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Experimental Studies and DFT Calculations of a Novel Molecule Having Thieno[3,2-*b*]thiophene Fragment

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Abstract: A novel molecule of thieno[3,2-*b*]thiophene-2,5-diylbis[*N*-(4-chlorophenyl)methanimine] **(TTBM)** was synthesized using thieno[3,2-*b*]thiophene fragment, and characterized using UV-Vis, FTIR, ^{1}H NMR and LC-MS spectroscopy. Quantum chemical properties of **TTBM** were investigated via DFT method using B3LYP hybrid functional with 6-311G(d,p) basis set. Optimized molecular structure, UV, FTIR, HOMO-LUMO energies and Molecular Electrostatic Potential (MEP) characteristics of **TTBM** were studied by means of DFT. The assignments of the vibrations in the molecular structure were performed by using the VEDA4 program with potential energy distribution (PED). The experimental spectra of **TTBM** (UV-Vis and FTIR) were compared in detail with the theoretical results and were seen to be in a good agreement with each other.

Key words: DFT calculations, HOMO-LUMO energies, MEP, Vibrational analysis

Tiyeno [3,2-b]tiyofen Fragmentli Yeni Bir Molekülün Deneysel Çalışmaları ve DFT Hesaplamaları

Özet: Tiyeno[3,2-*b*]tiyofen fragmenti kullanılarak yeni bir molekül olan tiyeno[3,2-*b*]tiyofen-2,5-diilbis[N-(4-klorofenil)metanimin] **(TTBM)** sentezlendi ve UV-Vis, FTIR, ^{1}H NMR ve LC-MS spektroskopileriyle karakterize edildi. **TTBM**'nin kuantum kimyasal özellikleri, DFT metodunda B3LYP hibrit fonksiyonu ile 6-311G (d, p) temel seti kullanılarak incelendi. **TTBM**'nin optimize moleküler yapısı, UV, FTIR, HOMO-LUMO enerjileri ve moleküler elektrostatik potansiyel (MEP) özellikleri DFT yöntemi ile çalışıldı. Moleküler yapıdaki titreşimlerin atamaları, potansiyel enerji dağılımlarıyla (PED) birlikte VEDA4 programı kullanılarak gerçekleştirildi. **TTBM**'in deneysel spektrumları (UV-Vis ve FTIR) teorik sonuçlarla ayrıntılı olarak karşılaştırıldı ve birbiriyle iyi bir uyum içinde olduğu görüldü.

Anahtar kelimeler: DFT hesaplamaları, HOMO-LUMO enerjileri, MEP, Titreşim analizi

1. Introduction

The design and synthesis of conjugated organic molecules attracted attention due to their potential use as organic semiconductors in organic electronics. These molecules have important uses in solar cells, OLEDs, transistors, *etc*. Organic molecules can be processed from solution and can be applied to large area surfaces and can be modified to obtain the desired properties to be used in organic devices. These molecules can provide the advantages of tunability of physical and chemical properties via synthetic routes and also cost efficiency [1-3].

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Thiophene rings (Ts) also provide both increase of organic conjugation and stability to these organic molecules. The use of fused thiophene rings such as thienothiophene (TTs) causes the molecule to become even more electron-rich. In this case, it allows them to act as electron donors in semiconductors. Thienothiophenes have four isomers due to the orientation of the sulfur atoms in the thiophene ring, the most common of which is thieno 3,2-*b*. In molecules containing these fused ring systems, they are very important both in forming polymer structures and gaining desired electronic or optoelectronic properties. For this reason, known the theoretical and experimental properties together with the design of the structures of such small molecules will form a great basis in the formation of small or polymeric structures with the desired properties in advanced applications [2,4-6].

For this purpose, a novel molecule with thieno[3,2-*b*]thiophene fragment was designed in this study, its synthesis and characterization were carried out. The novel molecule has been both studied experimentally and theoretically. Synthesis, spectroscopic and computational studies of this title molecule (**TTBM**) are not available in the literature yet. In this presented study, spectroscopic properties were investigated by UV-Vis and FTIR, ^{1}H NMR and LC-MS spectroscopy. In addition, vibrational frequencies, optimized geometry, HOMO-LUMO energies and MEP surface properties were calculated using the DFT method.

2. Material and Method

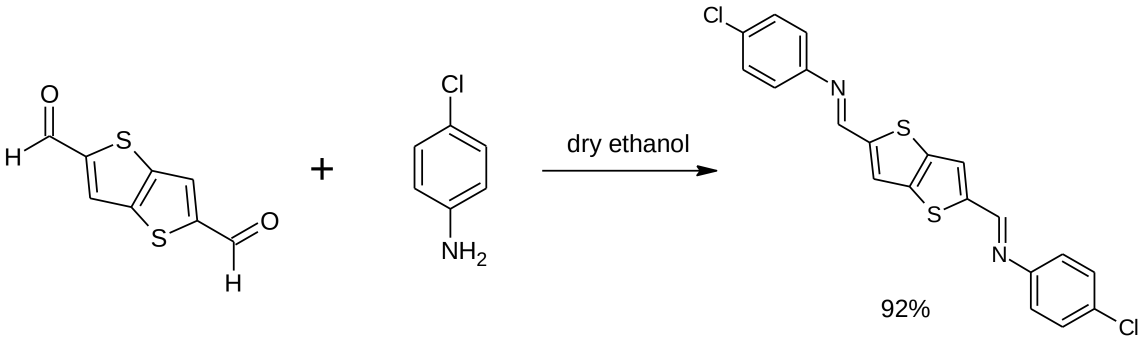
In this study, a dry environment was provided, and synthesis was performed by Schiff base condensation. The starting materials, thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde and 4-chloroaniline were purchased as Merck. Ethanol used as solvent was dried using standard methods.

