO} and ΔE values.

In the most common case, ionization potential (I) and electron affinity (A) are related to E_{HOMO} and E_{LUMO} respectively. The low I creates a better electron donor, and the large A makes a better electron acceptor. Using all the methods, the I of SRG is the lowest [7.332 eV (HF/6-31G(d,p)) and 5.299 eV (B3LYP/3-21 G)]. The A is found to be the highest for SIII with -0.563 eV (HF/6-311G) and for SOG with 3.119 eV (B3LYP/6-311G). The obtained values of I and A (Table 4) were considered for the calculation of global hardness (η), softness (σ), electronegativity (χ), chemical potential (Pi), and electrophilicity index (ω). These quantum chemical parameters were evaluated using Eqs. (2-4) and were listed as these values calculated with several basis sets in Table 5.

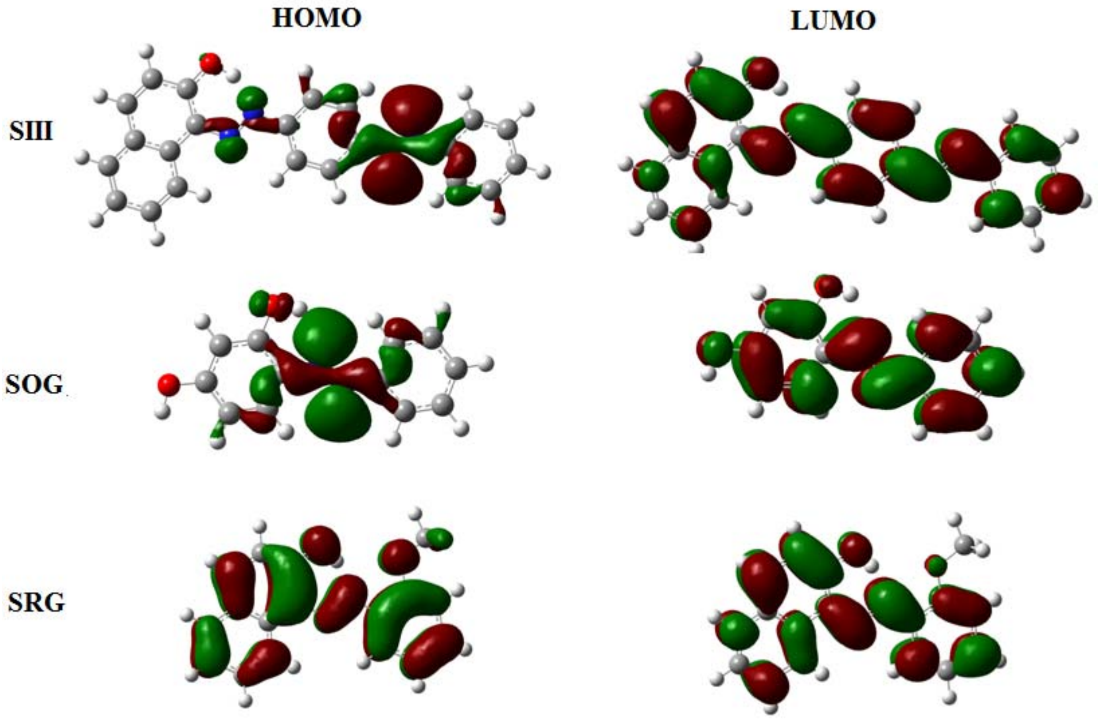


Fig. 4. 3D plots of HOMO and LUMO of studied molecules by B3LYP/6-31G(d,p) with energies.

Table 3. Calculated energy levels (in eV) of the HOMO, LUMO and ΔE.

		SIII			SOG			SRG		
Basis Sets		**E_{HOMO}(eV)**	**E_{LUMO}(eV)**	**ΔE (eV)**	**E_{HOMO}(eV)**	**E_{LUMO}(eV)**	**ΔE (eV)**	**E_{HOMO}(eV)**	**E_{LUMO}(eV)**	**ΔE (eV)**
3-21G	HF	-7.72368	0.76954	8.49322	-8.16151	1.57119	9.73270	-7.46926	1.46697	8.93622
	B3LYP	-5.61888	-2.86835	2.75053	-5.75276	-2.27433	3.47843	-5.29915	-2.34018	2.95897
6-31G	HF	-7.66763	0.70614	8.37376	-8.16668	1.41907	9.58576	-7.4513	1.38914	8.84044
	B3LYP	-5.69834	-2.96087	2.73747	-5.88065	-2.38181	3.49884	-5.43221	-2.38562	3.04659
6-31G(d)	HF	-7.52640	0.98206	8.50846	-7.91743	1.73092	9.64835	-7.33783	1.64112	8.97894
	B3LYP	-5.57616	-2.81339	2.76277	-5.70133	-2.19732	3.50401	-5.33343	-2.24113	3.09230
6-31G(d,p)	HF	-7.52096	0.98342	8.50438	-7.90763	1.73636	9.64399	-7.33184	1.64003	8.97187
	B3LYP	-5.57942	-2.82101	2.75842	-5.7046	-2.20140	3.50320	-5.3367	-2.2531	3.08360
6-31+G(d,p)	HF	-7.71253	0.62477	8.33730	-8.11389	1.26343	9.37732	-7.52477	1.24193	8.76670
	B3LYP	-5.88800	-3.15516	2.73284	-6.05481	-2.59297	3.46183	-5.65616	-2.6017	3.05448
6-31++G(d,p)	HF	-7.70355	0.62586	8.32941	-8.12287	0.85498	8.97786	-7.52422	1.00084	8.52506
	B3LYP	-5.88758	-3.15481	2.73277	-6.05329	-2.59318	3.46011	-5.65547	-2.60107	3.05440
6-311G	HF	-7.79715	0.56328	8.36043	-8.28097	1.26070	9.54168	-7.58518	1.23458	8.81976
	B3LYP	-5.93998	-3.19462	2.74536	-6.12365	-2.62590	3.49775	-5.6714	-2.61420	3.05720
6-311G(d)	HF	-7.67089	0.81226	8.48315	-8.04777	1.55078	9.59855	-7.4766	1.46778	8.94439
	B3LYP	-5.82324	-3.05584	2.76740	-5.94351	-2.43705	3.50646	-5.57425	-2.4792	3.09502
6-311G(d,p)	HF	-7.66899	0.81335	8.48234	-8.04804	1.55132	9.59936	-7.47497	1.46289	8.93786
	B3LYP	-5.82814	-3.06019	2.76794	-5.95113	-2.44386	3.50728	-5.57861	-2.48767	3.09094
6-311++G(d,p)	HF	-7.72368	0.76954	8.49322	-8.14655	0.97498	9.12153	-7.5596	0.94451	8.50411
	B3LYP	-5.94581	-3.19046	2.75535	-6.11386	-2.63297	3.48088	-5.71222	-2.63814	3.07407

