



## 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

Goncagül Serdaroglu<sup>\*a</sup> and Nesimi Uludağ<sup>b</sup>

<sup>a</sup>Faculty of Education, Mathematics and Science Education, Sivas Cumhuriyet University, 58140 Sivas, Turkey

<sup>b</sup>Department of Chemistry, Namik Kemal University, 59030 Tekirdag, Turkey

E-mail: goncagul.serdaroglu@gmail.com

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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  $\beta = 10.70 \times 10^{-30}$  esu by the B3LYP level.

Keywords: Dihydrospiro, FT-IR, NMR, FMO, NLO.

### Introduction

The substituted carbazole compounds have a main responsibility in synthetic chemistry due to their unique structure containing D- $\pi$ -A bridge promising in a potent usage in the pharmacological or medicinal sciences<sup>1,2</sup>. In addition, they have been used as a reagent material to synthesize of the uleine-type alkaloids<sup>3-5</sup>, which are able to be extracted from natural sources, due to their pharmacological properties<sup>6-8</sup> 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<sup>9-11</sup>.

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 Fig. 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.

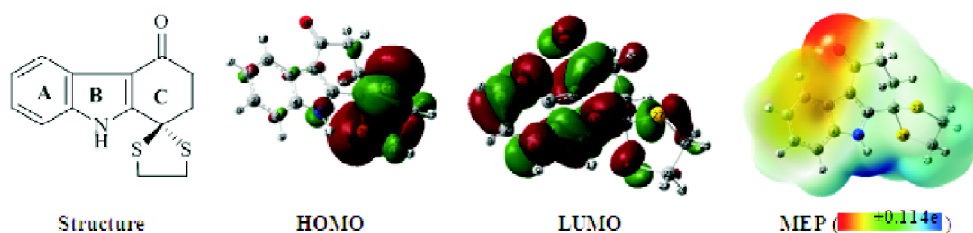
### Computational method

All calculations have been conducted by the G09W<sup>12</sup> package by using the hybrid DFT functionals (B3LYP and M06HF)<sup>13-16</sup> and the HF<sup>17-19</sup> method, in the three-calculation media, which are vacuum (Vac), chloroform (CHCl<sub>3</sub>) and dimethyl sulfoxide (DMSO). The PCM (polarize continuum model)<sup>20,21</sup> was used for the calculations employed in CHCl<sub>3</sub> and DMSO solvents. All calculated vibrations were assigned by VEDA<sup>22</sup> software via using the PED (potential energy distribution) method. The GIAO<sup>23,24</sup> approach was used to assign the <sup>1</sup>H and <sup>13</sup>C chemical shifts. The NLO analysis NLO<sup>25,26</sup> was used to predict whether a suitable substance was used for optoelectronic devices. The FMO<sup>27-29</sup> 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



**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.

from each other depending on the basis sets, solvents, and methods, but mostly by the used method. From Table 1,  $\Delta E$  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,  $\mu$  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,  $\eta$ ,  $\omega$ , and  $\Delta N$  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  $\Delta E$  value for all methods and basis sets has decreased as increasing of the solvent dielectric constant, which implies that the intramolecular inter-

actions are getting more possible than the intermolecular interactions by rising of the solvent dielectric constant. On the other hand,  $\eta$  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, Fig. 1 shows the FMO amplitudes and MEP plot 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

**Table 1.** The quantum chemical identifiers of the title compound

		Vac			CHCl <sub>3</sub>			DMSO		
		B3LYP	M06HF	HF	B3LYP	M06HF	HF	B3LYP	M06HF	HF
HOMO (-I)	6-31+g(d,p)	-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
$\Delta E$		4.596	8.919	8.919	4.594	9.341	9.341	4.587	9.480	9.480
$\mu$		-3.814	-4.403	-4.403	-3.912	-4.349	-4.349	-3.975	-4.366	-4.366
$\eta$		2.298	4.459	4.459	2.297	4.671	4.671	2.294	4.740	4.740
$\omega$		3.165	2.174	2.174	3.331	2.024	2.024	3.445	2.011	2.011
$\Delta N$		1.660	0.987	0.987	1.703	0.931	0.931	1.733	0.921	0.921
HOMO (-I)	6-311++g(d,p)	-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
$\Delta E$		4.623	8.435	8.887	4.622	8.858	9.274	4.616	9.000	9.383
$\mu$		-3.855	-4.722	-3.624	-3.956	-4.680	-3.559	-4.020	-4.702	-3.576
$\eta$		2.311	4.217	4.443	2.311	4.429	4.637	2.308	4.500	4.692
$\omega$		3.215	2.643	1.478	3.385	2.472	1.365	3.500	2.456	1.363
$\Delta N$		1.668	1.120	0.816	1.712	1.057	0.767	1.742	1.045	0.762

\* $\Delta E$ ,  $\chi$ ,  $\eta$ ,  $\omega$  and  $\Delta N_{\max}$  are in eV; HOMO and LUMO energies are in au. Abbreviations are  $\Delta E$ , energy gap;  $\chi$ , electronic chemical potential;  $\eta$ , global hardness;  $\omega$ , electrophilicity;  $\Delta N_{\max}$ , charge transfer capability index.

electrophilic attack and nucleophilic attack sites of the title compound have been determined by FMO and MEP analyses.

