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Normal coordinate analysis and crystal structure of N,N-dimethyl-N'-(2-chloro-benzoyl)thiourea

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Abstract

In the present paper, the crystal structural and vibrational analysis of the *N*,*N*-dimethyl-*N'*-(2-chloro-benzoyl)thiourea molecule is reported. The molecular structure of the title compound was determined by single crystal X-ray diffraction method. The compound crystallizes monoclinic, space group P_{21}/c with a = 5.6601(13) Å, b = 10.748(2) Å, c = 17.778(4) Å, $\beta = 94.266(5)^{\circ}$, and V = 1078.5(4) Å³ with Z = 4 for $d_{calc} = 1.495$ g/cm³. Calculations of the vibrational frequencies have been carried out on the basis of normal coordinate analysis using simple general valence force field in Wilson's GF matrix method with the SPSIM computer program. With the help of this modern technique we were able to complete the assignment of the vibrational spectrum of the title compound.

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Keywords: Crystal structure; Vibrational analysis; Normal coordinate analysis; Valence force field; Benzoyl thiourea

1. Introduction

N,N'-dialkyl-N'-benzoylthioureas are versatile ligands, able to coordinate to transition metal centres either as monoanions or as dianions [1–3]. There have been many studies of benzoylsubstituted thioureas and related ligands coordinated to metals [4], where the ligand typically bonds as a monoanion through S and O, giving a six-membered ring system, though complexes with neutral ligands are also known [5]. Study of compounds of these type thioureas has recently received attention because of their potential use as highly selective reagents for the preconcentration and separation of metal cations [6–8]. In addition, thioureas have been shown to possess antitubercular, antithroid, antihelmintic, antibacterial, insecticidal and rodenticidal properties [9–11].

We have recently begun to examine the coordination behaviour of some series of N,N'-dialkyl-N'-benzoylthioureas that posses a number of interesting properties [12–24]. We discuss here the structure of one of them, N,N-dimethyl-N'-(2chloro-benzoyl)thiourea (HL). In addition, vibrational spectrum of this compound is recorded and then normal coordinate calcu-

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lations are performed. Thus, whole vibrational spectrum of title compound is explained.

2. Experimental

2.1. Synthesis

N,*N*-dimethyl-*N'*-(2-chloro-benzoyl)thiourea was obtained as described in the literature [14]. A solution of 2-chlorobenzoyl chloride (0.01 mole) in acetone (50 cm³) was added dropwise to a suspension of potassium thiocyanate (0.01 mole) in acetone (30 cm³). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of dimethyl amine (0.01 mole) in acetone (10 cm³) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1N, 300 cm³) was added and then the solution filtered. The solid product was washed with water and purified by recrystallisation from ethanol/dichloromethane mixture (1:1).

2.2. Instrumentation and crystal structure determination

The solid-state infrared spectrum of HL studied was recorded using in the form of KBr pellet by BOMEN MB102 FT-IR instrument in the 4000–200 cm⁻¹ ranges; the resolution was 1 cm⁻¹. Single crystal X-ray data were collected on a Bruker

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AXS SMART APEX CCD [25] using monochromated Mo K α (λ = 0.71073 Å) radiation. Semi-empirical absorption corrections has been carried out from equivalents [25]. The structure was solved [25] by direct and conventional Fourier methods. Full-matrix least-squares refinement [25] based on F^2 . Further details concerning data collection and refinement are given in Table 1.

2.3. Normal coordinate analysis

Calculations of the frequencies and vibrational activities were performed by using computer programs developed by Schrader et al. [26,27] employing Wilson's GF matrix method [28]. *N*,*N*dimethyl-*N'*-(2-chloro-benzoyl)thiourea is calculated as an isolated molecule with C_s point group symmetry. The 72 normal modes of HL are distributed between the two species (*A'* and *A''*) of the C_s point group as

$$\Gamma_{\rm vib} = 47A' + 25A''$$

All of the species are both IR and Raman active. The geometric parameters are transferred from single crystal X-ray structure and to save C_s symmetry small adjustments were made on the torsion angles of the title compound (Fig. 1, Table 2). A total of 87 force constants (61 diagonal and 26 non-diagonal) were used for the HL to define the *F*-matrix. The initial set of valence force constant and the corresponding non-diagonal constant were transferred from related systems [29–40]. A zero order calculation with the transferred force constant was performed. The results indicated the reasonable agreement between the calculated and the observed frequencies. The initial set of force constant was refined by the method of least square technique by keeping some interaction force constants fixed throughout the refinement process. The only final diagonal force constants and their description were shown in Table 3.

