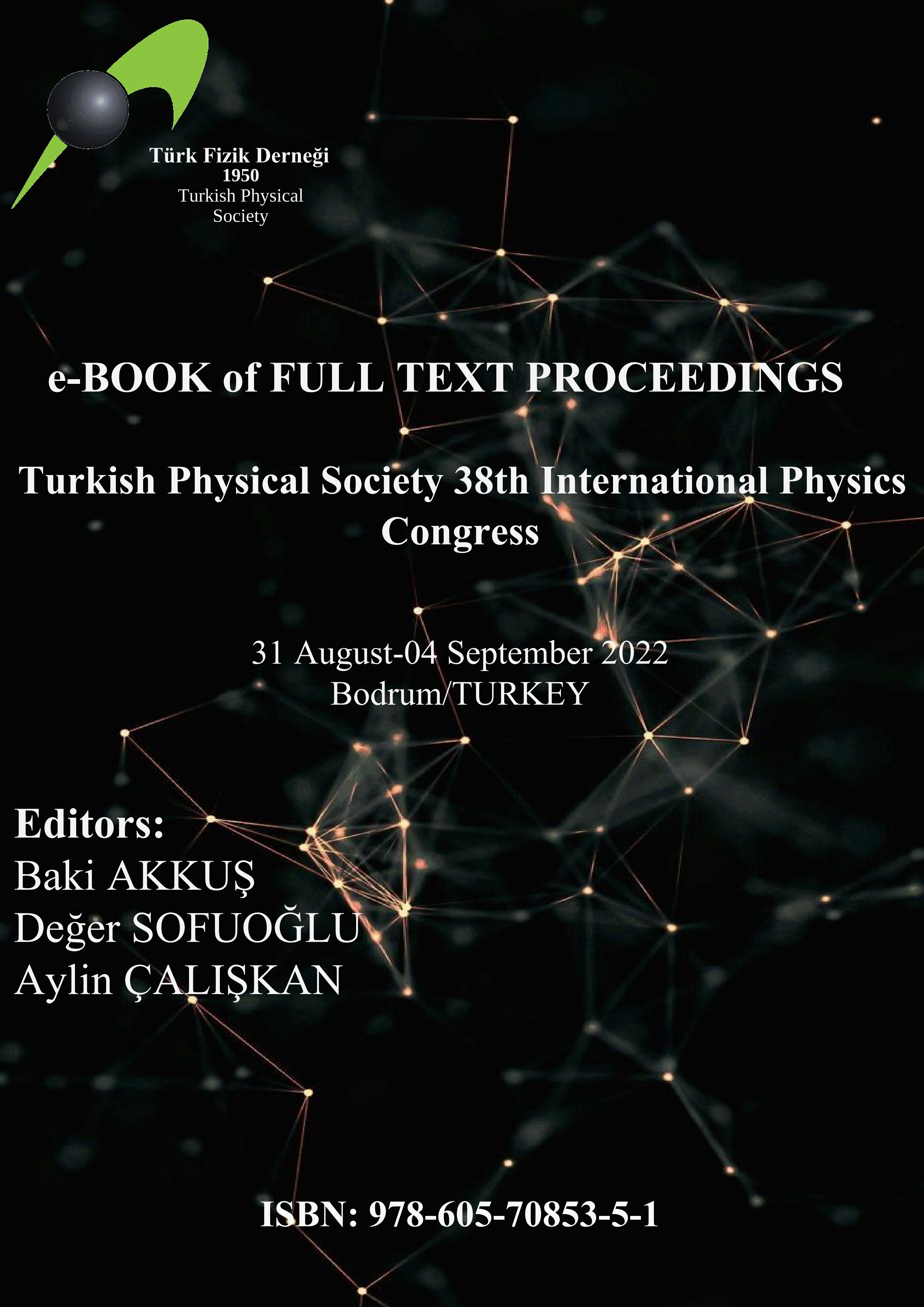

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DFT calculations on structural, spectroscopic and non-linear optical parameters of Diiodobis(2-aminopyridine)Cadmium(II)

