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Theoretical and Vibrational Analysis of Substituted Hydrazones: Valence Force Field

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Anahtar Kelimeler
Değerlik Kuvvet Alanı,
GF Matrix,
DFT Hesaplamaları

Abstract: The vibrational spectroscopic and theoretical investigation of some diketo hydrazones derivatives; (2Z)-2-[2-(4-methylphenyl)hydrazinylidene]-1-(naphthalen-2-yl)butane-1,3-dione(NBTMH), (2Z)-2-[2-(4bromophenyl)hydrazinylidene]-1-(naphthalen-2-yl)butane-1,3-dione (NBTBH), and (2Z)-2-[2,4-(phenyl)hydrazinylidene]-1-(naphthalen-2-yl) butane-1,3-dione (NBTBFH) were made in this study. Theoretical investigations of these compounds includes conformational, NBO and vibrational analyses to see the most stable structure, possible hydrogen bondings and chemical bond diversities of the compounds, respectively. The potential energy surfaces of the compounds were obtained by DFT method regarding the selected degree of torsional freedom, which was varied from 0° to 360° in 18° steps. The geometries of the compounds were optimized through conformational analysis followed by the minimum energy conformer. Possible hydrogen bonds were searched by NBO analysis. The vibrational frequencies were calculated using the optimized geometry (bond lengths, bond angles), the atomic masses, and the force constants as the input. The atomic radii and the electronegativities of the compounds were also used as the input to calculate IR and RAMAN activities. Wilson's GF Matrix method was used for the calculation of vibrational frequencies and the activities. The experimentally measured vibrational spectra were elucidated through theoretical calculations.

Dallanmış Hidrazonların Teorik ve Titreşim Analizi: Değerlik Kuvvet Alanı

AnahtarKelimeler
Diketon Hidrazon,
Değerlik kuvvet Alanı,
GF Matrix,
DFT hesaplamaları

Öz: Bazı diketo hidrazon türevlerinin, (2Z) -2- [2- (4-metilfenil) hydrazinylidene] -1-(naftalen-2-il) bütan-1,3-dion (NBTMH), (2Z) -2- [2- (4-bromofenil) hidraziniliden] -1-(naftalen-2-il) bütan-1,3-dion (NBTBH) ve (2Z) -2- [2 Bu çalışmada 4- (fenil) hidraziniliden] -1- (naftalen-2-il) bütan-1,3-dion (NBTBFH), titreşim spektroskopik ve teorik olarak incelenmesi yapılmıştır. Bu bileşiklerin teorik çalışmaları sırasıyla; konformasyonları, en kararlı yapıların NBO ve titreşim analizleri, olası hidrojen bağları ve kimyasal bağ türlerini içermektedir. Bileşiklerin potansiyel enerji yüzeyleri, 0° ila 360° arası 18°'lik aralıklarla değişen torsiyon değerinden bağımsız olarak DFT yöntemi ile elde edilmiştir. Bileşiklerin konformasyon analizi ardından minimum enerjili konformerleri optimize edilmiştir. Olası hidrojen bağları NBO analizi ile araştırılmıştır. Titreşim frekansları, optimize edilmiş geometrileri (bağ uzunlukları, bağ açıları), atom kütleleri ve kuvvet sabitleri kullanılarak hesaplanmıştır. Bileşiklerin atomik yarıçapları ve elektronegatiflikleri de IR ve RAMAN aktivitelerini hesaplamak için kullanıldı. Titreşim frekanslarının ve aktivitelerin hesaplanmasındaWilson'ın GF Matrix yöntemi kullanılmıştır. Deneysel olarak ölçülen titreşimspektrumları teorik hesaplamalarla açıklanmıştır.

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1. Introduction

Some diketo hydrazone compounds are present in chemical structure of some important pigments. Depending on the type and the position of the side functional groups they show different color characteristics. The most important yellow classical pigments are a group of acetoacetanilide series of compounds. These are known as diarylide yellow compounds [1-3]. These yellow colored compounds are used in printing inks, painting and coloring of plastic materials. They are available in markets commercially in different tautomeric forms [4]. Due to general insolubility of these compounds, they are usually dispersed in solid form in the matrix of polymeric structure and used as coloring material. Their structures are examined through x-ray methods [5, 6].

In this study, the novel compounds; (2Z)-2-[2-(4-methylphenyl)hydrazinylidene]-1-(naphthalen-2-yl)butane-1,3-dione (NBTMH), (2Z)-2-[2-(4-bromophenyl)hydrazinylidene]-1-(naphthalen-2-yl)butane-1,3-dione (NBTBH), and (2Z)-2-[2,4-(phenyl)hydrazinylidene]-1-(naphthalen-2-yl)butane-1,3-dione (NBTBFH) as azo dyes were examined from several aspects regarding spectroscopic and physicochemical properties to clarify some of their behaviors. Conformer analysis through geometry optimization, vibrational analysis, and NBO analysis were performed. The three diketo hydrazone compounds differ from each other by substitution of R group as shown in Figure 1.

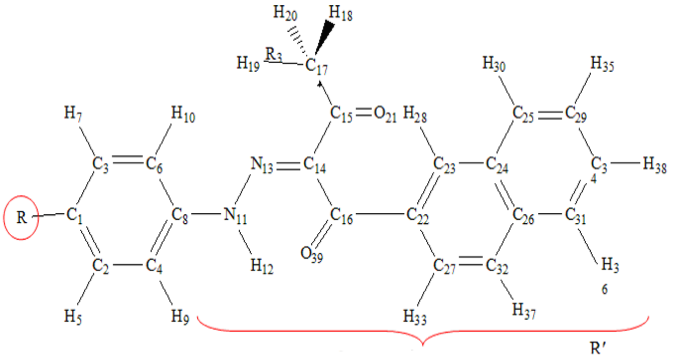

Figure 1. Numbering of atoms in NBTMH (where R= CH3, Br, R′).

The experimental IR and Raman spectra of these azo dyes were recorded and assigned by normal coordinate analysis using Wilson's GF matrix method. The advantage of using GF matrix is that it makes the problem more coherent and even the force constants in terms of these internal coordinates have a more easily visualized physical meaning than others. The force constants can be transferred from one molecule to another if they belong to the same chemical group. The geometry optimizations of these molecules were made by theoretical calculations to obtain most stable conformer employing DFT/B3LYP method. The intramolecular interactions and the hydrogen bondings were searched by NBO analysis. The theoretical results were compared with the experimental analogs and found to be in good agreement.

2. Material and Method

2.1. Experimental

The novel compounds; NBTMH, NBTBH, and NBTBFH as azo dyes were synthesized [6]. In this study, Jasco FTIR spectrometer was used in 400-4000 cm^{-1} wave number region for both compounds. 30 scans were made for each spectrum. All samples were prepared in 1-3 % (w/w) KBr pellets to measure IR absorption signals as shown in Figure 2.

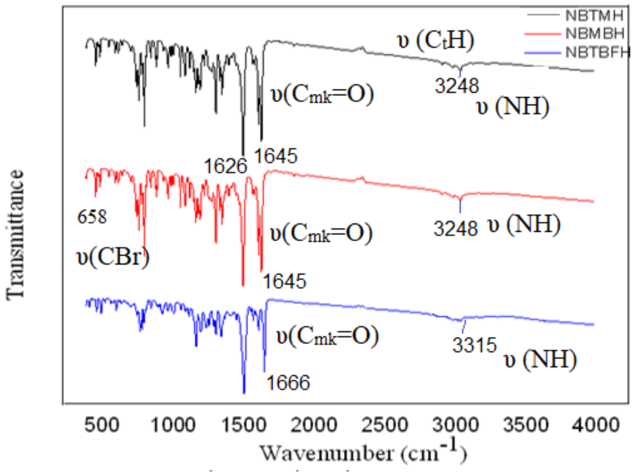

Figure. 2. Experimental FT-IR Spectra.

The Raman spectra were recorded on a Horiba Jobin Yvon Labram Model HR 80 Raman spectrometer. The spectrometer is equipped with a Nd: YAG LASER operated at 20 mW with a wavelength 532.1 nm. The collected signals were transmitted into a 600 grooves/mm holographic grating with a resolution of 3 cm^{-1}. The Raman spectra were collected by manually placing the 10x lens near the desired point of the sample on silicon wafer and all the spectra were calibrated according to the silicon peak at 522 cm^{-1}. An increasing photoluminescence effect above 1700 cm^{-1} of the spectrum for NBTMH negatively affected the Raman bands in this region. A similar destructive effect was also observed in the Raman spectrum of NBTBH, NBTBFH compounds. Only visible Raman signals exceeding the fluorescence bands were taken to the frequency lists additionally to IR bands for assignments of vibrational modes.

2.2 Computational Procedures

The conformer analyses were performed in two successive steps employing Spartan 08 [7] and Gaussian 09 programs [8]. The possible conformers of the compounds NBTMH, NBTBH were determined first by Spartan 08 program employing MMF method. The imaginary frequencies in calculated vibrational spectra, the overlapping structures and the structures having energies above 2 kcal/mol were eliminated. Using DFT/B3LYP/6-31 G [9] method the lowest relative energy conformer was determined as the most stable structure in Spartan 08 for practical and fast treatment and the output was transferred to Gaussian 09 program as input for further calculations. Gauss View 3.09 program [10] was also employed to form the molecular structure and to visualize 3D appearance; NBTMH, NBTBH and NBTBFH have been illustrated on Figures 4, 5 and 6, respectively. The critical torsional angles of flexible bonds affecting the conformational structures were determined as T ($C_{22}C_{16}C_{14}C_{15}$), T ($C_8N_{11}N_{13}C_{14}$), and T ($N_{13}C_{14}C_{15}C_{17}$). The potential energy surfaces were obtained through rotating the related bonds by 18°increaments for 20 times to get 360° full scan using DFT B3LYP/6-31G method, they were showed figure 7. More precise scanning was applied around the minimum energy regions by 2° to get more correct minimum energy value.

The optimized geometrical parameters including only the bond lengths and the bond angles for NBTMH, NBTBH and NBTBFH (**Appendix A**, **Appendix B**, **Appendix C**, respectively) were listed in supplementary data the internal coordinates can be seen on Figure 3 and the optimized structures of these compounds have been illustrated on Figures 4, 5 and 6, respectively. The calculated potential energy surfaces can be seen in Figure 7

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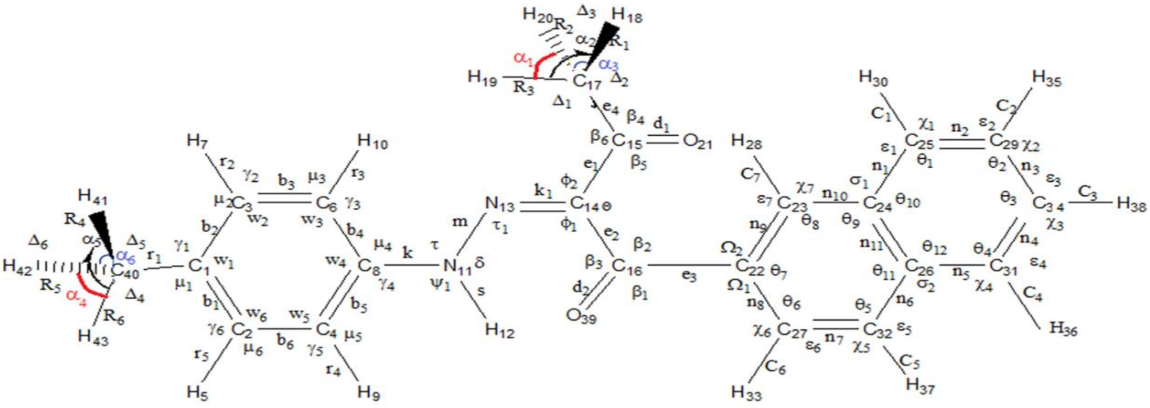


Figure 3. Internal coordinates of NBTMH.

