Research Article

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Quantum chemical studies on structural, spectroscopic, nonlinear optical, and thermodynamic properties of the 1,2,4-triazole compound

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Abstract: In this study, the structure of 4-[4-(diethylamino)-benzylideneamino]-5-benzyl-2H-1,2,4-triazol-3(4H)-one (DBT) was examined through spectroscopic and theoretical analyses. In this respect, the geometrical, vibrational frequency, ^1H and ^{13}C -nuclear magnetic resonance (NMR) chemical shifts, thermodynamic, hyperpolarizability, and electronic properties including the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energies of DBT as a potential non-linear optical (NLO) material were investigated using density functional theory at the B3LYP level with the 6-311G basis set. ^1H and ^{13}C -NMR chemical shifts of DBT with the gauge-invariant atomic orbital and continuous set of gauge transformation methods (in the solvents) were estimated, and the computed chemical shift values displayed excellent alignment with observed ones. Time-dependent density-functional theory (TD-DFT) calculations with the integral equation formalism polarizable continuum model within various solvents and gas phases in the ground state were used to evaluate UV-vis absorption and fluorescence emission wavelengths. Thermodynamic parameters including enthalpy, heat capacity, and entropy for DBT were also calculated at various temperatures. Moreover, calculations of the NLO were carried out to obtain the title compound's electric dipole moment and polarizability properties. To illustrate the effect of the theoretical method on the spectroscopic and structural properties of DBT, experimental

data of structural and spectroscopic parameters were used. The correlational analysis results were observed to indicate a strong relationship between the experimental and theoretical results.

Keywords: schiff bases, density functional theory, quantum chemical calculations, NLO, IR spectroscopy, UV/Vis spectroscopy

1 Introduction

1,2,4-Triazole and its heterocyclic derivatives have drawn much attention in recent years on account of their structural properties such as ease of accessibility and good coordination diversity, the existence of π -conjugated heterocyclic system possessing good coordination abilities, the existence of nitrogen atoms as receptors of hydrogen bonds along with aromatic systems that contribute to π – π stacking leading to a variety of secondary non-covalent interactions [1–8]. However, their wide range of biological uses, such as the broad spectrum of biological activity, materials with optoelectronic properties, electrochemical applications, and possible energetic materials, have generated substantial interest in these compounds [9–12].

Schiff bases have a wide range of applications in many fields, including analytical chemistry, material science, and biological and pharmaceutical research. In this respect, the heterocyclic derivatives of Schiff bases derived from 1,2,4-triazole display a wide variety of biological activities such as anti-inflammatory, antibacterial, antifungal, and antileishmanial antitubercular, antioxidant, analgesic, antitumor, and pesticidal properties [13–18]. In the past two decades, a considerable amount of literature has been published on their synthesis, pharmacological, and biological properties [19–24].

Over the last decade, extensive experimental and theoretical research on the structural, spectral, electronic,

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and thermal properties of non-linear optical (NLO) materials has been conducted due to their prospective uses in laser technology, optical communication, visual information processing, and high-density optical disc data storage. The research for new and improved NLO materials is vital to meet the demands of evolving technologies. Particularly, molecular systems having π -conjugate demonstrate a significant NLO response, and these systems are thus extensively explored [25–29].

A comprehensive literature survey shows that neither theoretical calculation nor extensive spectroscopic analysis has yet been published on the structure of 4-[4-(diethylamino)-benzylideneamino]-5-benzyl-2*H*-1,2,4-triazol-3(4*H*)-one (DBT). Therefore, the primary purpose of this investigation is to develop an understanding of the structural, electrical, and spectroscopic, thermodynamic, and NLO properties for DBT through experimental and theoretical methods. This study will focus on the structural, electrical, thermal, NLO, and spectroscopic properties of 1,2,4-triazole-based azomethine, DBT, in the light of DFT-based quantum chemical calculations.

2 Materials and methods

2.1 Computational details

In accordance with the aims of the study, the optimized molecular structures, ^1H and ^{13}C nuclear magnetic resonance (NMR) chemical changes, vibrational frequencies, UV-vis spectroscopy properties, thermodynamic properties, atomic charges, and frontier molecule orbitals of DBT were determined using the DFT/B3LYP method with the 6-311G basis set. All calculations were conducted with the Gauss-View and Gaussian09 molecular programs [30,31]. The accurate molecular structure and vibrational calculations of DBT were computed using Becke-3-Lee Yang-Parr [32,33] density functional methods with the 6-311G basis set. The measured vibrational wavenumbers for the optimized molecular structure showed that the structure was stable. However, the values computed for vibrational wavenumbers involved the known systematic errors [17]. Therefore, the determined vibrational wavenumbers were scaled to 0.9614, ranging from 1,700 to 4,000 cm^{-1} , and scaled to 1.0013 below 1,700 cm^{-1} for the B3LYP/6-311G basis set. In addition, fundamental molecular vibration mode assignments were conducted using the VEDA 4 program based on the analysis of total energy distribution [34]. The optimized molecular geometries for NMR calculations of DBT were first obtained with 6-311G basis set in the gas

phase ($\epsilon = 1$), CCl_4 ($\epsilon = 2.24$), CHCl_3 ($\epsilon = 4.9$), and DMSO ($\epsilon = 46.7$) solvents through the system of integral equation formalism polarizable continuum model. The ^1H and ^{13}C NMR chemical shifts of DBT in different solvents were determined with the gauge-invariant atomic orbital (GIAO) and continuous set of gauge transformation (CSGT) methods at the B3LYP/6-311G basis set [35–41]. In the same way, UV-vis spectroscopic computations of DBT were conducted utilizing the TD-DFT/B3LYP method in the CHCl_3 ($\epsilon = 4.9$), ethanol ($\epsilon = 24.5$), and water ($\epsilon = 78.39$) solvents [42]. In addition, HOMO-1, HOMO, LUMO, and LUMO+1 energies and energy gaps of DBT were determined through the B3LYP/6-311G basis set. Meanwhile, the orbital shapes (HOMO-1, HOMO, LUMO, and LUMO+1) of the mentioned molecule were mapped in three-dimensional (3D) with the B3LYP/6-311G basis set. Using the optimized molecular structure with the B3LYP/6-311G basis set, the molecular electrostatic potential (MEP) map of DBT was drawn. Finally, Mulliken atomic charges, thermodynamic characteristics (i.e., enthalpy, entropy, and thermal capacity) at various temperatures, and NLO properties (i.e., the first hyperpolarizability and polarizability) of DBT were examined.

3 Results and discussion

3.1 Molecular structure

The optimized molecular structure for DBT is presented in Figure 1. The optimized molecular geometric properties

Figure 1: The chemical structure (top) and optimized molecular 50 structure (bottom) for DBT.