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Abstract. The principles of nonlinear optics are of great importance as they are frequently used in many laser and electro-optical device designs and in areas such as ultra-short pulse transmission in fiber optics. In this respect, Diiodobis(2-aminopyridine)Cadmium(II) (**DIAC**) synthesized and characterized [1] was examined by using the HSEh1PBE and ωB97XD levels of density functional theory (DFT) with LanL2DZ basis set. The structural parameters (bond lengths and angles, and dihedral angles), ^{1}H NMR chemical shifts, vibrational wavenumbers, isotropic and anisotropic polarizability (α and $\Delta\alpha$), first- and second-order hyperpolarizability (β and γ) parameters of the complex (**DIAC**) were calculated at HSEh1PBE/LanL2DZ and ωB97XD/LanL2DZ levels. Furthermore, the absorption wavelengths and oscillator strengths for **DIAC** in the gas phase were performed at the TD-HSEh1PBE/ LanL2DZ and TD-ωB97XD/ LanL2DZ levels. Consequently, a detailed comparison of the theoretical and experimental structural, spectroscopic and electronic parameters of the DIAC complex was presented and a good agreement between these parameters was observed.

INTRODUCTION

The principles of nonlinear optics are of great importance as they are frequently used in many laser and electro-optical device designs and in areas such as ultra-short pulse transmission in fiber optics. Currently, the NLO property of materials with high first- and second-order hyperpolarizability has become an important study topic in the field of fiber optic communication technology, thanks to electro-optic modulators with very high frequency (THz) low voltage modulation [1-5]. By considering a previously reported experimental study, the aim of this study is theoretical investigation of the effective complex (**DIAC**) as the potential NLO candidate. In this context, the molecular structural parameters (bond lengths and angles), isotropic and anisotropic polarizability (α and $\Delta\alpha$), first- and second-order hyperpolarizability (β and γ) parameters of Diiodobis(2-aminopyridine) Cadmium(II) (**DIAC**) synthesized and characterized [1] were investigated by using DFT levels (HSEh1PBE/LanL2DZ and ωB97XD/LanL2DZ) in the gas phase. Furthermore, ^{1}H NMR chemical shifts, vibrational wavenumbers for **DIAC** were calculated at same methods. Besides, the TD-HSEh1PBE/ LanL2DZ and TD-ωB97XD/ LanL2DZ levels were applied in the gas phase to investigate electronic absorption spectra for the complex. Briefly, detailed experimental and theoretical structural and spectroscopic properties of the complex were presented comparatively.

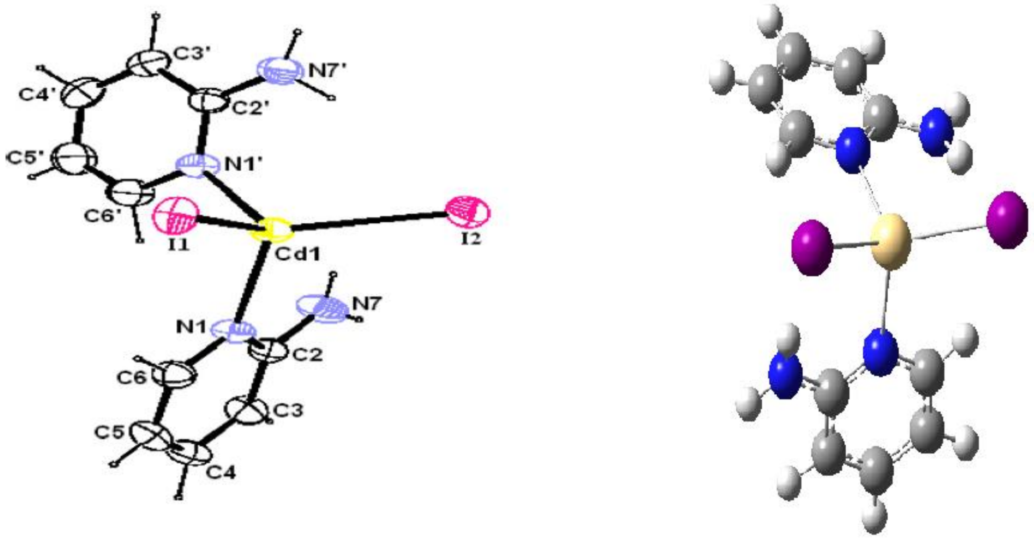
Computational Details

All calculations were performed by using the Gaussian 16W program [6] and the output files were visualized by GaussView 6.1 software [7]. The bond lengths and angles, ^{1}H NMR chemical shifts, vibrational wavenumbers, isotropic and anisotropic polarizability (α and $\Delta\alpha$), first- and second-order hyperpolarizability (β and γ) parameters for **DIAC** were calculated at HSEh1PBE [8]/LanL2DZ and ωB97XD [9]/LanL2DZ [10] levels. Furthermore, the absorption wavelengths and oscillator strengths for **DIAC** in the gas phase were obtained at the TD-HSEh1PBE/LanL2DZ and TD-ωB97XD/LanL2DZ levels. The frontier energies (HOMO and LUMO), chemical hardness, electronegativity parameters were calculated at the same levels.