2.1. Physical measurements

UV-Vis spectrum was recorded using Perkin Elmer Lambda 25 UV-Vis spectrometer and chloroform was used as the solvent. FTIR measurements were determined in solid form (ATR) with a NICOLET iS10 FTIR spectrometer. The ^{1}H NMR spectrum was performed with the TMS standard and using the DMSO-d_6 solvent. The mass spectrum (LC-MS) was recorded on Agilent 1200 Infinity HPLC/Agilent 6460 Jet Stream spectrometer.

2.2. Synthesis of the thieno[3,2-b]thiophene-2,5-diylbis[N-(4-chlorophenyl)methanimine], (TTBM)

Thieno[3,2-*b*]thiophene-2,5-dicarboxaldehyde (0.196 g, 1 mmol), 4-chloroaniline (0.255 g, 2 mmol) and dry ethanol (15 mL) were mixed and refluxed under inert atmosphere for 4 hours. The obtained light brown solid was filtered off and purified by crystallization from chloroform/methanol. m.p. 138-140 °C, yield: 92%. UV-vis: λmax = 400 nm. FTIR (ATR): ν(cm^{-1}): 3076, 2933, 1664. ^{1}H NMR (DMSO-d_6, 500 MHz): δ= 8.50 (s, 2H, -CH=N), 8.32 (s, 2H, thiophene H), 7.52 (d, 4 ArH, J=8.5 Hz), 7.29 (d, 4 ArH, J=8.5 Hz) ppm. LC-MS: m/z = 415.0 [M]$^+$ (calculated for $C_{20}H_{12}Cl_2N_2S_2$, 415.3).



Scheme 1. Synthesis of **TTBM**

3. Computational details

All computations made to investigate both spectroscopic and electronic properties of **TTBM** were performed using the Gaussian 09W program package [7]. Results obtained from theoretical calculations were depicted by means of the GausView5 program [8]. As a first step, **TTBM** was optimized and simultaneously harmonic wavenumbers in FTIR spectra were calculated using DFT/B3LYP method with the 6-311G (d,p) basis set [9]. To explain vibration frequencies in more detail, assignments were performed depending on PED analysis with VEDA 4 program [10]. All computed vibrational frequencies were scaled with 0.967 for B3LYP/6-311G(d,p) level [11]. The HOMO-LUMO energy levels were obtained from optimized molecule using the same method and basis set. By means of the optimized molecular geometry and parameters of **TTBM**, the UV-Vis values for **TTBM** were calculated via TD-DFT method with B3LYP/6-311G(d,p) level in vacuum.

4. Results

4.1. Optimized molecular geometry and HOMO-LUMO analyses

The molecular structure of **TTBM** has been optimized under DFT/B3LYP calculation and its optimized structure and ground state energy (as atomic unit [a.u.]) are presented in Figure 1. As can be seen from Figure 1, chlorine substiuted benzene rings (ring 1 and ring 4) located on both sides of thiophenes are bent where dihedral angles (in degrees) for $C_{12}N_{16}C_{17}C_{19}$ and $C_{11}N_{15}C_{27}C_{29}$ are 35.42 and -35.43, respectively.

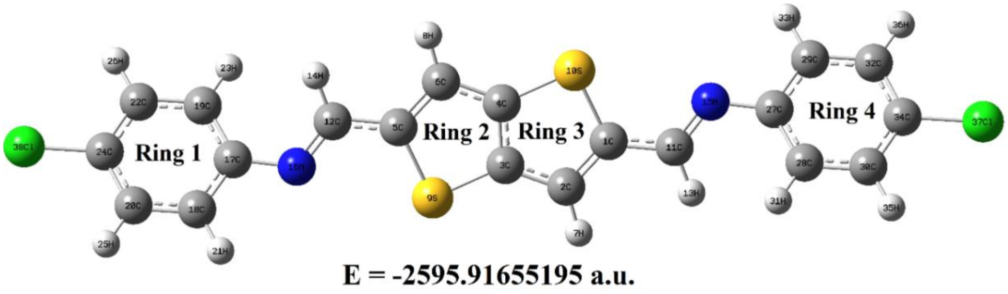


Figure 1. The optimized molecular geometry and ground state energy of the **TTBM** molecule

This structural feature, which the molecule bears, is important for their potential use in organic bulk heterojunction solar cells. Because completely planar molecular structures for donor and acceptor molecules are not desired to achieve ideal phase separation and aggregation in organic solar cells [12].

HOMO-LUMO analyzes have considerable importance to explain the electronic properties and energy values of compounds. Therefore, the frontier molecular orbitals of **TTBM** and their energy levels have been determined using DFT/B3LYP method. For **TTBM** molecule, the frontier molecular orbitals that are from HOMO-3 to LUMO+3 and their energy values are depicted in Figure 2.

