Vibrational assignment and structure of N-phenylthiobenzamide - A DFT approach

Mohammad Vakili, Raheleh Afzali, Sayyed Faramarz Tayyari[*]

Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran

Abstract

FTIR and Raman spectra of an anti-bacterial compound, N-phenylthiobenzamide (NptbH), were recorded in the solid phase and in solution. The harmonic vibration wavenumbers, for both the tautomeric forms of NptbH, as well as for its dimeric complex, have been calculated, using density functional B3LYP method involving several basis sets and the results were compared with the experimental values. Conformational studies have been also carried out regarding its tautomeric monomer forms as well as the dimer form. According to all calculations the thione form of NptbH (II) is about 41.2- 75.3 kJ/mol more stable than the thiol form (I) and the dimeric conformation (III) predicted to be more stable than the monomeric conformations (I) and (II). Vibrational assignments have been made, and it is found that the calculated normal mode frequencies of dimeric (III) and monomeric (II) molecules are required for the analysis of IR and Raman spectra of the NptbH in the solid and solution states. The intermolecular sulfur – nitrogen distance in N-H···S hydrogen bond system was found to be in the 3.421-3.448 Å range from these calculations. The calculated hydrogen bond strength was estimated to be in the 27.7-31.5 kJ/mol range (13.9-15.8 kJ/mol per bond).

Keywords: Vibrational spectra; DFT calculations; Thione-Thiol tautomerism; N-Phenylthiobenzamide (NptbH); NptbH dimer

1. Introduction

Thiobenzamides are used as an influenza inhibitor [1]. Furthermore, they have increasing interest as a lube oil additive [2]. Thiobenzamides are found to be inhibitor on the corrosion of mild steel [3] and have been used as inhibitor in enzymatic reactions [4]. These compounds have been used in many reactions [5-8]. Therefore, the spectra and structure of N-phenyl thiobenzamide has remained a subject of great interest.

One of the most interesting properties of NptbH is the possibility of existing two tautomeric forms, thiol (I) and thione (II). This molecule is also capable to be associated by hydrogen bonding into a dimeric structure (III) (see Figure 1).
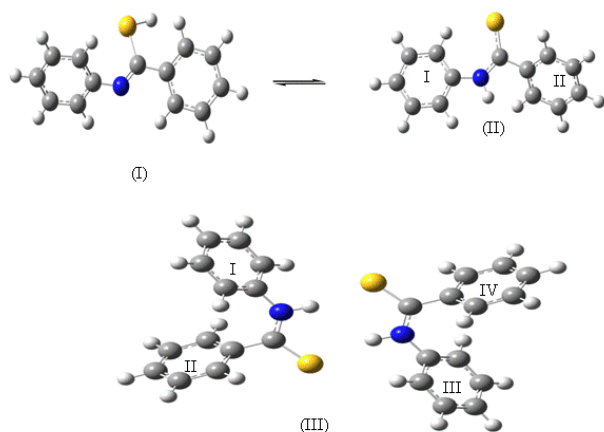

Figure 1. Optimized geometry of NptbH monomer in thiol (I), thione (II) tautomeric equilibrium, and dimer (III) form at B3LYP/6-311G**.

Similar behavior has been reported for other compounds, such as 2-mercaptobenzothiazole (MBT) [9], which are completely in the thione form. It is interesting that NptbH can serve as a ligand in formation of metal complexes [10], which NptbH in these complexes appears in the thiol form. Therefore, the conformational investigation and vibrational analysis of this compound could be interesting.

The aim of the present work is study of geometrical structure, conformational analysis, and vibrational assignment of the NptbH molecule by aid of Density Functional Theory (DFT) methods. Therefore, the geometry of possible thiol, thione, and dimer structures are optimized by DFT methods and the energy of fully optimized structures are compared. The vibrational wavenumbers, IR, and Raman intensities are calculated and compared with the observed values.

2. Experimental Details

N-Phenyl-Thiobenzamide was prepared according to the reported procedure [11].

The IR spectra of NptbH were recorded on a Bomem MB-154 Fourier Transform Spectrophotometer in region 4000-600 cm^{-1} by averaging 20 scans with a resolution of 2 cm^{-1}. The spectra were measured in the solid phase and CCl$_4$ solution.

The FT-Raman spectrum of NptbH in the solid phase was recorded employing a 180° back-scattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtration was afforded by two sets of two holographic technology filters. The spectra were accumulated for 1500 scans with a resolution of 2 cm^{-1}. The laser power at the sample was 300 mW.