#### 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  $\mu$  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  $\Delta\alpha$  value of the compound has been calculated as 18.68, 16.75 and  $15.27 \times 10^{-24}$  esu in Vac, and predicted as 22.53 (B3LYP), 19.49 (M06HF) and  $17.32 \times 10^{-24}$  (HF) in DMSO. Also, the  $\beta$  for the compound has been calculated as 5.35, 1.42, and  $1.74 \times 10^{-30}$  esu in Vac and as 10.70 (B3LYP), 5.81 (M06HF) and  $3.77 \times 10^{-30}$  (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  $\beta$  value of the urea molecule was reported<sup>30</sup> as  $0.6230 \times 10^{-30}$  esu by B3LYP/6-311++G(d,p) level. Thus, the title compound might be used for optoelectronic tools because its  $\beta$  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<sup>31</sup> 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  $\Pi^*$  C4-C5 and  $\Pi^*$  C11-C15 with the stabilization energy ( $E^{(2)}$ ) of 33.75 and 47.03 kcal/mol, respectively. Besides, the  $E^{(2)}$  for the interactions  $\Pi$  C11-C15  $\rightarrow$   $\Pi^*$  C14-O31 has remarkable provide stabilization of the compound with  $E^{(2)} = 27.90$  kcal/mol ( $ED_j = 0.21881e$ ).

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

	B3LYP			M06HF			HF		
	Vac	CHCl <sub>3</sub>	DMSO	Vac	CHCl <sub>3</sub>	DMSO	Vac	CHCl <sub>3</sub>	DMSO
$\mu$ (Debye)									
$\mu$	6.36	8.41	9.42	6.57	8.56	9.49	6.79	8.79	9.75
$\alpha$ , esu ( $\times 10^{-24}$ )									
$\alpha_0$	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
$\beta$ , esu ( $\times 10^{-30}$ )									
$\beta_x$	4.43	8.04	10.48	1.36	3.02	4.47	1.08	2.52	3.76
$\beta_y$	-0.17	-0.23	-0.24	-0.05	-0.01	-0.04	-0.14	-0.21	-0.25
$\beta_z$	2.99	0.76	-2.12	0.42	-1.75	-3.71	1.36	0.83	-0.04
$\beta$	5.35	8.08	10.70	1.42	3.49	5.81	1.74	2.67	3.77

\*The abbreviations are as  $\mu$ , static dipole moment;  $\alpha_0$ , the mean polarizability;  $\Delta\alpha$ , the anisotropy of the polarizability;  $\beta$ , 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)	$ED_j/e$	Acceptor (j)	$ED_j/e$	$E^{(2)}/\text{kcal mol}^{-1}$	$E(j)-E(i)/\text{a.u.}$	$F(i,j)/\text{a.u.}$
IIC1-C6 (2)	1.71037	$\Pi^*$ C2-C3	0.32438	19.90	0.28	0.067
		$\Pi^*$ C4-C5	0.47115	18.47	0.28	0.067
IIC2-C3 (2)	1.71687	$\Pi^*$ C1-C6	0.30766	17.86	0.29	0.065
		$\Pi^*$ C4-C5	0.47115	19.81	0.28	0.070
IIC4-C5 (2)	1.59655	$\Pi^*$ C1-C6	0.30766	19.08	0.28	0.067
		$\Pi^*$ C2-C3	0.32438	18.54	0.28	0.066
		$\Pi^*$ C11-C15	0.37643	17.34	0.27	0.061
IIC11-C15 (2)	1.72323	$\Pi^*$ C4-C5	0.47115	17.78	0.29	0.068
		$\Pi^*$ C14-O31	0.21881	27.90	0.28	0.081
LP(1) N16	1.58167	$\Pi^*$ C4-C5	0.47115	33.75	0.30	0.090
		$\Pi^*$ C11-C15	0.37643	47.03	0.29	0.106

From Table 3, it can be said that the resonance interactions ( $n \rightarrow \Pi^*$  and  $\Pi \rightarrow \Pi^*$ ) existed in the compound are mainly responsible for the stabilization of the compound.

#### Vibrational analysis and NMR shifts:

The calculated vibrational modes of the compound at B3LYP/6-311++G(d,p) level have been scaled down<sup>32</sup> 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, NH stretching mode for B3LYP/6-311++G(d,p) level has been assigned in  $3471 \text{ cm}^{-1}$  for DMSO and  $3490 \text{ cm}^{-1}$  for Vac. On the other hand, the same mode has been determined by HF/6-311++G(d,p) level in  $3529 \text{ cm}^{-1}$  for Vac and in  $3504 \text{ cm}^{-1}$  for DMSO. By B3LYP/6-311++G(d,p) level,  $\nu\text{CH}(\text{ar.})$  and  $\nu\text{CH}(\text{al.})$  ring modes have been assigned in  $3078\text{--}3043 \text{ cm}^{-1}$  and  $3002\text{--}2902 \text{ cm}^{-1}$ , respectively. The  $\nu\text{C}=\text{O}$  stretching mode has been assigned in  $1600 \text{ cm}^{-1}$  with a strong IR intensity. Recently, the  $\nu\text{NH}$  mode was reported in  $3395 \text{ cm}^{-1}$  and assigned in  $3505 \text{ cm}^{-1}$  by the same theory level<sup>33</sup>.

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  $^{13}\text{C}$  NMR shift for dasycarpidone compound was observed in 193.2 ppm and determined in 200.6 ppm by B3LYP level<sup>34</sup>. Besides, the aromatic ring  $^{13}\text{C}$  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  $^1\text{H}$  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  $\beta$  value.

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