RESULTS AND DISCUSSION

Geometry Optimization

The bond lengths obtained using DFT methods and reported experimentally for **DIAC** molecule (Figure 1) are listed in Table 1. In the calculations of the theoretical results, two different DFT methods and different basis sets were used.



(a) (b)

FIGURE 1. (a) The theoretical molecular structure of **DIAC**, (b) The experimental molecular structure of **DIAC**

When the results obtained for the bond lengths were compared, it was observed that the results obtained with the HSEh1PBE method were consistent. In addition, bond angles calculated at two methods and basis sets data are consistent with corresponding XRD ones.

TABLE 1. Selected experimental and theoretical bond length and angles for **DIAC**

Parameters	XRD	HSEh1PBE	ωB97XD
Bond length (Å)			
Cd1–N1	2.265(4)	2.34789	2.35271
Cd1–N1^{i}	2.267(4)	2.34786	2.34139
Cd1–I1	2.7081(5)	2.80321	2.78600
Cd1–I2	2.7292(5)	2.80320	2.78890
N1–C2	1.343(5)	1.36521	1.36259
N1–C6	1.358(6)	1.36388	1.36589
C2–N7	1.352(6)	1.36397	1.36909
N1^{i}– C2^{i}	1.337(5)	1.36521	1.36174
N1^{i}– C6^{i}	1.355(7)	1.36389	1.36588
C2^{i}– N7^{i}	1.365(7)	1.36397	1.36413

TABLE 1. Contiued

Parameters	XRD	HSEh1PBE	ωB97XD
Bond angles (^{o})			
N1– Cd1– N1^{i}	98.76(13)	97.02305	91.95000
N1– Cd1– I2	110.59(10)	104.24706	105.94634
N1^{i} – Cd1– I2	112.65(10)	109.37628	109.81171
I1– Cd1– I2	116.066(16)	128.26853	128.23716
C2– N1– Cd1	123.0(3)	125.96392	127.67076
C6– N1– Cd1	118.7(3)	114.78334	113.25481
C2^{i} – N1^{i} – Cd1	123.2(3)	125.97164	128.49220
C6^{i} – N1^{i} – Cd1	118.6(3)	114.77725	112.34604

IR Spectroscopy

Vibrational frequencies for DIAC were compared at HSEh1PBE/ LanL2DZ and ωB97XD/ LanL2DZ levels and experimental one. The theoretically obtained vibrational wavenumbers were scaled down 0.96 to get closer to FT-IR spectra. Table 2 shows that there is a good agreement between the theoretical and experimental data.

TABLE 2. The comparison of experimental and theoretical characteristic vibrational frequencies for **DIAC**

FT-IR (cm^{-1})[1]	HSEh1PBE	ωB97XD	Assignments via PED%
	LanL2DZ		
3430	3610	3643	υ NH 92% asymmetric
3336	3364	3398	υ NH 91% symmetric
3213	3154	3135	υ CH 85% ring
1629	1643	1653	β HNH 69% amine
1564	1568	1579	υ CN 21% ring
1490	1499	1502	υ CN 28% ring
1444	1435	1448	β HCC 50% ring
1332	1325	1332	β HCC 48% ring
1261	1295	1281	υ CN 49% ring
1157	1163	1175	β HCC 87% ring
1050	1042	1045	υ CC 37% ring
1008	1021	984	β HCN 39% amine
769	781	786	τ HCCC 12%+ τ HCCN 12%+γ NNCN 30% ring
641	642	657	τ HNHI 38%+ τ IHNC 44% ring
511	521	523	γ NNCN 30% ring

^{1}H NMR

^{1}H NMR chemical shifts parameters of **DIAC** were calculated at HSEh1PBE/ LanL2DZ and ωB97XD/ LanL2DZ level in the gas phase. These parameters were compared with corresponding experimental data. The theoretical ^{1}H NMR chemical shifts parameters calculated with the Gaussian W16 program largely agree with the experimental data [1]. The variation of these chemical shift parameters obviously shows that the proton shift is owing to metal–ligand coordination in this complex.