Table 1: The calculated bond lengths, dihedral angles and bond angles for DBT

Bond lengths (Å)	B3LYP	Bond angles (°)	B3LYP	Dihedral angles (°)	B3LYP
C1–C14	1.495	C14–C1–N45	126.404	N45–C1–C14–C15	0.799
C1–N45	1.314	C14–C1–N46	122.391	N45–C1–C14–H37	124.048
C1–N46	1.396	N45–C1–N46	111.205	N45–C1–C14–H38	–122.445
C2–N44	1.374	N44–C2–N46	101.767	N46–C1–C14–C15	–179.274
C2–N46	1.421	N44–C2–O49	129.621	N46–C1–C14–H37	–56.026
C2–O49	1.249	N46–C2–O49	128.613	N46–C1–C14–H38	57.482
C3–C4	1.453	C4–C3–H22	117.736	C14–C1–N45–N44	179.939
C3–H22	1.084	C4–C3–N47	120.766	N46–C1–N45–N44	0.005
C3–N47	1.303	H22–C3–N47	121.498	C14–C1–N46–C2	–179.958
C4–C5	1.409	C3–C4–C5	123.224	C14–C1–N46–N47	0.136
C4–C9	1.407	C3–C4–C9	119.426	N45–C1–N46–C2	–0.021
C5–C6	1.384	C5–C4–C9	117.349	N45–C1–N46–N47	–179.928
C5–H23	1.081	C4–C5–C6	121.493	N46–C2–N44–H21	–179.958
C6–C7	1.423	C4–C5–H23	118.776	N46–C2–N44–N45	–0.026
C6–H24	1.078	C6–C5–H23	119.731	O49–C2–N44–H21	0.045
C7–C8	1.419	C5–C6–C7	121.406	O49–C2–N44–N45	179.978
C7–N48	1.391	C5–C6–H24	118.321	N44–C2–N46–C1	0.027
C8–C9	1.388	C7–C6–H24	120.273	N44–C2–N46–N47	179.922
C8–H25	1.078	C6–C7–C8	116.852	O49–C2–N46–C1	–179.976
C9–H26	1.083	C6–C7–N48	121.494	O49–C2–N46–N47	–0.081
C10–C11	1.537	C8–C7–N48	121.652	H22–C3–C4–C5	179.360
C10–H27	1.091	C7–C8–C9	121.066	H22–C3–C4–C9	–0.558
C10–H28	1.092	C7–C8–H25	120.547	N47–C3–C4–C5	–0.889
C10–N48	1.473	C9–C8–H25	118.387	N47–C3–C4–C9	179.193
C11–H29	1.093	C4–C9–C8	121.823	C4–C3–N47–N46	–179.815
C11–H30	1.091	C4–C9–H26	119.263	H22–C3–N47–N46	–0.074
C11–H31	1.090	C8–C9–H26	118.914	C3–C4–C5–C6	179.886
C12–C13	1.538	C11–C10–H27	109.435	C3–C4–C5–H23	–0.348
C12–H32	1.091	C11–C10–H28	110.085	C9–C4–C5–C6	–0.195
C12–H33	1.092	C11–C10–N48	114.735	C9–C4–C5–H23	179.571
C12–N48	1.473	H27–C10–H28	106.001	C3–C4–C9–C8	–179.854
C13–H34	1.090	H27–C10–N48	107.093	C3–C4–C9–H26	0.288
C13–H35	1.090	H28–C10–N48	109.096	C5–C4–C9–C8	0.224
C13–H36	1.093	C10–C11–H29	110.212	C5–C4–C9–H26	–179.635
C14–C15	1.516	C10–C11–H30	111.051	C4–C5–C6–C7	–0.513
C14–H37	1.093	C10–C11–H31	111.431	C4–C5–C6–H24	179.326
C14–H38	1.093	H29–C11–H30	108.026	H23–C5–C6–C7	179.724
C15–C16	1.401	H29–C11–H31	108.126	H23–C5–C6–H24	–0.438
C15–C20	1.401	H30–C11–H31	107.870	C5–C6–C7–C8	1.148
C16–C17	1.397	C13–C12–H32	109.432	C5–C6–C7–N48	–178.253
C16–H39	1.083	C13–C12–H33	110.081	H24–C6–C7–C8	–178.687
C17–C18	1.397	C13–C12–N48	114.717	H24–C6–C7–N48	1.912
C17–H40	1.082	H32–C12–H33	106.029	C6–C7–C8–C9	–1.116
C18–C19	1.397	H32–C12–N48	107.094	C6–C7–C8–H25	178.838
C18–H41	1.082	H33–C12–N48	109.094	N48–C7–C8–C9	178.284
C19–C20	1.396	C12–C13–H34	111.450	N48–C7–C8–H25	–1.763
C19–H42	1.082	C12–C13–H35	111.004	C6–C7–N48–C10	–0.283
C20–H43	1.083	C12–C13–H36	110.195	C6–C7–N48–C12	–179.649
H21–N44	1.001	H34–C13–H35	107.882	C8–C7–N48–C10	–179.655
N44–N45	1.409	H34–C13–H36	108.125	C8–C7–N48–C12	0.979
N46–N47	1.394	H35–C13–H36	108.064	C7–C8–C9–C4	0.455
		C1–C14–C15	114.125	C7–C8–C9–H26	–179.686
		C1–C14–H37	108.134	H25–C8–C9–C4	–179.499
		C1–C14–H38	108.156	H25–C8–C9–H26	0.360
		C15–C14–H37	110.384	H27–C10–C11–H29	–61.307
		C15–C14–H38	110.368	H27–C10–C11–H30	58.365

(Continued)

Table 1: Continued

Bond lengths (Å)	B3LYP	Bond angles (°)	B3LYP	Dihedral angles (°)	B3LYP
		H37–C14–H38	105.260	H27–C10–C11–H31	178.649
		C14–C15–C16	120.623	H28–C10–C11–H29	54.812
		C14–C15–C20	120.644	H28–C10–C11–H30	174.484
		C16–C15–C20	118.732	H28–C10–C11–H31	–65.231
		C15–C16–C17	120.724	N48–C10–C11–H29	178.315
		C15–C16–H39	119.481	N48–C10–C11–H30	–62.013
		C17–C16–H39	119.794	N48–C10–C11–H31	58.271
		C16–C17–C18	120.090	C11–C10–N48–C7	–82.396
		C16–C17–H40	119.823	C11–C10–N48–C12	96.990
		C18–C17–H40	120.087	H27–C10–N48–C7	155.940
		C17–C18–C19	119.637	H27–C10–N48–C12	–24.674
		C17–C18–H41	120.181	H28–C10–N48–C7	41.632
		C19–C18–H41	120.182	H28–C10–N48–C12	–138.982
		C18–C19–C20	120.094	H32–C12–C13–H34	–178.801
		C18–C19–H42	120.080	H32–C12–C13–H35	–58.521
		C20–C19–H42	119.826	H32–C12–C13–H36	61.157
		C15–C20–C19	120.723	H33–C12–C13–H34	65.049
		C15–C20–H43	119.477	H33–C12–C13–H35	–174.671
		C19–C20–H43	119.801	H33–C12–C13–H36	–54.994
		C2–N44–H21	126.194	N48–C12–C13–H34	–58.435
		C2–N44–N45	113.897	N48–C12–C13–H35	61.845
		H21–N44–N45	119.908	N48–C12–C13–H36	–178.477
		C1–N45–N44	104.322	C13–C12–N48–C7	81.387
		C1–N46–C2	108.808	C13–C12–N48–C10	–98.000
		C1–N46–N47	120.918	H32–C12–N48–C7	–156.963
		C2–N46–N47	130.273	H32–C12–N48–C10	23.650
		C3–N47–N46	118.998	H33–C12–N48–C7	–42.622
		C7–N48–C10	121.243	H33–C12–N48–C10	137.991
		C7–N48–C12	121.058	C1–C14–C15–C16	91.215
		C10–N48–C12	117.696	C1–C14–C15–C20	–89.136
				H37–C14–C15–C16	–30.806
				H37–C14–C15–C20	148.843
				H38–C14–C15–C16	–146.748
				H38–C14–C15–C20	32.900
				C14–C15–C16–C17	179.609
				C14–C15–C16–H39	–0.525
				C20–C15–C16–C17	–0.046
				C20–C15–C16–H39	179.820
				C14–C15–C20–C19	–179.611
				C14–C15–C20–H43	0.562
				C16–C15–C20–C19	0.044
				C16–C15–C20–H43	–179.784
				C15–C16–C17–C18	0.018
				C15–C16–C17–H40	–179.948
				H39–C16–C17–C18	–179.848
				H39–C16–C17–H40	0.187
				C16–C17–C18–C19	0.012
				C16–C17–C18–H41	–179.939
				H40–C17–C18–C19	179.978
				H40–C17–C18–H41	0.026
				C17–C18–C19–C20	–0.014
				C17–C18–C19–H42	–179.986
				H41–C18–C19–C20	179.938
				H41–C18–C19–H42	–0.034
				C18–C19–C20–C15	–0.014

(Continued)

Table 1: Continued

Bond lengths (Å)	B3LYP	Bond angles (°)	B3LYP	Dihedral angles (°)	B3LYP
				C18–C19–C20–H43	179.813
				H42–C19–C20–C15	179.957
				H42–C19–C20–H43	–0.216
				C2–N44–N45–C1	0.014
				H21–N44–N45–C1	179.951
				C1–N46–N47–C3	179.938
				C2–N46–N47–C3	0.055

(bond lengths, bond angles, and dihedral angles) of DBT are given in Table 1.