Empirical formula	C ₁₀ H ₁₁ ClN ₂ OS
Formula weight (g)	242.72
Temperature (K)	120(2)
Wavelength (Mo Kα) (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{1}/c$
Unit cell dimensions	
<i>a</i> (Å)	5.6601(13)
<i>b</i> (Å)	10.748(2)
<i>c</i> (Å)	17.778(4)
β (°)	94.266(5)
Volume (Å ³)	1078.5(4)
Ζ	4
Density (calculated) (Mg/m ³)	1.495
Absorption coefficient (mm^{-1})	0.521
<i>F</i> (000)	504
Crystal size (mm ³)	$0.43 \times 0.20 \times 0.11$
Theta range for data collection ($^{\circ}$)	2.22-28.54
Index ranges	$-7 \le h \le 7$
	$-13 \le k \le 14$
	$-23 \le l \le 23$
Reflections collected	10874
Independent reflections	2724 [R(int) = 0.0993]
Completeness to theta = 28.54°	99.2%
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.9450 and 0.8072
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2724/1/146
Goodness-of-fit on F^2	1.175
Final R indices $[I > 2 \text{sigma}(I)]$	R1 = 0.0675, wR2 = 0.0807
R indices (all data)	R1 = 0.1064, wR2 = 0.0850
Largest difference peak and hole ($e Å^{-2}$)	0.979 and -0.668



Fig. 1. Molecular structure of N,N-dimethyl-N'-(2-chloro-benzoyl)thiourea. Thermal ellipsoids are shown at the 50% probability level.

Table 1		
Crystal data and	structure refinement	for title compound

Table 2	
Selected bond lengths (Å) and angles ($^{\circ}$)	

Bond lengths			
C7-O1	1.199(3)	C1C11	1.716(3)
C8-S1	1.669(3)	C1-C6	1.383(4)
N1-C7	1.383(3)	C5-C6	1.390(4)
N1-C8	1.398(3)	C1-C2	1.381(4)
N2-C8	1.314(3)	C2–C3	1.361(4)
N2-C9	1.450(3)	C3C4	1.365(4)
N2-C10	1.452(3)	C4–C5	1.371(4)
C6–C7	1.500(4)		
Bond angles			
O1-C7-N1	123.5(3)	C7-C6-C1	123.3(3)
O1-C7-C6	124.2(3)	C7-C6-C5	119.2(3)
C7-N1-C8	125.6(2)	C6C1C1	120.6(2)
N1-C8-S1	118.6(2)	C6-C1-C2	122.0(3)
S1-C8-N2	124.5(2)	C1C2C3	117.8(3)
C8-N2-C9	124.6(2)	C2-C3-C4	122.6(3)
C8-N2-C10	121.2(2)	C3-C4-C5	118.7(3)

3. Results and discussion

3.1. The crystal structure

The molecular structure of *N*,*N*-dimethyl-*N'*-(2-chlorobenzoyl)thiourea, is depicted in Fig. 1. Selected bond distances and angles of the title compound are presented in Table 2. There are no significant differences in the bond distances and bond angles from other thiourea derivatives [12,20-22,41,42]. The bond distances and angles in the thiourea moiety are typical for these compounds with the S1–C8 = 1.669(3) Å and C7–O1 = 1.199(3) Å bonds showing the usual double-bond character. Also, the C–N bond distances C7–N1, C8–N1 and C8–N2 are significantly shorter than the normal C–N single bond of about 1.48 Å. The shortening of these C–N bonds confirms the well-known effect of resonance in this part of the molecule.

3.2. Normal coordinate analysis

FT-IR part of the vibrational spectrum of the title compound was the only spectral source. This was not a serious problem in the compound because of both A' and A'' modes are active in both Raman and infrared in C_s point group symmetry. The IR spectrum of the N,N-dimethyl-N'-(2-chloro-benzoyl)thiourea molecule is shown in Fig. 2. The frequencies observed in the IR spectrum along with their relative intensities, the corresponding calculated frequencies together with the respective potential energy distributions (PEDs) and mode assignments are collected in Table 4. Here, the normal mode description following each fundamental in the last column is due to Wilson [28]. As seen from Table 4, the agreement between experimental and calculated frequencies for fundamental is good. The calculated frequencies do not differ so much from the experimental ones that the maximum difference between two spectra is not more than $10 \,\mathrm{cm}^{-1}$. The average absolute error of the calculated frequencies was found less than 0.1%. We also studied the relativity between the calculation and the experimental values, obtained