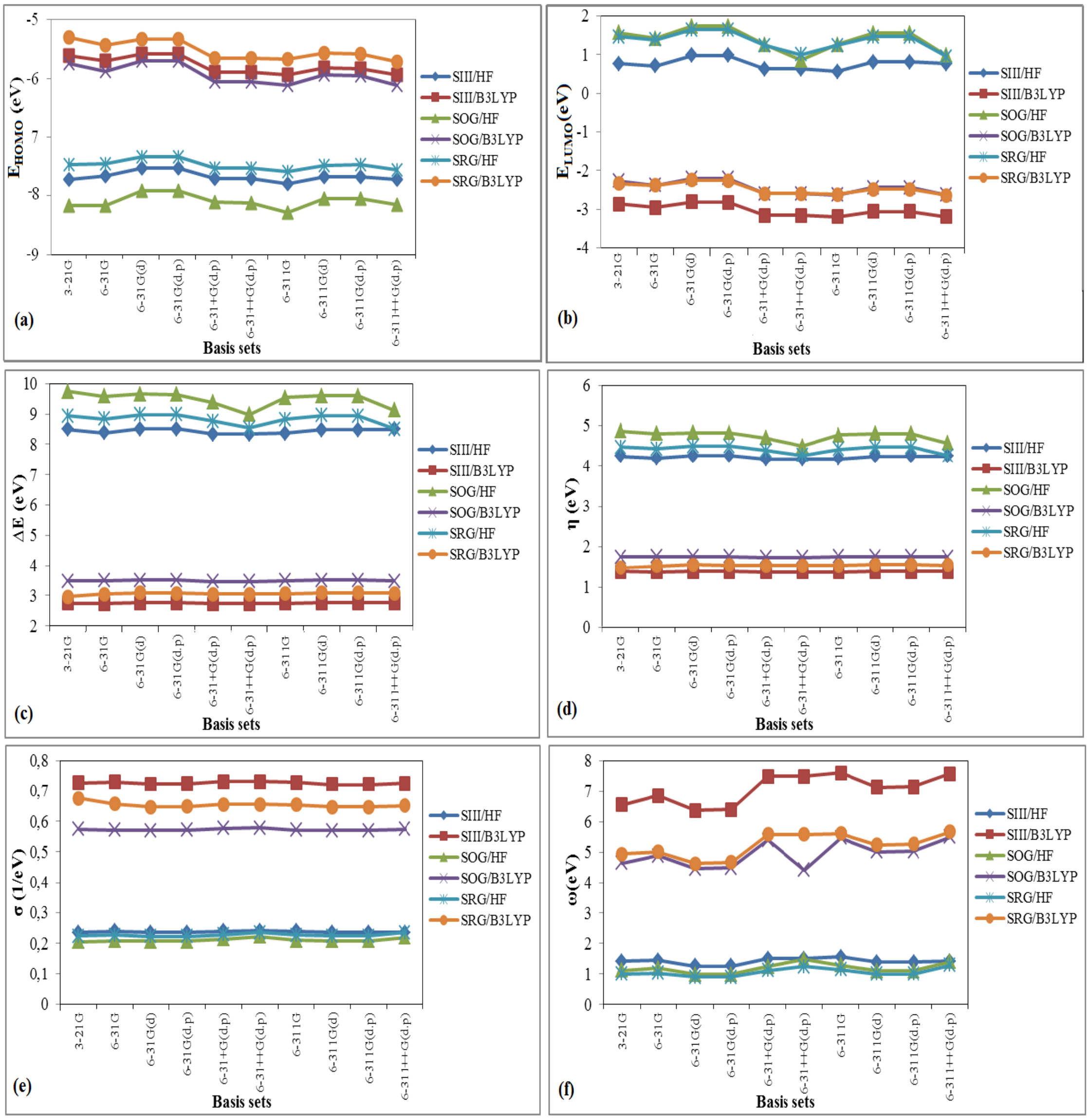


Fig. 5. Variation of (a) E_{HOMO} (eV) (b) E_{LUMO} (eV) (c) HOMO-LUMO energy gap (ΔE, in eV) (d) hardness (η, in eV) (e) softness (σ, in 1/eV) (f) global electrophilicity index (ω, in eV) of sudan dyes with HF and B3LYP methods and different basis sets.

Table 4: Electron affinities (A) and ionization potentials (I) values of SIII, SOG and SRG.

		SIII		SOG		SRG	
Basis Sets		$I=-E_{HOMO}$	$A=-E_{LUMO}$	$A=-E_{LUMO}$	$I=-E_{HOMO}$	$A=-E_{LUMO}$	$I=-E_{HOMO}$
3-21G	HF	7.72368	-0.76954	8.16151	-1.57119	7.46926	-1.46697
	B3LYP	5.61888	2.86835	5.75276	2.27433	5.29915	2.34018
6-31G	HF	7.66763	-0.70614	8.16668	-1.41907	7.45130	-1.38914
	B3LYP	5.69834	2.96087	5.88065	2.38181	5.43221	2.38562
6-31G(d)	HF	7.52640	-0.98206	7.91743	-1.73092	7.33783	-1.64112
	B3LYP	5.57616	2.81339	5.70133	2.19732	5.33343	2.24113
6-31G(d,p)	HF	7.52096	-0.98342	7.90763	-1.73636	7.33184	-1.64003
	B3LYP	5.57942	2.82101	5.70460	2.20140	5.33670	2.25310
6-31+G(d,p)	HF	7.71253	-0.62477	8.11389	-1.26343	7.52477	-1.24193
	B3LYP	5.88800	3.15516	6.05481	2.59297	5.65616	2.60170
6-31++G(d,p)	HF	7.70355	-0.62586	8.12287	-0.85498	7.52422	-1.00084
	B3LYP	5.88758	3.15481	6.05329	2.59318	5.65547	2.60107
6-311 G	HF	7.79715	-0.56328	8.28097	-1.26070	7.58518	-1.23458
	B3LYP	5.93998	3.19462	6.12365	2.62590	5.67140	2.61420
6-311G(d)	HF	7.67089	-0.81226	8.04777	-1.55078	7.47660	-1.46778
	B3LYP	5.82324	3.05584	5.94351	2.43705	5.57425	2.47920
6-311G(d,p)	HF	7.66899	-0.81335	8.04804	-1.55132	7.47497	-1.46289
	B3LYP	5.82814	3.06019	5.95113	2.44386	5.57861	2.48767
6-311++G(d,p)	HF	7.72368	-0.76954	8.14655	-0.97498	7.55960	-0.94451
	B3LYP	5.94581	3.19046	6.11386	2.63297	5.71222	2.63814

Table 5. Global hardness (η), softness (σ), electronegativity (χ), chemical potential (Pi) and electrophilicity index (ω) of SIII, SOG and SRG.

