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Theoretical studies of molecular structure and vibrational spectra of *O*-ethyl benzoylthiocarbamate

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Abstract

O-Ethyl benzoylthiocarbamate has been synthesized and characterized by elemental analysis and FT-IR. The crystal structure was determined by X-ray diffraction analysis. Title compound crystallizes in the orthorhombic space group $Pna2_1$, with $Z = 4$. Unit cell parameters $a = 9.941(3)$ Å, $b = 9.352(3)$ Å, $c = 10.962(3)$ Å and $V = 1019.1(5)$ Å^3. The molecular geometry and vibrational frequencies of *O*-ethyl benzoylthiocarbamate in the ground state has been calculated using the Hartree–Fock and density functional using Becke's three-parameter hybrid method with the Lee, Yang, and Parr correlation functional (B3LYP) methods with 3-21G and 6-31G(d) basis sets. The computational frequencies are in good agreement with the observed results. Comparison of the observed fundamental vibrational frequencies of *O*-ethyl benzoylthiocarbamate and calculated results by density functional B3LYP and Hartree–Fock methods indicate that B3LYP is superior to the scaled Hartree–Fock approach for molecular vibrational problems.

Keywords: *O*-Ethyl benzoylthiocarbamate; Crystal structure; DFT; HF; Infrared spectrum; Molecular calculations

1. Introduction

Thiocarbamate derivatives have received much attention due to their interesting technological [1] and biological applications [2]. Most notably, acylthiocarbamate derivatives are used as biosensors [3], elastase inhibitors [4], and they can exhibit antineoplastic and antiinflammatory [5] effects. *O*-Alkyl-*N*-acylthiocarbamate derivatives have been proposed as intermediates for regio- and chemoselective deoxygenation of primary and secondary aliphatic alcohols [6]. In addition, *O*-alkyl-*N*-aroylthiocarbamates are useful as selective extractants of heavy metal ions in water solutions [7]. These derivatives are also employed in studies of liquid–liquid extractions of silver(I) ions [8]. The synthesis, characterization and structure on some thiocarbamate derivatives have been studied [9–15]. The crystal structures of some derivatives have been reported in the literature are those of *O*-isopropyl-*N*-(2-furoyl)thiocarbamate [9], *O*-benzyl-*N*-(2-furoyl)thiocarbamate [10], *O*,*O*′-diethyl-*N*,*N*′-(*p*-phenylenedicarbonyl)-bis(thiocarbamate) [11], and *O*,*O*′-dimethyl-*N*,*N*′-(*m*-phenylenedicarbonyl)-bis(thiocarbamate) [12].

IR spectroscopy is usually considered as the most important experimental method for chemists. The experimental and theoretical vibrational spectrum assignment of thiocarbamate derivatives has not been studied previously. Consideration of all these factors motivated us to undertake the vibrational spectroscopic studies of *O*-ethyl benzoylthiocarbamate.

The aim of this work is to calculate the molecular geometry and vibrational spectra of *O*-ethyl benzoylthiocarbamate by applying the Hartree–Fock and density functional using Becke's three-parameter hybrid method with the Lee, Yang, and Parr correlation functional methods with 3-21G and 6-31G(d) basis sets. The calculated geometric parameters and vibrational frequencies were analyzed and compared with obtained experimental results.

2. Experimental

2.1. Synthesis

A solution of benzoyl chloride (0.01 mol) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate

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(0.01 mol) in acetone (30 cm^3). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of ethanol (0.01 mol) in acetone (30 cm^3) was added dropwise and the resulting mixture was stirred for 2 h. Cold water (250 cm^3) was added and then the solution filtered. The solid product was washed with water and purified by recrystallisation from ethanol/dichloromethane mixture (1:1). Anal. Calcd. for $C_{10}H_{11}NO_2S$: C, 57.4.; H, 5.3; N, 6.7. Found: C, 57.2; H, 5.2; N, 6.8.

2.2. Instrumentation

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of the *O*-ethyl benzoylthiocarbamate were registered using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000–525 cm^{-1}; number of scans: 250; resolution: 1 cm^{-1}). Elemental analyses were carried out on a Carlo Erba MOD 1106 instrument. Single crystal X-ray data were collected on a Bruker AXS Smart Apex CCD, using monochromated Mo Kα radiation. The structure was solved by direct and conventional Fourier methods. Full-matrix least-squares refinement based on F^2. All but hydrogen atoms refined anisotropically, H-atoms on idealized positions with 'riding' model. Programs used for calculations: SHELXTL [16]. Further details concerning data collection and refinement are given in Table 1.

Table 1
Summary of crystallographic data and parameters of the title compound

Empirical formula	$C_{10}H_{11}NO_2S$
Formula weight	209.26
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pna*2(1)
Unit cell dimensions	$a = 9.941(3)$ Å, $b = 9.352(3)$ Å, $c = 10.962(3)$ Å
Volume	1019.1(5) $Å^3$
Z	4
Density (calculated)	1.364 Mg/m^3
Absorption coefficient	0.290 mm^{-1}
F(0 0 0)	440
Crystal size	0.40 mm × 0.22 mm × 0.20 mm
Theta range for data collection	2.86–28.08°
Index ranges	$-13 \leq h \leq 13$, $-12 \leq k \leq 12$, $-14 \leq l \leq 13$
Reflections collected	7685
Independent reflections	2135 [R(int) = 0.0497]
Completeness to theta = 28.08°	99.2%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.9443 and 0.8929
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2135/1/127
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0444$, $wR2 = 0.1014$
R indices (all data)	$R1 = 0.0524$, $wR2 = 0.1052$
Absolute structure parameter	0.14(12)
Largest difference between peak and hole	0.342 and −0.278 einstein $Å^{-3}$