Table 1. The absolute total electronic energies (Hartree), N…S distance, E_{HB}, and the energy differences of NptbH at different basis sets [a].

Calculation levels	Dimer			Monomer		
	R	E	E_{HB}	E (thione)	E (thiol)	ΔE
B3LYP/6-31G*	3.448	-1909.919173	31.53	-954.953582	-954.937667	41.79
B3LYP/6-31G**	3.421	-1909.958360	29.68	-954.973528	-954.956727	44.11
B3LYP/6-311G**	3.438	-1910.242921	27.70	-955.116185	-955.100509	41.16
B3LYP/LanL2DZ	3.430	-1133.570208	29.58	-566.779472	-566.750808	75.26

[a] R: optimized N···S distance (Å); E: absolute electronic energy (hartree); ΔE: energy difference between thione and thiol at kJ/mol; E_{HB}: the energy difference between thione electronic energy and dimmer electronic energy at kJ/mol.
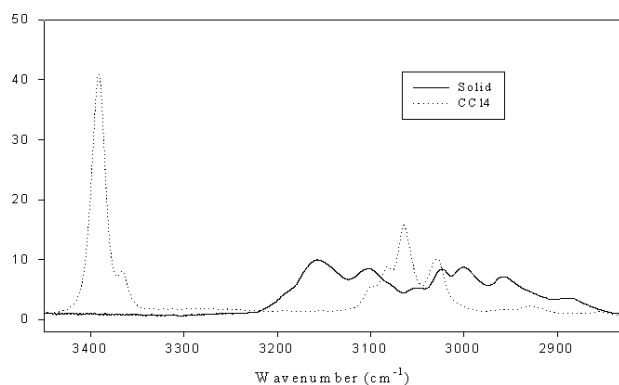
Figure 2. The IR spectra of NptbH (in KBr pellet and CCl₄ solution) in the CH and NH− stretching region.

The Far-IR spectra in the 500 cm⁻¹ region were collected employing a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of 2 cm⁻¹ by averaging the results of about 60 scans.

3. Computational Details

All calculations were performed using Gaussian 03 program [12]. Geometry optimizations for the monomeric and dimeric forms of NptbH (I, II, and III) were calculated at the B3LYP [13, 14] level using 6-31G*, 6-31G**, 6-311G**, and LanL2DZ basis sets. Vibrational data are calculated at the B3LYP/6-311G** level. Approximate frequency assignments are done using GaussView 4.0 program [15], the most dominant mode among others are selected.

4. Results and Discussion

4.1. Optimized geometry and conformational studies

The dimer and the two tautomeric monomer forms of NptbH were subjected to geometry optimization at various levels of theory using the Gaussian03 package [12]. The optimized geometry in various forms of this molecule is shown in the Figure 1. According to our calculations, the both monomeric tautomers of the NptbH (I) and (II) have **C1** symmetry and the dimer form of NptbH has **Ci** and/or **C2** symmetries, but our calculations showed the **Ci** is more stable than **C2** symmetry. The intermolecular sulfur-nitrogen distance in N-H···S hydrogen bond of dimeric form was found to be 3.421 Å at the B3LYP/6-31G** level. This H-bond
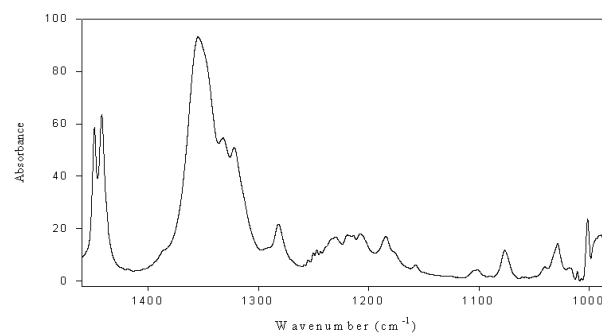
Figure 3. The IR spectra of NptbH in the CCl₄ solution (in the 1500-900 cm⁻¹ region).

distance is about 0.071 Å longer than the corresponding value in MBT, 3.35 Å [9], so the intermolecular hydrogen bonding (IHB), of NptbH is weaker than that of MBT.

The N···S bond length, as an important geometrical parameters of dimer form of NptbH, the calculated total electronic energies of dimer and monomers (in Hartree), and hydrogen bond strength, E_{HB}, (the energy difference between dimmer electronic energy and thione electronic energy) are tabulated in Table 1. According to this table, the N···S distance is in the 3.421- 3.448 Å range.