Basis Sets		SIII					SOG					SRG				
		η (eV)	σ (1/eV)	χ (eV)	Pi (eV)	ω (eV)	η (eV)	σ (1/eV)	χ (eV)	Pi (eV)	ω (eV)	η (eV)	σ (1/eV)	χ (eV)	Pi (eV)	ω (eV)
3-21G	HF	4.2466	0.2355	3.4771	-3.4771	1.4235	4.8664	0.2055	3.2952	-3.2952	1.1156	4.4681	0.2238	3.0012	-3.0012	1.0079
	B3LYP	1.3753	0.7271	4.2436	-4.2436	6.5472	1.7392	0.5750	4.0136	-4.0136	4.6310	1.4795	0.6759	3.8197	-3.8197	4.9307
6-31G	HF	4.1869	0.2388	3.4808	-3.4808	1.4469	4.7929	0.2086	3.3738	-3.3738	1.1874	4.4202	0.2262	3.0311	-3.0311	1.0393
	B3LYP	1.3687	0.7306	4.3296	-4.3296	6.8477	1.7494	0.5716	4.1312	-4.1312	4.8779	1.5233	0.6565	3.9089	-3.9089	5.0153
6-31G(d)	HF	4.2542	0.2351	3.2722	-3.2722	1.2584	4.8242	0.2073	3.0933	-3.0933	0.9917	4.4895	0.2227	2.8484	-2.8484	0.9036
	B3LYP	1.3814	0.7239	4.1948	-4.1948	6.3690	1.7520	0.5708	3.9493	-3.9493	4.4512	1.5461	0.6468	3.7873	-3.7873	4.6385
6-31G(d,p)	HF	4.2522	0.2352	3.2688	-3.2688	1.2564	4.8220	0.2074	3.0856	-3.0856	0.9873	4.4859	0.2229	2.8459	-2.8459	0.9027
	B3LYP	1.3792	0.7251	4.2002	-4.2002	6.3956	1.7516	0.5709	3.9593	-3.9593	4.4748	1.5418	0.6486	3.7949	-3.7949	4.6703
6-31+G(d,p)	HF	4.1687	0.2399	3.5439	-3.5439	1.5064	4.6887	0.2133	3.4252	-3.4252	1.2511	4.3834	0.2281	3.1414	-3.1414	1.1257
	B3LYP	1.3664	0.7318	4.5216	-4.5216	7.4811	1.7309	0.5777	4.3239	-4.3239	5.4006	1.5272	0.6548	4.1289	-4.1289	5.5813
6-31++G(d,p)	HF	4.1647	0.2401	3.5389	-3.5389	1.5035	4.4889	0.2228	3.6340	-3.6340	1.4709	4.2625	0.2346	3.2617	-3.2617	1.2479
	B3LYP	1.3664	0.7319	4.5212	-4.5212	7.4800	1.7301	0.5780	4.3232	-4.3232	5.4017	1.5272	0.6548	4.1283	-4.1283	5.5797
6-311 G	HF	4.1802	0.2392	3.6169	-3.6170	1.5648	4.7708	0.2096	3.5101	-3.5101	1.2913	4.4099	0.2268	3.1753	-3.1753	1.1430
	B3LYP	1.3727	0.7285	4.5673	-4.5673	7.5984	1.7489	0.5718	4.3748	-4.3748	5.4717	1.5286	0.6542	4.1428	-4.1428	5.6139
6-311G(d)	HF	4.2416	0.2358	3.4293	-3.4293	1.3863	4.7993	0.2084	3.2485	-3.2485	1.0994	4.4722	0.2236	3.0044	-3.0044	1.0092
	B3LYP	1.3837	0.7227	4.4395	-4.4395	7.1220	1.7532	0.5704	4.1903	-4.1903	5.0075	1.5475	0.6462	4.0267	-4.0267	5.2389
6-311G(d,p)	HF	4.2412	0.2358	3.4278	-3.4278	1.3852	4.7997	0.2084	3.2484	-3.2484	1.0992	4.4689	0.2238	3.0060	-3.0060	1.0110
	B3LYP	1.3840	0.7226	4.4442	-4.4442	7.1355	1.7536	0.5702	4.1975	-4.1975	5.0236	1.5455	0.6471	4.0331	-4.0331	5.2626
6-311++G(d,p)	HF	4.2466	0.2355	3.4771	-3.4771	1.4235	4.5608	0.2193	3.5858	-3.5858	1.4096	4.2521	0.2352	3.3076	-3.3076	1.2864
	B3LYP	1.3777	0.7259	4.5681	-4.5681	7.5736	1.7404	0.5746	4.3734	-4.3734	5.4948	1.5370	0.6506	4.1752	-4.1752	5.6707

The global hardness (η), softness (σ), electronegativity (χ), chemical potential (Pi) and electrophilicity index (ω) have been used by a number of workers [37, 53, 54] to assess a priori of the reactivity of chemical properties from their intrinsic electrical properties. Global hardness and softness are important properties to measure the molecular stability and reactivity. A hard molecule has a large energy gap, and a soft molecule has a small one. Soft molecules are more reactive than hard ones because they could easily offer electrons to an acceptor. For the simplest transfer of electrons, absoption could occur at the part of the molecule where softness, which is a localised, has the highest value. Evaluating the values of the hardness in Table 5 shows that SOG has the greatest. This means that SOG has the largest potential chemical resistance to change the number of electrons among the other molecules. It can be noted that the hardness of the molecules follows the order SOG > SRG > SIII using all the methods. Also, it can be seen in Table 5 that SIII is the compound that displays the greater reactivity in relationship to the others as a result of the high value of global softness. The softness of the molecules follows the order SIII > SRG > SOG using all the methods. The electrophilicity index, ω, encompasses both; the propensity of the electrophile to acquire an additional electronic charge driven by Pi^2 (the square of chemical potential) and the resistance of the system to exchange an electronic charge with the environment described by η simultaneously. Therefore, a good electrophile is characterized by a high value of Pi and a low value of η. We have computed the electrophilicity indexes and the corresponding values are shown in Table 5. SIII indicates the highest value of electrophilicity, which confirms its high capacity to accept electrons. For the other two molecules, the differences in the electrophilicity index remain relatively constant, with only minor variations. From Table 5, the variations of the ground state electrophilicity indexes of the studied compounds are similar to the different basis sets and methods. Global hardness, softness and electrophilicity index have been found to remain unchanged at the different basis sets (see Fig. 5(d)-(f)).