2.3. Calculations

The molecular structure of the *O*-ethyl benzoylthiocarbamate in the ground state is optimized by Hartree–Fock and density functional using Becke's three-parameter hybrid method with the Lee, Yang, and Parr correlation functional methods with the standard 3-21G and 6-31G(d) basis sets. The vibrational frequencies were also calculated with these methods. These calculations were carried out using Gaussian 03W program package on a double Xeon/3.2 GHz processor with 4 GB RAM [17]. The frequency values computed at these levels contain known systematic errors [18]. We therefore, have used the scaling factor values of 0.8929, 0.9613, 0.9085, and 0.9614 for HF/6-31G(d), B3LYP/6-31G(d), HF/3-21G, and B3LYP/3-21G, respectively [19]. The assignment of the calculated wavenumbers is aided by the animation option of GaussView 3.0 graphical interface for gaussian programs, which gives a visual presentation of the shape of the vibrational modes [20].

3. Results and discussion

The molecular structure and packing diagram of *O*-ethyl benzoylthiocarbamate is depicted in Figs. 1 and 2, respectively. Selected bond lengths and angles of the compound are presented in Table 2. The C(8)–O(2) bond distance (1.318(3) Å) indicates double bond character in agreement with literature data (d(C–O) = 1.290(6) Å [9] and d(C–O) = 1.300(7) Å [15]. The C(7)–N(1) (1.378(3) Å) and C(8)–N(1) (1.370(3) Å) distances show usual C sp^2–N sp^2 single bond character. Thus π–π conjugation is observed along the S(1)–C(8)–O(2), but not along O(1)–C(7)–N(1) and N(1)–C(8)–S(1), as reported by Schröder et al. [21] and Morales et al. [9]. S(1)–C(8) (1.619(3) Å) and O(1)–C(7) (1.205(3) Å) are double bonds. O(1)–C(7) bond length compares well with that from other thiourea derivatives (d(C=O) = 1.213(3) [22]; 1.224(2) [23]; 1.216(2) [24]) but S(1)–C(8) bond is shortened (d(C=S) = 1.676(4) [25]; 1.664(2) [22]; 1.6696(17) [23]; 1.666(2) [24]). Crystal packing shows intermolecular hydrogen bonds N1–H···O1($x + 0.5$, $-y + 0.5$, z) which link molecules to endless rows along [1 0 0].

The structure of the title compound shown in Fig. 1 is very flexible. It has got several conformations (Fig. 3). To establish the most stable conformation as the initial point for further calculations, the molecule was submitted to a rigorous conformation analysis around the free rotation bonds. This study was performed with the software Spartan 04 [26]. Energetics gathered in Table 3 shows that the Conformer 1 is the most stable. But comparison of the theoretical and experimental geometry of the title compound shows that the X-ray parameters fairly well reproduce the geometry of the Conformer 4. Therefore, further in this paper, we focus on this particular form of the title compound.

The optimized structure parameters of *O*-ethyl benzoylthiocarbamate calculated at ab initio-HF and density functional theory-B3LYP levels with the standard 3-21G and 6-31G(d)