Table 3	
Force constant of N N-dimethyl- $N'_{-}(2-chloro-henzoyl)$ thiourea	

Force	constant	Related internal	Force constant	Reference
No	Symbola	coordinate	value ^b	101010100
1		C N	5 7002	[20]
1	K(1) K(2)	$C_7 - N_1$	5.7902	[29]
2	K(2) K(3)	$C_7 = O_1$	1.9290	[30]
3	$\mathbf{K}(3)$	$C_7 - C_6$	4.3240	[31]
4 5	K(4) K(5)	N ₁ -C ₈	5 5075	[32]
5	K(5) K(6)	$N_1 - n_1$	3.3073	[32]
7	K(0) K(7)	$C_8 - S_1$	6 2350	[32]
8	K(7) K(8)	$C_8 = I N_2$	5 7142	[32]
0	K(0)	$C_6 = C_5$	J.7142 4 9261	[33]
10	K(f) K(10)	$C_6 - C_1$	6 1827	[33]
11	K(10) K(11)	$C_5 = H_{c_1}$	5 1874	[33]
12	K(11) K(12)		6.0274	[33]
12	K(12) K(13)	$C_4 = C_3$	5 1874	[33]
17	K(13) K(14)	$C_4 - \Pi_{4A}$	3 / 303	[34]
15	K(14) K(15)	$C_1 = C_1$ No = Co	5 2537	[35]
16	K(15) K(16)	Co-Hot	4 8679	[36]
17	K(10) K(17)	Co-Hon	4.8679	[36]
18	H(18)	$N_{t} = C_{\pi} = O_{t}$	0.5401	[36]
10	H(10) H(10)	$N_1 = C_7 = C_1$	1.0530	[36]
20	H(20)	$\Omega_1 = C_7 = C_6$	0.5401	[36]
20	H(20)	$C_1 - C_7 - C_6$	1 8231	[30]
21	H(22)	$C_7 = N_1 = C_8$	0.3375	[27]
22	H(22)	$C_7 - N_1 - \Pi_1$	0.3373	[37]
25 24	H(23) H(24)	$C_8 - N_1 - \Pi_1$	1.0200	[37]
24 25	H(25)	$N_1 = C_8 = S_1$ $N_4 = C_8 = N_8$	1.6050	[32]
25 26	H(25)	$N_1 = C_8 = N_2$	1.0050	[32]
20 27	H(20)	$S_1 = C_8 = 1 \sqrt{2}$	1.0290	[32]
28	H(28)	$C_7 - C_6 - C_5$	0.9340	[33]
20	H(20)	$C_5 - C_6 - C_1$	1 4832	[33]
30	H(20)	$C_6 - C_5 - C_4$	0.4752	[33]
31	H(31)	$C_6 - C_5 - H_{5A}$	0.5120	[33]
32	H(32)	$C_4 = C_5 = \Pi_{5A}$	0.8649	[33]
32	H(32) H(33)	$C_3 = C_4 = C_3$	0.4230	[33]
34	H(34)	$C_5 C_4 \Pi_{4A}$	1 2059	[33]
35	H(35)	$C_6 C_1 C_2$	0.8283	[34]
36	H(36)	$C_0 = C_1 = C_1$	0.8283	[34]
37	H(30) H(37)	$C_2 = N_2 - C_0$	1 6400	[38]
38	H(38)	$C_8 - N_2 - C_{10}$	1 2685	[38]
39	H(39)	$C_0 - N_2 - C_{10}$	1 3570	[38]
40	H(40)	$N_2 - C_0 - H_{0A}$	0.6130	[39]
41	H(41)	N2-Co-Hop	0.5563	[39]
42	H(42)	HoA-Co-Hop	0.5164	[39]
43	H(43)	Hoa-Co-Hoc	0.4686	[39]
44	H(44)	Hop-Co-Hoc	0.5554	[39]
45	A(45)	C ₇	0.5698	[36]
46	A(46)	N ₁	0.0660	[32]
47	A(47)	C ₈	0.5820	[32]
48	A(48)	Č ₆	0.2860	[33]
49	A(49)	Č5	0.2467	[33]
50	A(50)	C ₄	0.2983	[33]
51	A(51)	C_1	0.4319	[40]
52	A(52)	N_2	0.2792	[38]
53	T(53)	C_7-N_1	0.0706	[29]
54	T(54)	$C_7 - C_6$	0.0090	[33]
55	T(55)	N ₁ -C ₈	0.2000	[32]
56	T(56)	C_8-N_2	0.2000	[32]
57	T(57)	C ₆ -C ₅	0.0390	[33]
58	T(58)	C_6-C_1	0.0390	[33]
59	T(59)	C_5-C_4	0.0390	[33]
60	T(60)	C_2-C_1	0.0390	[33]
61	T(61)	N_2-C_9	0.0270	[38]