Figure 1 shows the optimized molecular structure of DBT together with the atom numbering system. A potential energy surface analysis was performed to demonstrate the orientation of the imine group and phenyl in DBT. Scanning of the whole potential energy surface around N47–C3–C4–C9 was carried out using the DFT/B3LYP/6-311G level of theory. All the geometrical parameters were simultaneously relaxed during the computation, while the N47–C3–C4–C9 torsional angles were varied in steps of 0, 1, 2, 3,..., 360°. According to the potential energy surface diagram, it was observed that the C1 configuration had the lowest energy structure. The energies of C1, C2, and C3 conformations were observed to be –1124.87163 a.u. (for C1), –1124.85626 a.u. (for C2), and –1124.85629 a.u. (for C3), respectively (Figure 2). The structure was then re-optimized using the DFT/B3LYP method,

using the 6-311G basis set. The optimized geometry of DBT confirmed that the vibrational spectrum did not contain imaginary wavenumbers on true local minimum on the potential energy surface.

In contrast, the calculated values were observed to agree with the X-ray results [43]. The phenyl ring's C–C bond lengths were changed due to the introduction of the triazole ring, imine, and diethylamino group in DBT. The shortest C1–C14 bond length was 1.495 Å, while the longest C5–C6 bond was noted to be 1.384 Å by DFT/6-311G. The C–C bond lengths in the aromatic ring were recorded to be in the range of about 1.380–1.405 Å by Kalaichelvan et al. [44]. The computed C–N (C1–N46, C2–N46, C2–N44, triazole, and C7–N48, C10–N48, and C12–N48 in triazole ring) bond lengths were at 1.396, 1.421, and 1.374 Å in triazole ring and 1.391, 1.473, and 1.473 Å in the ring, respectively. In contrast, the experimentally observed C–N (C1–N46,

Figure 2: The scanned potential energy surface for DBT with DFT/B3LYP/6-311G level.

C2–N46, and C2–N44) bond lengths in the triazole ring were 1.348, 1.329, and 1.377 Å, respectively [43]. The computed bond lengths of double-bonded C1=N44 in triazole ring and C3=N47 in the imine group for DBT were 1.314 and 1.303 Å, while the bond lengths of some similar structure were reported to be at the interval of 1.300–1.320 Å [45]. Furthermore, the calculated N–N (N44–N45 and N45–N47) bond lengths in the 4-amino-1,2,4-triazole ring were 1.409 and 1.394 Å, respectively. These bond lengths were recorded as 1.380 Å for related structures [43]. The double-bonded C2=O10 bond length was determined to be 1.249 Å, which reasonably agreed with previously published values for related structures [46]. The N–H length was computed as the shortest bond in this structure with 1.001 Å. The N–H length value for related structures had been found at 0.990 Å in the literature [43]. The lengths of all C–H bonds in aromatic rings were measured in the range of 1.050–1.010 Å and agreed well with the lengths of C–H bonds in aromatic rings [44]. The N46–C1–N45 bond angle of DBT was observed to be 101.767°, and the value reported for similar structures in literature was 113.8° [43]. Moreover, the computed triazole C1–N46–C2 and N46–C2–N44 bond angles were at 108.808 and 101.767°, while bond angles reported for triazole ring were found to be 105.7 and 108.7° in the literature [43]. The geometric parameters computed by utilizing the B3LYP method and the 6-311G level were in good agreement with the experimental results in the literature [43–46].

3.2 Vibrational frequencies

The DBT had 45 atoms, and thus the standard vibration numbers were 129. All vibrations under C_1 symmetry were active in IR. The observed and computed vibrational frequencies, IR intensities, and assignments for DBT are summarized in Table 2. Moreover, the experimental IR and simulated spectra of DBT by utilizing the B3LYP/6-311G level are presented in Figure 3. In order to make a comparison between the computed wavenumbers and experimental ones, the linear correlation coefficients (R^2) shown in Table 2 are displayed in Figure 4, as well. Here, we have reported the (R^2) value of DBT as (R^2) = 0.9867 for the IR wavenumbers.

3.2.1 NH and CH vibrations

The NH stretching mode for DBT was found at 3,165 cm^{-1} in the experimental IR spectral data [17]. The NH stretching

vibration mode for DBT in our calculation was 3,574 cm^{-1} at B3LYP/6-311G level. Moreover, the NH in-plane bending vibration modes were recorded at 1,351, 1,336, and 1,146 cm^{-1} for DBT. Likewise, for DBT, the NH out-of-plane bending vibration modes existed at 540 and 319 cm^{-1} .

In aromatic compounds, the C–H stretching vibration modes emerged above 3,000 cm^{-1} [47–49]. The aromatic C–H stretching vibration modes were noted at 3,034, 3,037, 3,041, 3,040, 3,058, 3,067, 3,071, 3,090, and 3,093 cm^{-1} . Moreover, the modes that were found as combined with other vibrational ones at 1,338, 1,291, and 1,164 cm^{-1} for DBT resulted from C–H in-plane bending vibration modes and the modes found at 987, 964, 943, 895, 822, and 802 cm^{-1} for DBT were caused by C–H out of plane bending vibration modes. Calculated wavenumber values and assignments of DBT for C–H stretching, in-plane and out-plane bending modes, and other vibration modes are shown in Table 2.

3.2.2 CH₂ and CH₃ vibrations

The C–H stretching vibration modes for the aliphatic =C–H group produced from sp^2 hybrid were not observed [50–52]. From Table 2, it could be observed that the bands at 2,990, 2,982, 2,972, 2,969, 2,949, 2,939, 2,911, 2,907, 2,904, and 2,902 cm^{-1} resulted from the CH₂ and CH₃ symmetric and asymmetric stretching vibration modes for DBT. Additionally, the observed modes at 1,516, 1,501, and 1,489 cm^{-1} could be attributed to scissoring modes in the CH₂ and CH₃ groups. Moreover, symmetry bending modes of the CH₂ and CH₃ groups may be assigned to the observed modes at 1,484, 1,476, 1,475, 1,469, and 1,396 cm^{-1} for compound DBT. Similarly, rocking modes of CH₂ and CH₃ groups of DBT were recorded at 1,242, 1,164, and 1,072 cm^{-1} . The computed vibrational modes in Table 2 were found to be consistent with the experimental ones.

3.2.3 CC, CN, and NN vibrations

The vibrational CC stretching bands in aromatic rings were reported at 1,627, 1,516, 1,486, and 1,313 cm^{-1} , and the bands at 1,018, 995, 643, 631, and 626 cm^{-1} could be attributed to the vibrational CCC in-plane modes.

The C=N stretching vibration modes in 1,2,4-triazole and ring were recorded at 1,610 and 1,588 cm^{-1} in IR for DBT; the computed wavenumbers were 1,555 and 1,508 cm^{-1} . The recorded bands at 1,273, 1,146, 1,015, 988, and 657 cm^{-1} could be explained with CN stretching vibration modes in the 1,2,4-triazole ring. The detected bands at 1,205, 1,015, and 762 cm^{-1} , on the other hand, could be related to the NN stretching vibrational mode combined with others.

Table 2: Experimental and calculated (unscaled and scaled) B3LYP/6-311G level vibrational frequencies (cm^{-1}), IR intensity (km mol^{-1}), Raman intensity, force constant ($\text{mdyne } \text{\AA}^{-1}$) and probable assignments for DBT

