A Computational Study of 2,3-dihydrospiro[carbazole-1,2'-[1,3]dithiolan]-4(9H)-one compound: Structure, FT-IR, NMR, NLO, and NBO Analyses

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The 2,3-dihydrospiro[carbazole-1,2'-[1,3]dithiolan]-4(9H)-one compound as a polycyclic aromatic alkaloid, was investigated by using the quantum chemical tools. All calculations were performed by DFT hybrid functionals (B3LYP and M06HF) and HF method, in three solvent environments (vacuum, chloroform, DMSO), using the 6-31+G(d,p) and 6-311++G(d,p) basis sets. The calculated FT-IR and NMR spectral data of the compound are compared with those of the observed values. The frontier molecular orbital amplitudes show that the nucleophilic attack site is mostly located over the dithiolane ring, and the electrophilic attack site is mainly located on all rings and oxygen atom of the studied compound. NLO analysis indicates that the title compound might be used as an available material in the optoelectronic tools because of the higher β=10.70x10^{-30} esu by the B3LYP level.

Keywords: *dihydrospiro*, FT-IR, NMR, FMO, NLO

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Introduction

The substituted carbazole compounds have a main responsibility in synthetic chemistry due to their unique structure containing D- π-A bridge promising in a potent usage in the pharmacological or medicinal sciences[1,2]. In addition, they have been used as a reagent material to synthesize of the uleine-type alkaloids[3-5], which are able to extracted from natural sources, due to their pharmacological properties[6-8] such as antibacterial, anti-inflammatory, antimalarial activity, etc.Recently, the quantum chemical investigations on the heterocyclic compounds have been reported to support the experimental results in terms of the results of structure and spectroscopic[9-11].

In this study, it has been intended to evaluate the electronic structure, inter- and intramolecular interactions, chemical reactivity trend/site, and optical properties of the title compound (given Figure 1) after the NMR and FT-IR spectral investigations. Hope, the obtained results from the quantum chemical calculations will provide useful information to both the synthetic and computational chemists.

Computational Method

All calculations have been conducted by the G09W[12] package by using the hybrid DFT functionals (B3LYP and M06HF)[13-16] and the HF[17-19] method, in the three-calculation media, which are vacuum (VAC), chloroform (CHCl$_3$) and dimethyl sulfoxide (DMSO). The PCM (polarize continuum model)[20,21] was used for the calculations employed in CHCl$_3$ and DMSO solvents. All calculated vibrations were assigned by VEDA[22] software via using the PED (potential energy distribution) method.

The GIAO[23,24] approach was used to assign the ^{1}H and ^{13}C chemical shifts. The NLO analysis NLO[25,26] was used to predict whether a suitable substance was used for optoelectronic devices. The FMO[27-29] analysis was employed to estimate/elucidate the chemical reactivity tendency/ site of the compound.

Results and Discussion

Frontier Molecular Orbital Analysis

Table 1 shows the global reactivity tensors calculated for all methods, solvents, and basis sets. Accordingly, the quantities of all tensors have been calculated in different trend from each other depending on the basis sets, solvents, and methods, but mostly by the used method. From Table 1, ΔE for B3LYP, M06HF, and HF in vac has been calculated as 4.596, 8.919 and 8.919 eV at 6-31+G(d,p) basis set, respectively; but they have been predicted as 4.623, 8.435 and 8.887 eV for 6-311++G(d,p) basis set. Besides, μ for these methods (B3LYP, M06HF, and HF) have been estimated by 6-31+G(d,p) basis set in -3.975, -4.366, -4.366 eV and by 6-311++G(d,p) basis set in -4.020, -4.702, -3.576 eV, in DMSO. Also, η, ω, and ΔN values for HF method are predicted in 4.692, 1.363, and 0.762 eV, while these tensors are calculated by B3LYP functional in 2.308, 3.500 and 1.742 eV,

respectively, in DMSO and at 6-311++G(d,p) basis set. Here, it should be noted that ΔE value for all methods and basis sets has decreased as increasing of the solvent dielectric constant, which implies that the intramolecular interactions are getting more possible than the intermolecular interactions by rising of the solvent dielectric constant. On the other hand, η value for B3LYP has decreased as the solvent dielectric constant increases, while the hardness for M06HF and HF has increased by the dielectric constant, at 6-31+G(d,p) basis set.