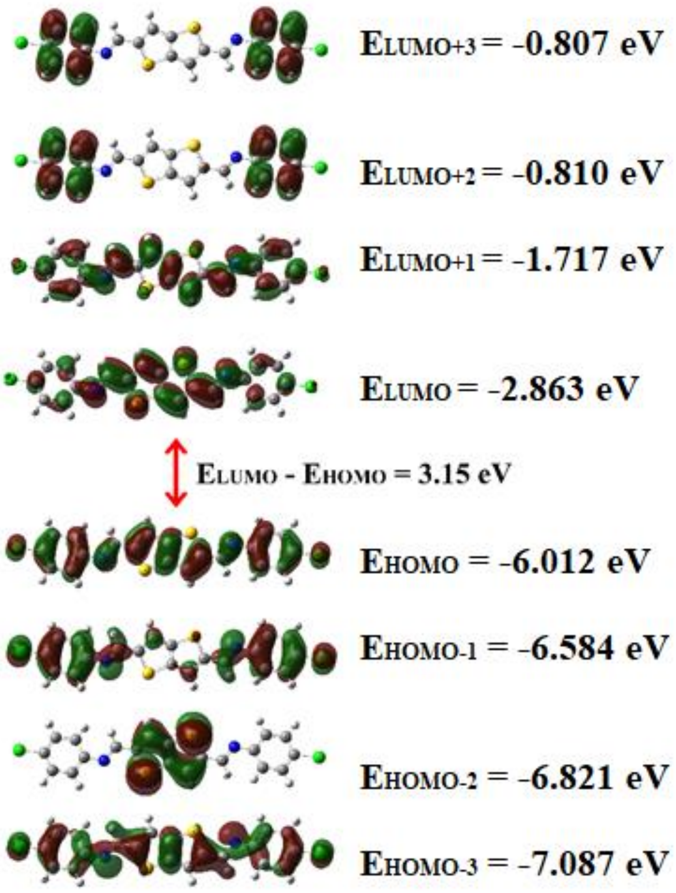


Figure 2. The frontier molecular orbitals and their energy levels for **TTBM**

HOMO-LUMO energy levels of TTBM were calculated as -6.01 eV and -2.86 eV, respectively. The electronic band gap was calculated as 3.15 eV as seen in Figure 1. HOMO orbital is almost localized on the molecule, similarly LUMO orbital is mostly localized on both thiophene rings and cyano (CN) groups. That's why, **TTBM** might be expected to function more as a donor molecule.

4.2 Experimental and theoretical analysis of UV-vis

UV-vis spectroscopy of **TTBM** was investigated both experimentally and theoretically. Experimental UV-vis spectrum of **TTBM** was recorded in the range of 300 and 800 nm in chloroform solution. Theoretical calculations for UV-vis were performed using TD-DFT/B3LYP with 6-311G (d,p) basis set. Both experimental and theoretical computed UV-vis. spectra of **TTBM** are shown in Figure 3.

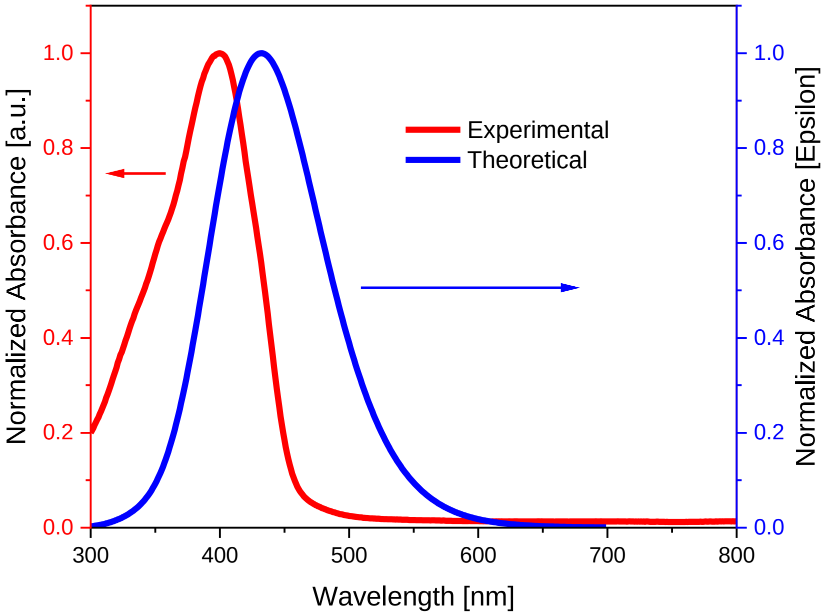


Figure 3. Experimental and computed UV-vis. spectra of molecule

As shown in Figure 3, the strong absorption maxima for **TTBM** was recorded at 400 nm and 432 nm experimentally and theoretically, respectively. The experimental and the theoretical UV-vis. parameters, related transitions and excitation energies for **TTBM** are given in Table 1.