Experimental frequencies		B3LYP 6-311G				Characterization of normal modes with potential energy distribution (PED) (%)
FTIR ^a		Unscaled	Scaled	IR intensity / _{IR}	Raman intensity S_{Raman}	
1	—	10	10	0.01	2.79	τCCCC (17) in ring + τCNNC (58) in triazole
2	—	15	15	0.13	6.07	$[\tau\text{CNNC}$ (20) + γNCCN (12)] in triazole + $[\tau\text{CCCC}$ (13) + τCNCC (12) + τCNCC (12)] in ring
3	—	29	28	0.32	3.56	$\delta\text{C}_3\text{N}_{47}\text{N}_{46}$ (20) + $\delta\text{N}_3\text{C}_1\text{C}_{14}$ (13) + $\delta\text{C}_4\text{C}_3\text{N}_{47}$ (23)
4	—	30	29	0.12	5.74	τCNNC (33) in triazole + τCCCC (40) in ring
5	—	36	35	0.31	0.2	τCCCC (56) in ring
6	—	45	43	0.63	1.55	τCNNC (10) in triazole + τCCCC (14) + τCNCC (22) + τCCNC (22) in ring
7	—	73	70	0.36	2.55	δCCC (15) + γCCCC (26) in ring
8	—	85	81	0.21	0.46	τCNNC (10) + τNCCN (16) + τCCCN (12) + τNCCN (22) in triazole
9	—	102	98	0.68	2.42	τCCNC (68) in ring
10	—	104	100	0.13	1.53	τCNCC (23) + τCCNC (32) in ring
11	—	123	119	2.61	2.1	τNNCC (25) + γNCNC (10) in triazole + γCCCN (17) in ring
12	—	146	140	2.98	1.87	$[\delta\text{NCC}_{\text{imine}}$ (17) + τCCNC (12)] in triazole ring
13	—	161	155	1.29	1.52	$[\tau\text{NNCC}$ (31) + γNCNC (10)] in triazole ring
14	—	178	171	3.64	1.33	τCCCC (12) in ring
15	—	192	185	1.1	0.55	$[\delta\text{CNC}$ (10) + τHCNC (14) + τHCCN (28)] in ring
16	—	208	200	0.91	0.48	$[\tau\text{HCCN}$ (10) + τHCCN (22)] in ring
17	—	218	210	3.5	0.74	τCCCC (26) in ring
18	—	237	228	1.85	5.13	τCCCC (39) in ring
19	—	276	266	1.97	1.12	$[\delta\text{NCC}$ (19) + τHCNC (14)] in ring
20	—	289	278	3.39	3.47	τCCCC (23) in ring + $\tau\text{C}_3\text{C}_4\text{N}_{46}\text{N}_{47}$ (10) + γNCCN in triazole (24)
21	—	312	300	0.1	0.57	$[\delta\text{CNC}$ (10) + δCCN (34)] in ring
22	—	331	319	2.2	0.44	$[\tau\text{CNNC}$ (34) + γONNC (14) + γNCNC (10)] in triazole
23	—	338	325	0.84	0.08	$[\delta\text{CCC}$ (58) + τHCCC (16)] in ring
24	—	343	329	13.23	1.19	$[\delta\text{OCN}$ (10) + δNNC (11)] in triazole + $[\delta\text{NCC}$ (16) + δCCN (15)] in ring
25	—	401	385	0.67	0.91	δCCN (14) + τCCCC (15) in ring + $\tau\text{C}_4\text{C}_3\text{N}_{47}\text{N}_{46}$ (19)
26	—	423	406	27.5	1.79	$[\delta\text{OCN}$ (20)] in triazole + τHCCC (16) in ring
27	—	423	407	0.05	0.07	τHCCC (12) in ring
28	—	438	421	1.83	1.59	$[\delta\text{CNC}$ (10) + τCCCC (19)] in ring
29	—	448	430	6.63	0.63	$[\delta\text{CNC}$ (15) + τCCCC (24)] in ring
30	—	471	453	16.99	0.92	$[\delta\text{CCN}$ (26) + τCCCC (12)] in ring
31	—	492	473	2.5	3.03	$[\tau\text{CCCC}$ (31) + γCCCC (21)] in ring
32	—	519	499	2.12	0.25	$[\delta\text{NCC}$ (12) + δCNC (23) + τCCN (13)] in ring
33	—	548	527	27.07	0.89	δCNC (13) + γNCCC (13) in ring
34	—	562	540	89.01	2.22	τHNNC (41) in triazole
35	—	566	544	42.94	1.04	τHNNC (43) in triazole + γNCCC (12) in ring
36	—	571	549	34.49	5.87	δOCN (16) in triazole + δCCC (15) in ring
37	—	622	598	16.52	3.16	$[\delta\text{OCN}$ (12) + δCNN (11) in triazole] + δCCC (19) in ring
38	—	651	626	4.01	1.57	δCCC (10) in ring + $\gamma\text{N}_{46}\text{C}_{14}\text{N}_{45}\text{C}_1$ (24)
39	—	657	631	3.99	4.84	δCCC (27) in ring + $\gamma\text{N}_{46}\text{C}_{14}\text{N}_{45}\text{C}_1$ (12)
40	683 m	669	643	0.51	11.57	$[\nu\text{CC}$ (10) + δCCC (56)] in ring
41	—	684	657	18.2	4.53	νNC (14) in ring
42	—	720	692	12.35	0.38	$[\tau\text{CNNC}$ (12) + γONNC (67)] in triazole
43	—	721	693	1.15	20.9	τCCCC (43) in ring
44	770 s	730	702	82.6	12.16	τHCCC (69) in ring

(Continued)

Table 2: Continued

Experimental frequencies		B3LYP 6-311G				Characterization of normal modes with potential energy distribution (PED) (%)
FTIR ^a		Unscaled	Scaled	IR intensity I_{IR}	Raman intensity S_{Raman}	
45	—	757	727	2.5	1.79	[τ HCCC (10) + τ CCCC (13) + γ CCCC (23)] in ring + γ N ₄₈ C ₆ C ₈ C ₇ (31)
46	—	779	749	3.06	8.71	δ HNC (19) in triazole + τ HCCC (13) in ring
47	—	792	762	2.44	6.3	[ν NC (14) + ν NN (17) + δ CNN (22)] in triazole
48	—	810	778	5.52	1.83	τ HCCN (48)
49	—	812	780	27.02	8.74	τ HCNC (22) in ring
50	—	818	786	13.36	9.38	ν CC (15) in ring
51	817 m	834	802	3.72	0.88	τ HCCC (91) in ring
52	—	852	819	12.19	23.25	ν CC (10) in ring
53	—	855	822	59.95	0.59	τ HCCC (74) in ring
54	—	874	840	0.02	1.37	τ HCCC (53) in ring
55	—	888	854	7.14	19.56	ν CC (31) in ring + δ C ₄ C ₃ N ₄₇ (14)
56	—	919	883	0.34	12.81	ν CC (19) in ring
57	—	931	895	0.58	7.64	ν CC (66) in ring
58	—	948	911	0.29	0.75	[δ HCC (30) + τ HCCC (30)] in ring
59	—	953	916	2.64	2.06	τ HCCC (55) in ring
60	—	981	943	0.31	0.57	τ HCCC (73) in ring
61	—	998	960	0.03	0.02	[τ HCCC (16) + τ CCCC (22)] in ring
62	—	1,003	964	0.09	0.89	τ HCCC (55) in ring
63	—	1,022	983	48.56	20.17	ν CC (14) in ring + δ N ₄₄ N ₄₅ C ₁ (24)
64	—	1,026	987	0.07	1.23	[τ HCCC (63) + τ CCCC (21)] in ring
65	—	1,028	988	46.32	31.8	ν NC (23) + ν CC (50) in ring
66	—	1,032	992	8.37	1.06	δ CCC(30) in ring
67	—	1,035	995	16.31	29.27	[ν CC (28) + δ CCC (31)] in ring
68	—	1,055	1,014	15.8	9.8	τ H ₂₂ C ₃ N ₄₇ N ₄₆ (80)
69	—	1,056	1,015	27.69	61.75	[ν NC(17) + ν NN (50)] in triazole
70	—	1,059	1,018	13.81	1.77	[δ CCC(44) + δ HCC (11)] in ring
71	—	1,096	1,054	5.45	5.93	ν N ₄₈ C ₁₀ (14) + ν CC(28) + τ HCCN (13) + τ HCNC (13) in ring
72	—	1,115	1,072	6.72	0.28	[ν CC (36) + δ HCC (22)] in ring
73	—	1,123	1,080	40.49	18.94	[ν CC (10), τ HCNC (33)] in ring
74	—	1,134	1,090	27.68	1.02	[ν NC(24) + τ CCN (12) + τ HCCN (17)] in ring
75	—	1,165	1,120	5.94	56.46	[δ NCC (13) + δ HCC(28)] in ring
76	—	1,192	1,146	36.67	311.39	ν N ₄₄ C ₂ (33)
77	—	1,201	1,154	43.8	6.76	δ H ₂₄ C ₆ C ₅ (24) + ν N ₄₄ C ₂ (10)
78	—	1,211	1,164	0.03	3.32	δ HCC (66) in ring
79	—	1,226	1,178	0.83	9.66	[ν CC (21) + δ HCC (55)] in ring
80	—	1,234	1,186	71.33	326.11	[ν CC (10) + δ HCC (22)] in ring
81	—	1,236	1,188	0.13	5.03	[ν C ₁₅ C ₂₀ (10) + δ HCC (64)] in ring
82	—	1,237	1,190	105.64	300.71	[ν NC (13) + δ HCC (39)] in ring
83	—	1,243	1,195	2.56	28.79	[ν CC (37) + δ HCC (10)] in ring
84	—	1,253	1,205	91.07	354.63	[ν NC (12) + ν NN (11) + δ CNN (25)] in triazole
85	—	1,292	1,242	20.77	61.65	[ν C ₅ C ₄ (25) + δ HCC (12)] in ring
86	—	1,318	1,267	374.3	6.12	[ν NC (14) + δ HCC(21)] in ring
87	—	1,324	1,273	105.76	7.28	[ν CC (12) + τ HCCC(12)] in ring, [ν NC (11) + δ HCN (11)] in triazole
88	—	1,336	1,284	32.9	35.99	[ν CC (11) + δ HCC (31)] in ring
89	—	1,346	1,294	0.11	2.29	[ν CC (68) + δ HCC (25)] in ring
90	—	1,365	1,313	32.89	62.97	ν CC (26) in ring
91	—	1,383	1,329	9.39	32.25	δ HCC (56) in ring
92	—	1,390	1,336	69.43	13.29	ν O ₄₉ C ₂ (12) + δ H ₂₁ N ₄₄ N ₄₅ (70)