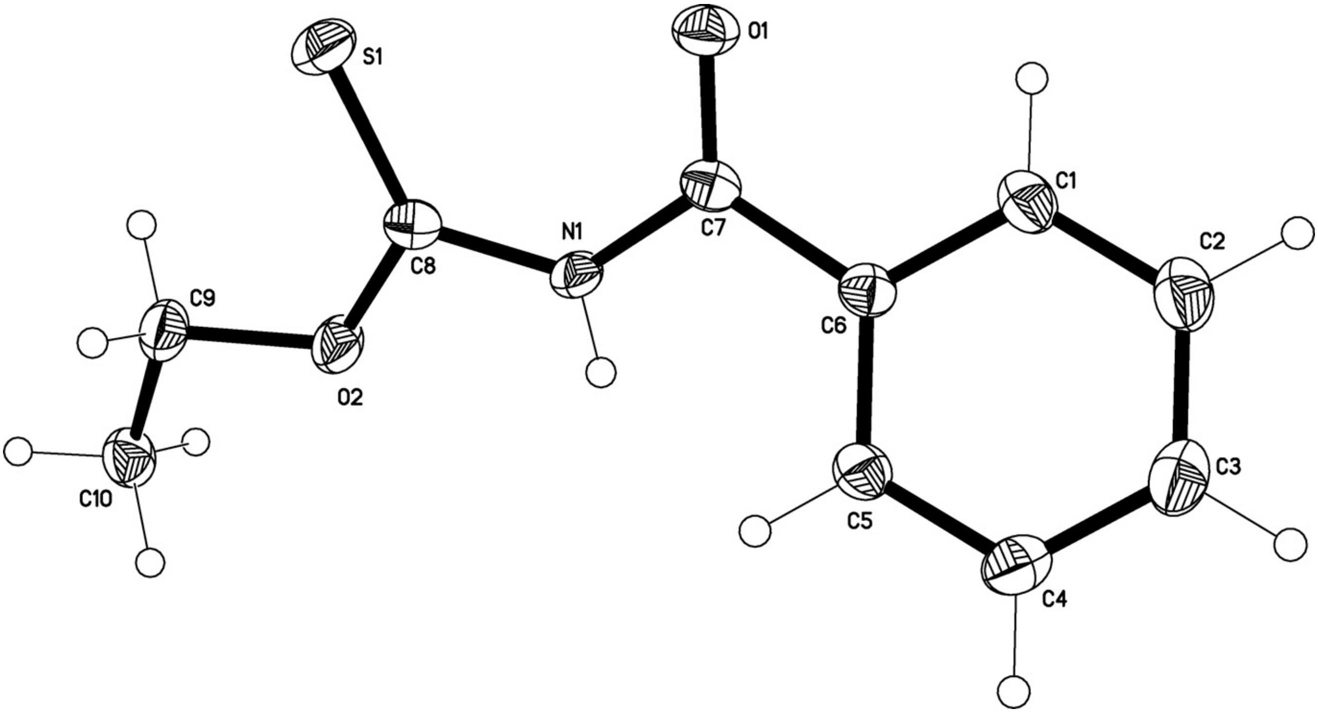


Fig. 1. The structure of *O*-ethyl benzoylthiocarbamate. Thermal ellipsoids are shown at the 50% probability level.

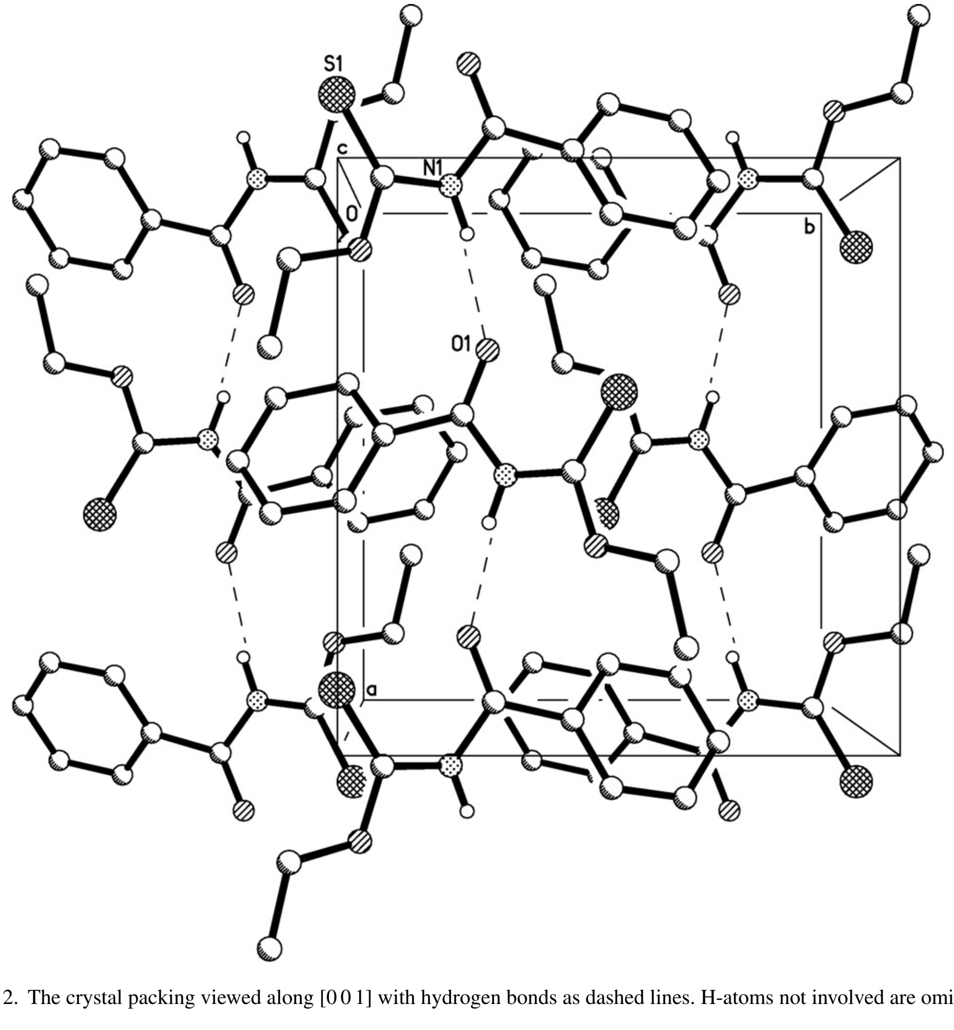


Fig. 2. The crystal packing viewed along [0 0 1] with hydrogen bonds as dashed lines. H-atoms not involved are omitted.