^a K, stretching; H, in-plane; A, out-of-plane bending; T, torsion force constant.
 ^b Units: K (mdyn/Å); H (mdynÅ/rad²).



Fig. 2. Infrared spectrum of the title compound.

linear function formula y = 1.0007x - 1.6793, $r^2 = 0.9999$. The linear corrected is shown in Fig. 3. The linear properties of the equation are very satisfactory. The vibrational bands observed in IR spectrum gave sufficient proof for the control of the accuracy of the valence force field developed for the compound.

One band with strong at 3166 cm^{-1} was observed in the *N*,*N*-dimethyl-*N'*-(2-chloro-benzoyl)thiourea spectrum. On the basis of NCA calculations and literature data, this band was assigned to the N–H stretching absorption [14,21,22,32]. Because this band is disappear in the nickel complex [14,23,24,43–45]. The N–H stretching force constant given by Bleckmann et al. [32] was modified to give a better fit to the experimental value and used as 5.5075 mdyn/Å (Table 3, No. 5).

Characteristic C_{ar} -H stretching vibrations of substituted benzenes are expected to appear in 3060–3095 cm⁻¹ frequency ranges. Our calculations confirmed the assignment of absorption at 3091 cm⁻¹ to C_{ar} -H stretching vibrations, which is in agreement with the literature data [33].

Two bands at 3019 and 2924 cm⁻¹ were observed in the spectrum. First band is asymmetric C–H stretching band and the other band symmetric C–H stretching band for methyl group. For these bands, a force constant of 4.8679 mdyn/Å (Table 3, No. 16) was used after modification of C–H stretching force constant as given by Ozpozan [36].

The strong absorb $\nu_{C=0}$ band in the IR spectrum of compound appears at about 1710 cm^{-1} . Our calculations confirmed the assignment of one absorption at 1705 cm^{-1} to C=O stretching vibration in agreement with the literature data [14,21,22,30,44]. $\nu_{C=O}$ vibration frequency (1710 cm^{-1}) of the title compound decreases by ca. 102 cm^{-1} in the complex form and this information is good agreement with the literature data [14,19,23,24,43-45]. Similar interpretations are valid for $\nu_{C=S}$ band. The C=S stretching vibration is calculated in 1199 cm^{-1} that is in agreement with the literature data [32,43,45]. For C=S stretching, a force constant of 4.0809 mdyn/Å (Table 3, No. 6) was used after the modification of C=S stretching force constant of thiourea as given by Bleckmann et al. [32].

The C–N stretching vibrations are calculated in 1641, 1484, 1240 and 1160 cm⁻¹ that is in agreement with the literature data [29,32,35]. For conjugated systems with aromatic ring attached to the carbon atom, the C–N absorption was observed at high frequencies in comparison with other systems where this absorption was observed in the 1641 and 1484 cm⁻¹ frequencies.

The characteristic skeletal stretching modes of semiunsaturated carbon–carbon bonds lead to appearance of a group of four bands in the $1663-1509 \text{ cm}^{-1}$ region. A change of the dipole-moment of substituted benzenes during the stretching modes generally occurs and as a result the bands of strong to



Fig. 3. The linear corrected between the calculation and FT-IR spectrum.