Table 1. The experimental and computed UV-Vis. parameters of the **TTBM** molecule

Exp. λ (nm)	**Transitions**	**The calculated UV-Vis. parameters with DFT-B3LYP/6-311 G(d,p) level**			
		$\lambda_{max.}$ (nm)	**Major transition**	**Excitation energy (eV)**	***f* (oscillator strength)**
400	π→π*	432.36	H→L	2.8676	1.6337
-	π→π*	354.61	H-2→L	3.4964	0.0577

The strong absorption peak (π→π*) is at 400 nm in experimental measurement. Theoretical band (π→π*) obtained from computed spectra is at 432 nm. The most possible electron transition in a molecule is known to be probable between HOMO (H) and LUMO (L) energy levels. Using computed UV-vis. results in Table 1, It can be said that the highest oscillator strength value, which is 1.6337 corresponds to HOMO and LUMO transition. The other oscillator strength value (0.0577) from computed results and its major contribution, which was observed at 354.61 nm can be assigned π→π* electronic transition.

4.3 Vibrational analysis

The thieno[3,2-*b*]thiophene-2,5-diylbis[N-(4-chlorophenyl)methanimine] molecule **(TTBM)** consists 38 atoms and gives 108 vibrational modes. In this study, experimental infrared vibrations are compared to calculated IR and Raman vibrations (Table 2). The experimental FTIR (ATR) and simulated IR and Raman spectra of the **TTBM** molecule are presented in Figure 4.

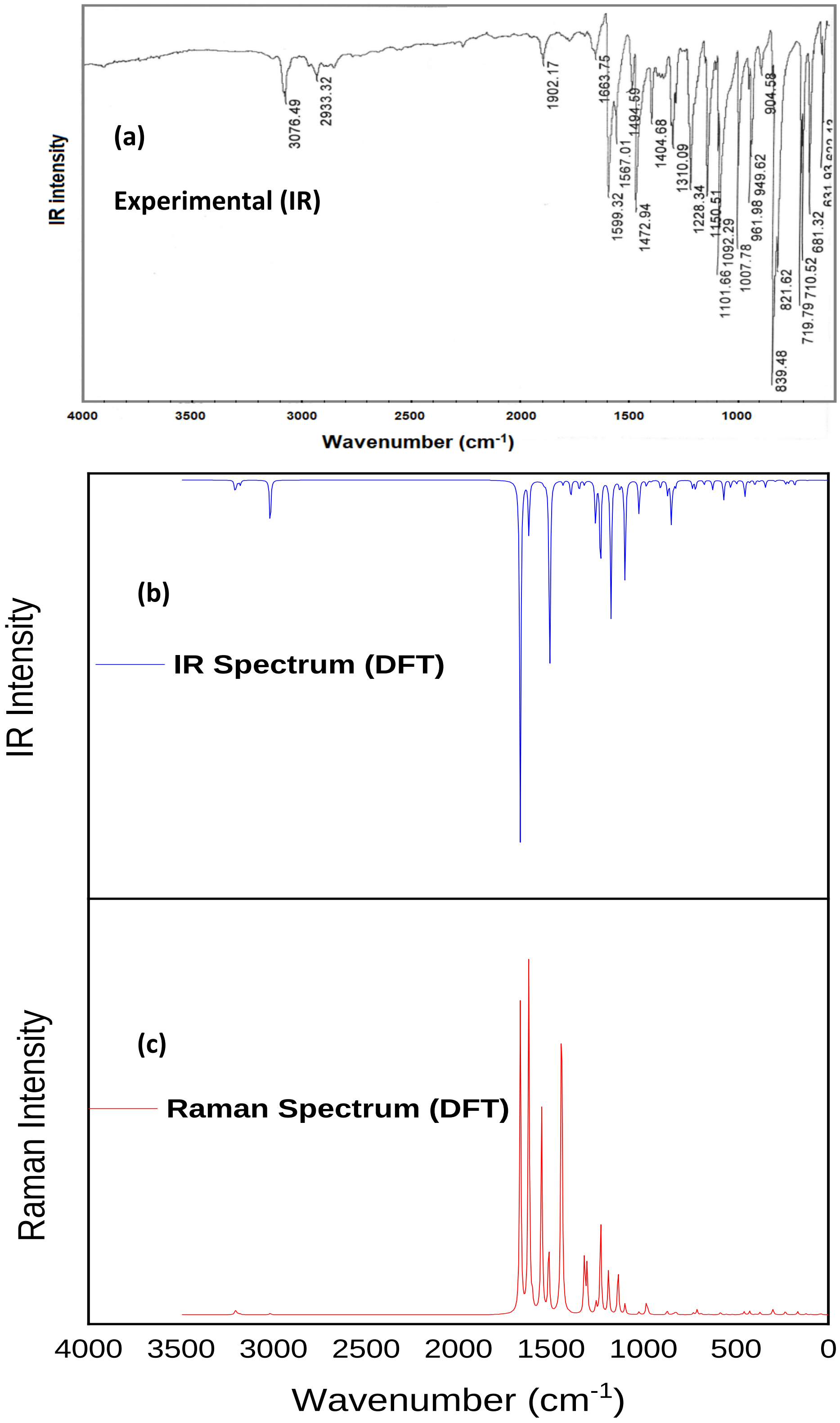


Figure 4. Experimental (a) and simulated (b) FTIR spectrum and simulated Raman spectrum (c) of the **TTBM** molecule.

Table 2. Vibrational frequencies (experimental and computed (cm^{-1})) with their assignments for the **TTBM** molecule.