The energy difference between the thione and thiol forms obtained from DFT method is 44.1 kJ/mol (calculated at the B3LYP/6-31G** level), which is about the same obtained in MBT (44.09 kJ/mol) [9]. According to all calculations, the thione form of NptbH (II) is predicted to be more stable than the thiol tautomer, which is consistent with the experimental results. Because of hydrogen bonding formation, dimerisation of NptbH considerable reduces the energy, *ca.* 27.7- 31.5 kJ/mol. These values indicate that the dimer form is quite stable in comparison to its monomeric form. The energy difference between dimer and thione forms suggests that the hydrogen bond strength in the dimeric form is about 13.9- 15.8 kJ/mol per hydrogen bond.

4.2. Vibration spectrum

The observed and calculated vibrational data for the dimeric and stable monomer (thione form) of NptbH are collected in Tables 2 and 3 (see Appendix), respectively. The IR spectra in the solid state and in CCl₄ solution are shown in Figures 2-4. The Raman spectrum of NptbH in the solid state is illustrated in Figure 5.

Both monomeric tautomers of NptbH (I) and (II) have 72 vibrational modes Raman and IR active. According to the calculations, the dimmer form of NptbH belongs to **Ci** point
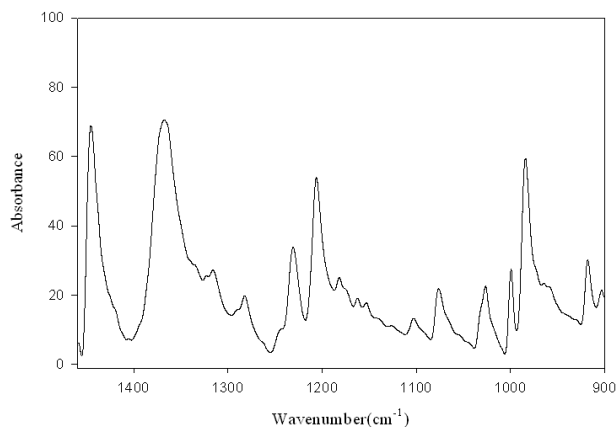
Figure 4. The IR spectra of NptbH in the solid phase (in the 1500-900 region).

Figure 5. The Raman spectra of NptbH in the solid phase.

group; therefore, half of its 150 vibrational modes are IR active and the others are Raman active. Assignments for the phenyl group are given in Wilson's notation [16].

4.3. Comparison between calculated and experimental spectra

Experimental wavenumbers obtained from IR and Raman spectra of this molecule have been compared with the calculated values in both conformations of monomers and dimer molecule. The experimental values are found to be in good agreement with the calculated values for the hydrogen bonded dimer conformation (III) and also with the values for thione monomer conformation (II). The most of the vibrational frequencies were scaled to the experimental frequencies. Mainly two scale factors 0.96 and 0.98 which are used for over and below 2000 cm^{-1}, respectively. The predicted relative intensity also found to be in agreement with the experimental values for most of the vibration modes.

The calculation at the B3LYP/6-311G** level and experimental wavenumbers and relative intensity for all 150 fundamental modes of vibration for NptbH dimer with their corresponding vibrational assignments are given in Table 2 (see Appendix). The calculated normal mode wavenumbers and their relative intensities for the thione form of NptbH (II) obtained at the B3LYP/6-311G** level with the corresponding observed values are given in Table 3 (see Appendix).

4.3.1. Region 4000-2000 cm^{-1}

In the IR spectrum of solid NptbH there was not observed any band over 3300 cm^{-1}, therefore existence of any detectable amount of monomeric form is unlikely. As it is shown in Table 2 (see Appendix) and Figure 2, the IR spectrum of solid NptbH indicates a relatively broad and strong band centered at 3156 cm^{-1}, which disappear in the solution and a strong and narrow band appears at 3392 cm^{-1}. According to our calculations, we assigned this band to the NH stretching modes in the dimeric form, respectively. Rai et al. [9] reported the corresponding bands in 2-mercaptobenzothiazole at 3112 and 3080 cm^{-1}. Therefore, the intermolecular H-bond in NptbH dimer is weaker than that in the 2-mercaptobenzothiazole dimer.