(Continued)

Table 2: Continued

Experimental frequencies		B3LYP 6-311G				Characterization of normal modes with potential energy distribution (PED) (%)
FTIR ^a		Unscaled	Scaled	IR intensity I_{IR}	Raman intensity S_{Raman}	
93	—	1,392	1,338	0.5	0.28	δHCC (76) in ring
94	—	1,403	1,348	241.89	85.33	[δHCC (10) + τHCCN (37)] in ring
95	—	1,405	1,351	33.5	13.3	τHCNC (60) in ring
96	—	1,418	1,363	65.64	245.01	[νCC (12) + τHCCC (26)] in ring + δH ₂₂ C ₃ N ₄₇ (27)
97	—	1,444	1,388	9.98	4.22	wCH ₂ (58)
98	—	1,448	1,392	39.03	79.94	[νNC (12) + δHCC (27) + wCH ₂ (25)] in ring
99	—	1,452	1,396	24.96	4.4	wCH ₂ (68)
100	—	1,464	1,464	130.25	118.62	δH ₂₂ C ₃ N ₄₇ (28)
101	—	1,476	1,419	13.97	311.77	vCC (36) in ring
102	—	1,502	1,444	5.95	0.73	[vCC (24) + δHCC (42)] in ring
103	—	1,510	1,452	40.87	36.86	δH ₃₈ C ₁₄ H ₃₇ (89)
104	—	1,528	1,469	3.02	11.22	wCH ₂ (50)
105	—	1,535	1,475	6.85	32.45	wCH ₂ (50)
106	—	1,536	1,476	0.95	21.54	wCH ₂ (70)
107	—	1,544	1,484	6.44	30.09	wCH ₂ (32)
108	—	1,546	1,486	14.55	0.27	[vCC (11) + δHCC (56)] in ring
109	—	1,548	1,489	6.15	3.46	wCH ₂ (79)
110	—	1,562	1,501	37.35	50.41	wCH ₂ (43)
111	1,588 s	1,569	1,508	172.28	3.64	[νN ₄₈ C ₇ (11) + δHCC (13)] in ring
112	—	1,577	1,516	16.01	1167.3	[vCC (40) + δCCC (12)] in ring
113	—	1,604	1,542	85.19	29.59	νNC (56) in triazole + τHCCC (10) in ring
114	1,610 s	1,618	1,555	166.72	4836.81	νNC (38) in triazole + δH ₂₂ C ₃ N ₄₇ (14)
115	—	1,627	1,564	1.17	10.38	[vCC (59) + δCCC (11)] in ring
116	—	1,649	1,585	14.41	51.36	vCC (47) in ring
117	—	1,654	1,590	323.29	361.6	vCC(48) in ring
118	1,700 s	1,703	1,637	400.78	61.51	[νOC (61) + νNC (13)] in triazole
119	—	3,019	2,902	6.17	48.4	v _s CH ₂ (23) + v _s CH ₃ (46)
120	—	3,021	2,904	49.47	148.84	v _s CH ₂ (65) + v _s CH ₂ (22)
121	—	3,024	2,907	35.45	58.28	v _s CH ₂ (49) + v _s CH ₃ (36)
122	—	3,028	2,911	83.38	324.07	v _s CH ₂ (31) + v _s CH ₃ (49)
123	—	3,029	2,911	10.22	125.72	v _{as} CH ₂ (99)
124	—	3,057	2,939	4.99	38.13	v _{as} CH ₂ (80) + v _{as} CH ₂ (99)
125	—	3,057	2,939	2.23	24.96	v _{as} CH ₂ (85)
126	—	3,068	2,949	30.01	221.3	v _{as} CH ₃ (47) + v _{as} CH ₂ (44)
127	—	3,088	2,969	63.93	168.86	v _{as} CH ₃ (60) + v _{as} CH ₂ (28)
128	—	3,092	2,972	51.26	70.1	v _{as} CH ₃ (12) + v _{as} CH ₂ (56)
129	—	3,105	2,984	9.55	8.82	v _{as} CH ₃ (93)
130	—	3,110	2,990	83.41	32.77	v _{as} CH ₃ (50) + v _{as} CH ₂ (28)
131	—	3,153	3,031	0.87	21.44	νC ₃ H ₂₂ (96) in triazole
132	—	3,156	3,034	9.31	9.07	vCH (97) in ring
133	—	3,159	3,037	2.46	108.51	vCH (94) in ring
134	3,054 s	3,163	3,041	12	73.76	vCH (100) in ring
135	—	3,170	3,048	21.79	111.29	vCH (67) in ring
136	—	3,181	3,058	55.42	42.72	vCH (94) in ring
137	—	3,191	3,067	4.44	32.65	vCH (94) in ring
138	—	3,195	3,071	30.53	374.28	vCH (86) in ring
139	—	3,215	3,090	24.59	33.59	vCH (95) in ring
140	—	3,217	3,093	21.07	165.95	vCH (97) in ring
141	3,165 m	3,717	3,574	89.44	219.64	νNH (100)

v, stretching; δ, bending; γ, out-of-plane bending; τ, torsion; s, strong; m, medium; w, weak; v, very. IR intensities (km mol⁻¹); S_R, Raman scattering activities (Å⁴ amu⁻¹).

^aThe experimental frequency values have been taken from ref. [17].

Figure 3: IR spectra simulated for DBT with DFT/B3LYP/6-311G level.

3.2.4 CO vibrations

The stretching C=O vibration modes usually appear as a strong peak in the mid-transition area at $870\text{--}1,540\text{ cm}^{-1}$ [51–53]. In this area, the position of the C=O stretching mode depends on the electronic/mass effects and physical situation of the surrounding substitutes, intermolecular and intramolecular hydrogen bonding as well as conjugations [50–54]. Thus, the peak at $1,700\text{ cm}^{-1}$ could be allocated to the C=O vibration mode in the triazole ring from Table 2, while the recorded band was $1,637\text{ cm}^{-1}$ [17]. In this respect, the band showing the CO stretching vibration of the studied molecule was found at $1,336\text{ cm}^{-1}$. Furthermore, the computed values at 692, 598, 549, 400,

and 329 cm^{-1} could be referred to as the CO bending modes.

3.3 ^{13}C and ^1H NMR isotropic chemical shift analysis

The isotropic chemical shift analysis in NMR spectroscopy enables us to classify relative ionic species and measure reliable magnetic properties that provide precise predictions of molecular geometries [55–58]. In this respect, the compound's optimized molecular geometries were obtained with the B3LYP/6-311G level utilizing the IEFPCM solvent model in CCl_4 ($\epsilon = 2.2$), chloroform ($\epsilon = 4.9$), and

Figure 4: The correlation graph of IR wavenumbers for DBT.