Furthermore, Figure 1 shows the FMO amplitudes and MEP pilot of the compound. Accordingly, the HOMO is mostly located over the pentacyclic ring containing the sulphur atoms and on the N atom while the LUMO is mostly expanded over the whole molecular surface and partly on the S- pentacyclic ring of the compound. Besides, the oxygen atom (red color) around and aromatic ring (orange color) of the compound have been determined as the electron-rich region and nitrogen atom around (dark blue), and the other rings (light blue) have been predicted as the electron-poor region. Here, the electrophilic attack and nucleophilic attack sites of the title compound have been determined by FMO and MEP analyses.
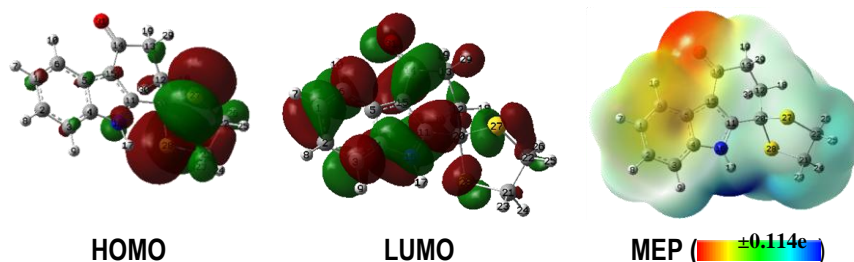

| Structure | HOMO | LUMO | MEP (±0.114e) |

Fig. 1. FMO amplitudes (isoval:0.02) and MEP (isoval:0.0004) plot of the title compound at B3LYP/6-311++G(d,p) in DMSO environment

		Vac			CHCl$_3$			DMSO		
		B3LYP	M06HF	HF	B3LYP	M06HF	HF	B3LYP	M06HF	HF
HOMO (-I)		-0.225	-0.326	-0.326	-0.228	-0.331	-0.331	-0.230	-0.335	-0.335
LUMO (-A)		-0.056	0.002	0.002	-0.059	0.012	0.012	-0.062	0.014	0.014
ΔE		4.596	8.919	8.919	4.594	9.341	9.341	4.587	9.480	9.480
μ	6-31+g(d,p)	-3.814	-4.403	-4.403	-3.912	-4.349	-4.349	-3.975	-4.366	-4.366
η		2.298	4.459	4.459	2.297	4.671	4.671	2.294	4.740	4.740
ω		3.165	2.174	2.174	3.331	2.024	2.024	3.445	2.011	2.011
ΔN		1.660	0.987	0.987	1.703	0.931	0.931	1.733	0.921	0.921
HOMO (-I)		-0.227	-0.329	-0.296	-0.230	-0.335	-0.301	-0.233	-0.338	-0.304
LUMO (-A)		-0.057	-0.019	0.030	-0.060	-0.009	0.040	-0.063	-0.007	0.041
ΔE		4.623	8.435	8.887	4.622	8.858	9.274	4.616	9.000	9.383
μ	6-311++g(d,p)	-3.855	-4.722	-3.624	-3.956	-4.680	-3.559	-4.020	-4.702	-3.576
η		2.311	4.217	4.443	2.311	4.429	4.637	2.308	4.500	4.692
ω		3.215	2.643	1.478	3.385	2.472	1.365	3.500	2.456	1.363
ΔN		1.668	1.120	0.816	1.712	1.057	0.767	1.742	1.045	0.762

*ΔE, χ,η, ω and ΔNmax are in eV; HOMO and LUMO energies are in au. Abbreviations are ΔE, Energy Gap; χ, electronic chemical potential;η, global hardness; ω, electrophilicity; ΔN, max. charge transfer capability index.

Non-Linear Optic Analysis

Table 2 summarized the NLO tensors of the title compound calculated by the 6-311++G(d,p) basis set. In Vac, the μ value of the compound has been predicted as 6.36 (B3LYP), 6.57 (M06HF) and 6.79 D (HF), while it has been estimated as 9.42 (B3LYP), 9.49 (M06HF) and 9.75 D (HF) in DMSO. Also, the Δα value of the compound has been calculated as 18.68, 16.75 and 15.27x10^{-24} esu in Vac, and predicted as 22.53 (B3LYP), 19.49 (M06HF) and 17.32x10^{-24} (HF) in DMSO. Also, the β for the compound has been calculated as 5.35, 1.42, and 1.74x10^{-30} esu in Vac and as 10.70 (B3LYP), 5.81 (M06HF) and 3.77x10^{-30} (HF) in DMSO. As known well, the urea is used for the comparison purpose of deciding/ predict the availability of using in the optic technology. In the past, the β value of the urea molecule was reported[30] as 0.6230x10^{-30} esu by B3LYP/6-311++G(d,p) level. Thus, the title compound might be used for optoelectronic tools because its β value is higher, approximately nine (Vac) and seventeen (DMSO) times than that of the urea.

Natural Bond Orbital Study

The results of second-order perturbative energy analysis in the NBO[31]basis are given in Table 3. It can be seen that the greatest contribution to the stabilization of the compound comes from the electron transfer from the lone pair of N atom to each of unfilled orbitals Π* C4-C5 and Π* C11-C15 with the stabilization energy (E$^{(2)}$) of 33.75 and 47.03 kcal/mol, respectively. Besides, the E(2) for the interactions Π C11-C15→ Π* C14-O31 has remarkable provide stabilization of the compound with E$^{(2)}$ =27.90 kcal/mol (ED$_j$= 0.21881e). From Table 3, it can be said that the resonance interactions (n→ Π* and Π → Π*) existed in the compound are mainly

responsible for the stabilization of the compound.

