

ARTICLE

Synthesis, Characterization and Quantum Chemical Study of New Biaryl Backbone Ligands in Bis (Oxamato) Type Compounds**Albara I. S. Alrawashdeh***Department of Chemistry and Chemical Technology, Tafila Technical University, Tafila, Jordan.**Received on: 9th Jan. 2018;**Accepted on: 6th Feb. 2018*

Abstract: A straightforward consecutive synthesis methodology for the preparation of two derivatives of bis (oxamato) type based on biarylbackbone compounds **2-4** is presented. All compounds were isolated and tested to be soluble in common organic solvents. Compound **2** was readily converted into its saponified form (namely **3**) when treated with four equivalents of [ⁿBu₄N]OH and the subsequent addition of Pd (OAc)₂. Compound **3** could be isolated smoothly from the reaction mixture as a fine brown solid. Treatment of **2** with an excess amount of methylamine in dry ethanol gave compound **4** as crystalline colorless material. The synthesized compounds **2** and **4** were characterized by IR-, NMR-spectroscopy, elemental analysis, mass spectroscopy and melting point. Density functional theory (DFT) calculations were carried out to correlate the structural features of compound **2**.

Keywords: Diethyl 2,2'-dibromo-4,4'-dimethylbiphenyl-6,6'-dioxamate, biaryl, DFT, HOMO.

Introduction

In the past decade, the chemistry of bis(oxamato) chelating ligands has seen tremendous development, thus many strategies have been explored to synthesize such ligands^[1]. In general, the synthesis of bis (oxamato) transition metal complexes is obtained by treating the chelating ligands diethyl N,N'-bis (oxamates) with four equivalents of hydroxide, followed by the subsequent addition of the appropriate transition metal salt solution^[2-5].

A wide variety of transition metal complexes containing such ligands have been utilized as a (pre) catalyst in a variety of organic transformations, such as cross-coupling reactions^[6]. Due to the importance of the structural studies of the transition metal

complexes of biaryl backbone ligands and in continuation with our investigations on coordination chemistry of 6,6'-dibromo and 6,6'-bis (dimethylamino) substituted 2,2'-diphosphinobiphenyls as well as 2,2',6,6'-tetraphosphino biphenyl^[7-9]; we report here the synthesis, characterization and structure properties of two derivatives of biaryl backbone ligands as well as the coordination behavior of diethyl 2,2'-dibromo-4,4'-dimethylbiphenyl-6,6'-dioxamate **2** towards the common Pd²⁺ precursor Pd(OAc)₂. Moreover, density functional theory (DFT)^[10-11] calculations were used to examine and characterize the structural features of the diethyl 2,2'-dibromo-4,4'-dimethylbiphenyl-6,6'-dioxamate ligand **2**.