Table 2
The experimental and calculated structure parameters of the *O*-ethyl benzoylthiocarbamate

Parameters	Experimental	Calculated (6-31G(d))		Calculated (3-21G)	
		HF	B3LYP	HF	B3LYP
Bond lengths (Å)					
S(1)–C(8)	1.619(3)	1.642	1.645	1.700	1.693
O(1)–C(7)	1.205(3)	1.185	1.213	1.204	1.231
O(2)–C(8)	1.318(3)	1.317	1.352	1.335	1.353
O(2)–C(9)	1.449(3)	1.432	1.448	1.465	1.485
N(1)–C(8)	1.370(3)	1.367	1.384	1.352	1.375
N(1)–C(7)	1.378(3)	1.397	1.407	1.400	1.409
C(1)–C(2)	1.373(4)	1.382	1.392	1.380	1.391
C(1)–C(6)	1.391(4)	1.391	1.402	1.387	1.401
C(2)–C(3)	1.371(4)	1.387	1.398	1.385	1.398
C(3)–C(4)	1.373(4)	1.385	1.396	1.384	1.397
C(4)–C(5)	1.373(4)	1.385	1.395	1.383	1.395
C(5)–C(6)	1.390(4)	1.390	1.403	1.387	1.401
C(6)–C(7)	1.481(3)	1.501	1.503	1.492	1.500
C(9)–C(10)	1.478(4)	1.516	1.520	1.524	1.528
r		0.9924	0.9937	0.9891	0.9906
Bond angles (°)					
C(8)–O(2)–C(9)	119.0(2)	122.9	120.4	123.3	119.2
C(8)–N(1)–C(7)	127.5(2)	130.2	129.9	129.6	128.7
C(2)–C(1)–C(6)	119.9(3)	120.2	120.4	120.3	120.5
C(3)–C(2)–C(1)	120.3(3)	120.0	120.1	119.9	119.9
C(2)–C(3)–C(4)	120.2(2)	120.1	120.0	120.1	119.9
C(5)–C(4)–C(3)	120.4(3)	120.0	120.1	120.0	120.1
C(4)–C(5)–C(6)	119.8(3)	120.2	120.3	120.0	120.1
C(5)–C(6)–C(1)	119.4(2)	119.5	119.3	119.7	119.4
C(5)–C(6)–C(7)	123.0(2)	123.2	123.8	123.8	124.8
C(1)–C(6)–C(7)	117.5(2)	117.2	116.9	116.5	115.7
O(1)–C(7)–N(1)	122.2(2)	124.1	123.9	123.6	123.6
O(1)–C(7)–C(6)	122.3(2)	122.2	122.5	122.4	122.4
N(1)–C(7)–C(6)	115.5(2)	113.7	113.7	113.9	113.9
O(2)–C(8)–N(1)	107.0(2)	106.4	105.7	107.0	105.9
O(2)–C(8)–S(1)	125.3(2)	126.1	126.7	124.7	126.0
N(1)–C(8)–S(1)	127.71(19)	127.5	127.5	128.3	128.1
O(2)–C(9)–C(10)	107.0(2)	110.9	110.1	109.7	109.9
r		0.9633	0.9784	0.9695	0.9806

basis sets are listed in Table 2 in accordance with the atom numbering scheme given in Fig. 1. The correlation between the experimental and calculated geometric parameters obtained by the several methods is shown in Table 2. Owing to our calculations, DFT method correlates well for the bond length and angle compare with the HF method. The largest difference between experimental and calculated DFT bond length and angle is about 0.042 Å and 3.1° for the 6-31G(d) basis set. As a result, the optimized bond lengths and angles by DFT method show the best agreement with the experimental values.

FT-IR spectrum of *O*-ethyl benzoylthiocarbamate is given in Fig. 4. Table 4 lists the vibrational frequencies obtained using ab initio-HF/6-31G(d), 3-21G and DFT-B3LYP/6-31G(d) and 3-21G calculations together with the experimental frequencies and

Table 3
Energies of the different conformations of the title compound calculated at the DFT-B3LYP/6-31G(d) level

Conformer	*E* (Hartree)	Δ*E* (kcal/mol)	E_0 (Hartree)	Dipole moment (*D*)
1	−991.089382	0.0000	124.565600	2.4784
2	−991.088162	0.7655	124.666710	2.3349
3	−991.088059	0.8298	124.678950	2.4229
4	−991.084483	3.0743	124.290090	5.9063
5	−991.083553	3.6578	124.401190	5.7150
6	−991.083490	3.6973	124.380160	5.7716
7	−991.078116	7.0693	124.537420	5.5980
8	−991.076703	7.9557	124.473490	5.1666

E: total energies; E_0: energies corrected for zero-point energy vibrational.

Table 4
Experimental and calculated vibrational frequencies (in cm^{-1}) of *O*-ethyl benzoylthiocarbamate