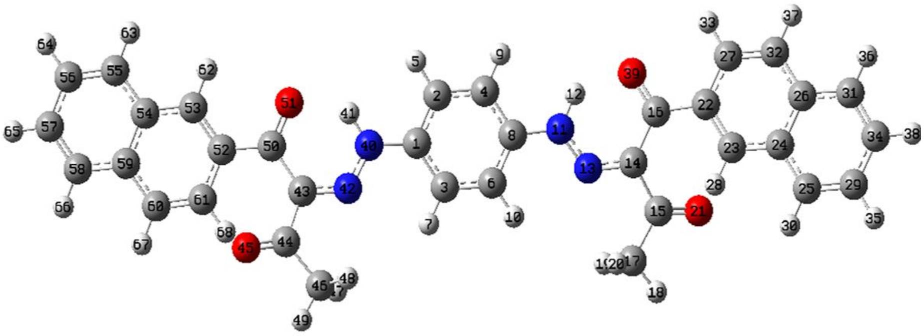


Figure 4. Optimized geometry of the NBTBFH.

Figure 5. Optimized geometry of the NBTMH.

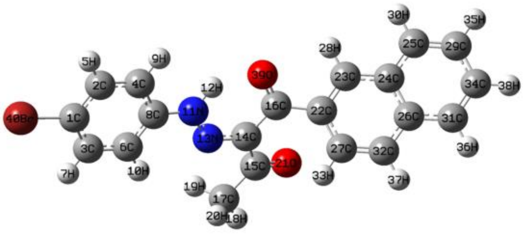
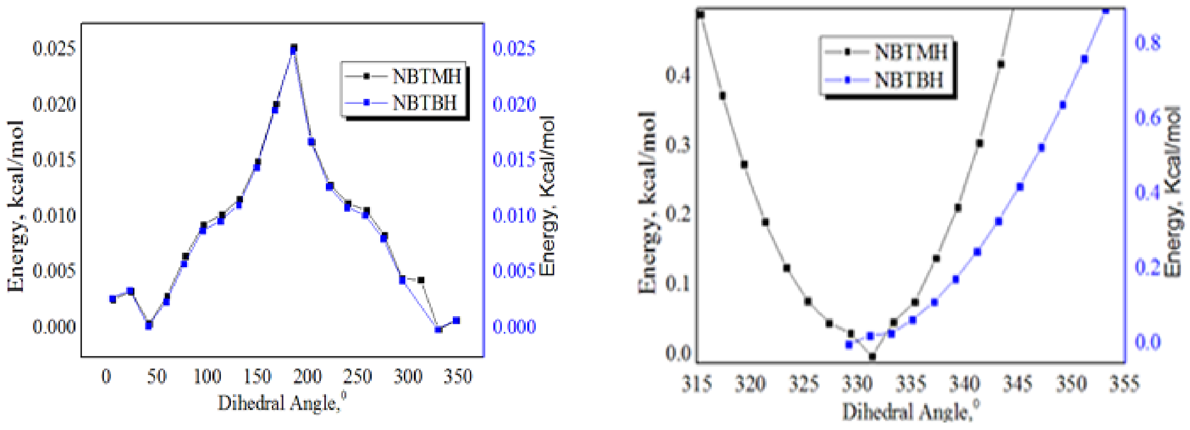
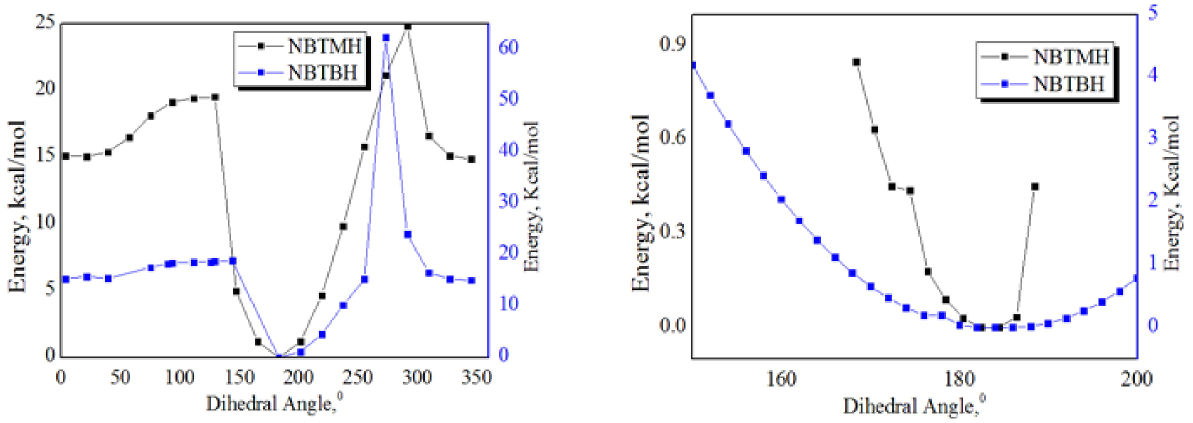


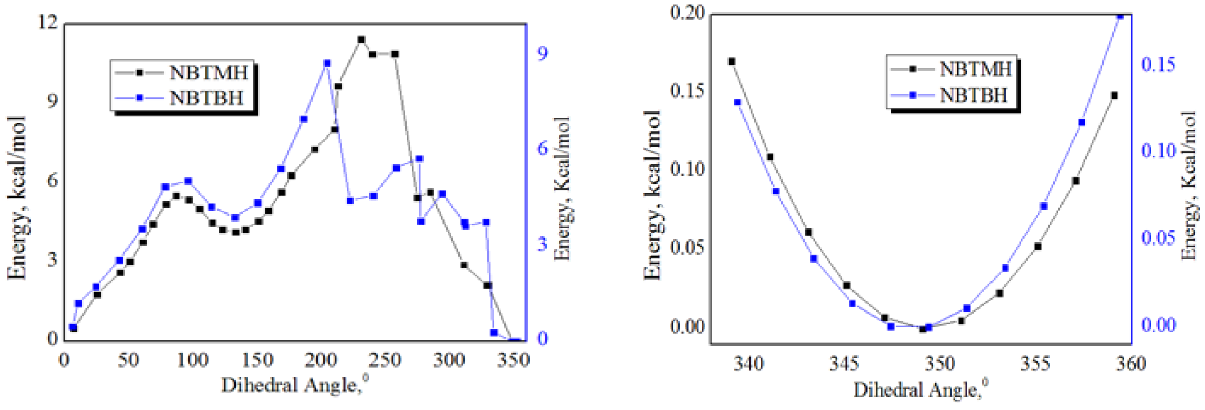
Figure 6. Optimized geometry of the NBTBH.



7a. Energy vs. rotational angle of $C_{16}C_{14}$ (18^0)   **7b.** Energy vs. rotational angle of $C_{16}C_{14}$ (2^0)



7c. Energy vs. rotational angle of $N_{11}N_{13}$ (18^0)   **7d.** Energy vs. rotational angle of $N_{11}N_{13}$ (2^0)



7f. Energy vs. rotational angle of $C_{14}C_{15}$ (18°)   **7g.** Energy vs. rotational angle of $C_{14}C_{15}$by (2^0)

Figure 7. Energy vs. scanned rotational angles of flexible bonds by 18° and 2° increments.

The Normal Coordinate Analysis was made by Wilson's GF matrix method [11]. The frequencies were calculated by the program written originally by Shimanouchi [12], the activities (IR & Raman) and the normal coordinate treatment of the related compounds to interpret their vibrational spectra have been performed by the program SPSIM developed by Schrader et al. [13-17].The valence force constants transferred from similar compounds were refined to calculate vibrational frequencies in AXS and NCF modules then IR and Raman activities were calculated in ACT module of SPSIM program [16].Additional calculation of vibrational frequencies were performed by DFT/B3LYP 6-31G(d, p) method to compare the results with the semiemprical method used in SPSIM program. Intra molecular H bondings were investigated through NBO analysis and the criteria for H bond classification were considered as given by Jeffry [18].

3. Results

3.1 Conformer Distribution and NBO Analysis

The critical torsional angles and the corresponding molecular energies before and after the conformational analysis of NBTMH and NBTBH can be seen on Table 1. The critical torsional angles of NBTMH and NBTBH calculated by the two programs did not differ too much as can be seen from the graphs given in Figure 7. This result was expected since the initial geometrical parameters for the calculation in Gaussian were obtained from the calculation of the molecule in Spartan using the same method DFT-B3LYP in both. This procedure is usually preferred because of easy, fast and practical conformational analysis in Spartan and more accurate molecular energy calculations [19]. The critical torsional angles for the third compound NBTBFH were transferred from the compound NBTMH in the final form because of very similar duplicated structure of NBTMH. After optimization of the geometries the possible H-bondings of the most stable conformer were determined depending on the Jeffry's classification of hydrogen bonding. No strong H-bonding was observed in any of the compounds NBTMH and NBTBH. A medium H-bonding were found between $H_{12}\cdots O_{39}$ atoms of NBTMH and $H_{12}\cdots O_{39}$ atoms of NBTBFH with respect to this classification. A weak H bondings were also found between $H_{28}\cdots O_{21}$ atoms in NBTMH and $H_{28}\cdots O_{21}$ atoms in NBTBH molecules. No energy transfer was found for NBTMH and NBTBH molecules originate from the electron transfer but NBTBFH molecule has shown energy transfer in the NBO analysis.

Depending on the conjugative effect in NBTBFH molecule, the atoms $H_{12}\cdots O_{39}$ came closer and leading to increase in N_{11}-$H_{12}\cdots O_{39}$ angle. This causes easy energy transfer from O_{39} lone pair electrons to N_{11}-H_{12} antibonding electrons. The similar conjugative effect can be observed between O_{51} lone pair electrons and N_{40}-H_{41} antibonding electrons of the same molecule. The increase in size of the molecule causes more conjugations and more interaction sites between donors and acceptors along the molecule. A-H…B angles of NBTMH and NBTBH can be seen Table 2. A-H…B angles of NBTBFH and NBO for NBTBFH analyses were given in Table 3, Table 4, respectively.

Table 1. The comparison of the critical torsional angles and the energies before and after conformational analysis of the molecules.

NBTMH			NBTBH		
Critical Torsional Angles	Initial Values[a]	Final Values[b]	Critical Torsional Angles	Initial Values	Final Values
$T(N_{13}C_{14}C_{15}C_{17})$	170.79247	-170.77227	$T(N_{13}C_{14}C_{15}C_{17})$	170.69264	-170.69110
$T(C_8N_{11}N_{13}C_{14})$	-176.55079	-176.55156	$T(C_8N_{11}N_{13}C_{14})$	176.55079	-176.57896
$T(C_{22}C_{16}C_{14}C_{15})$	010.90706	-10.878450	$T(C_{22}C_{16}C_{14}C_{15})$	010.907060	-011.61980

Table 2 A-H…B angles of NBTMH and NBTBH.

Bond	Bond Angle (º)	Bond	Bond length (Aº)
$\cdot H_{28}$ -C_{23}	97.10458	O_{21}	28
$\cdot H_{12}N_{11}$-	132.66725	O_{39}	01
$H_{10}C_6$	94.66316	H_{10}	18
$C_{61}H_{68}$	97.10458	H_{68}	91
$N_{40}H_{41}$	132.66725	H_{41}	08
$C_{46}H_{48}$	80.67206	H_{48}	12
C_3H_7	94.66316	H_7	85

Table 3. A-B angles of NBTBFH.

NBTMH				NBTBH			
Bond	Bond Angle,º	Bond	Bond Length, Aº	Bond	Bond Angle, º	Bond	Bond Length, Aº
C_{24}-$H_{28}\cdot\cdot O_{21}$	96.77593	$H_{28}\cdot\cdot O_{21}$	2.56455	C_{24}-$H_{28}\cdot\cdot O_{21}$	96.77780	$H_{28}\cdot\cdot O_{21}$	2.58221
N_{11}-$H_{12}\cdot\cdot O_{39}$	132.35344	$H_{12}\cdot\cdot O_{39}$	1.77235	N_{11}-$H_{12}\cdot\cdot O_{39}$	132.26133	$H_{12}\cdot\cdot O_{39}$	1.77543

Table 4. NBO for NBTBFH.