Experimental Section

Synthesis of diethyl 2,2'-dibromo-4,4'-dimethylbiphenyl-6,6'-dioxamate, **2**

The 6,6'-dibromo-4,4'-dimethylbiphenyl-2,2'-diamine **1** (0.5g, 0.877 mmol) and Et₃N (0.177g, 1.754 mmol) were suspended in dry THF (40 mL) and cooled to 0 °C. Then, ethyloxalyl chloride (0.24g, 1.754 mmol) was added dropwise with continuous stirring maintaining the temperature at 0 °C. The resulting reaction mixture was refluxed at 65 °C for 40 min with continuous stirring, then the reaction mixture was cooled down to room temperature and the volume was reduced to ca. 15 mL. Slow addition of ice water resulted in the precipitation of crude product as off-white powder. The solid was collected by centrifugation, washed thoroughly with water and recrystallized from ethanol/water mixture and dried in vacuum to yield pure off-white solid of compound **2**. (**Yield** 86%), **M.p.**: 197 (dec.)°C, **Elemental analysis (%)** for compound **2**; C₂₂H₂₂Br₂N₂O₆ (570.22 g·mol⁻¹) calcd (%): C 46.34, H 3.89, N 4.91; Found: C 46.65, H 4.03, N 4.90. **IR**: $\nu = 3556$ (b), (NH); 2983(m) (CH); 1652(s) (CO). **¹H NMR** (500 MHz, CDCl₃): $\delta = 1.31$ (t, 6H, CH₂CH₃), 2.46 (s, 6H, CH₃ group on the aromatic ring), 4.27 (q, 4H, CH₂CH₃), 7.45 (s, 2H, aromatic ring), 8.24 (s, 2H, aromatic ring), 8.57 (s, 2H, NH), **¹³C{¹H} NMR** (126 MHz, CDCl₃): $\delta = 14.01$, 21.92, 63.83, 121.17, 124.47, 125.95, 130.67, 136.00, 139.44, 142.53, 153.82, 157.14 (CO), 160.03 (CO). **ESI-TOF MS**: calcd. for [C₂₂H₂₂Br₂N₂O₆+H]⁺ 570.09; found 568.99.

Synthesis of 6,6'-dibromo-4,4'-dimethylbiphenyl-2,2'-bis(N'-methyloxamide), **4**

Compound **4** was synthesized in analogy to Ruiz et al.[2]. A ethanoic solution (35 mL) of **2** (0.0045 mol, 2.56 g) was treated at ambient temperature with an excess amount of methylamine (33% in ethanol) under continuous vigorous stirring, where upon a white solid immediately precipitated. Then, the solution was refluxed at 50°C for 45 minutes and the resulting solution was evaporated under vacuum, washed three times with methanol and diethyl ether to precipitate the product, which after being dissolved in dichloromethane (12 mL) was flash filtered through a pad of silica gel and dried in *vacuo*. to obtain compound **4** as crystalline colorless material. (**Yield** 78%), **M.p.**: 219

(dec.)°C, **Elemental analysis (%)** for compound **4**; C₂₀H₂₀Br₂N₄O₄ (540.205 g·mol⁻¹) calcd. (%): C 44.47, H 3.73, N 10.37; Found: C 44.46, H 3.78, N 9.99. **IR**: $\nu = 3253$ (m), 3371(s) (NH); 2963(m) (CH); 1696(s), 1689(s) (CO). **¹H NMR**: $\delta = 2.36$ (s, 6H, CH₃ group on the aromatic ring), 3.43 (d, 6H, NHCH₃), 8.39 (q, 2H, NHCH₃), 7.39 (s, 2H, aromatic ring), 7.47 (s, 2H, aromatic ring), 9.29 (s, 2H, NHAr). **¹³C{¹H} NMR**: $\delta = 13.7$, 19.73, 26.69, 120.3, 125.3, 129.3, 133.4, 134.5, 139.2, 139.7, 159.96, 160.06, 161.55 (CO), 164.89 (CO). **ESI-TOF MS**: calcd. for [C₂₀H₂₀Br₂N₄O₄+H]⁺ 540.90; found 538.99.

Materials and Methods

Optimized geometries and the respective energies were calculated for compound **2** at the DFT/ωB97X-D level of theory with the polarized 6-31G(d,p) basis set. All reactions were performed under an inert atmosphere of argon by using Schlenk and vacuum-line techniques. THF and diethyl ether (Et₂O) were purified by distillation from sodium/benzophenone ketyl. Ethanol was purified by distillation from magnesium. All chemicals were purchased from commercial sources (Merck®, Aldrich® and Arcos®) and used as received without further purification. 6,6'-dibromo-4,4'-dimethylbiphenyl-2,2'-diamine was synthesized *via* the literature modified procedure which was reported by our group^[7-9]. Flash column chromatography purifications were carried out using Merck silica gel 60 (230e400 meshASTM). The structures of the isolated compounds were confirmed by IR-, NMR-spectroscopy, elemental analysis, mass spectroscopy and melting point. NMR spectra were recorded on a Bruker Avance III 500 spectrometer; chemical shifts for ¹H and ¹³C are referenced internally to the residual protons and to the ¹³C NMR signal of the deuterated solvent. Elemental analysis for C, H and N was performed on a Thermo Flash AE 1112 analyzer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrophotometer as KBr pellets. Mass spectra were recorded on a Bruker micrOTOF-QIIa mass spectrometer operating in ESI mode.