Another important molecular feature of its electronic properties is its polarizability. The π electrons of unsubstitued aromatic molecules do not contribute to the polarizability in a direction perpendicular to the plane; however, in the case of sudan dyes the π electrons may contribute to the polarizability via –OH group [54]. It has been documented that the hydroxy group is an electron donor via a π-bond and an electron acceptor via σ-bond. However, the polarizability of molecules in the perpendicular direction is mainly due to the polarizability of the σ-bonds. This would suggest that certain orientations of dipoles can have a disadvantageous effect on the order parameter. On the other hand, the dipole moment of the C-OH bond seems to be significant because the C-OH dipole may lead to both attraction and repulsion, and the net effect may be very small [54]. Ghanadzadeh et al. [54] investigated the experimental parameters (e.g. dichroic ratio R and order parameter) of five sudan dye solutions including SIII by measuring the intensity of the absorption bands in the visible region of parallel aligned samples. In that study, the polarized absorption of the Sudan dyes were measured, but no data on the polarizability of those dyes was provided [54]. Therefore, we have not compared this experimental data with our theoretical values for the polarizabilities of sudan dyes.

The calculated components of the polarizability tensor α, the polarizability <α> and the anisotropy of the polarizability <Δα> for studying the molecules are listed in Table 6. The variation of <α>, <Δα> in the atomic units and <α> in esu ($x10^{-24}$) for studying the molecules are in the same order as SOG < SRG < SIII with HF and B3LYP levels.

The concepts of hardness and softness of atoms and molecules are however, intimately linked with their polarizabilities and also the sizes. Softness and polarizability are assumed to be related: "a soft species is also more polarizable." Thus, a hard (soft) species is known to correspond to a low (high) value of the polarizability as well as a small (large) size [54]. Indeed, one expects the SIII, the most polarizable member of the family, to be the "softest." In contrast, the SOG, the less polarizable molecule of the family, is expected to be the "hardest." As seen in Fig. 6(a)-(b), the variation of <α> and <Δα> values for SIII, SOG, and SRG, and that it decreases from the largest molecular structure (SIII) to the smallest molecular structure (SOG) is obvious.

The dipole moment in a molecule is an important property, which is mainly used to study the intermolecular interactions involving the nonbonded type dipole–dipole interactions, because the higher the dipole moment, the stronger the intermolecular interactions will be. The dipole moments of the studied dyes obtained using HF and DFT calculations are summarized in Table 7. The higher values of dipole moments in the cases of SIII (1.72 D), SOG (3.59 D) and SRG (2.84 D) using B3LYP/3-21G, HF/6-31G and HF/6-31 basis sets, respectively, is mainly attributed to an overall imbalance in the charge from one side of a molecule to the other. The variations of the ground state dipole moments of studied sudan dyes are shown in Fig. 6(c). As can be seen Fig. 6(c), results show that there is approximately increase in μ when the calculation is done at 6-31G and 6-311G basis sets when compared to other basis sets.

In general, the stronger the donor, the smaller the energy difference between ground and excited states, and the longer the wavelength of UV-visible absorption. This red shift suggests an increase of molecular hyperpolarizability, according to theoretical and experimental NLO studies [55]. In previous studies, the UV-visible absorption spectra of azo dyes in different solvents were investigated by several authors [12, 21, 54]. Sudan dyes contain intramolecular charge-transfer chromophores which have large and stable NLO responses. The absorption spectrum of Sudan I was recorded by the UV-VIS-NIR spectrometer [12]. The absorption bands of Sudan I in solution is strong at 488 and 532 nm in the visible region. He and Wang [12] have investigated the nonlinear optical property of Sudan I under pulse 532 nm. They found the second hyperpolarizability to be $1.83x10^{-30}$ esu [12].

Santos et al. [21] have reported the experimental UV-visible spectrum of SIII, but they have given any information regarding the solution for the recorded spectrum. Two absorption bands of SIII were observed at 351 and 513 nm in the experimental spectrum. The band close to 350 nm was not affected by the tautomeric equilibrium [52]. The lowest energy transition, responsible for the absorption band at 484 nm obtained with B3LYP, involves the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) with the Configuration interaction (CI) contribution equal to 86% (HOMO → LUMO). Also, Ghanadzadeh et al. [54] investigated the maximum absorption wavelengths of SIII in isotropic and anisotropic solvents. They found these wavelengths to be between 495 and 520 nm. The absorption maxima of SOG were observed at 254 and 382 nm in all solvents.

For DHAB, the absorption maxima at 256 and 382 nm in a non-polar solvent suggests the presence of an intramolecular hydrogen bonding interaction (IHB) between –OH···N=N– groups [57].

The investigation of the first static hyperpolarizability is explained by the calculation of the frontier molecular orbital energies, which helps to use intramolecular charge transfer to explain the hyperpolarizability. Therefore previous and present calculations show the inverse relationship between the polarizability and HOMO-LUMO energy gaps [58].

As the experimental values for the first hyperpolarizability of sudan dyes in the literature are not reported, it is difficult to conclude which basis set computes reliable values of β. The 6-31G basis set has been a common strategy for study in many previous theoretical investigations of the NLO properties of organic molecules [59, 60]. Though it is well established that diffuse and polarization functions are required for a quantitative description of both the electronic and NR (hyper) polarizabilities of medium size organic molecules [61], it has previously been noted that the 6-31G basis is adequate in obtaining semiquantitative results [62-64]. In this study, the values of the first hyperpolarizability obtained using the above Eq.9 have been calculated using HF and B3LYP methods with different basis sets and are given in Table 8. From Table 6-8, it was suggested that these compounds are polar having non-zero dipole moment, hyperpolarizabilities, and hence have positive microscopic NLO behavior [65, 66]. On the other hand, the first polarizability values obtained using HF/6-31G level for SIII and SOG are generally lower than the other basis sets. In this sense, due to the deficiency of the electron correlation, we expect that the results obtained from B3LYP level are larger than ab initio HF level calculations using different basis sets. This study reveals that the SIII and SOG have large first static hyperpolarizability, and have the potential applications for the development of NLO devices.

Urea is one of the prototypical molecules used in this study for the NLO properties of the molecular systems for comparative purposes. It can be seen from Table 8, the calculated β values of SIII, SOG and SRG using HF/6-31G(d,p) and B3LYP/6-31G(d,p) levels (the β of urea is 0.1947 x10^{-30} esu) were found nearly 42, 46 and 14 (with HF) and 225, 87 and 12 (with B3LYP) times more than that of urea, respectively.

Fig. 6(d) shows that the variation of the first hyperpolarizability for studying Sudan dyes. It can be seen from Fig. 6(d) that the relative changes from one basis set to another are nearly the same for studying Sudan dyes. The variation of β for SIII, SOG and SRG are the order of SRG < SIII < SOG with HF levels, and SRG < SOG < SIII with B3LYP levels although the results of obtained with B3LYP level are bigger than ab initio HF level calculations using different basis sets. However, as seen in Figure 6(d), when diffuse functions are added to these basis sets on heavy atoms and hydrogen atoms, the magnitude of β increases significantly. The β values obtained using the DFT method with different exchange and correlation functionals are higher than those from the HF methods. Figure 6(d) shows that the value of β obtained using B3LYP/3-21G for SRG is slightly different from those of other methods.