Donor NBO (i) electron	Acceptor NBO (J) electron	^{1}E(2)^a (kcal/mol)	^{2}E(i)-E(j)^b (au)	^{3}F(i,j)^c (au)
LP (2) O_{21}	BD*(1) $C_{27} - H_{33}$	124.14	1.39	379
LP (1) O_{21}	BD*(1) $C_{27} - H_{33}$	10.25	1.23	105
LP (1) O_{21}	BD*(1) $C_{14} - C_{15}$	44059	0.82	103
LP (1) O_{21}	BD*(1) $C_{15} - C_{17}$	7.92	0.81	73
LP (2) O_{39}	BD*(1) $N_{11} - H_{12}$	1.23	0.70	26
LP (1) O_{39}	BD*(1) $N_{11} - H_{12}$	0.63	1.13	24
LP (1) O_{45}	BD*(1) $C_{53} - H_{62}$	8.57	1.30	99
LP (2) O_{45}	BD*(1) $C_{53} - H_{62}$	146.36	1.41	417
LP (1) O_{45}	BD*(1) $N_{40} - H_{41}$	14.83	0.67	90
LP (1) O_{51}	BD*(1) $N_{40} - H_{41}$	0.57	1.13	23
LP (2) O_{51}	BD*(1) $N_{40} - H_{41}$	1.13	0.70	25
LP (1) N_{42}	BD*(1) $C_{46} - H_{48}$	0.72	0.80	22

[1]Hyperconjugative interactions

[2]. Energy difference between donor and acceptor NBO orbitals

[3]. Fock matrix energy between donor and acceptor NBO orbitals, F(i, j)

3.2 Vibrational assignments

In all the frequencies calculations of the three compounds, the geometrical parameters are taken from the DFT/B3LYP/631G (d, p) calculations for each compound in Gaussian 09 program following the determination of the most stable conformer. Predicted spectra of the compounds NBTMH, NBTBH, NBTBFH at B3LYP/6-31G* level were given figure 8.

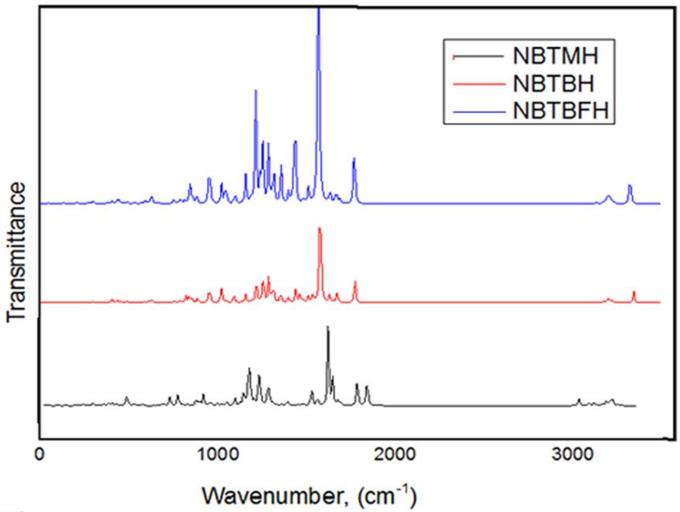


Figure 8. Predicted spectra of the compounds NBTMH, NBTBH, NBTBFH **at B3LYP/6-31G* level.**

The compound NBTMH has 43 atoms and C_1 symmetry. 123 vibrational degrees of freedom are active both in IR and Raman spectra. 163 internal coordinates (Figure 1.) are required for the calculation of the frequencies of the compound. Totally 162 force constants (118 diagonal + 44 nondiagonal) were used in F matrix to calculate the frequencies of NBTMH. The force constants were transferred from the similar small molecules such as naphthalene [20], benzene [20], ethylmethylketone [21], toluene [22], hydrazine [23], saturated hydrocarbons [25] and aniline [24, 26]. Only the diagonal force constants were listed in **Appendix D**. The calculated Raman spectra of the compounds (NBTMH, NBTBH, NBTBFH at B3LYP/6-31G* level) were given figure 9.

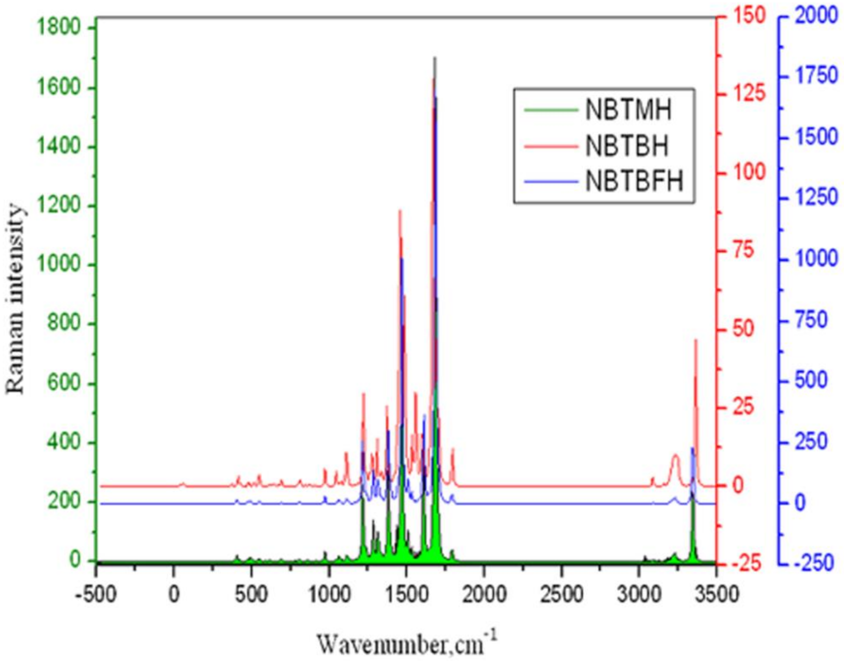


Figure 9. The calculated Raman spectra of the compounds NBTMH, NBTBH, NBTBFH at B3LYP/6-31G* level.

The part of these values as vibrational frequencies and their assignments in comparison with other compounds are given in Table 5. The compound NBTBH has 40 atoms and the fourth atom on the phenyl ring of NBTMH was replaced by Bromine atom instead of the methyl group. The molecule was assumed to have C_1 symmetry. 114 vibrational degrees of freedom are active both in IR and Raman. 153 internal coordinates are required for the calculation of the normal vibrational frequencies. 161 force constants (114 diagonals + 47 nondiagonals) were employed in the F matrix to calculate the vibrational frequencies of NBTBH. The force constants were transferred from the similar small molecules as used in the previous calculations of NBTMH. Additionally, bromophenol compound was used for transferring the force constants [27].

The NBTBFH molecule is nearly a duplicate of NBTMH and has 68 atoms. The molecule assumed to have C_1 symmetry. 198 vibrational degrees of freedom are active both in IR and Raman spectra. 166 force constants (125 diagonals + 45 nondiagonals) were required in F matrix to calculate the frequencies of NBTBFH. The list of the force constants used for the last three molecules were given on Supplementary data. The IR and Raman activities of these three compounds were also calculated using atomic radii, atomic electronegativities as input data in ACT module of the program [28]. A new valance force field (VFF) was developed for the compounds. All the bands in the vibrational spectra were assigned by means of theoretically calculated spectra. The theoretically calculated spectra were found to be in good agreement with the experimental frequencies as can be seen in Figure 10. The R^2 values of the correlation graphics of experimental vs. theoretical frequencies (by GF method) were found to be 0.9999, 0.9998, and 0.9999 for NBTMH, NBTBH, and NBTBFH compounds, respectively. The relative % errors of the theoretical frequencies of the same compounds were calculated as 0.79% for NBTMH, 0.97% for NBTBH and 0.65% for NBTBFH molecule

Table5. Assigments for NBTMH, NBTBH, NBTBFH.

		NBTMH			NBTBH			NBTBFH		
No.	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
1	υ (NH)	3248	-	3248	3248	-	3248	3315,33	-	3322,33
2	$\upsilon(C_nH)$	3097,3078, 3072	3083	3094,3083, 3069	3097, 3078	-	3095,31	3097 3069	-	3097,3096, 3082, 3070
3	$\upsilon(C_bH)$	3055	3060	3057,3056,3050, 3049	3055, 3050	3065	3069, 3057-3055- 3048	3069 3055 -	-	3067 3058,3055, 3050,3049
4	$\upsilon(C_nH)$	3037 3006	-	3038,3030 3014,3013	3039 3008	-	3038,3032, 3022,3014	3035 3013	-	3039,3032, 3031, 3017,3015
5	υ (C_tH)	2999	-	3005,3	-	-	-	-	-	-
6	$\upsilon(C_mH)$	2960 2896	-	2969, 2959, 2887	2999, 2979 2922	- 2933	2980, 2971 2899	2999, 2966 2941, 2912 2851	-	2972,2966, 2941,2912, 2851
7	$\upsilon(C_tH)$	2924	2928	2924	-	-	-	-	-	-
8	$\upsilon(C_{mk}=O)$	1645	1644	1655	1645	1650	1658	1666	1653	1665
9	$\upsilon(C_{nk}O)$	1626	1624	1642	-	-	-	1657		1650,16
10	$\upsilon(C_{nk}O)$, $\upsilon(C_{mk}O)$	-	-	-	1625	1627	1636	-	-	-
11	$\upsilon(C_bC_b)$	-	-	-	1625, 1593	1627, 1601	1625,16	1605	1601	1604
12	$\upsilon(C_nC_n)$	1614	-	1630	1625, 1582	1627, 1570	1628,16	1657,16	-0,16	1649,16
13	$\upsilon(C_nC_n)$, $\upsilon(C_nC_{nk})$							1624,16	1616, 1592	1590,16
14	$\upsilon(C_bC)+\upsilon(C_nC)$							1605	1572	1568
15	$\upsilon(C_bC_b)$	1596	1587	1594,16	-	-	-	1520	1510	1526

Table 5. Cont.

		NBTMH			NBTBH			NBTBFH		
No.	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
16	$\upsilon(C_bC)$, $\delta(C_bC_bN)$	-	-	-	-	-	-	-	-	
17	$\upsilon(C_nC_n)$	1593	1587	1575	-	-	-	1569	1572	1567,1561,1560
18	υ (C=N), $\upsilon(C_nC_n)$	-	-	-	1515	-	1541	1469	-	1455
19	υ (C=N), $\upsilon(C_{mk}O)$	-	-	-	1506	1505	1533	-	-	-
20	υ(C=N)	1514	1516	1538	-	-	-	1500	-	1511
21	$\upsilon(C_nC_n)$	1508	-	1530	1487	1496	1485	1537,1520 1500,1487	1537, 1510 1502	1536,1513,1502, 1494
22	$\delta(HC_mH)$,$\upsilon(C_hC_{mk})$	1487	1487	1497	-	-	-	1537	1537	1545
23	δ(NNH), $\delta(C_bNH)$	1487	1466	1492	1464	1463	1472	-	-	-
24	δ (NNH), $\upsilon(C_nC_n)$	-	-	-	-	-	-	1429	-	1439
25	$\delta(HC_tH)$, $\delta(C_tC_tH)$	1464	1466	1473	-	-	-	-	-	-
26	$\delta(HC_mH)$	1464	1466	1463	1458	-	1443,14	1469,14	-	1468, 1449
27	$\delta(HC_mH)$	1430	1434	1442	-	-	-	1429,14	-	1435, 1416
28	$\upsilon(C_nC_n)$, $\delta(HC_mH)$	1430	-	1440	-	-	-	-	-	-
29	$\delta(HC_tH)$	1430	-	1439	-	-	-	-	-	-
30	$\delta(HC_mH)$, $\delta(C_bC_tH)$	1430	-	1438	-	-	-	-	-	-

Table 5. Cont.