DMSO ($\epsilon = 46.7$). The ^1H and ^{13}C NMR chemical shift values were computed at the same level using the GIAO and CSGT approaches, based upon the compound's optimized molecular geometries. The experimentally obtained and computed chemical shifts of the mentioned molecule are presented in Table 3. In comparing the computed ^1H and ^{13}C NMR chemical shift values with the experimental ones, we presented the linear correlation graphics of the compound by presenting the results given in Table 3. Accordingly, the values (R^2) for ^{13}C NMR chemical shift values of DBT in various solvents (DMSO, carbon tetrachloride, and chloroform) were found to be 0.9977 (DMSO), 0.9978 (CCl_4), and 0.9978 (CHCl_3) with the GIAO approach and 0.9937 (DMSO), 0.9940 (CCl_4), and 0.9939 (CHCl_3) with the CSGT approach, respectively. Furthermore, the values (R^2) for ^1H NMR chemical shift values were recorded to be 0.8939 (DMSO), 0.8893 (CCl_4), and 0.8882 (CHCl_3) with the GIAO approach and 0.5827 (DMSO), 0.5830 (CCl_4), and 0.5689 (CHCl_3) with the CSGT approach, respectively (Figure 5).

Our data analysis showed that ^{13}C NMR chemical shift values for the title molecule were significant, as predicted [57,58]. In Table 3, the ^{13}C NMR chemical shift value of DBT was noted at 155.74 ppm for the C2 carbon atom double-bonded to the oxygen in a carbonyl group [17]. The computed ppm values for the C2 atom in CCl_4 ($\epsilon = 2.2$), chloroform ($\epsilon = 4.9$), and DMSO ($\epsilon = 46.7$) solvents were theoretically determined to be 153.04 (DMSO), 152.59 (CCl_4), and 152.83 ppm (CHCl_3) with the GIAO approach and 147.60 (DMSO), 147.44 (CCl_4), and 147.54 ppm (CHCl_3) with the CSGT approach, respectively. Based on the ^{13}C NMR chemical shift values of the C1 carbon atom bound to electronegative nitrogen atoms in 1,2,4-triazole ring and C3 carbon atom with sp^2 hybridized in imine group, we observed 150.53 and 152.18 ppm, respectively [17]. Likewise, the ^{13}C -NMR chemical shift values for these carbon atoms (C1 and C3 bound to nitrogen atoms in the triazole ring) were recorded as 154.07 (DMSO), 152.94 (CCl_4), and 153.47 ppm (CHCl_3) with the GIAO approach and 154.21 (DMSO), 153.39 (CCl_4), and 153.77 ppm (CHCl_3) with the CSGT approach, respectively. Moreover, the ^{13}C -NMR chemical shift values for these carbon atoms (C10 and C12) which bound to other nitrogen atoms in the compound were found to be 44.47 ppm, while these values of the carbons mentioned above in DMSO, CCl_4 , and chloroform were observed to be 60.65 (DMSO), 60.72 (CCl_4), and 60.69 ppm (CHCl_3) with the GIAO approach and 60.62 (DMSO), 60.68 (CCl_4), and 60.65 ppm (CHCl_3) with the CSGT approach, respectively. The carbon atoms in the aromatic ring were observed at the interval 111.70–146.78 ppm, while these values of the carbons mentioned above were reported at the interval 107–149 ppm.

On the other hand, the recorded ^1H NMR chemical shifts at intervals 6.69 and 7.54 ppm may be allocated to the hydrogen atoms in the aromatic ring [42]. The ^1H -NMR chemical shift values for the hydrogen atoms bound to the diethylamino group in the compound were found to be 1.09 and 3.37 ppm, while these computed values were observed at the interval 0.09–5.10 ppm.

The experimentally observed and theoretically computed shift values of all protons and carbon atoms in alkyl groups, triazole, and aromatic rings are presented in Table 3.

The computed and experimental values were found to be closely correlated (Figure 5);

$$\delta_{\text{exp}}(\text{ppm}) = 0.9780\delta_{\text{calc}} + 3.6122 \quad (R^2 = 0.9977) \quad (\text{in DMSO for } ^{13}\text{C-NMR/GIAO method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 0.9827\delta_{\text{calc}} + 3.2340 \quad (R^2 = 0.9978) \quad (\text{in } \text{CCl}_4 \text{ for } ^{13}\text{C-NMR/GIAO method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 0.9804\delta_{\text{calc}} + 3.4171 \quad (R^2 = 0.9978) \quad (\text{in } \text{CHCl}_3 \text{ for } ^{13}\text{C-NMR/GIAO method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.397\delta_{\text{calc}} - 19.505 \quad (R^2 = 0.9937) \quad (\text{in DMSO for } ^{13}\text{C-NMR/CSGT method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.145\delta_{\text{calc}} - 19.999 \quad (R^2 = 0.9940) \quad (\text{in } \text{CCl}_4 \text{ for } ^{13}\text{C-NMR/CSGT method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.1424\delta_{\text{calc}} - 19.759 \quad (R^2 = 0.9939) \quad (\text{in } \text{CHCl}_3 \text{ for } ^{13}\text{C-NMR/CSGT method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.0416\delta_{\text{calc}} + 0.7677 \quad (R^2 = 0.8939) \quad (\text{in DMSO for } ^1\text{H-NMR/GIAO method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.0482\delta_{\text{calc}} + 0.8188 \quad (R^2 = 0.8893) \quad (\text{in } \text{CCl}_4 \text{ for } ^1\text{H-NMR/GIAO method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.0434\delta_{\text{calc}} + 0.8011 \quad (R^2 = 0.8882) \quad (\text{in } \text{CHCl}_3 \text{ for } ^1\text{H-NMR/GIAO method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.6233\delta_{\text{calc}} - 3.226 \quad (R^2 = 0.5877) \quad (\text{in DMSO for } ^1\text{H-NMR/CSGT method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.5565\delta_{\text{calc}} - 2.7557 \quad (R^2 = 0.5630) \quad (\text{in } \text{CCl}_4 \text{ for } ^1\text{H-NMR/CSGT method})$$

$$\delta_{\text{exp}}(\text{ppm}) = 1.6091\delta_{\text{calc}} - 3.1072 \quad (R^2 = 0.5689) \quad (\text{in } \text{CHCl}_3 \text{ for } ^1\text{H-NMR/CSGT method}).$$

3.4 UV-vis spectroscopy and HOMO–LUMO analyses

The compound's experimental absorption wavelength values were found to be 358 and 216 nm in ethanol solvent. The absorption wavelengths (λ), oscillator strengths (f), and excitation energies of the UV-vis absorption spectra for DBT were determined utilizing TD-DFT/B3LYP methods with 6-311G level in various solvents (in chloroform [$\epsilon = 4.9$], ethanol [$\epsilon = 24.55$], and water [$\epsilon = 78.39$]). The theoretical absorption wavelengths of DBT were 352.54,

Table 3: The calculated and experimental ^{13}C and ^1H NMR isotropic chemical shifts for DBT (with respect to TMS, all values in ppm)