The IR spectrum of NptbH in the CCl_4 solution indicates a very strong band at 3392 cm^{-1} and a weak band at 3366 cm^{-1}, which the former is assigned to the NH stretching
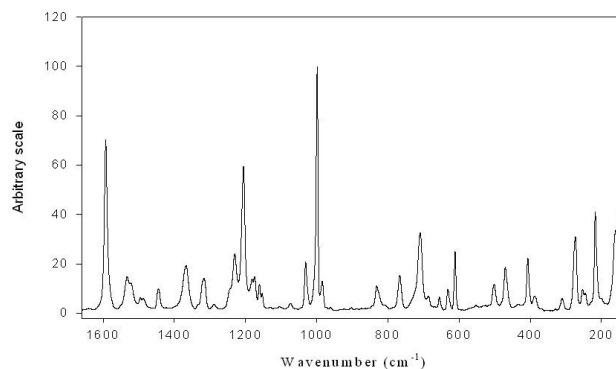
in the thione form and the latter was considered as a combination band. The absence of any band frequency in the 2500-2600 cm^{-1} range rules out the existence of any detectable amount of thiol tautomer in the sample.

The bands at 3082, 3052, 3025 cm^{-1} in the solid state and 3100, 3082, 3065, and 3029 cm^{-1} in the solution are attributed to the CH stretching of the phenyl groups.

4.3.1.1. Overtone and combination bands

The medium bands observed in this region at 3000, 2956, and 2885 cm^{-1} can be interpreted as overtone bands of the fundamental frequencies at 1496, 1484, and 1446 cm^{-1}, respectively.

4.3.2. Region 2000-1000 cm^{-1}

The medium band in the IR spectra of the solution and solid state at about 1590 cm^{-1} is attributed to 8a mode of the phenyl groups, which this band is somewhat coupled with the NH bending modes.

The strong band with a shoulder at 1534 and 1522 cm^{-1} in the solid state and its corresponding Raman band at 1521 cm^{-1} are assigned to the NH bending mode coupled to the N-C stretching. The corresponding band in the dimer of 2-mercaptobenzothiazole (2-MBT) appears at 1497 cm^{-1} [9].

The strong bands at 1496 and 1484 cm^{-1} in the solid state are attributed to the 19a. These bands in solution appear at 1499 and 1488 cm^{-1}. In the solution IR spectrum, two strong bands observed at 1449 and 1442 cm^{-1} are attributed to 19b. These bands are coupled to the NH bending mode. The corresponding bands in the solid state appear at 1446 and 1421 cm^{-1}.

The strong and relatively broad IR band in solid state at 1367 cm^{-1} is attributed to the asymmetric NC stretching coupled to 3 vibrational mode of the phenyl group. The red shift of this band to 1356 cm^{-1} in the solution confirms this coupling and is in agreement with theoretical results. The 3 and 14 vibrational modes of the phenyl rings are observed at about 1332-1281 cm^{-1} region for solution and solid states. The IR and Raman spectra in the solid state show a shoulder band at 1244 cm^{-1}, which is assigned to the N-Ph and C-Ph stretching modes, the corresponding stretching mode in solution appears at 1230 and 1218 cm^{-1}.

The 9a mode of the phenyl ring of both benzoylacetone conformers [17] is observed at 1200 and 1185 cm^{-1}, while in NptbH this mode appeared at 1205-1182 cm^{-1} in CCl_4 solution and solid state. The medium Raman

band at 1031 cm^{-1} is assigned to the 18a coupled to the asymmetric C=S stretching.

4.3.3. Region below 1000 cm^{-1}

The very strong Raman band observed at 998 cm^{-1}, according to our calculations, is caused by the 12 mode of the phenyl groups. The strength of both Raman and IR bands confirms this assignment. The corresponding modes in solution observed at 1001 and 995 cm^{-1}. The IR band in both states at about 990 cm^{-1} is attributed to the 5 mode of the phenyl groups.

The very strong IR bands at 709 and 685 cm^{-1} are assigned to the 11 and 4 vibrational modes of the phenyl groups, respectively. The corresponding modes in solution observe at about 700 cm^{-1}.

According to our calculation the out-of-plane NH bending is coupled with other vibrations. The bands at 773 and 768 cm^{-1} in the solid state are engaged with the out-of-plane NH bending. The corresponding bands in the CCl$_4$ solution are observed at 693, and 687 cm^{-1}, which are considerably shifted toward lower frequencies.