		NBTMH			NBTBH			NBTBFH		
	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
31	$\delta(HC_mH)$, $\delta(C_nC_nH)$	-	-	-	-	-	-	1404, 1381	1404, 1389	1401, 1393
32	$\delta(C_bC_tH)$	1430	-	1437	-	-	-	-	-	-
33	$\delta(C_bC_bH)$	1412	1410	1416	1430, 1350	1431, 1347	1431, 1341	1381	1389	1396
34	$\delta(C_bC_bH)$, $\upsilon(C_bC_b)$	-	-	-	-	-	-	1417	-	1413
35	$\upsilon(C_nC_n)$	1389	1392	1401	-	-	-	1429	-	1432
36	$\delta(C_nC_nH)$	1364	1374	1375	1412	-	1414	-	-	-
37	$\delta(C_nC_nH)$	1364, 1350	1374, 1347	1364, 1343	1382, 1364	1374, 1361	1378, 1362	-	-	-
38	$\upsilon(C_bC_b)$	1350	1347	1347	1389	1386	1396	-	-	-
39	$\delta(C_{mk}C_mH)$	-	-	-	1321	-	1340	1367	1374	1374
40	$\delta(C_{mk}C_mH)$, $\delta(HC_mH)$	1321	1323	1336	-	-	-	-	-	-
41	$\upsilon(C_nC_n)$, $\delta(C_bC_bH)$	1240	1241	1253	1379	1372	1299	-	-	-
42	δ (C_nC_nH),$\upsilon(C_nC_n)$	1269	1284	1299	-	-	-	-	-	-
43	$\upsilon(C_nC_n)$	1180,1	-0,1	1175, 1040	1020	1021	1048	-	-	-
44	$\upsilon(C_bN)$,$\delta(C_bC_bH)$	-	-	-	1238	1238	1249	-	-	-
45	$\delta(C_nC_nH)$, $\upsilon(C_nC_n)$	-	-	-	1269, 1209, 1096	-,1210, -	1274,1221,1088	1381,1367, 1198 1175	1389, 1374 --	1385,1369 1196,1187 1172
46	$\delta(C_nC_nH)$	1209,12	1204, 1180	1215, 1159	1134	1137	1157	1306, 1273 1259	1311, 1268 -	1306,1273 1231

Table 5. Cont.

		NBTMH			NBTBH			NBTBFH		
	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
47	$\delta(C_bC_bH)$	1290,12	1299, 1180	1315, 1175	1294, 1163	1299, 1161	1277, 1162	1321	1330	1326
48	$\upsilon(C_nC_{nk})$	1163	1164	1147	-	-	-	-	-	-
49	$\upsilon(C_nC_n)$, $\upsilon(C_nC_{nk})$	-	-	-	1178,11	1174,11	1173,12	-	-	-
50	$\delta(C_bC_bH)$	1163	1164	1156	-	-	-	-	-	-
51	$\upsilon(NN)$,$\upsilon(C_nC_n)$	1105	1102	1102	860	856	874	-	-	-
52	$\upsilon(NN)$	-	-	-	1103	1108	1103	1110,89	1112,88	1101,88
53	$\delta(C_{mk}C_mH)$, $\upsilon(NN)$	-	-	-	-	-	-	1110	1112	1110
54	$\upsilon(NN)$, $\upsilon(C_{nk}C_h)$	-	-	-	-	-	-	981	-	984
55	$\upsilon(C_bC_b)$	1095	-	1078	1096,92	-0,94	1088,93	-	-	-
56	$\upsilon(NN)$, $\delta(C_nC_nH)$	1136	1137	1137	-	-	-	-	-	-
57	$\upsilon(C_bC_b)$,$\delta(C_bC_tH)$	1071	1071	1066	-	-	-	-	-	-
58	$\delta(C_{mk}C_mH)$,$\delta(HC_mH)$	-	-	-	-	-	-	1217,12	1210,12	1225,12
59	$\delta(C_{mk}C_mH)$	1071,1	1071,1	1073,1	1071,1	-0,1	1069,1	1357,1072, 1011, 941,860	1359,- - -,-	1313,1065, 1006-1002 948-43,865
60	$\delta(CC_mH)+\delta(C_bC_bC)$	-	-	-	1005	-	1006	-	-	-
61	$\upsilon(C_nC_{nk})+\delta(C_nC_nC)$	-	-	-	-	-	-	1144	1148	1152
62	$\delta(C_{mk}C_mH)$,$\upsilon(C_nC_n)$	-	-	-	-	-	-	1072	-	1054
63	$\delta(C_{mk}C_mH)$,$\upsilon(C_bC_b)$	-	-	-	-	-	-	1034	-	1032
64	$\delta(C_bC_tH)$	986	983	983	-	-	-	-	-	-

Table 5. Cont.

		NBTMH			NBTBH			NBTBFH		
	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
65	δ(C_nC_nH)	970	-	969	-	-	-	-	-	-
66	υ(C_bC_b),δ ($C_bC_bC_b$)	970	-	964	-	-	-	-	-	-
67	γ(C_b)	949	958	940	984,97	-996	978,96	981,96	-	983,97
68	υ($C_{nk}C_h$),υ(C_mC_{mk})	949	-	933	958	958	946	-	-	-
69	δ(C_nC_nH)	908	-	922	-	-	-	1161	-	1167,12
70	δ(C_nC_nH), υ(C_nC_n)	-	-	-	779	-	786	1072, 1022, 935,831	-	1053,1016, 937,856
71	γ(C_n)	908,83	-	920,86	893,827,798	-,830,-	889,858,797	920,660,474	-	921,919,666-664,464
72	γ(C_b)	903,82	-901	907,84	949,78	-,-	945,77	-	-	-
73	γ (C_b)	903,76	-	903,75						
74	γ(C_n)	893	-	886	760	752	751	860,831 796785,762	-	856, 850,802-799-792,752
75	υ(C_nC_n)	860	859	879	903	901	923	1110, 1034 908,900 831,649,630	1112 -	1108-1102,1032, 911,896-892 850,650-647,632
76	δ(C_n C_nC_n),υ(C_nC_n)	656	658	652	779,66	-	786,66	474	484	469
77	δ(C_n C_nC_n)	798	-	785	893,82	-, -	890,8			
78	υ(C_bC_b)	775	769	759	760	769	758	785	772	791,783,
79	γ(C_b), γ(N)	759	-	754						
80	γ(N)	759	-	754						

Table 5. Cont.

		NBTMH			NBTBH			NBTBFH		
	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
81	υ(C_bC_b)	-	-	734	-	-	-	-	-	-
82	γ(C_b), τ(C_bC_b)	716	-	725	-	-	-	-	-	-
83	υ(C_bC_b)	-	696	702	-	-	-	709	-	722
84	γ(C_b), γ(N)	687	-	686	-	-	-	692	691	693
85	υ(CBr),δ(CNN)	-	-	-	658	-	667	-	-	-
86	γ(C_n)	656	658	656	658	-	657	-	-	-
87	δ($C_hC_{mk}O$)	635	631	621	635	-	639	-	-	-
88	δ($C_nC_{nk}O$),δ($C_bC_bC_b$)	629	-	611	-	-	-	981	976	892
89	δ($C_bC_bC_b$)	608	-	603	629	621	614	590	-	
90	γ(C_{nk})	608	-	600	629	621	619	958,58	-952	911
91	γ(C_b)	563	-	582	-	-	-	-	-	
92	υ($C_{mk}C_k$),δ($C_nC_nC_n$)	-	-	-	608,55	-601	603,54	-	-	
93	υ($C_{mk}C_k$)	553	-	566	-	-	-			
94	υ($C_{mk}C_k$),δ($C_mC_{mk}O$)	-	-	-	-	-	-	590	-	599
95	γ(C_n)	510	518	537	500	515	510	500	-	490
96	τ(C_nC_n)	-	-	-	-	-	-	615	-	622
97	γ(C_b),τ(C_bC_b)	500	-	527	608,46	-601	592,44	-	-	-

Table 5. Cont.

		NBTMH			NBTBH			NBTBFH		
	Assignment	IR	Raman	GF	IR	Raman	GF	IR	Raman	GF
98	$\gamma(C_n),\tau(C_nC_n)$	-	-	-	-	-	-	603, 509	- 515	604,602 520,505
99	$\delta(C_mC_{mk}O)$	-	-	-	-	-	-	576	-	566
100	$\gamma(C_b)$	488	-	497	460	441	445	-	-	-
101	$\delta(C_nC_nH)$	-	-	-	563,488,403	565,485,403	566,490,427	-	-	-
102	$\gamma(C_{mk})$	-0,4	-	477,42	-	-	-	451,42	-	458,43
103	Naphthalene ring def.	471	-	456	471	-	460	615,58	-	618,56
104	$\gamma(C_{nk})$, $\gamma(N)$	-	-	-	-	-	-	590	-	587
105	$\gamma(C_b)$, $\gamma(N)$	-	-	-	-	-	-	534	-	541
107	$\tau(C_nC_n)$, $\gamma(C_{nk})$	460	461	438	-	-	-	-	-	
108	$\delta(C_bC_bN)$	-	-	-	-	-	-	451	-	
109	$\delta(C_bC_bC_b),\delta(C_bC_bN)$	408	-	429	-	-	-	-	-	
110	$\gamma(C_{mk})$, $\tau(C_hN)$	-	-	-	-	-	-	424	-	
111	$\tau(C_hN)$	-	-	-	-	-	-	401	-	
112	$\gamma(C_{mk})$, $\tau(C_bC_b)$	-	-	-	-	-	-	451	-	
113	$\delta(C_nC_nC_n)$	-	-	390	-	-	-	-	-	
114	$\gamma(C_n)$	-	-	367	-	-	-			
115	$\gamma(C_n)$, $\tau(C_bC_b)$	-	-	362	-	-	-	941	928	
116	$\delta(C_bC_bC_b)$	-	-	339	-	-	-		-	
117	$\tau(C_bC_b)$, $\gamma(C_n)$	-	-	328	-	-	-	935	924	

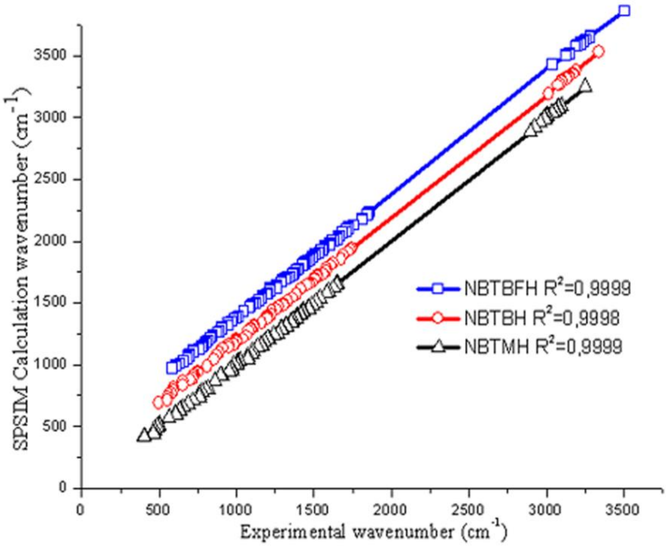


Figure 10. Correlation plot of experimental vs. theoretical frequencies

by GF.

The correlation between experimental and the calculated wave numbers by the method DFT/B3LYP/631G (d, p) for the three compounds can be seen in Figures 11-13. The R^2 (n) values of calculated frequencies by DFT were found to be 0.9929(n=97), 0.9961(n=88), and 0.9965(n=154), for the compounds NBTMH, NBTBH, and NBTBFH, respectively. The average percent relative error of the calculated frequencies of NBTMH in the present study was found to be 11 cm^{-1} and the maximum deviation is 27 cm^{-1} at 500 cm^{-1} corresponding to the out of plane $P(C_b)$ vibrations. The average percent relative error of the calculated frequencies for NBTBH was also found to be 9 cm^{-1} and the maximum deviation is 30 cm^{-1} at 828 cm^{-1} corresponding to C_n-C_n out of plane deformation vibration. The similar calculation was also performed for NBTBFH and the average percent relative error of the calculated frequencies was found to be 7. The maximum deviation is 28 cm^{-1} observed at 1259 cm^{-1} wavenumber corresponding to C_nC_nH in plane deformation vibration aromatic rings

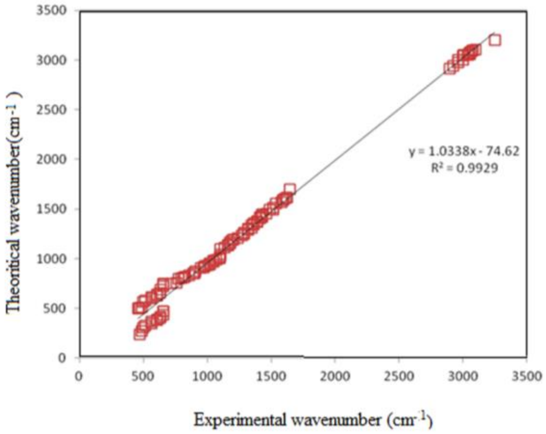


Figure 11. Correlation plot of experimental vs. theoretical frequencies of NBTMH.