Results and Discussion

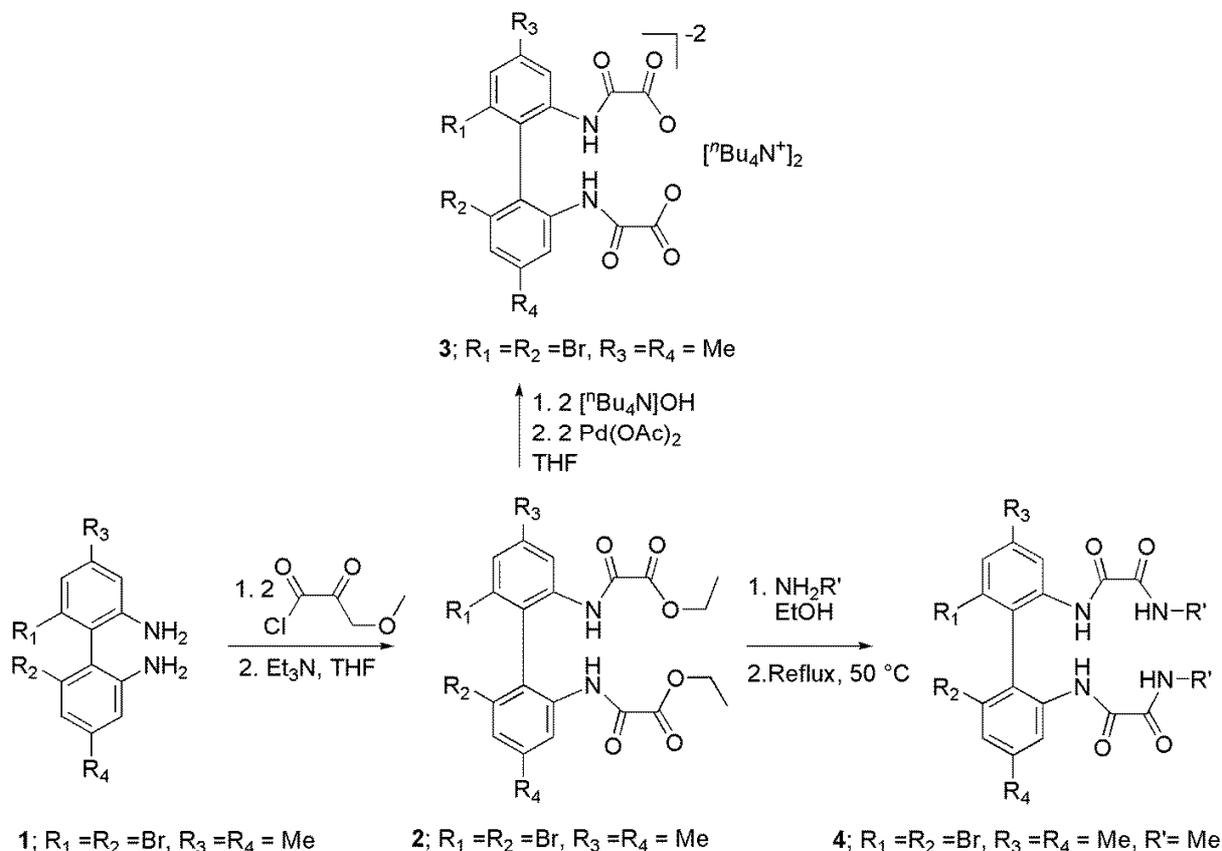
The diethyl 2,2'-dibromo-4,4'-dimethylbiphenyl-6,6'-dioxamate **2** was readily prepared *via* a two-step sequence from the direct reaction of 6,6'-dibromo-4,4'-dimethylbiphenyl-2,2'-diamine with two equivalents of ethoxalyl chloride in the presence of triethylamine as an acid scavenger in dry THF with a 86% overall isolated yield. As shown in Scheme 1, the treatment of compound **2** with an excess amount of 33% methylamine (3-fold at least) in absolute ethanol under continuous vigorous stirring at 50 °C results in the formation of a white powder which after being dissolved in dichloromethane was flash filtered through a pad of silica gel and dried *in vacuo* to obtain compound **4** as crystalline colorless material, in ca. 78% yield. This reaction was easily preceded with no complications. Compounds **2** and **4** are stable in both solid state and solution and soluble in a range of polar organic solvents. The treatment of compound **2** with four equivalents of [ⁿBu₄N]OH and the *in-situ* addition of Pd (OAc)₂ gave only