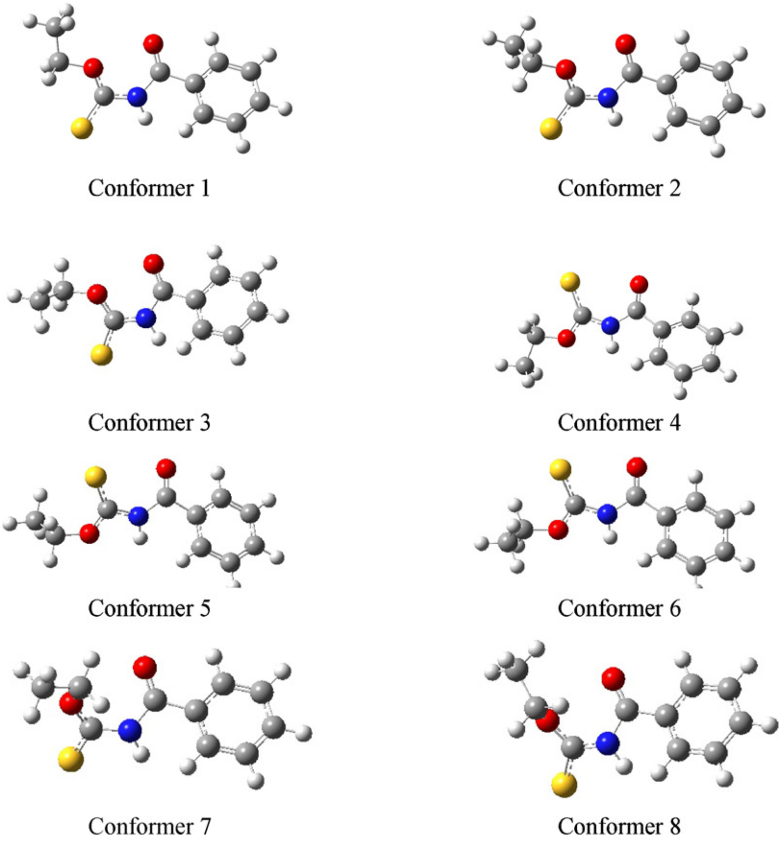
Experimental	HF/6-31G(d)			DFT-B3LYP/6-31G(d)			HF/3-21G			DFT-B3LYP/3-21G			Assignments
	Calc.	Corr.	Inten.	Calc.	Corr.	Inten.	Calc.	Corr.	Inten.	Calc.	Corr.	Inten.	
3256, w	3865	3451	58.96	3591	3452	27.99	3792	3445	74.11	3530	3394	33.17	ν_{NH}
3106, vw	3411	3046	3.94	3228	3103	4.69	3402	3091	3.70	3233	3108	6.46	ν_{CH}, sym, Ph
3090, vw	3393	3030	20.36	3214	3090	19.52	3389	3079	7.91	3222	3098	8.36	ν_{CH}, sym, Ph
3076, vw	3383	3021	29.88	3203	3079	24.47	3378	3069	18.74	3211	3087	15.02	ν_{CH}, asym, Ph
3065, vw	3371	3010	8.18	3193	3069	3.35	3367	3059	6.73	3200	3076	2.93	ν_{CH}, asym, Ph
3060, vw	3362	3002	1.51	3184	3061	7.22	3358	3051	0.66	3190	3067	8.69	ν_{CH}, asym, Ph
3042, vw	3355	2996	12.02	3158	3036	19.22	3344	3038	8.18	3165	3043	12.38	ν_{CH}, asym, et
3030, vw	3310	2955	26.93	3142	3020	6.24	3297	2995	13.86	3142	3021	2.10	ν_{CH}, asym, et
2993, w	3285	2933	44.24	3128	3007	21.50	3284	2984	26.41	3132	3011	19.12	ν_{CH}, asym, CH_3
2963, w	3277	2926	17.10	3093	2973	30.71	3271	2972	8.88	3095	2976	20.56	ν_{CH}, sym, CH_2
2942, vw	3217	2872	22.14	3062	2944	17.68	3215	2921	13.60	3067	2949	13.16	ν_{CH}, sym, CH_3
1697, s	2024	1807	262.47	1811	1741	149.80	1947	1769	166.58	1742	1675	84.93	$\nu_{C=O}$
1598, w	1809	1615	19.02	1661	1597	10.71	1777	1614	13.41	1633	1570	8.68	ν_{CC}
1582, vw	1783	1592	4.06	1640	1577	3.38	1752	1592	5.11	1614	1552	7.40	ν_{CC}
1518, s	1720	1536	588.31	1553	1493	379.77	1694	1539	482.90	1572	1511	11.46	δ_{NH}
1489, m	1669	1490	14.85	1539	1479	95.87	1675	1522	5.06	1553	1493	5.54	$\delta_{NH} + \delta_{CH}$, Ph
1472, m	1657	1480	19.17	1533	1474	82.44	1670	1517	47.28	1552	1492	119.85	δ_{CH}, $CH_3 + \delta_{NH}$
1452, m	1645	1469	2.83	1515	1456	3.36	1661	1509	64.98	1539	1480	156.56	δ_{CH}, CH_3
1449, w	1630	1455	2.17	1513	1454	33.27	1658	1506	6.92	1525	1466	206.86	δ_{CH}, CH_2
1437, w	1613	1440	6.90	1494	1436	5.06	1621	1473	6.53	1504	1446	11.59	δ_{CH}, Ph + ν_{CC}
1388, w	1577	1408	40.58	1442	1386	41.67	1577	1433	12.83	1459	1403	13.01	δ_{CH}, et
1358, vw	1547	1381	32.70	1421	1366	54.53	1544	1403	17.74	1416	1361	33.64	δ_{CH}, et
1325, w	1475	1317	9.65	1369	1316	1.40	1505	1367	9.29	1392	1338	29.24	δ_{CH}, Ph
1306, m	1463	1306	199.84	1359	1306	279.76	1456	1323	109.18	1349	1297	135.81	$\nu_{CC} + \delta_{CH}$, Ph
1289, vs	1428	1275	753.82	1348	1296	74.32	1432	1301	861.18	1337	1285	366.54	δ_{CH}, Ph + $\nu_{CN} + \delta_{CH}$, CH_3
1264, vs	1400	1250	201.05	1330	1279	319.24	1372	1246	136.90	1323	1272	170.29	$\nu_{CN} + \delta_{CH}$, $CH_3 + \nu_{C–O}$
1232, m	1348	1204	85.75	1271	1222	111.02	1362	1237	19.60	1256	1208	84.60	$\nu_{CC} + \nu_{CN} + \delta_{CH}$, Ph
1182, vs	1335	1192	507.51	1217	1170	11.86	1335	1213	9.06	1245	1197	67.98	δ_{CH}, Ph
1175, vs	1305	1165	23.65	1208	1161	328.14	1314	1194	374.99	1232	1184	16.11	$\delta_{NH} + \delta_{CH}$, Ph
1158, vs	1290	1152	73.91	1196	1150	2.74	1275	1158	174.68	1197	1151	160.68	δ_{CH}, Ph + $\nu_{C=S}$
1149, s	1246	1113	10.77	1171	1126	232.19	1258	1143	2.81	1150	1106	225.91	$\nu_{C–O} + \delta_{CH}$, $CH_3 + \delta_{CH}$, Ph
1094, s	1228	1096	3.76	1141	1097	8.53	1231	1118	29.21	1138	1094	16.61	$\delta_{NH} + \delta_{CH}$, Ph
1073, m	1207	1078	46.14	1123	1080	16.29	1209	1098	16.99	1131	1087	4.14	δ_{CH}, Ph + δ_{CH}, CH_3
1060, w	1187	1060	4.38	1109	1066	62.35	1202	1092	1.36	1087	1045	157.37	δ_{CH}, Ph + δ_{CH}, CH_3
1030, m	1141	1019	49.55	1062	1021	17.04	1181	1073	88.01	1063	1022	2.85	δ_{CH}, Ph + δ_{CO}
1011, vs	1136	1014	10.08	1039	999	131.29	1171	1064	1.17	1052	1011	6.58	$\nu_{CN} + \nu_{CC} + \delta_{CH}$, Ph
995, s	1117	997	108.08	1018	979	8.21	1140	1036	5.74	1041	1001	38.10	δ_{CCC}, Ph + ν_{CO}
962, m	1113	994	0.37	1008	969	0.36	1124	1021	60.51	1021	982	2.29	γ_{CH}, Ph
932, s	1091	974	1.49	981	943	1.46	1112	1010	31.18	1017	978	137.82	γ_{CH}, Ph + γ_{CCC}, Ph
916, m	1065	951	3.28	945	908	15.51	1088	988	131.22	970	933	1.73	γ_{CH}, Ph
910, m	1014	905	50.29	941	905	31.70	1001	909	26.35	939	903	41.80	γ_{CH}, Ph + γ_{CH}, CH_3
857, m	964	861	0.56	866	832	0.73	997	906	0.56	876	842	0.25	γ_{CH}, Ph
812, w	931	831	16.08	858	825	7.09	965	877	65.36	857	824	13.39	γ_{CH}, Ph
799, m	893	797	7.89	815	783	4.82	909	826	15.62	841	809	3.55	γ_{CH}, et
753, m	875	781	2.78	806	775	5.49	898	816	164.37	831	799	9.30	γ_{CH}, Ph
715, m	802	716	118.13	752	723	3.87	890	809	22.89	775	745	161.19	δ_{CCC}, Ph + ν_{CO}
705, vs	796	711	12.72	721	693	58.40	813	739	64.95	739	710	7.98	γ_{CH}, Ph + $\nu_{C=S} + \delta_{CNC}$
685, vs	765	683	10.16	700	673	0.67	793	720	6.82	730	702	31.09	γ_{CCC}, Ph
677, vs	750	670	56.75	681	655	41.81	777	706	13.19	720	692	5.94	δ_{CCC}, Ph
635, s	728	650	31.55	665	639	48.74	717	651	42.17	678	652	30.20	γ_{NH}
615, s	678	605	1.28	633	609	0.69	710	645	0.86	658	633	0.93	γ_{CCC}, Ph