Table 6. Calculated components of the polarizability tensor α, the polarizability <α> and the anisotropy of the polarizability <Δα> of studied molecules using different basis sets from HF and DFT calculations.

		Basis Sets	α_{xx}	α_{xy}	α_{yy}	α_{yz}	α_{zz}	α_{xz}	**<α> (a.u.)**	**<Δα> (a.u.)**	**<Δα>x10^{-24} (esu)**	**<α>x10^{-24} (esu)**
SIII	HF	3-21G	512.7124	14.0054	256.9934	-0.007	56.2879	0.0003	275.33	396.97	58.83	40.80
	B3LYP		514.4930	-0.0251	60.2755	0.0447	547.6547	-256.578	374.14	648.06	96.04	55.45
	HF	6-31G	531.3003	14.9071	267.8941	0.0067	71.8431	0.0030	290.35	400.16	59.30	43.03
	B3LYP		815.3230	-5.7292	287.8517	-0.0031	73.7069	-0.0072	392.29	661.16	97.98	58.14
	HF	6-31G(d)	525.5983	-12.0882	271.5904	0.0721	81.0533	-0.0244	292.75	386.86	57.33	43.39
	B3LYP		812.2345	4.1177	291.5687	-0.0106	81.8376	0.0035	395.21	651.41	96.54	58.57
	HF	6-31G(d.p)	527.1728	-12.1797	272.8884	0.0997	82.2482	-0.0364	294.10	387.20	57.38	43.59
	B3LYP		544.0592	-0.0742	82.9142	0.0615	563.8508	-261.396	396.94	653.57	96.86	58.83
	HF	6-31G+(d,p)	546.9250	-12.7054	294.5525	0.0458	139.5119	-0.0213	327.00	356.85	52.89	48.46
	B3LYP		849.7634	4.3190	320.7906	-0.0014	142.0397	0.0005	437.53	637.44	94.47	64.84
	HF	6-31++G(d,p)	546.9541	-12.6977	294.6132	-0.0038	140.3471	0.0089	327.31	356.21	52.79	48.51
	B3LYP		849.8573	-4.3182	320.9925	-0.0004	143.0036	-0.0035	437.95	636.84	94.38	64.90
	HF	6-311G	536.0901	15.5744	275.5163	0.0077	94.4568	0.0037	302.02	385.47	57.13	44.76
	B3LYP		820.5679	-6.0822	297.9721	-0.0020	95.8809	-0.0057	404.81	647.82	96.01	59.99
	HF	6-311G(d)	532.9824	-12.6386	280.2679	0.1048	101.3047	-0.036	304.85	376.30	55.77	45.18
	B3LYP		821.0457	-4.5072	302.3232	-0.0012	101.8877	-0.0042	408.42	642.87	95.27	60.53
	HF	6-311G(d.p)	534.1449	-12.7115	281.4437	0.1205	103.5589	-0.0525	306.38	375.42	55.64	45.41
	B3LYP		555.3009	0.03375	103.8758	-0.0397	570.2876	-259.473	409.82	642.46	95.21	60.74
	HF	6-311G++(d.p)	546.2762	-12.9042	295.0030	0.0266	141.1655	-0.0136	327.48	354.91	52.60	48.53
	B3LYP		839.3699	4.5427	319.2384	0.0145	142.5065	-0.0156	433.71	627.45	92.99	64.28
SOG	HF	3-21G	133.9712	0.0972	32.1929	0.0071	245.3824	-15.9331	137.18	186.74	27.68	20.33
	B3LYP		143.4127	-0.0236	34.3539	0.0537	333.5049	-19.5813	170.42	177.39	26.29	25.26
	HF	6-31G	256.0869	-0.7888	137.9212	0.0069	41.7317	-0.0023	145.25	185.97	27.56	21.53
	B3LYP		340.8651	3.2961	148.6110	0.0035	42.8643	-0.0005	177.44	261.74	38.79	26.30
	HF	6-31G(d)	257.8172	-0.2208	139.6777	0.0198	48.0890	-0.0086	148.53	182.12	26.99	22.01
	B3LYP		342.6691	3.4526	149.8313	0.0062	48.5775	-0.0018	180.36	258.84	38.36	26.73
	HF	6-31G(d.p)	258.5454	-0.1782	140.5138	0.0220	48.8171	-0.0101	149.29	182.11	26.99	22.13
	B3LYP		152.8770	0.4269	49.2534	0.0540	341.0530	-21.1868	181.06	258.83	38.36	26.83
	HF	6-31G+(d.p)	271.2372	-0.9434	152.9491	0.0243	82.2481	-0.0134	168.81	165.40	24.51	25.02
	B3LYP		363.3607	2.7156	167.1840	0.0154	84.7305	-0.0076	205.09	247.96	36.75	30.40
	HF	6-31G++(d,p)	271.2596	-0.9378	152.9751	0.0342	82.7871	-0.0189	169.01	164.99	24.45	25.05
	B3LYP		363.6625	2.7289	167.2883	0.0193	85.3368	-0.0101	205.43	247.78	36.72	30.45
	HF	6-311G	259.8738	-1.0449	142.1966	0.01172	55.1119	-0.0050	152.39	178.00	26.38	22.59
	B3LYP		346.1320	3.0927	154.2257	0.0059	56.2263	-0.0025	185.53	255.48	37.86	27.50

Table 6 Continued. Calculated components of the polarizability tensor α, the polarizability <α> and the anisotropy of the polarizability <Δα> of studied molecules using different basis sets from HF and DFT calculations.