the hydrolyzed form of compound **2**; namely **3**, and there was no complexation with Pd⁺² ion, Scheme 1. Moreover, the formation of dark orange and brown precipitate indicates the formation of Pd(OH)₂ and the hydrolyzed form of compound **2**, respectively. Probably, the formation of Pd(OH)₂ is due to the fact that the Pd(II) ion is weakly bonded to N,O-chelates^[12].

After the appropriate workup, the desired compound **3** was separated from the reaction mixture as a fine brown powder in 77% yield based on compound **1**. It is worth pointing out that all efforts made for the synthesis of compound **3** following the usually employed procedures of related bis (oxamato) type transition metal complexes were unsuccessful^[13].

On the other hand, the dibromo substituted compounds **2-4** are crystalline materials and remarkably stable towards oxidation in air. The synthesized compounds **2** and **4** were characterized by IR-, NMR-spectroscopy, elemental analysis, mass spectroscopy and melting point.

Scheme 1. General synthesis strategy of compounds 2-4.



NMR Spectroscopy

The ^1H NMR spectrum of compound **2** obtained in deuterated chloroform is shown in Figure 1 along with the predicted signals; i.e., the protons of the CH_3 groups on the phenyl rings appeared as a sharp singlet at $\delta = 2.46$ ppm, while the protons of the NH group appeared as a singlet at $\delta = 8.57$ ppm. Moreover, a triplet of CH_2CH_3 appeared at $\delta = 1.31$ ppm as well as a quartet of CH_2CH_3 at $\delta = 4.27$ ppm. In addition, the two different protons on the biaryl group appeared at $\delta = 7.45$ ppm and at $\delta = 8.24$ ppm, respectively. The same expected behavior is

IR Spectroscopy

The infrared-spectrum shows a strong band at 3556 cm^{-1} and (3253 cm^{-1} and 3371 cm^{-1}) for compounds **2** and **4**, respectively, which are attributed to stretching vibration of the secondary amine. Weak absorption at 882 cm^{-1} is consistent with the bending vibrations of the NH group of compound **2**. Moreover, the infrared-spectrum shows a strong band centered at 1652 cm^{-1} and (1696 cm^{-1} and 1689 cm^{-1}) for compounds **2** and **4**, respectively, which can be assigned to stretching vibration of the carbonyl groups of these bis (oxamato) ligands.