Table 4 (*Continued*)

Experimental	HF/6-31G(d)			DFT-B3LYP/6-31G(d)			HF/3-21G			DFT-B3LYP/3-21G			Assignments
	Calc.	Corr.	Inten.	Calc.	Corr.	Inten.	Calc.	Corr.	Inten.	Calc.	Corr.	Inten.	
592, s	657	587	33.19	610	586	24.05	662	601	8.32	607	584	12.83	γ_{NH}
580, m	636	568	4.27	593	570	7.20	597	542	3.85	569	547	8.54	γ_{CH}, et + γ_{COC}
–	536	479	5.02	490	471	3.38	539	481	7.99	487	468	3.77	$\tau_{CCCC} + \tau_{CCCN}$
–	477	426	6.32	441	424	3.85	473	422	1.30	440	423	1.19	δ_{CCO}
–	456	407	0.43	420	404	1.40	470	420	3.13	428	411	1.64	$\tau_{CCCC} + \tau_{CCNC}$
–	450	402	2.05	417	401	0.12	464	414	4.29	426	410	2.58	τ_{CCCC}
–	368	329	10.81	341	328	6.46	369	329	11.95	348	335	6.43	δ_{CO}
–	345	308	5.88	324	311	4.98	337	301	9.58	321	309	8.61	τ_{COC2H5}
–	286	255	3.79	268	258	3.94	288	257	5.52	273	262	5.23	τ_{COC2H5}
–	244	218	0.42	222	213	2.27	260	232	1.57	228	219	2.34	τ_{CCCH}, et
–	230	205	1.38	220	211	0.09	220	196	2.51	226	217	1.69	τ_{CCCN}
–	185	165	0.76	172	165	0.94	192	171	1.17	181	174	1.46	$\tau_{CCCC} + \tau_{CCNC}$
–	137	122	3.21	121	116	2.96	157	140	3.81	139	134	3.05	τ_{CNCO}
–	114	102	1.61	101	97	1.35	118	105	1.19	109	105	1.18	$\tau_{SCOC2H5}$
–	79	71	0.87	73	70	0.76	79	71	0.92	76	73	0.81	$\tau_{SCOC2H5}$
–	69	62	0.43	67	64	0.42	72	64	0.55	71	68	0.34	τ_{CNCO}
–	40	36	0.72	38	37	0.59	43	38	1.14	40	38	0.64	τ_{CNCO}
–	31	28	0.12	30	29	0.08	31	28	0.30	28	27	0.55	τ_{CNCS}, τ_{CCNC}