Table 4 Observed and calculated planar and non-planar fundamentals (\mbox{cm}^{-1})

No.	Species	Wavenumber		PED (%)	Assignments ^a	
		Observed (IR)	Calculated (IR-Raman)			
1	A'	3166	3166	99% K(5)	$\nu_{\rm N-H}$	
2	A'	3091	3095	74% K(11), 25% K(13)	VC-H	
3	A'	3091	3093	87% K(13), 12% K(11)	VC-H	
4	A'	3091	3091	96% K(13)	v _{C-H}	
5	A'	3091	3090	89% K(13), 10% K(11)	$\nu_{\rm C-H}$	
6	A'	3019	3028	54% K(17), 45% K(16)	ν_{C-H}	
7	$A^{\prime\prime}$	3019	3025	53% K(16), 47% K(17)	ν_{C-H}	
8	A'	3019	3015	91% K(16), 10% K(17)	ν_{C-H}	
9	$A^{\prime\prime}$	3019	3015	84% K(16), 16% K(17)	ν_{C-H}	
10	A'	2924	2920	62% K(16), 36% K(17)	ν_{C-H}	
11	A'	2924	2920	63% K(16), 36% K(17)	ν_{C-H}	
12	A'	1710	1705	25% K(2), 11% K(15)	vc=0	
13	A'	1663	1657	21% K(12), 13% K(8)	ν_{C-C}	
14	A'	1637	1641	38% K(7), 18% K(4), 17% K(15)	ν_{C-N}	
15	A'	1591	1600	25% K(10), 22% K(2)	ν _{C-C} , ν _{C=O}	
16	A'	1563	1556	23% K(12), 23% K(10), 15% K(2)	ν _{C-C} , ν _{C=O}	
17	A'	1509	1507	24% K(10), 17% H(33), 13% H(30), 13% H(31)	$\nu_{C-C}, \delta_{C-C-H}$	
18	A'	1484	1487	55% H(44), 12% K(4), 10% H(40)	δ_{H-C-H}	
19	A'	1471	1468	53% H(44), 16% H(42)	δ_{H-C-H}	
20	$A^{\prime\prime}$	1457	1457	39% H(42), 28% K(44), 11% H(40)	δ_{H-C-H}	
21	A'	1432	1438	28% H(33), 16% K(12), 13% K(10)	$\delta_{C-C-H}, \nu_{C-C}$	
22	A'	1430	1429	49% H(42), 15% H(40)	$\delta_{\mathrm{H-C-H}}$	
23	A'	1390	1384	66% H(43), 16% H(42)	δ_{H-C-H}	
24	A'	1375	1380	67% H(43), 16% H(42)	δ_{H-C-H}	
25	A'	1292	1291	30% K(3), 19% K(9), 11% K(12)	ν_{C-C}	
26	A'	1270	1271	21% K(9), 16% K(10), 13% K(12)	ν_{C-C}	
27	A'	1240	1238	16% H(40), 14% K(15), 15% K(4)	$\delta_{N-C-H}, \nu_{C-N}$	
28	A'	1201	1199	47% H(33), 11% K(6)	$\delta_{C-C-H}, \nu_{C=S}$	
29	A'	1160	1159	16% K(15), 15% H(41)	$\nu_{C-N}, \delta_{N-C-H}$	
30	A'	1130	1132	11% K(8), 11% H(23)	$\nu_{C-C}, \delta_{C-N-H}$	
31	A'	1093	1086	16% K(8), 10% K(10)	ν_{C-C}	
32	A'	1043	1033	41% H(33), 37% K(10)	$\delta_{C-C-H}, \nu_{C-C}$	
33	$A^{\prime\prime}$	1037	1033	84% H(40)	δ_{N-C-H}	
34	A'	1009	1009	63% H(33), 34% K(12)	$\delta_{C-C-H}, \nu_{C-C}$	
35	A'	972	978	35% K(12), 30% H(33)	$\nu_{C-C}, \delta_{C-C-H}$	
36	A'	962	960	25% K(1), 19% H(23), 19% H(41), 17% H(22)	$\nu_{C-N}, \delta_{C-N-H}$	
37	A''	952	955	94% H(40)	δ_{N-C-H}	
38	A'	909	910	66% H(41), 17% H(40)	δ_{N-C-H}	
39	A'	887	885	17% H(40), 18% K(15), 14% H(41)	$\delta_{N-C-H}, \nu_{C-N}$	
40	A''	869	869	86% A(50)	γc	
41	$A^{\prime\prime}$	815	823	25% K(15), 10% K(6)	$\nu_{C-N}, \nu_{C=S}$	
42	A''	782	779	73% A(50), 17% A(49)	γc	
43	A'	752	749	19% H(32), 10% K(14)	δ_{C-C-C} , ν_{C-Cl}	
44	$A^{\prime\prime}$	721	723	33% A(45), 16% A(48), 17% A(50), 14% A(49)	γc	
45	$A^{\prime\prime}$	694	696	46% A(47), 20% T(56), 12% A(52)	$\gamma_{\rm C}, \tau_{\rm C-N}$	
46	A'	684	682	18% H(32), 18% K(9), 12% H(29)	$\delta_{C-C-C}, \nu_{C-C}$	
47	$A^{\prime\prime}$	647	647	43% A(50), 20% A(45), 11% A(49)	γc	
48	A'	613	611	14% K(15), 13% K(8)	$\nu_{C-N}, \nu_{C=C}$	
49	<i>A''</i>	602	598	52% A(50), 37% A(49)	γc	
50	A'	547	544	21% H(39), 21% H(37), 16% K(15)	$\delta_{C-N-C}, \nu_{C-N}$	
51	<i>A''</i>	503	496	53% A(51), 13% A(48), 11% A(45)	γc	
52	A'	470	468	21% H(27), 14% K(8), 12% K(14)	δ_{C-C-C} , ν_{C-Cl}	
53	A''	449	445	42% <i>I</i> (55), 39% <i>A</i> (46), 15% <i>I</i> (53)	τ_{C-N}, γ_{C}	
54 55	A'	434	435	25% K(6), $25%$ H(38), $12%$ H(39)	$\nu_{C=S}, \delta_{C-N-C}$	
35	A'	-	369	20% K(14), 20% H(36)	$v_{C-Cl}, \delta_{C-C-Cl}$	
56	A''	-	365	38% A(4/), 32% T(56), 14% A(52)	$\gamma_{\rm C}, \tau_{\rm C-N}, \gamma_{\rm N}$	
57	A'	-	325	11% K(14), 10% H(35)	vc-cl, Sc-c-cl	
58 50	A' ^''	-	281	21% H(20), 15% H(18)	δ _{C-C-O} , δ _{N-C-O}	
39 60	A''	-	257 227	51% A(48), 22% A(51), 13% I(59)	$\gamma_{\rm C}, \tau_{\rm C-C}$	
00	A'	-	227	1/% $H(23)$, 14% $H(20)$, 13% $H(18)$	∂ _{N−C−N} , ∂ _{N−C−S}	
01	A''	-	202	$\delta 5\% I(59)$	τ_{C-C}	
02	A	-	180	43% A(32), 33% I(01), 18% I(30)	$\gamma_{\rm N}, \tau_{\rm C-N}$	