Mass Spectroscopy

Mass spectral data for compounds **2** and **4** was in accordance with their respective formulations. The ESI-MS spectra of compounds **2** and **4** reveal the corresponding molecular ions $[\text{M}^+]$ (m/z ; 568.99) and $[\text{M}^+]$ (m/z ; 538.99), respectively.

found for the $^{13}\text{C}\{^1\text{H}\}$ NMR, where one signal at 21.92 ppm represents the CH_3 group on the phenyl ring, while the signals that appeared at 14.01 ppm and at 63.83 ppm were assigned to CH_2CH_3 and CH_2CH_3 , respectively. Whereas, 8 signals in the range 121–160 ppm match well the structure of the aromatic part as well as carbon atoms of the carbonyl groups. The signals that appeared at 160.03 and 157.14 ppm were assigned to carbon atoms of the carbonyl groups, while the remaining signals were for carbon atoms of aromatic part. The NMR data of compound **4** is given in the experimental part.

Computational

All electronic structure calculations were performed using the Spartan 16 software package. The structure of compound **2** was fully optimized without any geometric or symmetry constraints at the DFT/ $\omega\text{B97X-D}$ level of theory with the polarized 6-31G(d,p) basis set in the gas phase. The absence of imaginary frequencies in the vibrational analysis confirmed that the optimized structure corresponds to a real minimum. The optimized ground state geometry of compound **2** at the $\omega\text{B97X-D}/6\text{-}31\text{G(d,p)}$ level of theory is illustrated in Figure 2 with the HOMO and LUMO plots depicted in Figure 3. Geometrical parameters of the optimized structure, such as angles ($^\circ$) and bond lengths (\AA), were retrieved. Selected calculated bond lengths (\AA) and angles ($^\circ$) are listed in Table 1.