5. Conclusions

The hydrogen bonded cyclic dimer form of NptbH (III) is more stable in comparison to its tautomric monomers (I, II). The quantum mechanical calculations for dimer of NptbH (III) are highly required for the interpretation of the solid IR and Raman spectra. According to the DFT calculations, which it is in agreement with the infrared spectrum in solution, the thione tautomeric form (II) is found to be more stable in comparison to the thiol form (I). There are very less spectral signs of the thione-thiol tautomeric equilibrium in the solid phase of NptbH, since its vibrational spectra are mostly consistent with the thione form alone. The predicted shift in NH-stretching vibration towards the lower wavenumber side with the B3LYP/6-311G** calculations for the most stable dimer form (III), is in better agreement with experimental results. The intermolecular sulfur-nitrogen distance in N-H…S hydrogen bonds was found to be 3.421-3.448 Å from these calculations, while in the case of MBT is 3.35 Å, this blue shift is also in agreement with the experimental value.

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Appendix

Table 2. Vibrational assignments, experimental, and calculated wavenumbers in cm^{-1} (with relative intensity) of NptbH dimer[a].

No.	Sym	Theoretical $F_1{}^b$	$F_2{}^b$	I_{IR}	A_R	Exp. IR	Raman	Assignment
						3185(sh)		2x1593
1	Au	3303	3171	2259	0	3156(m)		υ(NH)
2	Ag	3280	3148	0	2990		3178(vw, br)	υ(NH)
3	Ag	3206	3078	0	162		3075(sh)	(2, 20b) (I, III)
4	Au	3206	3078	5	0	3102(m)		(2, 20b)(I, III)
5	Ag	3200	3072	0	397		3075	2 (lI, IV)
6	Au	3200	3072	12	0	3082(vw)		2(II, IV)
7	Ag	3196	3068	0	104		3057(m)	(2, 20b)(II, IV)
8	Au	3196	3068	20	0	3052(vw)		(2, 20b)(II, IV)
9	Au	3194	3066	31	0	3052		20b(I, III)
10	Ag	3194	3066	0	565		3057	20b(I, III)
11	Ag	3186	3059	0	324		3057	20a(I, III)
12	Au	3186	3059	51	0	3052		20a(I, III)
13	Ag	3186	3058	0	154		3057	20a(II, IV)
14	Au	3186	3058	47	0	3052		20a(lI, IV)
15	Au	3176	3049	13	0	3025(m)		7b(l, III)
16	Ag	3176	3049	0	308		3023(vw)	7b(I, III)
17	Au	3176	3049	19	0	3025		7b(lI, IV)
18	Ag	3176	3049	0	274		3023	7b(lI, IV)
19	Ag	3167	3041	0	82		3023	13(I, III)
20	Au	3167	3041	2	0			13(I, III)
21	Ag	3165	3039	0	95		3023	13(lI, IV)
22	Au	3165	3039	0	0			13(lI, IV)
						3000(w)	3000(w)	2*1496
						2958(w)	2967(w)	2*1484
						2885(w)		2*1446
23	Au	1643	1610	16	0	1593(m)		8a(I, III), δ(NH)
24	Ag	1643	1610	0	369		1592(s)	8a(I, III), δ(NH)
25	Ag	1640	1607	0	359		1592	8a(lI, IV), δ(NH)
26	Au	1640	1607	5	0			8a(lI, IV), δ(NH)
27	Au	1635	1602	82	0	1577(sh)		8b(I, III), δ(NH)
28	Ag	1634	1602	0	82		1592	8b(I, III), δ(NH)
29	Au	1619	1586	14	0	1558(vw)		8b(lI, IV), δ(NH)
30	Ag	1618	1586	0	13		1532(m)	8b(lI, IV), δ(NH)
31	Au	1580	1548	305	0	1534(s)		δ(NH), ν(NC)
32	Ag	1570	1538	0	74	1522(sh)	1521(m)	δ(NH), ν(NC)
33	Ag	1527	1496	0	81		1492(w)	19a(I, III)
34	Au	1526	1496	142	0	1496(s)		19a(I, III)
35	Au	1523	1492	7	0	1484(sh)		19a(lI, IV)
36	Ag	1523	1492	0	42		1486 (w)	19a(lI, IV)
37	Au	1482	1452	51	0	1446(s)		19b(I- IV), δ(NH)
38	Ag	1480	1451	0	17		1444(w)	19b(I- IV), δ(NH)
39	Ag	1475	1445	0	7			19b(I- IV), δ(NH)
40	Au	1474	1444	5	0	1421(sh)		19b(I- IV), δ(NH)
41	Ag	1414	1386	0	293		1366(m)	υ(NC), 3(I- IV)
42	Au	1412	1384	602	0	1367(s)		υ(NC), 3(I- ,IV)
43	Au	1356	1329	21	0	1334(sh)		3(I, III)
44	Ag	1356	1329	0	8		1334(vw)	3(I, III)
45	Au	1354	1327	4	0	1334		3(lI, IV)
46	Ag	1354	1327	0	9		1334	3(lI, IV)
47	Au	1331	1305	31	0	1315(sh)		14(I, III)
48	Ag	1331	1304	0	29		1317(w)	14(I, III)
49	Au	1322	1296	3	0	1281(w)		14(lI, IV)
50	Ag	1322	1296	0	14		1287(vw)	14(lI, IV)