Table 2. The NLO tensors for the title compound, at 6-311++G(d,p) basis set

	B3LYP			M06HF			HF		
	Vac	CHCl$_3$	DMSO	Vac	CHCl$_3$	DMSO	Vac	CHCl$_3$	DMSO
μ (Debye)									
μ	6.36	8.41	9.42	6.57	8.56	9.49	6.79	8.79	9.75
α, Esu (x10^{-24})									
α_0	32.12	40.88	45.46	30.39	38.40	42.59	28.89	36.09	39.81
$\Delta\alpha$	18.68	22.28	22.53	16.75	19.59	19.49	15.27	17.56	17.32
β, esu (x10^{-30})									
β_x	4.43	8.04	10.48	1.36	3.02	4.47	1.08	2.52	3.76
β_y	-0.17	-0.23	-0.24	-0.05	-0.01	-0.04	-0.14	-0.21	-0.25
β_z	2.99	0.76	-2.12	0.42	-1.75	-3.71	1.36	0.83	-0.04
β	5.35	8.08	10.70	1.42	3.49	5.81	1.74	2.67	3.77

*The abbreviations are as μ, static dipole moment; α$_0$, the mean polarizability; Δα, the anisotropy of the polarizability; β, the frequency independent first-order hyperpolarizability.

Table 3. NBO analysis results of the title compound at the B3LYP/6-311++G(d,p) level in chloroform

Donor(i)	ED$_i$/e	Acceptor (j)	ED$_j$/e	E(2)/ kcalmol^{-1}	E(j)-E(i)/ a.u	F(i.j)/ a.u
ΠC1-C6 (2)	1.71037	Π* C2-C3	0.32438	19.90	0.28	0.067
		Π* C4-C5	0.47115	18.47	0.28	0.067
ΠC2-C3 (2)	1.71687	Π* C1-C6	0.30766	17.86	0.29	0.065
		Π* C4-C5	0.47115	19.81	0.28	0.070
ΠC4-C5 (2)	1.59655	Π* C1-C6	0.30766	19.08	0.28	0.067
		Π* C2-C3	0.32438	18.54	0.28	0.066
		Π* C11-C15	0.37643	17.34	0.27	0.061
ΠC11-C15 (2)	1.72323	Π* C4-C5	0.47115	17.78	0.29	0.068
		Π* C14-O31	0.21881	27.90	0.28	0.081
LP(1) N16	1.58167	Π* C4-C5	0.47115	33.75	0.30	0.090
		Π* C11-C15	0.37643	47.03	0.29	0.106

Vibrational Analysis and NMR Shifts

The calculated vibrational modes of the compound at B3LYP/6-311++G(d,p) level have been scaled down[32] by the factor 0.96 for C-H and N-H stretching region and by 0.988 for the remaining region of the IR spectra. Accordingly, N-H stretching mode for B3LYP/6-311++G(d,p) level has been assigned in 3471 cm^{-1} for DMSO and 3490 cm^{-1} for Vac. On the other hand, the same mode has been determined by HF/6-311++G(d,p) level in 3529 cm^{-1} for Vac and in 3504 cm^{-1} for DMSO. By B3LYP/6-311++G(d,p) level, vCH (ar.) and vCH (al.) ring modes have been assigned in 3078-3043 cm^{-1} 3002-2902 cm^{-1}, respectively. The vC=O stretching mode has been assigned in 1600 cm^{-1} with a strong IR intensity. Recently, the vNH mode was reported in 3395 cm^{-1} and assigned in 3505 cm^{-1} by the same theory level[33].

The highest chemical shift for the compound has been estimated for the C14

atom bonded to an electronegative oxygen atom in 203.9 for B3LYP, 269.6 for M06HF, and 201.9 ppm for HF, in DMSO solvent. In a previous study, the similar ^{13}C NMR shift for dasycarpidone compound was observed in 193.2 ppm and determined in 200.6 ppm by B3LYP level[34]. Besides, the aromatic ring ^{13}C NMR shifts have been calculated by 6-311++G(d,p) basis set in the range of 117.9-144.1 ppm for B3LYP, 160.7-182.0 ppm for M06HF and 118.8-143.7 ppm for HF method in DMSO at 6-311++G(d,p) basis set. Furthermore, the aromatic ^{1}H shifts have been determined in the range of 7.6- 8.5 ppm for B3LYP, 9.0- 10.0 ppm for M06HF, and 7.7-8.7 ppm for HF in DMSO at 6-311++G(d,p) basis set. The similar shifts have been calculated in the range of 7.4-8.7 ppm for B3LYP, 8.7- 10.1 ppm for M06HF and 7.5-8.9 ppm for HF by the same basis set in Vac. Thus, the NMR chemical shifts strongly depend on the calculation method or approach rather than both the basis set and solvent media.

Conclusions

In this work, the structural, electronic, and spectroscopic properties of the title compound have been investigated by quantum chemical tools. The calculated NMR and FT-IR values of the compound have agreed with the previous report. The FMO analysis and MEP pilot shows the chemical reactivity behavior and nucleophilic/ electrophilic site of the compound. NLO analysis has revealed that the title compound is an available material for optoelectronic technology purposes because of the higher β value.

Acknowledgements

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