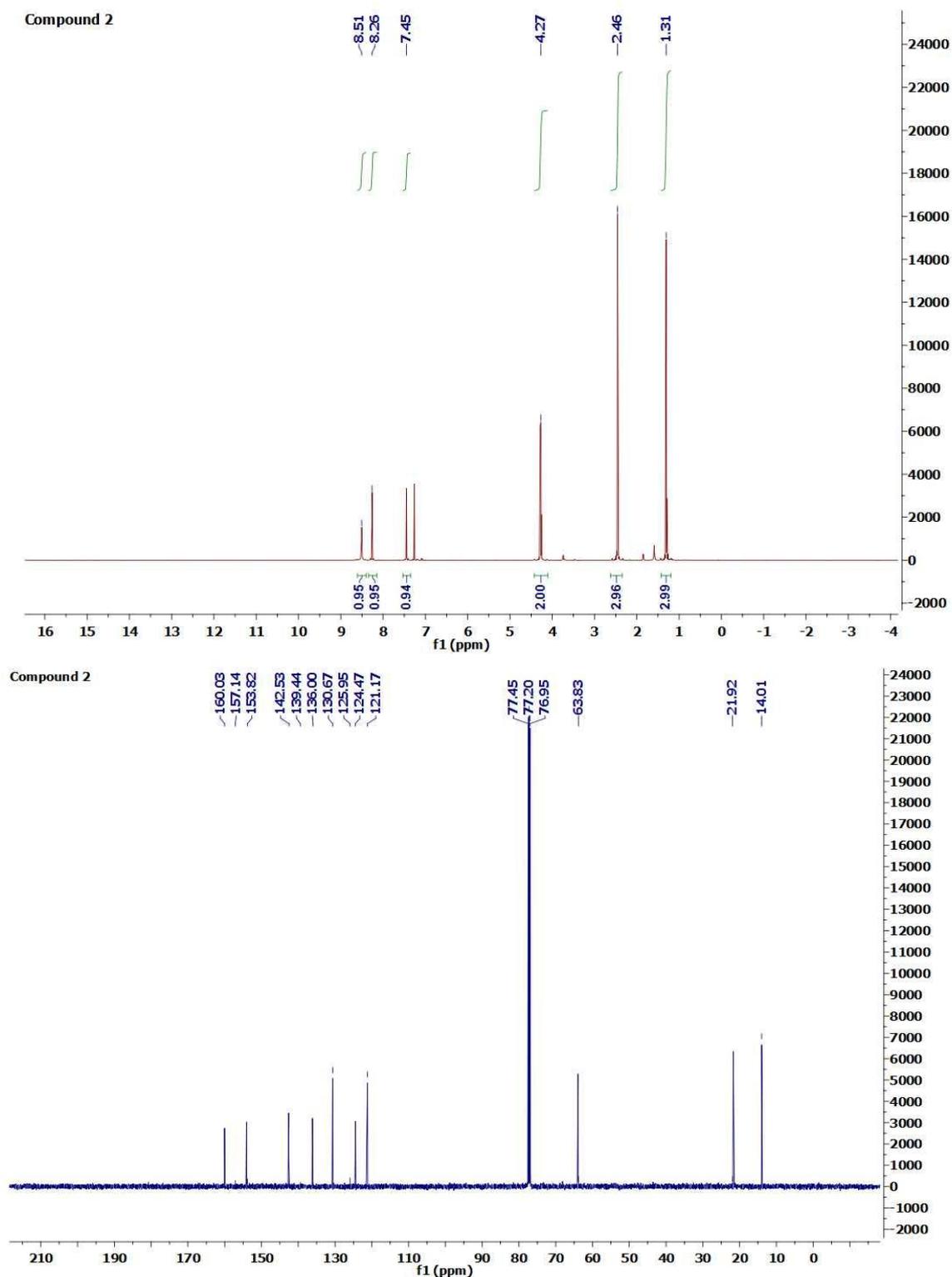


Figure 1. ^1H (above) and ^{13}C NMR (below) spectra of compound 2 in CDCl_3 at 25 $^\circ\text{C}$.

Table 1. Selected calculated bond lengths (Å) and angles (°) for compound 2.

Bond	Calc'd	Angle	Calc'd
C(1)-C(2)	1.395	C(2)-C(1)-C(7)	117.43
C(2)-Br(1)	1.901	C(2)-C(1)-C(12)	122.70
C(3)-C(4)	1.393	C(3)-C(2)-Br(1)	118.20
C(4)-C(5)	1.507	C(1)-C(2)-Br(1)	119.67
C(7)-N(1)	1.401	C(2)-C(3)-C(4)	119.70
C(8)-O(1)	1.213	C(6)-C(7)-N(1)	122.35
C(8)-N(1)	1.359	C(1)-C(7)-N(1)	116.79
C(8)-C(9)	1.544	O(1)-C(8)-N(1)	128.04
C(9)-O(3)	1.212	O(1)-C(8)-C(9)	122.51
C(9)-O(2)	1.318	N(1)-C(8)-C(9)	109.45
C(10)-O(2)	1.442	O(3)-C(9)-O(2)	126.18
C(10)-C(11)	1.517	O(3)-C(9)-C(8)	122.39
C(12)-C(13)	1.394	O(2)-C(9)-C(8)	111.43
C(13)-Br(2)	1.901	O(2)-C(10)-H(10)	108.80
C(18)-N(2)	1.401	C(14)-C(13)-Br(2)	118.22
C(19)-O(4)	1.213	C(12)-C(13)-Br(2)	119.67
C(19)-N(2)	1.359	C(17)-C(18)-N(2)	122.44
C(20)-O(5)	1.212	C(12)-C(18)-N(2)	116.72
C(20)-O(6)	1.318	O(4)-C(19)-N(2)	128.04
C(21)-C(22)	1.512	O(5)-C(20)-O(6)	125.80
C(21)-O(6)	1.441	C(9)-O(2)-C(10)	116.43

The vibrational frequencies of compound **2** have then been computed and compared with those obtained experimentally. The broad band observed at 3556 cm^{-1} in the IR spectrum and attributed to stretching vibration of the secondary amine is theoretically predicted at 3589 cm^{-1} . The computed FT-IR vibrational

analysis also reveals a weak absorption band at 1651 cm^{-1} attributed to the NH bending vibrations. Additionally, a strong absorption peak observed at 1848 cm^{-1} in the computed IR spectrum is assigned to the vibration of the carbonyl group of compound **2**.