No	Sym					IR exp	Raman exp	Assignment
51	Au	1250	1225	211	0	1244(sh)		ν(N-Ph), ν(C-Ph)
52	Ag	1250	1225	0	187		1244(sh)	ν(N-Ph), ν(C-Ph)
53	Au	1214	1190	137	0	1230(m)		ν(C=S), 19a
54	Ag	1212	1188	0	239		1230(m)	ν(C=S), 19a
55	Au	1203	1179	40	0	1205(s)		9a(I- IV)
56	Ag	1203	1179	0	81		1205(s)	9a(I- IV)
57	Au	1199	1175	19	0	1182(sh)		9a(I- IV)
58	Ag	1199	1175	0	206		1181(w)	9a(I- IV)
59	Ag	1184	1160	0	13		1174(w)	15(I- IV)
60	Au	1184	1160	0	0			15(I- IV)
61	Au	1183	1159	1	0	1162(sh)		15(I- IV)
62	Ag	1183	1159	0	12		1160(w)	15(I- IV)
63	Au	1111	1089	17	0	1103(w)		18b(I- IV)
64	Ag	1110	1088	0	7		1104(vw)	18b(I- IV)
65	Au	1105	1083	2	0	1075(m)		18b(I- IV)
66	Ag	1105	1083	0	8		1073(vw)	18b(I- IV)
67	Au	1059	1038	42	0	1026(sh)		18a(II, IV), ν(C=S)
68	Ag	1058	1037	0	63		1031(m)	18a(II, IV), ν(C=S)
69	Au	1050	1029	6	0	1026		18a(I, III)
70	Ag	1049	1029	0	41		1031	18a(I,III)
71	Au	1033	1013	92	0	1015(w)		12(II, IV), υ(C=S)
72	Ag	1031	1010	0	26		1007(sh)	12(II, IV), υ(C=S)
73	Ag	1017	996	0	193		998(vs)	12(I- IV)
74	Au	1017	996	0	0			12(I- IV)
75	Au	1016	996	4	0	999(m)		12(I- IV)
76	Ag	1016	996	0	48		984(w)	12(I- IV)
77	Au	1007	986	2	0	984(s)		5(II, IV)
78	Ag	1007	986	0	1			5(II, IV)
79	Au	1000	980	1	0			5(I, III)
80	Ag	1000	980	0	1			5(I, III)
81	Ag	987	967	0	1		962(vw)	17a(II, IV)
82	Au	987	967	3	0	959(sh)		17a(II, IV)
83	Au	980	960	1	0			17a(I, III)
84	Ag	980	960	0	1			17a(I, III)
85	Au	941	922	17	0	918(m)		10b(I- IV)
86	Ag	941	922	0	1			10b(I- IV)
87	Au	926	907	16	0	902(w)		10b(I- IV)
88	Ag	925	907	0	2		902(vw)	10b(I- IV)
89	Au	868	851	42	0	825(w)		γ(N-H), 6a(I- IV)
90	Ag	862	845	0	24		830(w)	γ(N-H), 6a(I- IV)
91	Au	857	840	5	0			10a(II, IV)
92	Ag	857	840	0	8		822(sh)	10a(II, IV)
93	Au	846	829	4	0	808(vw)		10a(I, III), γ(NH)
94	Ag	846	829	0	1		808(vw)	10a(I, III), γ(NH)
95	Au	828	811	70	0	773(sh)		γ(NH)
96	Ag	816	800	0	149		767(m)	γ(NH)
97	Ag	788	772	0	11		767	11(II, IV), γ(NH)
98	Au	788	772	61	0	768(s)		11(II, IV), γ(NH)
99	Au	773	758	27	0	738(vw)		11(I- IV)
100	Ag	771	756	0	13		732(sh)	11(I- IV)
101	Au	734	719	70	0	715(sh)		6a(II, IV),11(I, III), δ(CN-Ph)
102	Ag	732	718	0	27		715(sh)	6a(II, IV),11(I, III), δ(CN-Ph)
103	Au	710	696	51	0	709(vs)		11(II, IV)
104	Ag	710	695	0	5		709(s)	11(II, IV)
105	Au	708	694	72	0	685(vs)		4(I, III)
106	Ag	708	694	0	2		685(w)	4(I, III)
107	Au	653	640	9	0	669(m)		γ(C=S)
108	Ag	652	639	0	29		669(vw)	γ(C=S)
109	Au	633	621	2	0	655(sh)		6b(I, III)
110	Ag	633	620	0	13		655(w)	6b(I, III)
111	Au	628	615	4	0	631(sh)		6b(II, IV)
112	Ag	628	615	0	7		630(mw)	6b(II, IV)