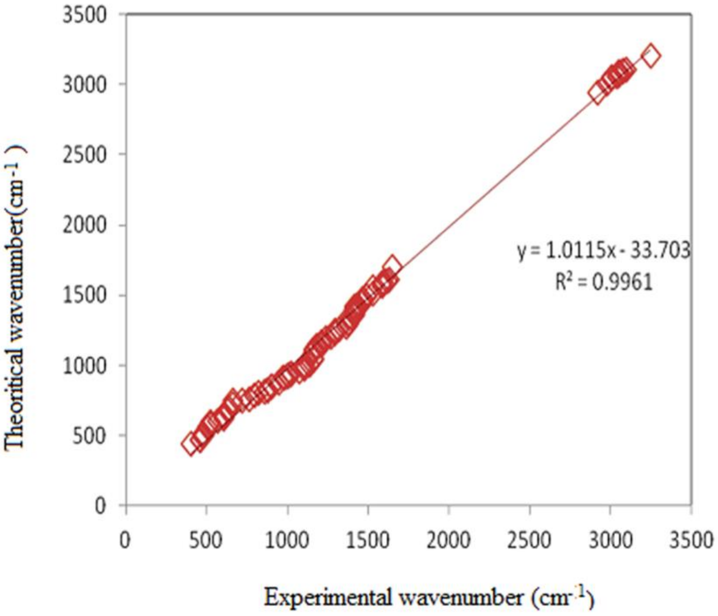


Figure 12. Correlation plot of experimental vs. theoretical frequencies of NBTBH.

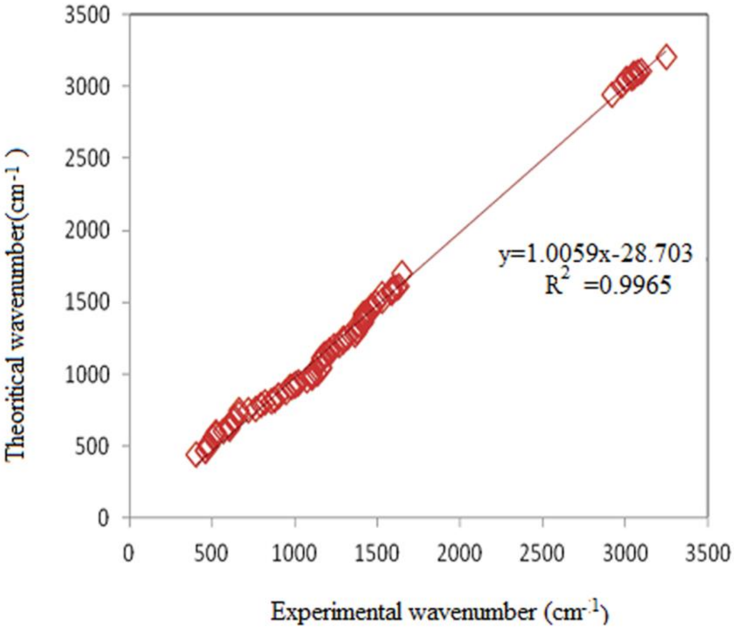


Figure 13. Correlation plot of experimental vs. theoretical frequencies of NBTBFH.

3.2.1N-H vibrations

N-H stretching mode observed usually at 3350-3200 cm^{-1}. N-H stretching vibration for a similar structure of p-CH_3 and m-CH_3cyanoformazone were calculated at 3230, 3222 cm^{-1} by Abdel Ghanı*et al*. [29].

The N-H stretching vibration of the hydrazine group of NBTMH was calculated at 3248 cm^{-1} by GF method same as the observed IR wave number value. Similarly, the N-H stretching vibration of NBTBH was calculated and observed at 3248 cm^{-1}. The same signal for NBTBFH was calculated at 3301 cm^{-1} and observed at 3315 cm^{-1}. The shift and broadening of the -NH stretching band and the shift of the C=O stretching band of the naphtyl keto group in NBTBFH corresponding to the same groups in NBTMH and NBTBH were mainly responsible for the weak hydrogen bonding [30] between the N-H of hydrazine and the C=O of the naphthyl keto groups as can be seen in Table 4.

NH bending mode observed usually at 1505-1570 cm^{-1} was calculated at 1505 cm^{-1} with a 37% contribution and at 1556 cm^{-1} with low percentage (17%) for diacetylmonoxime semicarbazone in the same work [31]. The deformation vibrations of NNH group for p-CH_3 substituted cyanoformazones were calculated at 1404 cm^{-1} and observed at 1400 cm^{-1}. The same band were observed at 1469 cm^{-1} and calculated at 1466 cm^{-1} for m-CH_3 substituted analog [29].

In the present study, NNH in plane bending of NBTMH was calculated at 1487 cm^{-1} with 18% contributions of NNH and %18 contributions of CNH internal coordinates. The same mode was calculated at 1472 cm^{-1} for NBTBH and at 1439 cm^{-1} for NBTBFH, respectively.

NH out of plane vibration of the hydrazone group was observed at 652 cm^{-1} and calculated at 654 by Doddof*etal*. [32]. The same mode for NBTMH was observed at 754, 686 cm^{-1} and calculated at 687 and 759 cm^{-1}. The out of plane vibration of NBTBFH was observed 692 cm^{-1} and calculated at 693 cm^{-1}.

3.2.2 C-H vibrations

The C–H stretching frequencies of monosubstituted benzenes are expected in the region 3010–3120 cm^{-1} and substituted groups do not alter much in this range very much [29, 33]. C-H in plane and out of plane bendings are usually observed at 1100-1500 cm^{-1} and in 800-1000 cm^{-1} regions, respectively [34]. Netto *etal.* Observed C-H stretching vibrations at 3073, 3064, 3056, 3057 cm^{-1} for benzene and at 3065, 3056, 3055, 3029, 3025, 2980 cm^{-1} for naphthalene. The C-H vibrations the C-H in plane bendings of benzene and naphthalene were observed at 1482, 1350, 1309, 1178, 1152 cm^{-1} and 1460, 1436, 1389, 1240, 1209, 1144, 1125, 1099 cm^{-1} respectively[20]. The aromatic C–H stretching vibrations of the naphthalene group in NBTMH were observed at 3097, 3078, 3072, 3037, 3006, cm^{-1} and calculated at 3094, 3083, 3069, 3038, 3014, cm^{-1} with a contribution of 100, 97, 98 and 100, 85 percents to the PED of the normal vibrations, respectively. The C–H stretching vibrations of benzene observed at 3055 cm^{-1} were attributed to the calculated wave numbers of 3057, 3056, 3050 cm^{-1} with 99% contributions each.

The C-H stretching vibrations of benzene ring belonging to NBTBH compound was calculated at 3054, 3049, 3048 cm^{-1} and observed at 3055 cm^{-1} as single band. The naphthalene's C-H stretchings vibrations of NBTBH compound were observed at 3097, 3078, 3039, 3008 cm^{-1} and calculated at 3095, 3081, (3038, 3032), (3022, 3014) cm^{-1} wavenumbers. C-H strechings belonging to benzene ring of NBTBFH was observed at 3069 and 3055 cm^{-1} and calculated at 3067 and (3058, 3055,3050, 3049) cm^{-1} The C-H stretchings belonging to naphthalene group of the same compound was observed at 3035, 3013 cm^{-1} and calculated at (3039, 3032, 3031) and (3017, 3015) cm^{-1} wavenumbers.

The C–H stretching vibrations of toluenicCH_3 group connected to hydrazone bridge of cyanoformazans, similar to our system, were calculated at 2998, 2960, 2946 cm^{-1} for asymmetrical stretchings and 2945, 2939, 2920 cm^{-1} for symmetrical stretchings of ortho- meta and para methhylated benzene ring, respectively [29]. The C-H stretching vibrations of methyl group connected to kethonic carbonyls in another study were observed at 2982, 2953 cm^{-1} wavenumbers [35]. The C-H vibrations of toluenic methyl group of NBTMH were observed at 2999, 2924 cm^{-1} and calculated at (3005, 2990), 2924 cm^{-1} while the C-H stretching vibrations of ketonic CH_3 group were observed at 2960, 2896 cm^{-1} and calculated at (2969, 2959), 2887 cm^{-1} for NBTMH. Since there are only ketonic C-H vibrations available as aliphatic C-H vibrations in NBTBH and NBTBFH molecules, the wavenumbers 2999, 2979, 2922 cm^{-1} were observed and calculated at 2980, 2971, 2899 cm^{-1} wavenumbers for this group of NBTBH. The same aliphatic C-H vibrations of NBTBFH were observed at 2999, 2966, 2941, 2912, 2851 cm^{-1} and calculated at 2972, 2966, 2941, 2912, 2851 cm^{-1}.

Toluenic HCH bendings of CH_3 in nitrotoluenes appear at 1477, 1469, 1374 cm^{-1} [22], in the same study C_bC_tH bending was observed at 997 cm^{-1}wavenumber. In another study, aliphatic HCH bendings were observed at 1440, 1380 cm^{-1}

wavenumbers. CCH bending belonging to CH_3 observed at 990 cm^{-1} and calculated at 990 cm^{-1} with 65% contribution [31]. The HCH bendings of ketonic CH_3 for NBTMH were observed at 1464, 1430 cm^{-1} wavenumbers and calculated at 1463, 1442 cm^{-1}. The HCH of toluenic methyl deformations were observed at 1465, 1430 cm^{-1} and calculated at 1473, 1439 cm^{-1} wavenumbers. The HCH deformation vibrations of ketonic methyl group for NBTBFH are observed at 1469, 1442, 1429, 1417 cm^{-1} and calculated at 1468, 1449, 1435, 1416 cm^{-1} wavenumbers, respectively.

CCH in-plane bendings of naphthalene groups are observed at 1460, 1209, 1008 cm^{-1} wavenumbers. The same bending vibrations of benzene ring are observed at 1482, 1350, 1178, 1010 cm^{-1} [36]. The CCH in-plane bending of naphthalene groups in NBTMH was observed at 1364, 1350 cm^{-1} and it was calculated at (1375, 1364), 1343 cm^{-1} wavenumbers. For NBTBH the same bendings were observed at the 1412, 1382, 1364, cm^{-1} wavenumbers and calculated at 1414, 1378, 1362 cm^{-1} wavenumbers. The same vibrations for NBTBFH was observed at 1381, 1367 cm^{-1} and calculated at 1385, 1369 cm^{-1} wavenumbers. The similar bending frequencies of benzene ring in all the three compounds were observed at 1412-1163 cm^{-1} wavenumber region as expected and calculated between 1416-1156 cm^{-1}

The out of plane bending vibrations of aromatic rings appear generally in the range 1000-650 cm^{-1} [29, 37]. The out of plane vibrations of the aromatic rings of the three compounds of the present study were observed in the range 984 to 460 cm^{-1}.

3.2.3 C=C Vibrations

C=C stretching vibrations of aromatic rings usually give strong bands between 1400 and 1600 cm^{-1}. Netto *et al.*, observed the C=C stretching vibrations of benzene at 1599,1309, 1037, 993 cm^{-1} and theoretically calculated them at 1602, 1316, 1026, 993 cm^{-1}, respectively [20]. The C=C stretching vibrations of naphthalene were observed by the same group at 1624,1595, 1579, 1509, 1361, 1379, 1144, 1025, 1008, 763 cm^{-1} and calculated them at 1625, 1597, 1577, 1529, 1357, 1368, 1136, 1013, 1007, 767 cm^{-1} respectively.