Nucleus	GIAO method				CSGT method		
	$\delta_{\text{exp.}}^*$	δ_{calc} (DMSO)	δ_{calc} (CCl_4)	δ_{calc} (Chloroform)	δ_{calc} (DMSO)	δ_{calc} (CCl_4)	δ_{calc} (Chloroform)
1-C	150.53	154.07	152.94	153.47	154.21	153.39	153.77
2-C	155.74	153.04	152.59	152.83	147.60	147.44	147.54
3-C	152.18	150.52	150.29	150.42	154.32	154.22	154.29
7-C	146.78	148.98	148.19	148.60	147.31	146.59	146.97
15-C	136.68	135.37	135.20	135.26	136.12	135.84	135.96
5-C	130.25	132.84	132.76	132.80	135.38	135.31	135.35
16-C	129.46	129.56	129.54	129.56	131.07	131.11	131.10
20-C	129.46	129.44	129.39	129.42	130.94	130.94	130.94
19-C	129.09	127.41	127.00	127.18	130.27	129.93	130.08
17-C	129.09	127.36	126.97	127.14	130.24	129.91	130.05
18-C	127.34	126.12	125.70	125.89	129.08	128.74	128.89
9-C	130.25	123.94	124.51	124.24	124.55	124.98	124.77
4-C	120.16	119.80	121.08	120.44	121.39	122.54	121.97
8-C	111.70	109.70	109.14	109.40	113.13	112.67	112.89
6-C	111.70	108.45	107.92	108.18	112.48	111.98	112.23
12-C	44.47	44.75	44.85	44.80	60.65	60.72	60.69
10-C	44.47	44.71	44.81	44.77	60.62	60.68	60.65
14-C	31.84	29.78	30.05	29.92	40.99	41.26	41.13
13-C	13.05	7.95	8.20	8.08	28.74	28.98	28.86
11-C	13.05	7.75	8.03	7.89	28.46	28.72	28.59
22-H	9.35	9.33	9.39	9.36	7.84	7.90	7.87
26-H	7.54	7.26	7.27	7.27	6.83	6.85	6.84
40-H	7.28	6.55	6.42	6.48	6.44	6.33	6.38
42-H	7.28	6.55	6.41	6.48	6.43	6.33	6.38
41-H	7.20	6.48	6.34	6.40	6.30	6.20	6.24
39-H	7.22	6.46	6.34	6.40	6.33	6.24	6.28
43-H	7.22	6.45	6.32	6.38	6.30	6.21	6.25
21-H	11.82	6.39	6.31	6.26	4.14	3.93	4.04
23-H	7.54	6.38	6.13	6.34	6.04	6.00	6.02
25-H	6.69	5.76	5.60	5.67	6.17	6.05	6.11
24-H	6.69	5.73	5.58	5.65	6.12	6.00	6.06
37-H	3.98	3.14	3.06	3.10	3.78	3.72	3.75
38-H	3.98	3.14	3.06	3.10	3.77	3.72	3.74
28-H	3.37	2.99	2.97	2.98	5.05	5.05	5.05
33-H	3.37	2.96	2.94	2.95	5.07	5.07	5.07
27-H	3.37	2.22	2.07	2.14	4.80	4.70	4.75
32-H	3.37	2.22	2.07	2.14	4.79	4.70	4.74
31-H	1.09	0.67	0.76	0.72	3.65	3.72	3.69
34-H	1.09	0.57	0.67	0.63	3.62	3.69	3.66
35-H	1.09	0.39	0.35	0.37	3.43	3.38	3.42
30-H	1.09	0.37	0.33	0.35	3.41	2.67	3.39
29-H	1.09	0.18	0.11	0.14	2.72	2.67	2.70
36-H	1.09	0.16	0.09	0.12	2.74	2.69	2.71

*The experimental ^{13}C and ^1H NMR isotropic chemical shift values have been taken from ref. [17].

287.01, and 277.00 nm in the chloroform/353.88, 287.74, and 278.74 nm in the ethanol solvent/353.85, 287.86, and 275.52 nm in water. The computed and experimentally observed UV parameters and simulated spectra of DBT are shown in Table 4 and Figure 6. The experimental

and computed absorption wavelength (λ) values were found to be significantly correlated:

$$\lambda_{\text{exp}}(\text{nm}) = 1.9725\lambda_{\text{calc}} - 337.37 \quad (R^2 = 1.000) \quad (\text{in } \text{CHCl}_3)$$

$$\lambda_{\text{exp}}(\text{nm}) = 1.9830\lambda_{\text{calc}} - 343.73 \quad (R^2 = 1.000) \quad (\text{in ethanol})$$

$$\lambda_{\text{exp}}(\text{nm}) = 1.9022\lambda_{\text{calc}} - 315.10 \quad (R^2 = 1.000) \quad (\text{in water}).$$

Figure 5: The correlation graphs for ^{13}C and ^1H NMR chemical shifts (a; in DMSO), (b; in CCl_4), (c; CHCl_3) with GIAO (1) and CSGT (2) methods for DBT.

It has been well acknowledged that the HOMO means the electron-filled outermost orbital and functions as an electron donor, and the LUMO is the first unoccupied innermost orbital to be unfilled by electron and acts as an electron acceptor which is called frontier molecular orbitals. Thus, the energy of the HOMO which is mainly related to the ionization potential defines the ability of electron-donating. In contrast, LUMO's energy has generally been related to the electron affinity and demonstrates electron-reception/electron-absorption capacity. Molecular chemical stability is indicated by the generated energy gap between HOMO and LUMO and is a critical parameter for determining the properties of molecular electrical transport [59]. The connections between the chemical reactivity, stability, polarizability, chemical

hardness-softness, and electronegativity of a molecule can be computed through HOMO and LUMO energy values [60]. The energy differences between HOMOs–LUMOs, electronegativity, and chemical hardness results of DBT are presented in Table 5, and the 3D representations of their HOMOs and LUMOs are displayed in Figure 7.

3.5 MEP

MEPs are used to determine the interaction between molecules, which have recently been used to interpret and predict relative sites of reactivity for the nucleophilic and electrophilic attack, to examine biological

Table 4: The experimental and calculated absorption wavelength (λ), excitation energies, and oscillator strengths (f) for DBT

Exp.* (in ethanol)	Transition	The calculated with B3LYP/6-311G level in CHCl_3 /Ethanol/Water		
		λ_{max} (nm)	Excitation energy (eV)	f (oscillator strength)
358 (17,280)	$n \rightarrow \pi^*$	352.54/353.88/353.85	3.5169/3.5035/3.5039	1.0433/1.0223/1.0156
	$\pi \rightarrow \pi^*$	287.01/287.74/287.86	4.3199/4.3089/4.3070	0.0573/0.0562/0.0558
209 (19,526)	$\pi \rightarrow \pi^*$	277.00/278.74/275.52	4.4760/4.4964/4.5001	0.0097/0.0128/0.0134

*The experimental absorption wavelength (λ) values have been taken from ref. [17].

Figure 6: UV-Vis spectra simulated with DFT/B3LYP/6-311G level in solvent phases for DBT.

identification, interactions with hydrogen bonding, molecular cluster, zeolite, and crystal behavior studies, and to compare and predict a broad range of macroscopic properties [61]. In addition, MEP defines the molecule's overall charge distribution; it demonstrates the similarities between the molecular properties such as dipole moments, partial charges, chemical reactivity, and electronegativity. The electrostatic potential on the surface is represented by different colors in our study (Figure 8). Thus, red regions indicate negative potential, and blue regions indicate positive potential. In addition, the green color sections reflect zero potential areas. The negative potentials were associated with the electrophilic attack, while the positive

Table 5: The calculated HOMO-1, HOMO, LUMO, and LUMO+1 energies, energy gap, electronegativity, and chemical hardness values for DBT

Parameters	B3LYP/6-311G
$E_{\text{HOMO-1}}$ (eV)	-6.329
E_{HOMO} (eV)	-5.323
E_{LUMO} (eV)	-1.408
$E_{\text{LUMO+1}}$ (eV)	-0.273
$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)	3.920
$E_{\text{HOMO}} - E_{\text{LUMO+1}}$ (eV)	5.056
$E_{\text{HOMO-1}} - E_{\text{LUMO}}$ (eV)	4.921
$E_{\text{HOMO-1}} - E_{\text{LUMO+1}}$ (eV)	6.056
χ (Electronegativity) (eV)	3.366
η (Chemical hardness) (eV)	1.957

Figure 7: The calculated HOMO-1, HOMO, LUMO, and LUMO+1 energy values, energy gap values for DBT.

Figure 8: The MEP map for DBT.

ones were associated with the nucleophilic attack. MEPs for the title molecule based on optimized molecular structure were determined by using B3LYP/6-311G level, and 3D

plots of MEPs are presented in Figure 8. The MEP map's negative regions were primarily located on the carbonyl oxygen atom (O49) and the nitrogen atom (N45) in the triazole ring due to their electronegative properties. The MEP map's positive region was located on the hydrogen atom bound to the nitrogen atom in the triazole ring representing the potential sites for nucleophilic attack. These sites included some knowledge of non-covalent molecular interaction regions.