No.	Sym	F1	F2	I.IR	A_R	IR	Raman	Assignment
113	Au	618	605	35	0	612(w)		6a(I, III)
114	Ag	618	605	0	22		611(m)	6a(I, III)
115	Au	566	555	71	0	551(m)		6a(I- IV)
116	Ag	559	548	0	8		552(vw)	6a(I- IV)
117	Au	509	499	6	0	501(vs) [#]		16b(II, IV)
118	Ag	508	498	0	5		501(m)	16b(Il, IV)
119	Ag	484	475	0	16		472(m)	16b(I- IV), νS···N
120	Au	484	475	12	0	466(w)		16b(I- IV), νS···N
121	Au	421	412	1	0			16a(I, III)
122	Ag	420	412	0	11		407(m)	16a(I, III)
123	Au	415	406	1	0	409(w)		16a(Il, IV)
124	Ag	415	406	0	9		407	16a(Il, IV)
125	Ag	366	359	0	9		389(vw)	16b(I- IV), νC=S
126	Au	364	357	11	0	388(vw)		16b(I- IV), νC=S
127	Au	337	330	5	0			γ(CNC)
128	Ag	337	330	0	4		311(vw)	γ(CNC)
129	Ag	275	269	0	8		274(m)	γ(N-Ph), γC-Ph,, δC=S
130	Au	273	268	1	0	273(vw)		γ(N-Ph), γC-Ph,, δC=S
131	Au	238	233	13	0	253(w)		δC=S , γ(N-Ph)
132	Ag	234	230	0	15		245(vw)	δC=S , γ(N-Ph)
133	Ag	204	200	0	14		217(m)	δ(C-Ph)
134	Au	202	198	2	0	214(w)		δ(C-Ph)
135	Au	156	153	13	0	149(s)		δ(N-Ph)
136	Ag	148	145	0	8		160(m)	δ(N-Ph)
137	Au	94	92	3	0			γC=S
138	Ag	91	89	0	14			γC=S
139	Ag	71	69	0	4			νNH···S
140	Ag	67	66	0	8			δNH···S
141	Au	65	64	0	0			τ(Ph-N)
142	Ag	54	53	0	10			τ(Ph-C), δNH···S
143	Au	53	52	0	0			τ(Ph-C)
144	Ag	45	44	0	8			τ(Ph-N-C)
145	Au	43	42	1	0	55(s)		τ(Ph-N), δNH···S
146	Ag	40	39	0	15			τ(Ph-N), γNH···S
147	Ag	35	34	0	3			γ(NPTBH-NPTBH)
148	Au	30	30	2	0			δ(NPTBH-NPTBH)
149	Au	12	12	0	0			τ(NPTBH-NPTBH)
150	Au	8	8	2	0			γ(NPTBH-NPTBH)

[a] IR, infrared; R, Raman; ν, stretching; δ, in plane bending; γ, out of plane bending; σ bending of two NptbH molecules against each other. v, very; s, strong; m, medium; w, weak; sh, shoulder; t, torsion, I.IR, infrared intensity in KM/Mole; A_R, Raman scattering activities in Å^4/AMU; # below 600 cm^{-1} obtained with different instruments.

[b] Unscaled (F1) and scaled (F2) frequencies (theoretical frequency scaled by 0.96, and 0.98 for the 3200–1700, below 1700 cm^{-1} regions, respectively) calculated at the B3LYP/6-311G** level.

Table 3. Vibrational assignments, experimental, and calculated wavenumbers in cm^{-1} of NptbH thione form[a].