Assignments (PED%≥10%)	**Experimental (cm^{-1})**	**The calculated vibrational parameters with B3LYP/6-311(d,p) level**			
	IR	**Unscaled frequencies (cm^{-1})**	**Scaled frequencies (cm^{-1})**	$\mathbf{I_{IR}}$	$\mathbf{S_{Raman}}$
Antisym. νCH(99) [in ring 2+ring 3]	-	3210	3104	14.533	0.183
Sym. νCH(98) [in ring 2+ring 3]	-	3210	3104	0.016	166.690
νCH(97) [in ring 1+ring 4]	-	3206	3100	0.769	355.009
νCH(97) [in ring 1+ring 4]	3076	3206	3100	8.660	31.573
νCH(73) [in ring 1+ring 4]	-	3201	3096	1.508	227.540
νCH(73) [in ring 1+ring 4]	-	3201	3096	7.488	45.832
νCH(95) in ring 1	-	3191	3086	2.147	89.569
νCH(95) in ring 4	-	3191	3086	2.568	74.918
νCH(82) in ring 1+ring 4	-	3179	3074	1.103	92.138
νCH(82) in ring 1+ring 4	-	3179	3074	9.711	10.452
Sym. ν[$C_{12}H_{14}$+ $C_{13}H_{13}$] (99)	-	3018	2919	0.114	189.887
Antisym. ν[$C_{12}H_{14}$+ $C_{13}H_{13}$] (99)	2933	3018	2918	104.656	0.206
ν $C_{11}N_{15}$ (39) + ν $C_{12}N_{16}$ (23)	-	1666	1611	13.622	30067.948
ν $C_{12}N_{16}$ (38) + ν $C_{11}N_{15}$ (22)	1664	1665	1611	777.336	524.579
[νCC in ring 1 + νCC in ring 4] (17)	1599	1620	1566	0.008	33645.730
[νCC in ring 1 + νCC in ring 4] (18)	-	1619	1566	120.830	2.370
νCC (54) in ring 1 + δring (11) in ring 4	1567	1600	1548	0.130	646.016
νCC (43) in ring 4 + δring (13) in ring 1	-	1600	1548	0.213	393.352
νCC (58) [in ring 2 + ring 3 +ring 4] + δHCC (14) [in ring 2 + ring 3]	1495	1551	1499	0	19549.888
νCC (43) [in ring 2 + ring 3 +ring 4]	-	1537	1487	6.655	0.007
δHCC (28) in ring 1 + δHCC (27) in ring 2	-	1512	1462	0	6845.455
δHCC (24) in ring 1 + δHCC (24)) in ring 4 + νCC (11) [in ring 2 + ring 3]	1473	1507	1457	458.211	0.003
νCC (54) [in ring 2 + ring 3]	-	1443	1395	0	32971.904
νCC (34) [in ring 1 + ring 2 + ring 3 +ring 4] + δHCC (17) in ring 4+ δHCC (16) in ring 1	1405	1435	1388	0	588.655
νCC (28) [in ring 1 + ring 2 + ring 3 +ring 4] + δHCC (18) in ring 1 + δHCC (17) in ring 4	-	1434	1387	9.855	0.016
δ$H_{13}C_{11}N_{15}$ (17) + δ$H_{14}C_{12}N_{16}$ (17)	-	1402	1356	0	60.144
νCC (40) [in ring 2 + ring 3]+ δHCC (15) [in ring 2 + ring 3] + δ$H_{13}C_{11}N_{15}$ (11) + δ$H_{14}C_{12}N_{16}$ (11)	-	1392	1346	39.940	0.001
νCC (27) [in ring 2 + ring 3] + δ$H_{13}C_{11}N_{15}$ (23) + δ$H_{14}C_{12}N_{16}$ (23)	1310	1347	1303	23.071	0
δHCC (26) in ring 1 + δHCC (26) in ring 4	-	1321	1277	0	1699.745
δHCC (43) in ring 4 + δHCC (42) in ring 1	-	1319	1276	9.9162	0.003
δHCC (19) in ring 1 + δHCC (19) in ring 4 + νCC (11) in ring 1	-	1318	1275	0	3902.106
νCC (42) in ring 1 + νCC (13) in ring 4	-	1308	1265	1.129	0.014

Table 2. (Continued)