The C=C stretching vibrations of NBTMH molecule including benzene and naphthalene rings were calculated at 1630, 1575, 1530, 1401, 1175, 1040 cm^{-1}. For naphthalene and 1594, 1591, 1347, 1078 cm^{-1} for benzene with a considerably high contribution of the related internal coordinate to the potential energy term. These frequencies were assigned to the observed bands of naphthalene at 1614, 1582, 1508, 1389, 1198, 1020 cm^{-1} and of benzene at 1596, 1593, 1350, 1095 cm^{-1}, respectively. The similar results were obtained for NBTBH and NBTBFH compounds. The C=C stretching bands of benzene and naphthalene groups of NBTBH were observed at 1627, 1625, 1601, 1593, 1582, 1570, 1496, 1487, 1389, 1386, 1096, 1021, 1020, 936, 921, 903, 901 and 769, 760 cm^{-1}, their corresponding wave numbers were calculated at 1625, 1596, 1577, 1485, 1396, 1088, 1048, 931, 923 and 758 cm^{-1}, respectively. The aromatic C=C stretching bands of NBTBFH were observed nearly at twice the number of aromatic C=C stretching bands due the additional naphthalene ring of NBTBFH with respect to previous compounds. The aromatic C=C stretching vibrations were observed at 1657, 1624, 1616, 1605, 1592, 1572, 1569, 1537, 1520, 1510, 1510, 1502, 1500, 1487, 1429, 1381, 1367, 1198, 1175, 1072, 1112, 1034, 908, 900, 831, 785,772, 709 , 649, 630, cm^{-1} and calculated at 1649, 1610, 1604, 1568, 1567, 1561, 1560, 1536, 1526, 1513, 1502, 1494, 1432, 1108, 1054, 1032,1002, 911, 896, 892, 850, 791, 783, 722, 650, 647, 632 cm^{-1}.

The C_nC_{nk} bond between naphthalene ring and carbonyl group frequency of NBTMH was calculated at 1147 cm^{-1} and observed at 1163 with a 41% C-C character. The other C-C bonds between naphtylketo carbon and hydrazone carbone ($C_{nk}C_h$) and between methyl carbon and ketonic carbon (C_mC_{mk}) were calculated at 933 cm^{-1} with nearly equal contribution to the PED in total of 30% and assigned to 949 cm^{-1}.

The stretching vibration of C_nC_{nk} belonging to NBTBH were calculated at 1173, 1152 cm^{-1} and observed at 1178, 1134 cm^{-1}. For the same compound, the $C_{nk}C_h$ and C_mC_{mk} aliphatic strechings were observed at 958 cm^{-1} and calculated at 946 cm^{-1}. For NBTBFH, the C_nC_{nk} streching vibration was observed at1144 cm^{-1} and calculated at 1152 cm^{-1} wavenumber.

3.2.4 C=O, C=N, N-N vibrations

The p-diketones, which have α-hydrogen, do not have the C=O stretching band at 1700-1750 cm^{-1}characteristic of normal conjugated ketones but instead they have very broad band between 1640-1530 cm^{-1}[30, 38]. This broad band has been attributed to a reduction of the double bond character by the resonance between forms H_{12}-$N_{11}$and H_{12}-O_{39}

The energy difference between keto and enol forms in NBTMH, NBTBH and NBTBFH compounds were found to be $1.2\cdot10^{-5}$, $8.2\cdot10^{-5}$ and $2.1\cdot10^{-5}$ kcal/mol, respectively in DFT method. According to the calculations the keto forms are more stable than enol forms for each three compounds.

The C=O stretching were appeared at 1645 and 1626 cm^{-1} in the vibrational spectra for NBTMH and these frequencies were calculated at 1655 and 1642 cm^{-1}. The same vibrations of NBTBH were observed at 1645, 1625 and calculated at 1658, 1636cm^{-1}. For NBTBFH there are more carbonyls therefore the bands at 1666, 1657 cm^{-1} are correspond to calculated, 1665, 1650, 1642 cm^{-1} numbers.

The stretching vibration of C=N group in NBTMH was observed 1516, 1514 cm^{-1} and was calculated at 1538 cm^{-1} with a 32% contribution of C=N stretching force constant. The C=N stretching vibrations for both NBTBH and NBTBFH were calculated at 1541, 1533 and 1511 cm^{-1} and observed 1515, 1506, 1505 and 1500 cm^{-1} respectively.

Doddof and his friends observed N-N stretching vibration for hydrazine at 1096 cm^{-1} wavenumbers. The N-N stretching vibration was calculated at 1136, 1105, 1005, 860 cm^{-1} wavenumbers [32]. The N-N stretching vibrations of NBTMH were observed at 1137, 1136, 1105, cm^{-1} and were calculated at 1137 and 1102 cm^{-1}wavenumbers. The same stretchings were observed at 1108, 1103 and 860 cm^{-1} for NBTBH and calculated at 1103 and 874 cm^{-1}. For NBTBFH the same stretching were observed at 1112, 1110 and 887 cm^{-1} wavenumbers and calculated at 1101 and 878 cm^{-1} wavenumbers.

3.2.5. C-Br vibrations

Krishnakumar *et al*, reported that C-Br vibrations were observed at 650- 400 cm^{-1} with a very intense band and they observed this vibrations at 609 cm^{-1} for 1-bromo-4-fluronaphthalene and at 544 cm^{-1} for 4-bromo benzonitrile [39]. The out of plane bending vibration of C-Br was observed at 279 cm^{-1}[40].

The C-Br stretching vibrations for NBTBH were calculated at 667 cm^{-1} and 358 cm^{-1} and the out of planes of the same group were calculated at 239, 220 cm^{-1} wavenumbers.

4. Discussion and Conclusion

The potential energy surfaces of the compounds were calculated by DFT/6-31G (d, p). Two remarkable H-bondings were obtained through NBO analysis in gas phase for NBTBFH. The most strong hyperconjugative interaction were calculated between the LP O_{21} atom and BD* (C_{23} – H_{28}) bond. The second remarkable interaction in gas phase was found between the LP O_{45} and BD* C_{61} – H_{68} for NBTBFH.

The complete vibrational analysis has been performed by emphasizing on the vibrations of O-H, C=N, C-H, C=O/C-O, C=C/C-C (stretchings), CCH, HCH,CCC, COH (deformations).Our study may hopefully be assistance, theoretical results for the title compound in reaction intermediates, theoretical chemistry and health science. The vibrational dynamics of Hydrazones can be satisfactorily interpreted from the normal modes of N=N, C=N as obtained by Wilson's GF matrix method for finite systems. The vibrational dynamics of Hydrazone derivates can also interpret satisfactorily through normal modes analysis by the other researchers.

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Appendices

AppendixA Geometrical parameters of NBTMH

Bonding Atoms	Bond lengths(Å)	Bonding Atoms	Bond angles	Bonding Atoms	Bond angles
C_2-C_1	1.39993	C_3-C_1-C_2	117,71	C_{34}-C_{29}-H_{35}	119.64413
C_3-C_1	1.40365	C_4-C_2-C_1	121.38655	C_{31}-H_{36}- C_{26}	118.80527
C_4-C_2	1.39248	C_2-C_1 -H_5	119.54116	C_{34}-C_{31}-H_{36}	120.44559
C_2-H_5	1.08666	C_2-C_4 -H_5	119.07222	C_{32}-H_{37}- C_{27}	120.27306
C_6-C_3	1.39010	C_6-C_3-C_1	121.84494	C_{26}-C_{32}-H_{37}	118.77647
C_3-H_7	1.08714	C_3-C_1-H_7	119.27556	C_{34}-H_{38}- C_{29}	119.54203
C_6-C_8	1.40099	C_6-C_3-H_7	118.87947	C_{34}-H_{38}- C_{31}	119.99280
C_8-C_4	1.39958	C_3-C_6-C_8	119.41237	O_{39}-C_{16}-C_{14}	118.62368
C_4 -H_9	1.08668	C_8-C_4-C_2	119.87881	C_{22}-C_{16}-O_{39}	117.71778
C_6-H_{10}	1.08314	5C_4-C_8-C_6	119.76303	C_2-C_1-C_{40}	121.33152
N_{11}-C_8	1.40462	C_6-C_8-H_{10}	119.45447	C_3-C_1-C_{40}	120.94615
N_{11}-H_{12}	1.02731	C_2-C_4-H_9	120.23740	C_{40}-H_{41}-H_{42}	107.94727
N_{13}-N_{11}	1.30532	C_8-C_4-H_9	119.88333	C_{40}-H_{41}-H_{43}	107.38534
C_{14}-N_{13}	1.32487	C_3-C_6-H_{10}	121.13233	C_{40}-H_{42}-H_{43}	107.07721
C_{15}-C_{14}	1.49221	N_{11}-C_8-C_6	122.28796	C_1-C_{40}-H_{41}	111.46868
C_{16}-C_{14}	1.48918	C_4-C_8-N_{11}	117.94893	C_1-C_{40}-H_{42}	111.43794
C_{17}-C_{15}	1.52148	C_8-N_{11}-H_{12}	121.32274	C_1-C_{40}-H_{43}	111.30667
C_{17}-H_{18}	1.09063	N_{11}-C_8-N_{13}	121.63454		
C_{17}-H_{19}	1.09367	N_{13}-N_{11}-H_{12}	116.99472		
C_{17}-H_{20}	1.09393	N_{13}-N_{11}-C_{14}	122.01574		
C_{15}-O_{21}	1.22329	N_{13}-C_{14}-C_{15}	113.48766		
C_{16}-C_{22}	1.49021	C_{16}-C_{14}-N_{13}	122.29952		
C_{22}-C_{23}	1.38306	C_{16}-C_{15}-C_{14}	123.95640		
C_{23}-C_{24}	1.41674	C_{17}-C_{15}-C_{14}	117.84447		
C_{23}-C_{25}	1.42159	C_{15}-H_{18}-C_{17}	107.89792		
C_{23}-C_{26}	1.43284	C_{15}-H_{19}-C_{17}	111.49341		
C_{27}-C_{22}	1.42481	C_{17}-H_{18}-H_{19}	109.49473		

Appendix A Geometrical parameters of NBTMH (Cont.)

Bonding Atoms	Bond lengths(Å)	Bonding Atoms	Bond angles	Bonding Atoms
C_{23}-C_{28}	1.08354	C_{15}-H_{20}-C_{17}	110.75544	
C_{25}-C_{29}	1.37597	C_{17}-H_{18}-H_{20}	106.89032	
C_{25}-H_{30}	1.08668	C_{17}-H_{19}-H_{20}	110.31096	
C_{26}-C_{31}	1.41905	C_{17}-C_{15}-O_{21}	120.50913	
C_{26}-C_{31}	1.42232	O_{21}-C_{15}-C_{14}	121.60007	
C_{27}-C_{32}	1.37150	C_{22}-C_{16}-C_{14}	123.52475	
C_{27}-H_{33}	1.08400	C_{23}-C_{22}-C_{16}	123.11197	
C_{29}-C_{34}	1.41653	C_{24}-C_{23}-C_{22}	121.18740	
C_{31}-C_{34}	1.37736	C_{31}-C_{26}-C_{24}	118.82753	
C_{29}-H_{35}	1.08583	C_{32}-C_{26}-C_{24}	118.62223	
C_{31}-H_{36}	1.08679	C_{32}-C_{22}-C_{27}	120.73476	
C_{32}-H_{37}	1.08675	C_{31}-C_{26}-C_{32}	122.54965	
C_{34}-H_{38}	1.08610	C_{27}-H_{33}- C_{22}	118.22933	
C_{16}-O_{39}	1.24550	C_{32}-C_{27}-H_{33}	121.03581	
C_{1}-H_{40}	1.50970	C_{34}-C_{29}-C_{25}	120.18789	
$C_{40}H_{41}$	1.09476	C_{29}-C_{34}-C_{31}	120.46517	
$C_{40}H_{42}$	1.09354	C_{34}-C_{31}-C_{26}	120.74912	
C_{40}-H_{43}	1.09719	C_{29}-H_{35}- C_{25}	120.16785	