		Basis Sets	**α_{xx}**	**α_{xy}**	**α_{yy}**	**α_{yz}**	**α_{zz}**	**α_{xz}**	**<α> (a.u.)**	**<Δα> (a.u.)**	**<Δα>x10^{-24} (esu)**	**<α>x10^{-24} (esu)**
	HF	6-311G(d)	262.5452	-0.0825	144.1468	0.0271	59.5082	-0.0128	155.40	176.64	26.18	23.03
	B3LYP		348.8353	3.6030	155.6340	0.0179	60.0943	-0.0079	188.19	254.86	37.77	27.89
	HF	6-311G(d.p)	263.1232	-0.1655	145.0442	0.0275	61.0399	-0.0130	156.40	175.84	26.06	23.18
	B3LYP		349.2726	3.5812	156.4527	0.0140	61.4904	-0.0089	189.07	254.06	37.65	28.02
	HF	6-311G++(d.p)	271.4019	-0.8673	153.2172	0.0388	83.3444	-0.0216	169.32	164.65	24.40	25.09
	B3LYP		361.1423	2.8138	166.2084	0.0250	85.1160	-0.0151	204.16	245.78	36.43	30.26
SRG	HF	3-21G	236.9889	-0.0089	49.9892	-0.0217	300.5881	-36.2811	195.86	234.21	34.71	29.03
	B3LYP		281.1446	-0.0641	52.9968	0.0632	355.1707	-76.0544	229.77	302.94	44.90	34.05
	HF	6-31G	315.4518	-3.4055	222.0131	0.0011	61.5155	-0.0012	199.66	222.54	32.98	29.59
	B3LYP		414.8095	-16.7054	246.3321	-0.0016	63.2011	-0.0022	241.45	305.96	45.35	35.78
	HF	6-31G(d)	313.2702	3.5648	225.1850	-0.0024	68.4782	0.0041	202.31	214.86	31.84	29.98
	B3LYP		413.0422	16.8719	249.0105	-0.0001	69.4496	-0.0019	243.84	299.09	44.33	36.14
	HF	6-31G(d.p)	232.4129	-0.0346	69.4902	0.4359	309.0442	-22.3757	203.65	215.42	31.93	30.18
	B3LYP		297.4114	-0.0077	70.3579	0.0027	368.2928	-76.7952	245.35	300.61	44.55	36.36
	HF	6-31G+(d.p)	331.7343	-3.0170	242.6564	-0.0010	110.8134	0.0021	228.40	192.59	28.54	33.85
	B3LYP		440.7732	17.4132	271.9494	-0.0022	113.8503	0.0007	275.52	284.78	42.20	40.83
	HF	6-31G++(d.p)	263.5977	-0.0074	114.1191	-0.0187	328.9846	-36.8986	235.57	201.19	29.82	34.91
	B3LYP		440.9511	-17.3822	272.1979	-0.0032	114.8718	0.0032	276.01	284.05	42.10	40.90
	HF	6-311G	320.2688	2.9760	227.3201	0.0001	77.7850	0.0011	208.46	299.75	44.42	30.89
	B3LYP		421.0262	-16.6259	253.6778	-0.0021	79.6493	0.0011	251.45	297.06	44.02	37.27
	HF	6-311G(d)	319.7444	3.0461	231.4406	-0.0015	82.9367	0.0031	211.37	207.35	30.73	31.33
	B3LYP		421.4001	-16.8989	256.8515	-0.0006	84.2773	0.0027	254.18	293.45	43.49	37.67
	HF	6-311G(d.p)	321.4529	2.7948	232.9205	-0.0012	84.6979	0.0030	213.02	207.25	30.72	31.57
	B3LYP		423.7359	16.8029	258.1454	0.0016	85.8377	0.0045	255.91	294.09	43.58	37.93
	HF	6-311G++(d.p)	332.4068	2.5330	243.4175	-0.0011	112.2035	0.0025	229.34	191.92	28.44	33.99
	B3LYP		437.9974	-16.6180	271.1306	-0.0023	114.3912	0.0034	274.51	281.77	41.76	40.68

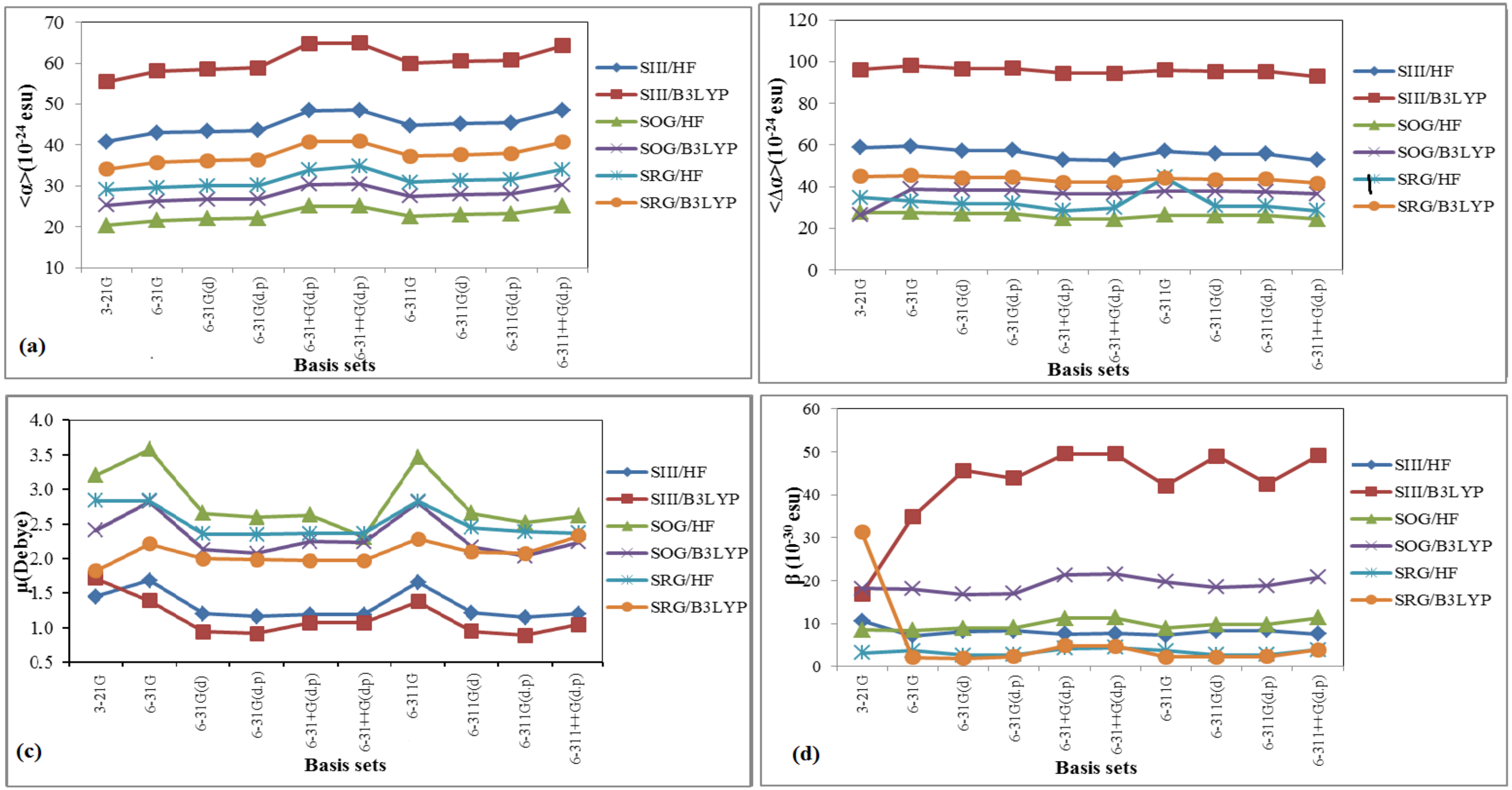


Fig. 6. Variation of (a) polarizability (<α>, in 10^{-24} esu) (b) the anisotropy of the polarizability (<Δα>, in 10^{-24} esu) (c) ground-state dipole moment (μ, in D) and (d) the first-order hyperpolarizability (β, in 10^{-30} esu) of sudan dyes with HF and B3LYP methods and different basis sets.