TABLE 3. The experimental and theoretical ^{1}H NMR chemical shifts for **DIAC**

Atom	**NMR (ppm) [1]**	**HSEh1PBE/ LanL2DZ**	**ωB97XD/ LanL2DZ**
		Gas	**Gas**
^{1}H			
H29	8.00	9.35	9.30
H17	8.00	9.35	8.80
H7	7.50	7.98	8.19
H15	7.50	7.98	8.07
H8	6.60	7.20	7.32
H16	6.60	7.07	7.10
H6	6.40	7.07	6.96
H14	6.40	6.68	6.84
H26	4.50-4.90	7.20	7.25
H25	4.50-4.90	6.68	6.80
H28	4.50-4.90	4.05	4.28
H24	4.50-4.90	4.05	4.25

UV-Vis Spectroscopy

The theoretical absorption wavelengths and oscillator strengths of DIAC calculated at TD-HSEh1PBE and TD-ωB97XD levels in the gas phase were given in Table 4. Obtained theoretical results at the range from 263.4 to 296.1 nm by TD-HSEh1PBE and ωB97XD levels were compared with the experimental λ_{max} value observed at 343 nm in crystal form [1]. These wavelengths were chiefly determined as contributions of HOMO→LUMO at 90 percent and HOMO-4→LUMO+1 at 85 percent. The UV cut-off wavelength observed at 343 nm was assigned as the $\pi \rightarrow \pi^*$ transition in the complex.

TABLE 4. The experimental and theoretical electronic absorption wavelengths and oscillator strength for **DIAC**.

Exp. λ (nm)[1]	**Gas**			
	λ (nm)	**Osc. strength**	**Major contributions determined via SWizard H:HOMO, L: LUMO**	
			TD-HSEh1PBE/ LanL2DZ	
343	296.1	0.0008	H→L (%90)	H−1→L+1 (%8)
	198.7	0.4865	H-6→L+4 (%80)	H→L+5 (%5)
			TD-ωB97XD/ LanL2DZ	
343	263.4	0.0815	H-4→L+1 (%85)	
	176.3	0.2952	H-7→L+4 (%30)	H-8→L (%8)

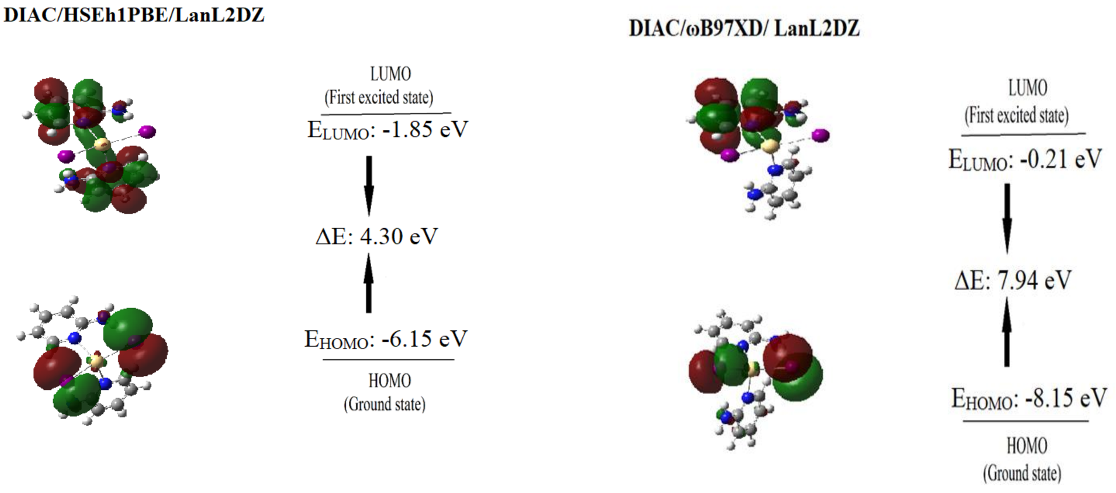
Homo-Lumo

The frontier molecular orbital (FMO) energies of **DIAC** were obtained by using HSEh1PBE and ωB97XD levels in the gas phase. HOMO and LUMO energies represent the electron donating and electron withdrawing ability, respectively. Using HOMO and LUMO energies, the chemical hardness (η) and electronegativity (χ) parameters were computed for the molecular parameters displaying molecular chemical stability, chemical reactivity, and hardness of the molecule. These parameters were given in Table 5.