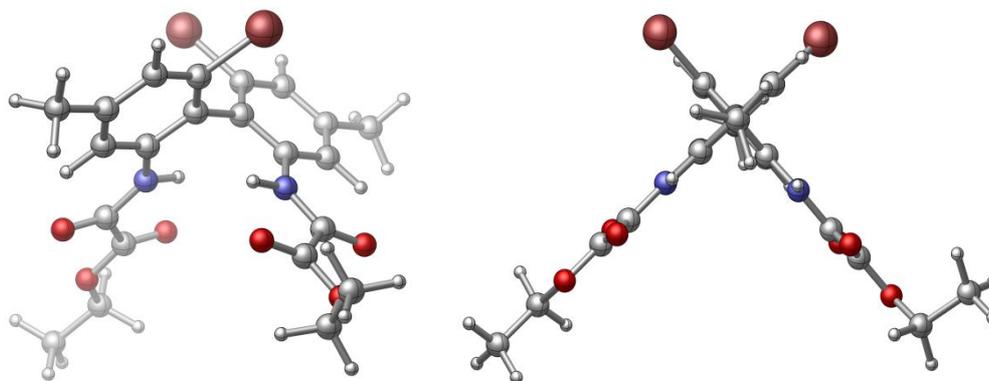


Figure 2. Side view (left) and perspective view (right) of the optimized ground state geometry of compound **2** at the ω B97X-D/6-31G(d,p) level of theory.

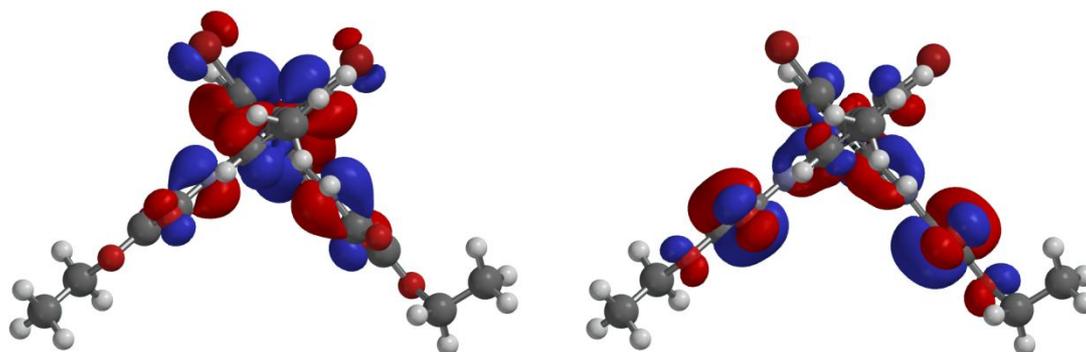


Figure 3. The HOMO (left) and LUMO (right) plots of the optimized ground state geometry of compound **2** at the ω B97X-D/6-31G(d,p) level of theory.

Conclusion

In the present study, starting from 6,6'-dibromo-4,4'-dimethylbiphenyl-2,2'-diamine **1**, we synthesized diethyl 2,2'-dibromo-4,4'-dimethylbiphenyl-6,6'-dioxamate **2**, and 6,6'-dibromo-4,4'-dimethylbiphenyl-2,2'-bis(N'-methyloxamide) **4**, with four donor atoms. To get a deeper understanding of the spectroscopic properties of such ligands, the vibrational frequencies of compound **2** are assigned based on DFT calculations.

The observed vibrational frequencies of **2** are in good agreement with the corresponding values calculated by density functional theory (DFT) at the ω B97X-D/6-31G(d,p) level of theory.

Further synthetic, single-crystal X-ray structure determination and coordination behavior investigations relating to the electronic impact of such ligands are currently in progress.

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