Table 4 (Continued)

No.	Species	es Wavenumber		PED (%)	Assignments ^a
		Observed (IR)	Calculated (IR-Raman)		
63	Α'	_	166	21% H(24), 17% H(21), 12% H(26)	$\delta_{N-C-S}, \delta_{N-C-N}$
64	A''	-	139	18% H(27), 16% H(25), 16% H(35)	$\delta_{C-C-C}, \delta_{N-C-N}, \delta_{C-C-C}$
65	A''	-	122	95% T(61)	$ au_{ m C-N}$
66	A''	-	110	33% T(59), 21% T(57), 20% T(60)	$\tau_{ m C-C}$
67	A''	-	86	38% A(46), 31% T(55)	$\gamma_{\rm N}, \tau_{\rm C-N}$
68	A'	-	61	37% H(19), 22% H(21), 22% H(27)	$\delta_{C-C-N}, \delta_{C-N-C}, \delta_{C-C-C}$
69	A''	-	53	30% T(58), 25% T(53), 16% T(60)	$\tau_{\text{C-C}}, \tau_{\text{C-N}}$
70	A''	-	42	38% T(61), 21% T(58), 11% T(56)	$\tau_{\text{C-N}}, \tau_{\text{C-C}}$
71	A''	-	27	47% T(53), 13% T(61)	$ au_{ m C-N}$
72	A''	-	10	92% T(54)	$ au_{ ext{C-C}}$

^a ν , stretching; δ , in-plane; γ , out-of-plane; τ , torsional vibrations.

medium intensity are expected for the aromatic CC modes. All observed bands are in full agreement with the literature data [33].

4. Conclusion

Molecular structure of title compound was determined by single crystal X-ray diffraction method. These crystal structure parameters were used in normal coordinate analysis calculations. A detailed IR study of the *N*,*N*-dimethyl-*N'*-(2-chloro-benzoyl)thiourea molecule on the basis of simple general valence force field and normal coordinate analysis calculations helped to assign the vibrational modes of the uncoordinated HL. It is apparent from Table 4 that out of the 72 fundamentals, 54 could be observed in the present case. The close agreements between the observed and calculated frequencies confirm the validity of the present assignment.

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with quotation number CCDC-273278 for HL and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk].

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