νCC (42) in ring 1 + δ$H_{13}C_{11}N_{15}$ (11) + δ$H_{14}C_{12}N_{16}$ (11)	-	1305	1262	0	4269.570
ν$C_{11}C_1$ (13)	1228	1258	1217	101.380	0.097
νCC (27) [in ring 2 + ring 3+ ring 4] +ν$C_{11}C_1$ (11)	-	1256	1215	0.0082	1053.159
ν$N_{15}C_{27}$ (12) + ν$N_{16}C_{17}$ (12) + δHCC (10) [in ring 2 + ring 3]	-	1232	1191	212.939	0.614
ν$N_{15}C_{27}$ (15) + ν$N_{16}C_{17}$ (15)	-	1231	1191	0.015	8356.809
δHCC (35) in ring 4 + δHCC (34) in ring 1	1151	1190	1151	4.816	0.007
δHCC (36) in ring 1 + δHCC (36) in ring 4	-	1189	1150	0	4008.986
δHCC (53) [in ring 2 + ring 3] + νCC (10) [in ring 2 + ring 3]	1102	1176	1137	304.362	0.0002
δHCC (52) [in ring 2 + ring 3] + νCC (15) [in ring 2 + ring 3]	-	1137	1099	0	4040.659
δHCC (34) in ring 4 + δHCC (28) in ring 1	-	1128	1091	15.576	2.872
δHCC (34) in ring 1 + δHCC (27) in ring 4	-	1128	1091	2.607	17.384
νCC (25) in ring 1 + νCC (23) in ring 4 + ν$Cl_{38}C_{24}$ (10)	-	1099	1063	0.129	901.089
νCC (27) in ring 1 + νCC (23) in ring 4 + ν$Cl_{37}C_{34}$ (10)	-	1099	1063	225.586	0.511
δHCC (49) in ring 1 + δHCC (24) in ring 4	1008	1024	990	0.009	240.396
δHCC (48) in ring 1 + δHCC (26) in ring 4	-	1024	990	78.360	0.026
τHCNC(53) + τHCCC (29) [in ring 2 + ring 3]	962	984	951	0.036	973.462
τHCNC(61) + τHCCC (10) [in ring 2 + ring 3]	-	984	951	12.828	2.686
τHCCC (37) in ring 4 + τHCCC (26) in ring 1	-	975	943	2.051	7.169
τHCCC (37) in ring 1 + τHCCC (27) in ring 4	-	975	943	0.042	355.181
τHCCC (30) in ring 1 + τHCCC (30) in ring 4	905	958	926	3.409	0.0003
τHCCC (31) in ring 1 + τHCCC (30) in ring 4	-	958	926	0	9.397
νSC (51) [in ring 2 + ring 3]	-	908	878	20.208	0
δCCC (11) in ring 1	-	872	843	0	319.276
δCCC (12) in ring 1	839	869	841	31.374	0.0003
τHCCC (19) in ring 1 + τHCCC (19) in ring 4	-	849	821	0.025	13.026
τHCCC (20) in ring 4 + τHCCC (19) in ring 1	822	849	821	97.644	0.004
τHCCC (77) [in ring 2 + ring 3]	-	839	811	0	73.835
τHCCC (72) [in ring 2 + ring 3]	-	837	809	10.509	0
τHCCC (29) in ring 1 + τHCCC (29) in ring 4 + δCCC (10) [in ring 2 + ring 3]	-	829	801	0	122.415
τHCCC (43) in ring 1 + τHCCC (43) in ring 4	-	825	798	13.860	0

Table 2. (Continued)

τHCCC (19) in ring 1 + τHCCC (19) in ring 4 + δCCC (14) [in ring 2 + ring 3] + νCC (11) [in ring 2 + ring 3]	-	822	795	0	172.351
τHCCC (10) in ring 1	720	734	710	17.180	0.0001
τHCCC (17) in ring 1	711	730	706	0	151.249
τHCCC (14) in ring 1	-	718	694	22.512	0
-	681	710	687	0	401.500
δSCC (51) [in ring 2 + ring 3]	-	688	665	0	104.772
δCCC (39) [in ring 2 + ring 3] + δSCC (13) [in ring 2 + ring 3]	-	672	650	10.621	0.0004
δCCC (28) in ring 4 + δCCC (22) in ring 1	-	647	625	0	31.325
δCCC (27) in ring 4 + δCCC (22) in ring 1	632	646	625	0.127	0.0001
[γ $S_9C_2C_4C_3$ + γ$S_{10}C_3C_6C_4$] (40)	-	634	613	0	6.695
νSC (12) [in ring 2 + ring 3]	-	626	605	21.008	0
ν$Cl_{37}C_{34}$ (11) + ν$Cl_{38}C_{24}$ (11) + δCCC (11) [in ring 2 + ring 3]	-	583	564	0	167.155
[τ$C_1C_2C_3C_4$ + τ$C_6C_5C_{12}N_{16}$ + τ$C_{28}C_{30}C_{34}C_{32}$ + τ$C_{32}C_{29}C_{27}C_{15}$] (19) + [γ$S_9C_2C_4C_3$ + γ$S_{10}C_3C_6C_4$] (10)	-	566	547	44.323	0
[γ$S_9C_2C_4C_3$ + γ$S_{10}C_3C_6C_4$] (13) + [τ$C_5C_{12}N_{16}C_{17}$ + τ$C_{11}C_1C_2C_3$] (11)	-	550	532	0	35.034
δ[$S_9C_3C_2$ + $S_{10}C_4C_6$] (10)	-	528	511	17.678	0
[γ$S_9C_2C_4C_3$ + γ$S_{10}C_3C_6C_4$] (10)	-	518	501	0	20.816
δ[$S_9C_3C_2$ + $S_{10}C_4C_6$] (24) + δCCC (13) [in ring 2 + ring 3]	-	496	480	8.242	0
δ$C_{29}C_{27}N_{15}$ (10) + δ$N_{16}C_{17}C_{19}$ (10)	-	471	456	0	45.751
νSC (59) [in ring 2 + ring 3] + δCCC (25) [in ring 2 + ring 3]	-	455	440	0	220.248
δ$N_{16}C_{17}C_{19}$ (10)	-	451	436	38.353	0
τCCCC (27) in ring 1 + τCCCC (25) in ring 4	-	426	412	5.001	0.0001
τCCCC (29) in ring 1 + τCCCC (26) in ring 4	-	426	412	0	262.591
τ[$C_5C_{12}N_{16}C_{17}$ + $C_{11}C_1C_2C_3$] (11)	-	398	384	11.610	0
ν$Cl_{37}C_{34}$ (17) + ν$Cl_{38}C_{24}$ (17)	-	394	381	0	27.186
δ[$S_9C_3C_2$ + $S_{10}C_4C_6$] (14)	-	374	361	2.944	0
γ $Cl_{37}C_{30}C_{32}C_{34}$ (14) + γ $Cl_{38}C_{20}C_{22}C_{24}$ (13)	-	370	358	0	168.535
τCCCC (13) [in ring 2 + ring 3] + γ $Cl_{37}C_{30}C_{32}C_{34}$ (12) + γ $Cl_{38}C_{20}C_{22}C_{24}$ (11)	-	341	329	16.069	0
δ$Cl_{38}C_{24}C_{22}$ (24) + δ $Cl_{37}C_{34}C_{32}$ (22)	-	304	294	0	88.326
[τ$C_5C_{12}N_{16}C_{17}$ + τ$C_{11}C_1C_2C_3$] (16) + τ$N_{15}C_{11}C_1C_2$ (12) + [γ$S_9C_2C_4C_3$ + γ$S_{10}C_3C_6C_4$] (12) + [τ$C_2C_3C_4C_6$ + τ$C_3C_4C_6N_5$ + τ$C_4C_6C_5C_{12}$ + τ$C_{29}C_{27}N_{15}C_{11}$] (10)	-	299	289	0	361.303
δ$Cl_{37}C_{34}C_{32}$ (33)+ δ$Cl_{38}C_{24}C_{22}$ (32)	-	287	278	3.352	0
δ$C_{11}C_1C_2$ (11)+ δ$Cl_{37}C_{34}C_{32}$ (10)	-	233	225	0	228.934
[γ$S_9C_2C_4C_3$ + γ$S_{10}C_3C_6C_4$] (45) + [τ$C_2C_3C_4C_6$ + τ$C_3C_4C_6N_5$ + τ$C_4C_6C_5C_{12}$ + τ$C_{29}C_{27}N_{15}C_{11}$] (12) + τ$N_{15}C_{11}C_1C_2$ (11)	-	231	223	8.958	0.0002
-	-	216	208	6.921	0