Table 7. The electric dipole moments , μ(D) of studied molecules derived from HF and DFT calculations.

		SIII				SOG				SRG			
Basis Sets		μ_x	μ_y	μ_z	μ(D)	μ_x	μ_y	μ_z	μ(D)	μ_x	μ_y	μ_z	μ(D)
3-21G	HF	-0.5922	1.3222	-0.0001	1.4488	1.7955	-2.6521	0.0014	3.2027	-2.7432	-0.7172	0.0007	2.8354
	B3LYP	1.2141	1.2129	-0.0001	1.7161	0.5343	-2.3475	0.0003	2.4076	-1.8119	-0.1749	0.0000	1.8203
6-31G	HF	-0.6338	1.5639	0.0002	1.6874	2.1616	-2.8510	0.0012	3.5778	2.6138	-1.1096	-0.0003	2.8396
	B3LYP	-0.1418	1.3847	0.0004	1.3919	1.1595	-2.5728	0.0005	2.8221	2.1419	-0.5499	0.0007	2.2114
6-31G(d)	HF	0.5867	1.0478	-0.0002	1.2009	1.3896	-2.2658	0.0015	2.6579	-2.2813	-0.5989	0.0009	2.3586
	B3LYP	0.1199	0.9359	0.0001	0.9436	0.4765	-2.0706	0.0005	2.1247	-1.9907	-0.1297	-0.0001	1.9950
6-31G(d.p)	HF	0.5724	1.0177	-0.0002	1.1676	1.3421	-2.2254	0.0016	2.5988	-2.2814	-0.5575	0.0001	2.3485
	B3LYP	0.1518	0.9049	0.0001	0.9176	0.4334	-2.0269	0.0083	2.0727	1.9801	-0.0845	0.0001	1.9819
6-31+G(d.p)	HF	0.6000	1.0288	-0.0003	1.1910	1.3999	-2.2226	0.0028	2.6267	2.3121	-0.4916	-0.0008	2.3638
	B3LYP	0.1248	1.0666	0.0003	1.0739	0.7044	-2.1298	0.0021	2.2433	-1.9605	-0.1953	-0.0007	1.9702
6-31++G(d.p)	HF	0.5985	1.0285	0.0002	1.1900	1.3948	-1.8320	0.2145	2.3125	2.3097	-0.4909	-0.0008	2.3613
	B3LYP	-0.1262	1.0648	0.0001	1.0723	0.7028	-2.1281	0.0027	2.2412	1.9594	-0.1962	0.0006	1.9692
6-311G	HF	-0.6801	1.5097	0.0003	1.6559	2.0907	-2.7699	0.0016	3.4704	-2.6293	-1.0409	0.0005	2.8279
	B3LYP	-0.0889	1.3776	0.0003	1.3805	1.1794	-2.5514	0.0007	2.8108	2.2210	-0.5219	0.0001	2.2815
6-311G(d)	HF	0.6713	1.0175	-0.0002	1.2190	1.3842	-2.2683	0.0021	2.6572	-2.3857	-0.5380	0.0007	2.4456
	B3LYP	-0.0745	0.9462	0.0003	0.9491	0.5051	-2.1087	0.0015	2.1683	2.0950	-0.1140	0.0001	2.0981
6-311G(d.p)	HF	0.6081	0.9742	-0.0004	1.1484	1.2967	-2.1559	0.0022	2.5159	-2.3427	-0.4595	0.0007	2.3873
	B3LYP	-0.1309	0.8791	0.0002	0.8888	0.4282	-1.9927	0.0013	2.0382	-2.0761	-0.0166	0.0002	2.0762
6-311++G(d.p)	HF	0.6236	1.0263	-0.0003	1.2009	1.4045	-2.2073	0.0042	2.6163	-2.3135	-0.4943	0.0008	2.3657
	B3LYP	0.1004	1.0440	0.0002	1.0488	0.7189	-2.1223	0.0024	2.2408	-2.3072	0.1246	0.2862	2.3282

Table 8. All β (a.u.) components and β ×10^{-30} (esu) values calculated using HF and DFT levels of theory for all compounds.

		Basis Sets	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	βx 10^{-30} (esu)
SIII	HF	3-21G	-1098.54	-19.07	133.52	17.71	5.91	4.02	-0.27	-7.77	-0.37	-0.09	10.58
	B3LYP		1333.27	-0.23	3.03	0.04	-670.18	-0.61	-4.95	420.32	1.59	-201.00	16.96
	HF	6-31G	-959.55	-47.98	128.87	18.29	4.11	2.78	0.38	-3.31	-0.91	-0.04	7.21
	B3LYP		4045.33	-681.42	-61.43	-0.84	0.71	0.93	0.41	-5.60	1.28	-0.24	34.87
	HF	6-31G(d)	1067.47	1.52	-136.56	16.30	-18.67	7.62	0.13	14.19	-0.32	0.07	8.17
	B3LYP		-5170.90	-560.43	91.50	15.97	-2.41	-0.62	2.28	1.80	1.51	-0.61	45.72
	HF	6-31G(d.p)	1087.37	-18.87	-144.11	16.90	-14.18	-7.00	-0.64	14.79	0.05	-0.087	8.28
	B3LYP		-1087.66	-0.13	1.86	-0.19	1628.05	1.09	-0.31	-2067.87	-1.53	2349.04	43.85
	HF	6-31G+(d,p)	1095.86	42.90	-229.01	61.76	-1.10	0.34	0.05	-1.05	52.76	0.07	7.60
	B3LYP		-5909.18	-484.83	198.23	44.51	-0.99	-0.66	-0.55	-6.45	57.59	-0.06	49.51
	HF	6-31++G(d,p)	1097.13	43.61	-229.21	63.73	-1.28	-0.31	-0.03	0.72	64.31	-0.38	7.65
	B3LYP		5915.47	-481.94	-195.55	45.78	0.53	-0.06	-0.61	6.49	72.12	-0.07	49.57
	HF	6-311G	-971.65	-25.89	140.92	24.02	6.41	3.71	0.52	-5.65	7.53	-0.021	7.23
	B3LYP		4907.22	-634.24	-70.17	23.61	-2.57	-1.14	-2.25	-2.89	13.30	-0.74	42.08
	HF	6-311G(d)	1095.38	-8.79	-152.08	27.43	-16.58	-8.06	-0.54	17.45	7.78	-0.15	8.31
	B3LYP		5767.84	-538.67	-105.59	39.19	-1.54	-0.08	-3.52	-4.37	11.89	-1.45	49.06
	HF	6-311G(d.p)	1103.43	-1.38	-153.34	27.93	-17.48	-9.05	-0.81	18.16	8.23	-0.20	8.37
	B3LYP		-1363.64	-0.20	-4.01	0.97	1876.69	0.49	-8.43	-2280.67	1.37	2487.13	42.48
	HF	6-311G++(d.p)	1066.15	52.36	-215.99	52.79	-7.14	4.00	-0.26	7.93	54.71	0.15	7.54
	B3LYP		-5850.98	-456.43	185.46	33.55	0.10	-0.87	-1.53	-8.96	58.32	-0.06	49.13
SOG	HF	3-21G	-66.81	-0.05	0.03	-0.00	-92.21	0.16	-1.14	-135.63	-0.04	1069.03	8.55
	B3LYP		-99.60	0.13	-1.99	0.02	-67.84	0.32	0.11	-169.62	1.01	2159.53	18.22
	HF	6-31G	1063.28	47.15	-90.59	-116.03	-0.37	0.17	0.08	-2.66	-0.13	0.01	8.40
	B3LYP		2144.67	107.23	-56.59	-144.28	0.80	0.47	0.05	-0.47	-2.15	0.09	18.04
	HF	6-31G(d)	1149.41	65.78	-108.86	-98.00	2.47	1.61	-0.24	-3.84	0.57	-0.13	8.96
	B3LYP		2013.58	106.10	-68.04	-120.42	-1.14	0.72	-0.50	-1.82	0.35	-1.55	16.79
	HF	6-31G(d.p)	1162.96	67.86	-109.64	-98.75	2.09	1.06	-0.79	-3.92	1.43	-0.33	9.07
	B3LYP		-90.63	-1.28	0.27	-1.51	-75.62	0.94	-2.04	-172.06	-0.54	2027.17	16.99
	HF	6-31G+(d.p)	1384.15	70.65	-135.30	-146.84	0.09	0.09	-0.01	49.80	-33.94	-0.01	11.26
	B3LYP		2489.93	114.46	-94.48	-192.41	-0.67	-0.31	-0.16	67.41	-37.65	0.10	21.30
	HF	6-31G++(d,p)	1385.23	69.91	-135.05	-147.59	0.08	0.06	-0.02	61.93	-38.45	-0.03	11.38
	B3LYP		2492.54	111.83	-92.91	-197.78	-0.46	0.11	0.72	85.43	-44.22	0.12	21.50
	HF	6-311G	1123.63	47.68	-94.45	-123.76	-1.99	0.91	0.076	5.97	-5.45	0.02	8.97
	B3LYP		2321.01	94.24	-49.52	-165.59	-0.38	-0.15	-0.41	11.91	-7.19	0.02	19.74
	HF	6-311G(d)	1235.32	64.13	-108.95	-110.10	2.91	1.11	-0.45	5.05	-3.92	-1.09	9.78
	B3LYP		2190.95	98.51	-62.80	-145.36	-1.62	1.62	-0.27	9.33	-4.81	-1.68	18.47