TABLE 5. Frontier molecular orbital (FMO) energies, electronegativity (χ) and hardness (η) for **DIAC**

Parameters	**HSEh1PBE/ LanL2DZ**	**ωB97XD/ LanL2DZ**
	Gas	**Gas**
E_{HOMO} (eV)	-6.15	-8.15
E_{LUMO}(eV)	-1.85	-0.21
ΔE (eV)	4.30	7.94
χ (eV)	4.00	4.18
η (eV)	2.15	3.97

The frontier molecular orbital (FMO) energies of DIAC were calculated by using the HSEh1PBE and ωB97XD levels in the gas phase. (see Figure 2).



(a) (b)

FIGURE 2. The frontier molecular orbital (FMO) energies and pictures of **DIAC** obtained by (a) the HSEh1PBE/LanL2DZ level in the gas phase, (b) the ωB97XD/LanL2DZ level in the gas phase.

NLO Analysis

NLO stands out in ongoing research for its importance in providing key functions such as frequency shifting, laser, fiber optic material logic and optical memory for emerging technologies in areas such as telecommunications, signal processing and optical interconnects [11-13]. The importance of polarizability and first-order hyperpolarizabilities of molecular systems depend upon the efficiency of electronic communication between acceptor and donor groups play a decisive role in determining the intramolecular charge. More effective NLO materials stand out with their higher hyperpolarizability values.

By comparing the theoretical results obtained for **DIAC** with the reference material pNA and urea values, it was investigated that **DIAC** could be a potential NLO material. It is seen from Table 6 that the values β of DIAC are higher than the values β of the reference substances pNA and urea. Which means that DIAC can be an NLO material.

TABLE 6. The dipole moment (μ, in Debye), the mean linear polarizability ($\langle\alpha\rangle$, in 10^{-24} esu), anisotropy of linear polarizability ($\Delta\alpha$, in 10^{-24} esu), mean first− and second−order hyperpolarizabilities ($\langle\beta\rangle$ and $\langle\gamma\rangle$ in 10^{-30} and 10^{-36} esu) for DIAC

Parameters	**HSEh1PBE**		**ωB97XD**	
	LanL2DZ			
	static	**532 nm**	**static**	**532 nm**
μ	11.58		11.41	
μ	6,20 [14] and 4,56 [15]			
$<\alpha>$	29.48	31.62	28.60	30.57
$<\alpha>$	17 [14]			
$\Delta\alpha$	11.17	12.34	4.02	4.58
$<\beta>$	11.15	13.51	10.43	12.46
$<\beta>$	9.2 [14], 0.32 [15] and 0.13 [16]			
$<\gamma>$	16.13	24.68	12.65	16.76
$<\gamma>$	15.0 [14] and 7 [15]			

CONCLUSION

The detailed molecular geometric parameters (bond lengths and angles) for **DIAC** were investigated. The isotropic and anisotropic polarizability (α and $\Delta\alpha$), first- and second-order hyperpolarizability (β and γ) parameters of **DIAC** synthesized and characterized were examined by using DFT levels (HSEh1PBE/ LanL2DZ and ωB97XD/LanL2DZ) in the gas phase. The UV cut-off wavelength observed at 343 nm was assigned as the $\pi\rightarrow\pi^*$ transition in the complex. It can be said that the absence of transition in the visible range may be owing to the occupied d^{10} orbital of the metal ion in the complex. The chemical hardness (η) and electronegativity (χ) parameters were calculated from FMOs energies. Vibrational frequencies for the complex calculated at HSEh1PBE/LanL2DZ and ωB97XD/ LanL2DZ levels were compared with the experimental ones. ^{1}H NMR chemical shift parameters of **DIAC** were calculated at HSEh1PBE/LanL2DZ and ωB97XD/LanL2DZ levels in the gas phase. These parameters were compared with corresponding experimental data. Tables 1-4 show that there is a good agreement between the theoretical and experimental data. From the first and second-order hyperpolarizability results obtained, it is seen that the DIAC values are higher than the pNA and urea values of the reference materials. These results show that DIAC could be an NLO material.

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