Appendix B Geometrical parameters of NBTBH

Bonding Atoms	Bond lengths(Å)	Bonding Atoms	Bond angles	Bonding Atoms	Bond angles
C_{2}-C_{1}	1.39350	C_{3}-C_{1}-C_{2}	120.81590	C_{17}-H_{19}-H_{20}	110.29219
C_{3}-C_{1}	1.39530	C_{2}-C_{1}-C_{40}	119.60775	C_{27}-C_{22}-C_{16}	117.24960
C_{1}-Br_{40}	1.90928	C_{3}-C_{1}-C_{40}	119.57620	C_{23}-C_{22}-C_{16}	123.04060
C_{4}-C_{2}	1.39180	C_{4}-C_{2}-C_{1}	119.40720	C_{24}-C_{23}-C_{22}	121.18140
C_{2}-H_{5}	1.08380	C_{2}-C_{1} -H_{5}	120.28750	C_{25}-C_{23}-C_{24}	121.85010
C_{6}-C_{3}	1.39090	C_{4}-C_{2}-H_{5}	120.30522	C_{25}-C_{24}-C_{26}	119.03861
C_{3}-H_{7}	1.08410	C_{6}-C_{3}-C_{1}	119.84790	C_{26}-C_{24}-C_{23}	119.11070
C_{8}-C_{4}	1.40150	C_{3}-C_{1}-H_{7}	120.02450	C_{27}-C_{23}-C_{22}	119.38038
C_{4}-H_{9}	1.08630	C_{6}-C_{3}-H_{7}	120.02446	C_{24}-H_{28}- C_{23}	118.19779
C_{6}-C_{8}	1.40148	C_{8}-C_{4}-C_{2}	120.20970	C_{22}-C_{24}-H_{28}	120.61820
C_{6}-H_{10}	1.08290	C_{2}-C_{4}-H_{9}	119.82220	C_{29}-C_{25}-C_{24}	120.72960
N_{11}-C_{8}	1.40160	C_{8}-C_{4}-H_{9}	119.96876	C_{25}-H_{30}- C_{24}	118.73450
N_{11}-H_{12}	1.02700	C_{3}-C_{6}-C_{8}	119.76845	C_{29}-C_{25}-H_{30}	120.53501
N_{13}-N_{11}	1.30900	C_{3}-C_{6}-H_{10}	120.72540	C_{31}-C_{26}-C_{32}	122.53279
C_{14}-N_{13}	1.32150	C_{6}-C_{8}-H_{10}	119.50642	C_{32}-C_{26}-C_{24}	118.64220
C_{15}-C_{14}	1.49420	N_{11}-C_{8}-C_{6}	122.11490	C_{31}-C_{26}-C_{24}	118.82400
C_{16}-C_{14}	1.49260	C_{4}-C_{8}-C_{6}	119.95061	C_{32}-C_{22}-C_{27}	120.69132
C_{17}-C_{15}	1.52060	C_{4}-C_{8}-N_{11}	117.93514	C_{27}-H_{33}- C_{22}	118.26129
C_{15}-O_{21}	1.22260	C_{8}-N_{11}-H_{12}	122.11490	C_{32}-C_{27}-H_{33}	118.26150
C_{16}-C_{22}	1.48840	N_{11}-C_{8}-N_{13}	121.38846	C_{34}-C_{29}-C_{25}	120.19008
C_{16}-O_{39}	1.24458	N_{13}-$N_{11}H_{12}$	121.38850	C_{29}-H_{35}- C_{25}	120.19000
C_{17}-H_{18}	1.09050	N_{13}-N_{11}-C_{14}	121.89230	C_{34}-C_{29}-H_{35}	119.64543
C_{17}-H_{19}	1.09390	N_{13} C_{14}-C_{15}	113.62640	C_{25}-C_{31}-C_{26}	120.16420
C_{17}-H_{20}	1.09380	C_{16}-C_{14}-N_{13}	122.36820	C_{31}-H_{36}- C_{26}	118.81520
C_{24}-C_{23}	1.41650	C_{16}-C_{15}-C_{14}	123.73487	C_{34}-H_{38}- C_{29}	119.53524
C_{22}-C_{23}	1.38350	C_{17}-C_{15}-C_{14}	117.91200	C_{56}-C_{57}-H_{65}	119.53460
C_{24}-C_{25}	1.42160	O_{21}-C_{15}-C_{14}	121.31790		
C_{24}-C_{26}	1.43290	C_{17}-C_{15}-O_{21}	117.91232		
C_{22}-C_{27}	1.42500	C_{34}-C_{31}-H_{36}	120.44608		
C_{23}-C_{28}	1.08360	C_{26}-C_{32}-C_{27}	120.96679		
C_{25}-C_{29}	1.37590	C_{26}-C_{32}-H_{37}	118.77030		
C_{25}-H_{30}	1.08670	C_{32}-H_{37}-C_{27}	120.26118		
C_{26}-C_{31}	1.41890	C_{29}-C_{34}-C_{31}	120.47832		
C_{26}-C_{32}	1.42250	C_{34}-H_{38}-C_{31}	119.98620		
C_{27}-C_{32}	1.37129	C_{22}-C_{16}-C_{14}	123.37090		
C_{27}-H_{33}	1.08400	O_{39}-C_{16}-C_{14}	118.47360		
C_{29}-C_{34}	1.41650	C_{22}-C_{16}-O_{39}	118.01944		
C_{29}-H_{35}	1.08580	C_{15}-H_{18}-C_{17}	108.94860		
C_{31}-C_{34}	1.37740	C_{15}-H_{19}-C_{17}	110.73900		
C_{31}-H_{36}	1.08670	C_{15}-H_{20}-C_{17}	111.45140		
C_{32}-H_{37}	1.08670	C_{17}-H_{18}-H_{19}	106.93207		
C_{34}-H_{38}	1.08600	C_{17}-H_{18}- H_{20}	109.47837		

Appendix C Geometrical parameters of NBTBFH (bond length (Å) and bond angle (°) as input to the SPSIM

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond angles(deg)	Bond	Bond angles(deg)	Bond	Bond angles(deg)
C_{2}-C_{1}	1.40161	C_{54}-C_{59}	1.43288	C_{3}-C_{1}-C_{2}	119.66980	C_{46}-C_{44}-O_{45}	117.86304	C_{29}-C_{25}-C_{24}	120.70410
C_{3}-C_{1}	1.40361	C_{17}-H_{20}	1.09055	C_{2}-C_{1}-N_{40}	118.10493	C_{22}-C_{16}-C_{14}	122.90070	C_{54}-C_{55}-C_{56}	120.73230
C_{1}-Br_{40}	1,4	C_{46}-H_{47}	1,09	C_{3}-C_{1}-N_{40}	122.22520	C_{43}-C_{50}-C_{52}	123.55840	H_{30}-C_{25}-C_{24}	118.73360
C_{4}-C_{2}	1.38852	C_{46}-H_{48}	1.09395	C_{4}-C_{2}-C_{1}	120.16870	O_{39}-C_{16}-C_{14}	118.65600	C_{54}-C_{55}-H_{63}	118.73690
C_{2}-H_{5}	1.08610	C_{22}-C_{27}	1.42375	H_{5}-C_{2}-C_{1}	119.95690	C_{22}-C_{16}-O_{39}	118.34345	C_{29}-C_{25}-H_{30}	120.56235
C_{6}-C_{3}	1.38660	C_{23}-H_{28}	1.08539	C_{4}-C_{2}-H_{5}	119.87449	C_{52}-C_{50}-O_{51}	117.84108	C_{56}-C_{55}-H_{63}	120.52952
C_{3}-H_{7}	1.08289	C_{25}-C_{29}	1.37597	C_{6}-C_{3}-C_{1}	120.16020	H_{18}-C_{17}-C_{15}	110.67760	C_{31}-C_{26}-C_{32}	122.53203
C_{8}-C_{4}	1.40150	C_{31}-C_{34}	1.37731	H_{7}-C_{3}-C_{1}	119.23820	H_{19}-C_{17}-C_{15}	111.41240	C_{58}-C_{59}-C_{60}	122.54030
C_{4} -H_{9}	1.08606	C_{57}-C_{58}	1.37738	C_{6}-C_{3}-H_{7}	120.60102	H_{20}-C_{17}-C_{15}	108.02300	C_{57}-C_{56}-H_{64}	119.64271
C_{6}-C_{8}	1.40356	C_{55}-C_{56}	1.37593	C_{8}-C_{4}-C_{2}	120.15880	C_{44}-C_{46}-H_{49}	107.92460	C_{54}-C_{59}-C_{60}	118.62720
C_{6}-H_{10}	1.08293	C_{25}-H_{30}	1.08669	C_{2}-C_{4}-H_{9}	119.87280	C_{44}-C_{46}-H_{48}	110.70020	C_{31}-C_{26}-C_{24}	118839
N_{11}-C_{8}	1.40072	C_{31}-H_{36}	1.08673	C_{8}-C_{4}-H_{9}	119.96847	C_{44}-C_{46}-H_{47}	111.50670	C_{54}-C_{59}-C_{58}	118.83193

Appendix C Cont.

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond angles(deg)	Bond	Bond angles(deg)	Bond	Bond angles(deg)
N_{11}-H_{12}	1.02834	C_{58}-H_{66}	1.08673	C_{3}-C_{6}-C_{8}	120.16082	H_{18}-C_{17}-H_{19}	106.93688	C_{32}-C_{27}-C_{22}	120.48058
N_{40}-H_{41}	1.02792	C_{55}-C_{63}	1.08668	C_{3}-C_{6}-H_{10}	120.61130	H_{18}-C_{17}-H_{20}	109.51418	H_{33}-C_{27}-C_{22}	119.8485
N_{13}-N_{11}	1.30764	C_{26}-C_{32}	1.42200	H_{10}-C_{6}-C_{8}	119.22750	H_{19}-C_{17}-H_{20}	110.27684	C_{61}-C_{60}-H_{67}	120.25543
N_{40}-N_{42}	1.30802	C_{53}-C_{54}	1.41656	N_{11}-C_{8}-C_{6}	122.22660	H_{49}-C_{46}-H_{48}	109.45134	C_{34}-C_{31}-C_{26}	120.72384
C_{14}-N_{13}	1.32369	C_{59}-C_{60}	1.42238	C_{4}-C_{8}-N_{11}	118.09290	H_{49}-C_{46}-H_{47}	110.31360	C_{57}-C_{58}-C_{59}	120.73670
N_{42}-N_{43}	1.32344	C_{27}-C_{32}	1.37203	C_{4}-C_{8}-C_{6}	119.68052	H_{47}-C_{46}-H_{48}	106.94430	C_{31}-H_{36}-C_{26}	118.83720
C_{2}-C_{1}	1.40161	C_{54}-C_{59}	1.43288	C_{3}-C_{1}-C_{2}	119.66980	C_{46}-C_{44}-O_{45}	117.86304	C_{29}-C_{25}-C_{24}	120.70410
C_{3}-C_{1}	1.40361	C_{17}-H_{20}	1.09055	C_{2}-C_{1}-N_{40}	118.10493	C_{22}-C_{16}-C_{14}	122.90070	C_{54}-C_{55}-C_{56}	120.73230
C_{1}-Br_{40}	1,4	C_{46}-H_{47}	1,09	C_{3}-C_{1}-N_{40}	122.22520	C_{43}-C_{50}-C_{52}	123.55840	H_{30}-C_{25}-C_{24}	118.73360
C_{4}-C_{2}	1.38852	C_{46}-H_{48}	1.09395	C_{4}-C_{2}-C_{1}	120.16870	O_{39}-C_{16}-C_{14}	118.65600	C_{54}-C_{55}-H_{63}	118.73690
C_{2}-H_{5}	1.08610	C_{22}-C_{27}	1.42375	H_{5}-C_{2}-C_{1}	119.95690	C_{22}-C_{16}-O_{39}	118.34345	C_{29}-C_{25}-H_{30}	120.56235
C_{6}-C_{3}	1.38660	C_{23}-H_{28}	1.08539	C_{4}-C_{2}-H_{5}	119.87449	C_{52}-C_{50}-O_{51}	117.84108	C_{56}-C_{55}-H_{63}	120.52952

Appendix C Cont.