s, strong; vs, very strong; m, medium; w, weak; vw, very weak; blank, not observed or measured; ν, stretching; δ, in-plane bending; γ, out-of-plane bending; τ, torsion; sym, symmetric; asym, asymmetric; et, ethyl group; Ph, phenyl group.

the approximate description of each normal modes. The vibrational bands' assignments have been made by using GausView molecular visualization program. To make comparison with experimental, we present correlation graphics in Figs. 5 and 6 based on calculations. As we can see from Figs. 5 and 6, experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for DFT-B3LYP than HF.



Conformer 1

Conformer 2

Conformer 3

Conformer 4

Conformer 5

Conformer 6

Conformer 7

Conformer 8

Fig. 3. Eight stable conformers of the title compound calculated at HF/6-31G(d) level.

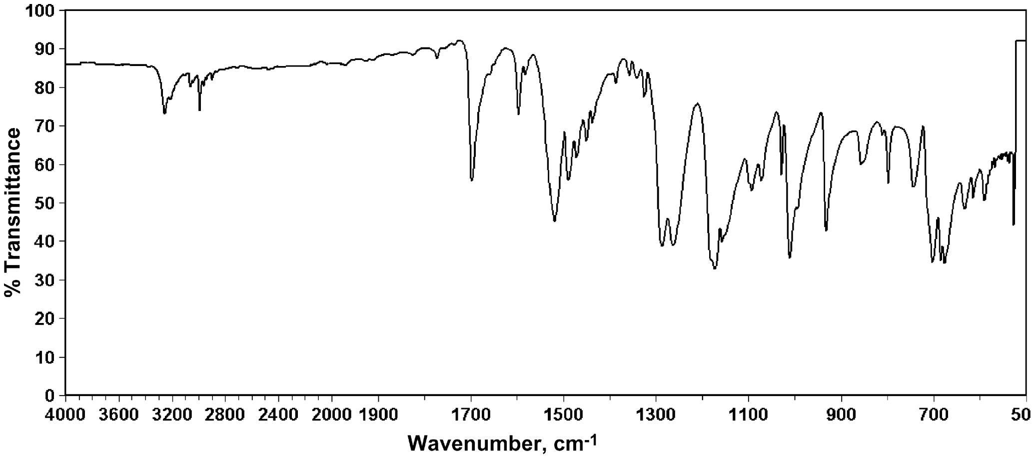


Fig. 4. FT-IR spectrum of *O*-ethyl benzoylthiocarbamate recorded at room temperature.

In the heterocyclic compounds, $\nu_{\text{N–H}}$ vibration occurs in the region 3500–3000 cm^{-1}. The IR band appearing at 3256 cm^{-1} is assigned to $\nu_{\text{N–H}}$ stretching mode of vibrations. This vibration mode calculated at 3451, 3452, 3445 and 3394 cm^{-1} for HF and DFT methods. This band is calculated and observed at 3632 cm^{-1} (non-scaling), 3491 cm^{-1} (scalling; 0.9613) and 3236 cm^{-1} by Zhou et al. for *N*-(morpholinothiocarbonyl)benzamide, respectively [27]. The difference between experimental and calculated $\nu_{\text{N–H}}$ stretching mode is about 196 cm^{-1} (DFT/6-31G(d)), 195 cm^{-1} (HF/6-31G(d)), 189 cm^{-1} (HF/3-21G) and 138 cm^{-1} (DFT/3-21G). This striking discrepancy can come from the formation of intermolecular hydrogen bonding with N–H. This interpretation is verifying with $\nu_{\text{C=O}}$ stretching vibration mode. The difference between experimental (1697 cm^{-1}) and calculated (1741 cm^{-1} with DFT-B3LYP/6-31G(d) method) $\nu_{\text{C=O}}$ is about 44 cm^{-1}. It can be easily observed in the correlation graphics of calculated and experimental frequencies of the title compound that the big difference is observed for $\nu_{\text{N–H}}$ and $\nu_{\text{C=O}}$ stretching vibrations (Fig. 5).