No.	Theoretical			Experimental	Assignment
	F_1[b]	F_2[b]	I.IR	IR	
1	3572	3429	8	3392(m)	ν(NH)
2	3242	3112	3	3100(vw)	(2, 20b)(l)
3	3203	3075	2		2(II)
4	3193	3065	8	3082(vw)	2(I)
5	3191	3063	7		(2, 20b)(II)
6	3180	3052	7	3065(w)	20a(II)
7	3179	3052	6		20a(I)
8	3170	3043	0		7b(II)
9	3169	3043	0		7b(I)
10	3162	3035	1		13(II)
11	3147	3021	4	3029(vw)	13(I)
12	1644	1611	5		8a(I), δ(NH)
13	1640	1607	6	1601(m)	8b(I) , δ(NH), 8a(II), υ(NC)
14	1638	1606	9	1595(sh)	8a(II, I), δ(NH)
15	1617	1585	0		8b(II)
16	1574	1542	72	1526(s)	δ(NH), 19b(I), ν(NC)
17	1527	1496	34	1499(vs)	19a(I)
18	1520	1489	1	1488(sh)	19a(II)
19	1479	1450	4	1449(s)	19b(I, II), δ(NH)
20	1474	1445	10	1442(s)	19b(I, II), δ(NH)
21	1383	1356	100	1356(vs)	3(I), ν(NC)
22	1353	1326	2		3(II)
23	1351	1324	33	1332(s)	3(I), νa(C-N-Ph)
24	1344	1317	7	1322(sh)	14(I, II), ν(N−C=S)
25	1318	1291	7	1281(w)	14(II), νN-CS
26	1246	1221	6	1230(w)	18a(I, II), υ(C-ph)
27	1226	1202	12	1218(w)	18a, υ(N-ph), δ(NH), ν(C=S)
28	1205	1181	1	1207(w)	9a(I)
29	1204	1180	2	1185(w)	9a(II)
30	1184	1161	0	1176(w)	15(I, II)
31	1184	1160	0		15(II, I)
32	1112	1090	2	1102(w)	18b(I)
33	1106	1084	3	1077(w)	18b(II)
34	1054	1033	1	1028(w)	18a(II, I)
35	1052	1031	3	1028	18a(I, II)
36	1015	995	1	1001(w)	12(II)
37	1014	994	1	1001	12(I), 1(I), ν(C=S)
38	1009	989	1	995(w)	[12, 5](II)
39	1005	985	5	991(w)	1 (II), n(C=S)
40	1004	984	4		1 (I), n(C=S)
41	986	966	1	973(vw)	17a(II)
42	975	956	0		17a(I)
43	940	921	1	920(vw)	17b(II)
44	919	901	2	901(vw)	17b(I)
45	858	841	1		10a(II)
46	839	822	0		10a(I)
47	835	818	1		6a(I,II), υ(NC), υ(C-Ph)
48	780	764	10		11(II)
49	773	757	20		11(I)
50	743	728	5		δ(CNC), υ(C=S)
51	713	698	9	711(w)	[11, 4](II)
52	704	690	16	702(sh)	[11, 4](I)
53	678	665	1		6a(I, II)
54	670	656	9	693(s)	γ(NH), 11(II)

55	633	620	1	687(m)	γ(NH), 6b(I, II)
56	631	618	0	671(vw)	6b(I)
57	616	604	3	615(w)	γ(NH), 6a(II)
58	573	561	5	558(w)	6a(I, II)
59	520	510	6	503(w)	16b(I), γ(NH)
60	487	478	1		16b(II)
61	417	409	0		16a(I, II)
62	416	408	0		16a(II, I)
63	357	350	0		δ(N-Ph)
64	304	298	0		δ(C-Ph)
65	272	267	0		γ(C-Ph), γ(N-Ph)
66	247	242	0		δ(C=S)
67	198	194	1		δ(C-ph), γ(N-ph)
68	170	166	0		γ(C-Ph), δ(C-N-Ph)
69	83	81	0		γ(C-Ph)
70	70	69	0		τPh-C-N
71	44	43	0		τPh
72	28	27	0		τPh

[a] IR, infrared; R, Raman; ν, stretching; δ, in plane bending; γ, out of plane bending ; v, very; s, strong; m, medium; w, weak; sh, shoulder; t, torsion; I.IR, infrared intensity in KM/Mole.

[b] Unscaled (F_1) and scaled (F_2) frequencies (theoretical frequency scaled by 0.96, and 0.98 for the 3200–1700, below 1700 cm^{-1} regions, respectively) calculated at the B3LYP level, using 6-311G** basis set.