Table 2. (Continued)

$\gamma Cl_{38}C_{20}C_{22}C_{24}$ (10) + $\gamma Cl_{37}C_{30}C_{32}C_{34}$ (10)	-	184	178	2.040	0
[$\tau C_2C_3C_4C_6$ + $\tau C_3C_4C_6N_5$ + $\tau C_4C_6C_5C_{12}$ + $\tau C_{29}C_{27}N_{15}C_{11}$] (50)	-	182	176	10.759	0
-	-	166	160	0	227.755
-	-	121	117	0	74.177
-	-	114	110	1.051	0
-	-	95	92	0	20.246
[$\tau C_2C_3C_4C_6$ + $\tau C_3C_4C_6N_5$ + $\tau C_4C_6C_5C_{12}$ + $\tau C_{29}C_{27}N_{15}C_{11}$] (18)	-	67	65	0.157	0
$\tau N_{15}C_{11}C_1C_2$ (13)	-	50	48	0	19.690
$\tau C_{12}N_{16}C_{17}C_{18}$ (12)	-	40	39	0	52.094
-	-	35	33	0	16.327
-	-	32	31	0.411	0.0001
-	-	19	18	0.5728	0
-	-	11	11	0.104	0
R^2	**0.9991**				

ν, stretching;, δ, in-plane bending; τ, torsion; γ, out-of-plane bending, I_{IR}, IR intensity (km/mol); S_{Raman}, Raman scattering activity (Å4/amu) PED, Potential Energy Distribution.

C-H vibrations

The presence of aromatic rings in the molecular skeleton and C-H bonds on the linker groups led to excessive C-H vibration. Generally, in FTIR, C-H stretching occurs in the 3300-3000 cm^{-1} as multiple medium and weak bands [13]. The CH stretching in ring 1 and ring 4 is recorded at 3076 cm^{-1} as experimentally and this band is assigned at 3100 cm^{-1} with 97% PEDs as theoretically. The C-H in plane bending vibration usually occurs as mixed with other vibrations in the range of 1400-900 cm^{-1}, while the CH out-of-plane bending (τHCCC or torsion CH) is observed in the region 650-1000 cm^{-1} [14,15]. The other determined vibrations in the region of CH in plane bending are 1008 (990), 1102 (1137), 1151 (1151), 1405 (1388) and 1473 (1457) cm^{-1} in experimental (scaled theoretical) notation. Also CH out of- plane bending vibrations are 711 (706), 720 (710), 822 (821) and 905 (926) cm^{-1}. The C-H in-plane vibrations for azomethine group are found at 1310 cm^{-1} and the corresponding theoretical value is 1303 cm^{-1}.