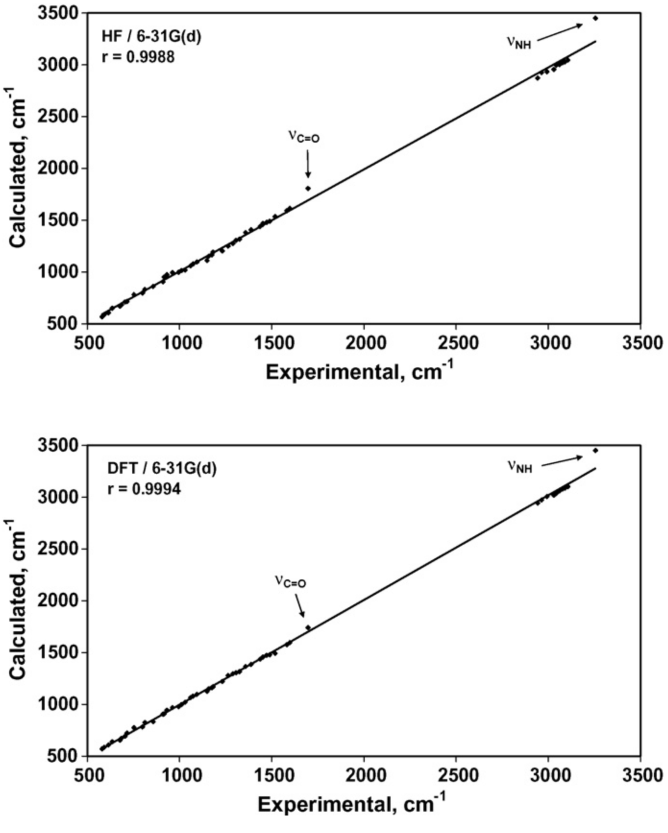


Fig. 5. Correlation graphics of calculated and experimental frequencies of the title compound.

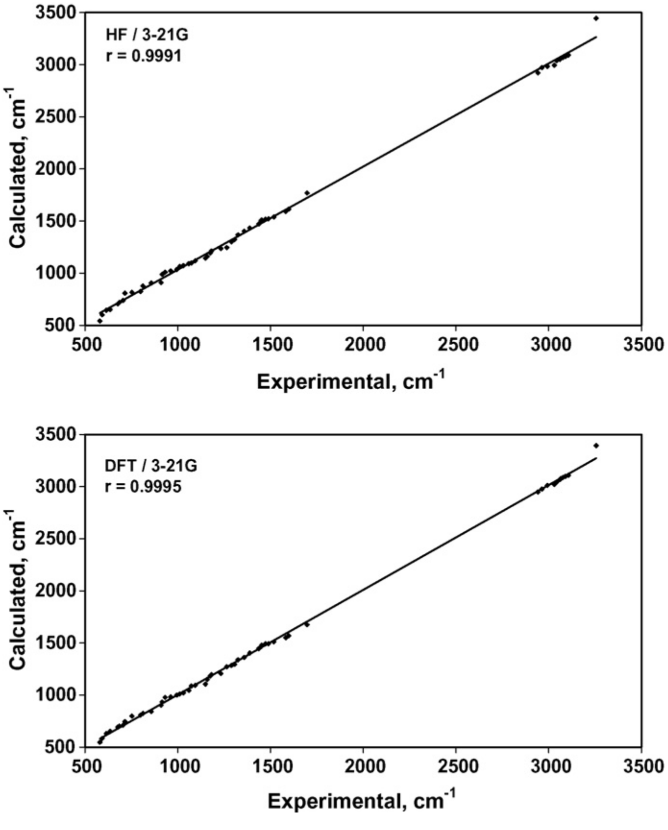


Fig. 6. Correlation graphics of calculated and experimental frequencies of the title compound.

Characteristic aromatic $\nu_{C–H}$ stretching vibrations of substituted benzenes are expected to appear in 3050–3100 cm^{-1} frequency ranges. Our calculations confirmed the assignment of absorption at 3106, 3090, 3076, 3065 and 3060 cm^{-1} to $\nu_{C–H}$ stretching vibrations, which is in agreement with the literature data [27,28]. Five bands at 3042, 3030, 2993, 2963 and 2942 cm^{-1} were observed in the spectrum. First three is asymmetric $\nu_{C–H}$ stretching band and the other bands symmetric $\nu_{C–H}$ stretching band for ethyl group. These assignments were also supported by the literature [29,30]. The two in-plane methyl hydrogen-bending modes (1472, and 1452 cm^{-1}) are also well established in the spectrum.

The carbon–carbon stretching vibrations of the title compound have been observed at 1598, 1582, 1437 and 1306 cm^{-1}. The in-plane and out-of-plane bending vibrations of C–C group are presented in Table 4. All these assignment are in good agreement with the literatures [27,29].

The identification of $\nu_{C–N}$ vibrations is a difficult task, since the mixing of vibrations is possible in this region. However, with the help of the animation option of GaussView 3.0 graphical interface for gaussian programs, the $\nu_{C–N}$ vibrations are identified and assigned in this study. The IR bands appearing at 1289, 1264 and 1232 cm^{-1} are assigned to $\nu_{C–N}$ vibrations with the δ_{PhH} for the title compound.

4. Conclusions

In this work, the crystal structure of title compound has been described here. Also, we have calculated the geometric parameters and vibrational frequencies of the *O*-ethyl benzoylthiocarbamate by using B3LYP and HF method with the standard 3-21G and 6-31G(d) basis sets. We have used the scaling factor values of 0.8929, 0.9613, 0.9085 and 0.9614 for HF/6-31G(d), B3LYP/6-31G(d), HF/3-21G, and B3LYP/3-21G respectively, to fit the theoretical results of vibration analysis with experimental ones. Scaling factors results gained seemed to be in a good agreement with experimental ones. In particular, the results of DFT-B3LYP method have shown better fit to experimental ones than ab initio-HF in evaluating vibrational frequencies. The difference between experimental and calculated vibrations mode can be considered as the difference of the state. Because it is clear that gas state vibration frequencies are larger than in the solid state.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-613207] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033 (internat.), E-mail: deposit@ccdc.cam.ac.uk].

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