Table 8 Continued. All β (a.u.) components and β ×10^{-30} (esu) values calculated using HF and DFT levels of theory for all compounds.

		Basis Sets	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	βx 10^{-30} (esu)
	HF	6-311G(d.p)	1231.57	64.61	-109.94	-109.31	1.96	1.23	0.10	5.74	-4.35	-1.13	9.75
	B3LYP		2228.84	97.53	-62.48	-139.96	-6.17	-2.18	-2.15	15.16	-3.28	-1.85	18.85
	HF	6-311G++(d.p)	1348.84	69.54	-132.13	-140.23	0.03	0.12	-0.01	55.04	-33.54	-0.11	11.33
	B3LYP		2432.10	112.08	-93.71	-186.35	-0.03	0.44	0.84	70.45	-36.73	0.08	20.83
SRG	HF	3-21G	-169.26	-1.31	-10.44	-0.12	71.80	1.08	29.70	-177.92	-1.04	-41.80	3.13
	B3LYP		1117.44	-2.08	-5.51	0.07	-1060.48	1.82	42.21	1229.00	-1.78	-1741.16	31.26
	HF	6-31G	338.94	-229.02	-26.58	-43.06	-2.33	-0.52	0.33	34.83	10.92	-0.00	3.75
	B3LYP		-135.25	-122.38	-100.86	-49.213	0.11	-0.32	-1.37	43.92	15.34	-0.10	2.14
	HF	6-31G(d)	-229.45	-203.36	50.00	-18.34	3.04	2.18	0.45	-33.92	8.27	-0.09	2.61
	B3LYP		67.72	-136.47	108.37	-53.68	-1.63	-0.91	2.57	-41.49	13.12	-0.09	1.92
	HF	6-31G(d.p)	104.11	1.62	-19.33	0.42	-118.52	-2.80	32.25	63.40	4.28	368.42	2.75
	B3LYP		34.13	-0.02	-5.57	2.07	-0.74	-0.73	42.80	-73.84	1.00	-305.22	2.31
	HF	6-31G+(d.p)	191.51	-303.31	-96.49	-93.98	-0.20	0.017	0.36	-10.43	-86.80	0.18	4.25
	B3LYP		101.38	-287.99	159.74	-118.47	-0.08	0.27	0.78	-1.39	-90.15	-0.12	4.84
	HF	6-31G++(d.p)	-144.88	-0.91	-76.07	-0.13	53.48	0.83	-87.58	-242.84	-0.31	-180.38	4.42
	B3LYP		-88.36	-281.47	-151.39	-112.11	-0.02	-0.33	-0.29	2.04	-104.96	0.06	4.77
	HF	6-311G	-312.27	-234.78	30.01	-51.60	3.07	0.83	0.14	-34.14	0.65	-0.23	3.68
	B3LYP		33.07	-195.60	-90.26	-73.66	-0.04	-0.67	-2.44	49.99	9.50	-0.56	2.25
	HF	6-311G(d)	-225.52	-211.89	51.20	-28.72	5.81	4.00	0.59	-40.98	0.26	-0.38	2.79
	B3LYP		41.93	-185.63	-100.53	-77.41	-2.13	-0.01	5.16	52.65	6.19	1.07	2.22
	HF	6-311G(d.p)	-216.63	-212.95	52.86	-30.25	6.14	3.89	1.39	-40.74	0.06	-0.35	2.75
	B3LYP		41.32	-182.08	117.97	-73.30	-0.39	2.80	3.86	-52.61	5.40	-0.80	2.35
	HF	6-311G++(d.p)	-197.64	-282.23	82.49	-73.10	0.63	0.19	-0.08	4.27	-84.04	0.26	3.92
	B3LYP		-18.10	-265.70	-126.16	-93.11	-0.38	0.01	0.92	17.50	-80.63	-0.02	3.95

4. Conclusions

The molecular structures and quantum chemical parameters of the Sudan III, Sudan Red G and Sudan Orange G were studied using the B3LYP and HF methods on several basis sets. Non-linear optical NLO behaviors of the studied molecules were investigated by determining the electric dipole moment μ, the polarizability α and the hyperpolarizability β using the same methods. The study showed that these Sudan dyes have valuable first-static hyperpolarizabilities, and may have potential applications in the development of NLO materials.

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