3.6 NLO properties

The significance of NLO features for molecular systems is contingent upon the efficacy of electrical communication between the donating and withdrawing groups involved in intramolecular charge transfer. NLO properties originate from electromagnetic field interactions in different media to generate new fields changing in terms of phase, frequency, amplitude, or other propagation properties from the incident fields [62]. Organic molecules with substantial NLO behavior usually have a π -electron conjugated moiety replaced through an electron donor group

Table 6: The total energy (Hartree), the electric dipole moment μ (Debye), the average polarizability α_{total} (10^{-24} cm⁵ esu⁻¹), and first hyperpolarizability β_{total} (10^{-30} cm⁵ esu⁻¹) for DBT

	Urea	B3LYP
E		-1124.8716
μ_x		-4.4673
μ_y		-2.5257
μ_z		0.2412
μ	1.3197	5.1375
α_{xx}		451.3983
α_{xy}		13.8852
α_{yy}		244.0924
α_{xz}		4.2412
α_{yz}		2.2514
α_{zz}		167.0458
α		42.6093
Δ_α (esu)		37.7500
β_{xxx}		773.3342
β_{xxy}		1248.6634
β_{xyy}		246.5077
β_{yyy}		-269.2251
β_{xxz}		84.7340
β_{xyz}		20.6039
β_{yyz}		0.2402
β_{xzz}		-89.7842
β_{yzz}		-70.6770
β_{zzz}		-1.2540
β	0.1974	10.9054

Table 7: The computed Mulliken atomic charges for DBT

Atoms	Mulliken atomic charges	Atoms	Mulliken atomic charges
1C	0.5431	26H	0.1664
2C	0.7695	27H	0.1746
3C	-0.0246	28H	0.1956
4C	-0.0575	29H	0.1776
5C	-0.1530	30H	0.1805
6C	-0.2113	31H	0.1988
7C	0.3900	32H	0.1751
8C	-0.2131	33H	0.1900
9C	-0.0766	34H	0.1968
10C	-0.2228	35H	0.1844
11C	-0.4900	36H	0.1683
12C	-0.2204	37H	0.2242
13C	-0.4903	38H	0.2183
14C	-0.5570	39H	0.1565
15C	0.0304	40H	0.1507
16C	-0.1005	41H	0.1463
17C	-0.1605	42H	0.1413
18C	-0.1326	43H	0.1478
19C	-0.1613	44N	-0.6099
20C	-0.1044	45N	-0.1644
21H	0.3684	46N	-0.6542
22H	0.2396	47N	-0.1681
23H	0.1649	48N	-0.6408
24H	0.1711	49O	-0.4204
25H	0.1633		

on one end of the conjugated structure and an electron receptor group on the other, forming a “push–pull” conjugated structure [63]. Numerous research groups have examined the compatibility of practical and theoretical methodologies for the construction and characterization of highly efficient NLO materials [64–67]. We investigated the linear polarizability (α), first hyperpolarizability (β) of DBT to offer a critical overview of the NLO parameters and to evaluate using the DFT model (B3LYP) in the gas phase. The linear polarizability (α), first hyperpolarizability (β), and total static dipole moment (μ) for DBT were described utilizing x , y , and z components as [68]:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\beta = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2}$$

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$

The linear polarizability (α), first hyperpolarizability (β), and total static dipole moment (μ) of DBT were computed

at the B3LYP/6-311G level. The computed polarizability (α), first hyperpolarizability (β), and total dipole moment (μ) for the mentioned compound were observed to be $42.6093 \times 10^{-24} \text{ cm}^5 \text{ esu}^{-1}$, $10.9054 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$, and 5.1375 D, respectively (Table 6). In this vein, urea is one of the essential molecules used to determine molecular systems' NLO properties. The computed β value was determined to be around 56 times higher than that of urea ($0.1947 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) [69]. As a result, DBT can provide a foundation for the future design of effective NLO materials.

3.7 Atomic charges and thermodynamic properties

The computed Mulliken atomic charges and thermodynamic parameters for DBT through B3LYP/6-311G level in the gas phase are reported in Table 7 and Figure 9 [70]. The electronegative N44, N45, N46, N47, N48, and O49 atoms in DBT had negative atomic charge values. The charge values of all those electronegative atoms mentioned above were determined to be as -0.6099 (N44),

Figure 9: Mulliken atomic charge graph for DBT.

Figure 10: Correlation graph for DBT (a) entropy and temperature, (b) heat capacity and temperature, and (c) enthalpy and temperature.

−0.1644 (N45), −0.6542 (N46), −0.1681 (N47), −0.6408 (N48), and −0.4204 (O49) a.u. The carbon atoms (C1, C2, and C7) bonded to electronegative atoms in DBT had positive atomic charge values. The charge values of all the above-mentioned carbon atoms were recorded to be 0.5431 (C1), 0.7695 (C2), and 0.3900 (C7) a.u. The C2 atom surrounded by three electronegative atoms (N44, N46, and O49), the

C1 atom surrounded by two electronegative atoms (N45 and N46), and the C7 atom surrounded by one electronegative atom (N48) had the highest positive charge values. The other carbon atoms of DBT had, on the other hand, positive/negative charge values. In addition, all charge values of the hydrogen atoms in the DBT compound were positive.

Table 8: The computed thermodynamic functions at different temperatures for DBT

T (°K)	S_m^0 (cal mol ⁻¹ K ⁻¹)	C_p^0 (cal mol ⁻¹ K ⁻¹)	ΔH_m^0 (kcal mol ⁻¹)
100	107.969	37.92	257.794
200	143.332	63.368	262.842
298.15	174.496	90.913	270.398
300	175.073	91.443	270.567
400	205.815	119.248	281.121
500	235.558	143.555	294.296
600	263.931	163.655	309.690
700	290.743	180.121	326.906
800	315.976	193.722	345.619
900	339.703	205.085	365.576
1,000	362.03	214.671	386.577

Many thermodynamic functions, including entropy S_m^0 , heat capacity C_p^0 , and enthalpy ΔH_m^0 , are listed in Figure 10 and Table 8. As the rate of molecular vibration increased with temperature, these thermodynamic parameters were found to rise with an increase in temperature varying from 100 to 1,000°K. The correlation parameters between entropy S_m^0 , heat capacity C_p^0 , and enthalpy ΔH_m^0 and temperatures were fitted utilizing quadratic formulas, and the related fitting factors (R^2) for these thermodynamic properties were 0.1000, 0.9903, and 0.9995, respectively. The related fitting equations were as follows:

$$S_m^0(\text{cal mol}^{-1} \text{K}^{-1}) = -0.00007T^2 + 0.362T + 73.009$$

$$(R^2 = 1.0000)$$

$$C_p^0(\text{cal mol}^{-1} \text{K}^{-1}) = -0.0001T^2 + 0.3495T + 0.9903$$

$$(R^2 = 0.9991)$$

$$\Delta H_m^0(\text{kcal mol}^{-1}) = 0.0001T^2 + 0.0346T + 251.96$$

$$(R^2 = 0.9995)$$

These values showed that thermodynamic parameters including entropy S_m^0 , heat capacity C_p^0 , and enthalpy ΔH_m^0 steadily increased with temperature. The thermodynamic data could provide all the knowledge needed for future studies on DBT.

4 Conclusion

The chemical structure, vibrational frequencies, UV-vis spectroscopy, proton and carbon NMR chemical changes, HOMO and LUMO studies, thermodynamic, NLO, and molecular electronic properties for DBT were all determined by utilizing from Density Functional Theory/B3LYP method and 6-311G level. The theoretical results (DFT/B3LYP) were found to be consistent with the experimental ones based upon the optimized structure analysis. By evaluating the

results of the experimental work [17], it was determined that the theoretical vibrational frequencies, ¹H and ¹³C-NMR chemical shift values and UV spectra fit the experimental data very well. The NLO functions of DBT were determined, which revealed that it could provide the basis for the future design of efficient NLO materials. Based upon the MEP surface, the compound's most reactive site for the electrophilic attack was found to be around the nitrogen and oxygen atoms, whereas the most reactive region for the nucleophilic attack was realized to be around the NH in the triazole ring. We used HOMO–LUMO energy values for DBT to calculate parameters like the HOMO–LUMO energy gap, electronegativity, and chemical hardness values. It was observed that DBT had good stability and high chemical hardness. The linear polarizability (α), the first hyperpolarizability (β), and dipole moment (μ) were calculated, and the results showed that it could provide the basis for the future design of efficient NLO materials. The findings revealed that the entropies, enthalpies, and heat capacities went up as temperature rose due to intensities of the molecular vibrations rising as a consequence of increasing temperature.

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Code availability: ChemDraw Ultra 8.0, Gaussian 0.9, GaussView 5.0, Veda 4, Chemcraft 1.8.

Data availability statement: The datasets generated during and/or analyzed during this study are available from the corresponding author on reasonable request.

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