C-C and C-N vibrations

Generally, the aromatic C-C stretching vibrations occur in the range of 1400-1650 cm^{-1} [16]. It is also intertwined with some vibrations in this range. The C-C stretching vibrations in aromatic groups of the **TTBM** are summarized in Table 2**.** These vibrational frequencies appear at 1473 (1457), 1495 (1499), 1567 (1548) and 1599 (1566) cm^{-1} with experimental (scaled theoretical) notation. The characteristic C=N stretching vibrations of azomethine compounds usually appear in 1600-1700 cm^{-1} [17-19]. The azomethine C_{11}=N_{15} stretching band was observed at 1664 cm^{-1} in FT-IR spectra while it is computed at 1611 cm^{-1}. The C-N single bond stretching vibration in the azomethine group is found at experimentally 1310 cm^{-1}, calculated as 1303 cm^{-1}.

C-S vibrations

In general, it is not easy to determine the band of the C-S stress vibration. It can be seen in various intensities and in a wide band range. In the thiophene ring, this band is usually seen at 873-650 cm^{-1} [15, 20-21]. In this study, since C-S stretching vibrations are in the fingerprint region, the vibration does not appear clearly, but theoretically it is assigned at 878 cm^{-1}.

C-Cl vibrations

The C-Cl stretching vibrations are usually in the band of 800-600 cm^{-1} [22]. In this work, the C-Cl stretching vibrations are observed at 564 cm^{-1}. The small changes for this band are expected in the different ring systems.

4.4 MEP Surface analysis

Molecular Electrostatic Potential (MEP) is a useful tool to explain the regional reactivity of compounds. MEP is comprised of interaction by nuclei and electrons in the molecular system. Molecular surface properties of a system can be determined by charge distribution on the surface of the compound [23]. The MEP surface of **TTBM** was investigated by DFT/B3LYP method with 6-311G(d,p) level. The three-dimensional charge distribution of MEP for **TTBM** is depicted in Figure 5.

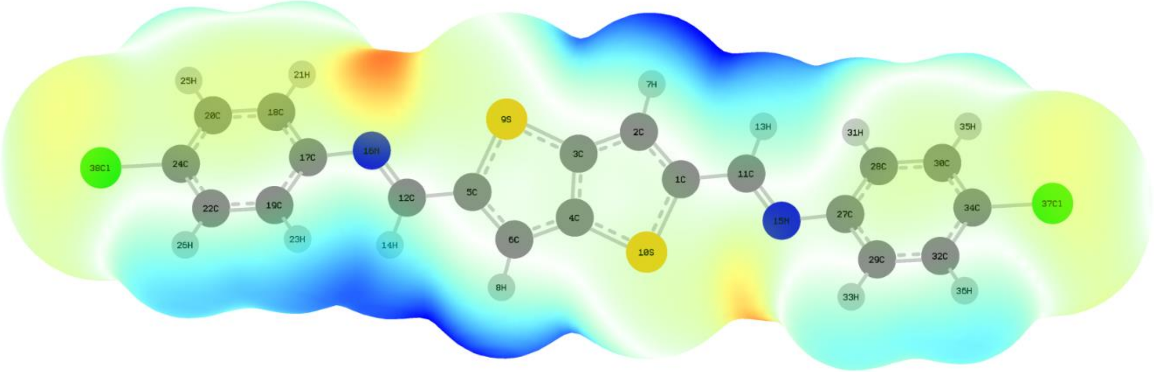


Figure 5. The MEP surface of **TTBM** molecule

As can be seen from Figure 5, negative electrostatic potential regions are represented with red color, whereas positive electrostatic potential regions are represented with blue color. The negative electrostatic potential regions (red sites) of **TTBM** are mainly located around N15 and N16 atoms and the calculated electron density value for both of the nitrogen atoms is found as -0.030 a.u. The positive electrostatic potential regions (blue sites) of **TTBM** are mainly placed around H7 and H8 atoms and the calculated electron density value for both of the hydrogen atoms is found as 0.037 a.u. Electron density values of nitrogen and hydrogen atoms located on TTBM molecule are found to be similar. This result might be attributed to the symmetrical structure of **TTBM** molecule.

5. Conclusion and Comment

A novel molecule called *thieno[3,2-b]thiophene-2,5-diylbis[N-(4-chlorophenyl)methanimine]* (**TTBM**) was investigated both as experimentally and theoretically. The optimized molecular structure, HOMO-LUMO analysis and related energies, MEP surface analysis and all computational processes for **TTBM** were performed using DFT/B3LYP method with 6-311G (d,p) basis set. FTIR spectra of **TTBM** were recorded experimentally and also were calculated using DFT/B3LYP method. Experimental and theoretical results were compared and found to be in agreement with the value of $R^2 = 0.9991$. For the title compound, experimental and computational UV-Vis absorption spectra were studied in detail to provide information about the electronic structure of the molecule. HOMO-LUMO analysis provided important data for charge transfer analysis in the molecule. In addition, the properties of the compound such as the susceptibility to reactions and reactivity were revealed by MEP surface analysis. The herein obtained results clearly show that the **TTBM** molecule can be used in many applications, especially in the field of photovoltaics.

Author Statement

Cigdem Yorur Goreci: Investigation/ Material/ Instrument Supply/ Formal Analysis/ Original Draft writing/ Review and Editing

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Conflict of Interest

As the author of this study, I declare that I do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the author of this study, I declare that I do not have any ethics committee approval and/or informed consent statement.

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