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond angles(deg)	Bond	Bond angles(deg)	Bond	Bond angles(deg)
N_{11}-H_{12}	1.02834	C_{58}-H_{66}	1.08673	C_3-C_6-C_8	120.16082	H_{18}-C_{17}-H_{19}	106.93688	C_{32}-C_{27}-C_{22}	120.48058
C_8-C_4	1.40150	C_{31}-C_{34}	1.37731	H_7-C_3-C_1	119.23820	H_{19}-C_{17}-C_{15}	111.41240	C_{58}-C_{59}-C_{60}	122.54030
C_4 -H_9	1.08606	C_{57}-C_{58}	1.37738	C_6-C_3-H_7	120.60102	H_{20}-C_{17}-C_{15}	108.02300	C_{57}-C_{56}-H_{64}	119.64271
C_6-C_8	1.40356	C_{55}-C_{56}	1.37593	C_8-C_4-C_2	120.15880	C_{44}-C_{46}-H_{49}	107.92460	C_{54}-C_{59}-C_{60}	118.62720
C_6-H_{10}	1.08293	C_{25}-H_{30}	1.08669	C_2-C_4-H_9	119.87280	C_{44}-C_{46}-H_{48}	110.70020	C_{31}-C_{26}-C_{24}	118839
N_{11}-C_8	1.40072	C_{31}-H_{36}	1.08673	C_8-C_4-H_9	119.96847	C_{44}-C_{46}-H_{47}	111.50670	C_{54}-C_{59}-C_{58}	118.83193
N_{11}-H_{12}	1.02834	C_{58}-H_{66}	1.08673	C_3-C_6-C_8	120.16082	H_{18}-C_{17}-H_{19}	106.93688	C_{32}-C_{27}-C_{22}	120.48058
N_{40}-H_{41}	1.02792	C_{55}-C_{63}	1.08668	C_3-C_6-H_{10}	120.61130	H_{18}-C_{17}-H_{20}	109.51418	H_{33}-C_{27}-C_{22}	119.8485
N_{13}-N_{11}	1.30764	C_{26}-C_{32}	1.42200	H_{10}-C_6-C_8	119.22750	H_{19}-C_{17}-H_{20}	110.27684	C_{61}-C_{60}-H_{67}	120.25543
N_{40}-N_{42}	1.30802	C_{53}-C_{54}	1.41656	N_{11}-C_8-C_6	122.22660	H_{49}-C_{46}-H_{48}	109.45134	C_{34}-C_{31}-C_{26}	120.72384
C_{14}-N_{13}	1.32369	C_{59}-C_{60}	1.42238	C_4-C_8-N_{11}	118.09290	H_{49}-C_{46}-H_{47}	110.31360	C_{57}-C_{58}-C_{59}	120.73670
N_{42}-N_{43}	1.32344	C_{27}-C_{32}	1.37203	C_4-C_8-C_6	119.68052	H_{47}-C_{46}-H_{48}	106.94430	C_{31}-H_{36}-C_{26}	118.83720

Appendix C Cont.

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond angles(deg)	Bond	Bond angles(deg)	Bond	Bond angles(deg)
C_{15}-C_{14}	1.49181	C_{60}-C_{61}	1.37132	H_{12}-C_{8}-N_{11}	121.59860	C_{23}-C_{22}-C_{16}	117.36020	C_{59}-C_{58}-H_{66}	118.80544
C_{43}-C_{44}	1.49381	C_{27}-H_{33}	1.08302	C_{1}-N_{40}-H_{41}	121.59380	C_{50}-C_{52}-C_{53}	123.14430	C_{34}-C_{31}-H_{36}	120.43889
C_{16}-C_{14}	1.48877	C_{29}-H_{35}	1.08585	N_{11}-C_{8}-N_{13}	121.54390	C_{27}-C_{22}-C_{16}	123.07820	C_{57}-C_{58}-H_{66}	118.80540
C_{43}-C_{50}	1.49106	C_{32}-H_{37}	1.08653	C_{1}-N_{40}-N_{42}	121.50150	C_{50}-C_{52}-C_{61}	117.18072	C_{26}-C_{32}-C_{27}	121.19467
C_{17}-C_{15}	1.52021	C_{34}-H_{38}	1.08607	H_{12}-N_{13}-N_{11}	116.81209	C_{24}-C_{23}-C_{22}	121.43470	C_{59}-C_{60}-C_{61}	120.95790
C_{44}-C_{46}	1.52101	C_{56}-H_{64}	1.08579	H_{41}-N_{40}-N_{42}	116.83312	C_{52}-C_{53}-C_{61}	119.35270	C_{26}-C_{32}-H_{37}	118.76680
C_{15}-O_{21}	1.22308	C_{57}-H_{65}	1.08606	N_{13}-N_{11}-C_{14}	121.64650	C_{25}-C_{24}-C_{23}	122.08000	C_{32}-C_{27}-H_{33}	119.66010
C_{44}-O_{45}	1.22276	C_{60}-H_{67}	1.08672	N_{40}-N_{42}-C_{43}	121.86210	C_{52}-C_{53}-C_{54}	121.18110	C_{34}-C_{29}-C_{25}	120.21830
C_{16}-C_{22}	1.49091	C_{53}-H_{62}	1.08351	N_{13}- C_{14}-C_{15}	113.86171	C_{25}-C_{24}-C_{26}	119.04011	C_{55}-C_{56}-H_{57}	120.19220
C_{50}-C_{52}	1.48887	C_{61}-H_{68}	1.08396	N_{42}-C_{43}-C_{44}	113.45000	C_{53}-C_{54}-C_{55}	121.83550	C_{29}-C_{25}-H_{35}	120.15480
C_{16}-O_{39}	1.24544	C_{29}-C_{34}	1.41671	C_{16}-C_{14}-N_{13}	122.59970	C_{55}-C_{54}-C_{59}	119.03136	C_{55}-C_{56}-H_{64}	120.16499
C_{50}-O_{51}	1.24561	C_{56}-C_{57}	1.41652	N_{42}-C_{43}-C_{50}	122.33649	C_{26}-C_{24}-C_{23}	118.87760	C_{34}-C_{29}-H_{35}	119.62687

Appendix C Cont.

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond angles(deg)	Bond	Bond angles(deg)	Bond	Bond angles(deg)
C_{17}-H_{18}	1.09395	C_{61}-C_{52}	1.42504	C_{16}-C_{15}-C_{14}	123.29030	C_{53}-C_{54}-C_{59}	119.13230	C_{59}-C_{60}-H_{67}	118.78490
C_{17}-H_{19}	1.09384	C_{52}-C_{53}	1.38335	C_{44}-C_{43}-C_{50}	122.33650	C_{27}-C_{22}-C_{23}	119.34282	H_{37}-C_{32}-C_{27}	120.03763
C_{54}-C_{55}	1.42160	C_{46}-H_{49}	1.09059	C_{17}-C_{15}-C_{14}	118.06210	C_{52}-C_{61}-C_{60}	120.72040	C_{29}-C_{34}-C_{31}	120.47469
C_{59}-C_{58}	1.41891	C_{24}-C_{23}	1.41560	C_{43}-C_{44}-C_{46}	117.86300	H_{28}-C_{23}-C_{22}	119.00310	C_{56}-C_{57}-C_{58}	120.47490
C_{50}-C_{52}	1.48887	C_{24}-C_{25}	1.42170	O_{21}-C_{15}-C_{14}	121.47330	C_{52}-C_{61}-H_{68}	120.63939	C_{34}-H_{38}-C_{31}	119.98990
C_{22}-C_{23}	1.38422	C_{26}-C_{31}	1.41908	C_{43}-C_{44}-O_{45}	121.47330	C_{24}-C_{23}-H_{28}	119.56183	C_{58}-C_{57}-H_{65}	119.53460
C_{24}-C_{26}	1.43313			C_{17}-C_{15}-O_{21}	120.80647	C_{60}-C_{61}-H_{68}	121.02840	C_{34}-H_{38}-C_{29}	119.53537

Appendix D Force constants for NBTMH

Force const.		Internal coordinate	Force const. [b]	Ref.[c]	Force const.		Internal coordinate	Force const. [b]	Ref.[c]
No	Sym.[a]				No	Sym.[a]			
1	K_{b1}	C_2-C_1	500000	[20]*	23	K_{R3}	C_{17}-H_{19}	470300	[25]
2	K_{b2}	C_3-C_1	500000	[20]*	24	K_{R2}	C_{17}-H_{20}	470300	[25]
3	K_{r1}	C_1-H_{40}	430030	[22]	25	K_{n10}	C_{23}-C_{26}	490000	[20]*
4	K_{b6}	C_4-C_2	507330	[20]*	26	K_{n9}	C_{22}-C_{23}	699800	[20]
5	K_{r5}	C_2 -H_5	507000	[20]*	27	K_{n2}	C_{24}-C_{25}	485600	[20]*
6	K_{b3}	C_6-C_3	507330	[20]*	28	K_{n1}	C_{24}-C_{26}	603400	[20]
7	K_{r2}	C_3 -H_7	507000	[20]*	29	K_{n8}	C_{22}-C_{27}	487820	[20]*
8	K_{b5}	C_8-C_4	505000	[20]*	30	K_{C7}	C_{23}-H_{28}	490000	[20]*
9	K_{r4}	C_4 -H_9	505900	[20]*	31	K_{n3}	C_{25}-C_{29}	588800	[20]*
10	K_{b4}	C_6-C_8	505000	[20]*	32	K_{C1}	C_{24}-H_{30}	502200	[20]
11	K_{r3}	C_6-H_{10}	505900	[20]*	33	K_{n11}	C_{26}-C_{31}	485600	[20]*
12	K_k	N_{11}-C_8	512580	[22]	34	K_{n6}	C_{26}-C_{32}	430000	[20]*
13	K_s	N_{11}-H_{12}	581760	[22]*	35	K_{n7}	C_{27}-C_{32}	600000	[20]*
14	K_m	N_{13}-N_{11}	580000	[21]*	36	K_{C6}	C_{27}-H_{33}	507970	[20]*
15	K_{k1}	C_{14}-N_{13}	690000	[26]*	37	K_{n4}	C_{29}-C_{34}	590100	[20]
16	K_{e1}	C_{15}-C_{14}	401700	[21]	38	K_{C2}	C_{29}-H_{35}	507970	[20]*
17	K_{e2}	C_{16}-C_{14}	399900	[21]*	39	K_{n5}	C_{31}-C_{34}	588800	[20]*
18	K_{e4}	C_{17}-C_{15}	399900	[21]*	40	K_{C4}	C_{31}-H_{36}	502200	[20]
19	K_{d1}	C_{15}-O_{21}	798000	[21]*	41	K_{C5}	C_{32}-H_{37}	505050	[20]*
20	K_{c3}	C_{16}-C_{22}	430030	[22]	42	K_{C3}	C_{34}-H_{38}	507970	[20]*
21	K_{d2}	C_{16}-O_{39}	800000	[21]*	43	K_{R4}	$C_{40}H_{41}$	469850	[22]*
22	K_{R1}	C_{17}-H_{18}	470300	[25]	44	K_{R5}	C_{40}-H_{42}	469850	[22]*

Appendix D Cont.

Force const.		Internal coordinate	Force const. [b]	Ref.[c]	Force const.		Internal coordinate	Force const. [b]	Ref.[c]
No	Sym.[a]				No	Sym.[a]			
45	K_{R6}	C_{40}-H_{43}	469850	[22]*	62	H_{w4}	C_4-C_8-C_6	110000	[20]*
46	H_{w1}	C_3-C_1-C_2	92000	[20]	63	$H_{\gamma 4}$	C_4-C_8-N_{11}	105.00	[26]*
47	$H_{\mu 1}$	C_2-C_1-C_{40}	86080	[22]	64	$H_{\psi 1}$	C_8-N_{11}-H_{12}	56000	[26]*
48	$H_{\gamma 1}$	C_3-C_1-C_{40}	86080	[22]	65	H_{δ}	C_8-N_{11}-N_{13}	64800	[26]*
49	H_{w6}	C_4-C_2-C_1	92000	[20]	66	H_{τ}	N_{13}-N_{11}-H_{12}	60000	[26]*
50	$H_{\gamma 6}$	C_1-C_2 -H_5	50800	[20]	67	$H_{\tau 1}$	N_{11}-N_{13}-C_{14}	64800	[26]*
51	$H_{\mu 6}$	C_4-C_2-H_5	50800	[20]	68	$H_{\Phi 2}$	N_{13}-C_{14}-C_{15}	139160	[23]
52	H_{w2}	C_6-C_3-C_1	92000	[20]	69	$H_{\Phi 1}$	C_{16}-C_{14}-N_{13}	139160	[23]
53	$H_{\mu 2}$	C_1-C_3-H_7	50800	[20]	70	H_{Θ}	C_{16}-C_{14}-C_{15}	50800	[21]*
54	$H_{\gamma 2}$	C_6-C_3-H_7	50800	[20]	71	$H_{\beta 6}$	C_{17}-C_{15}-C_{14}	50800	[21]*
55	H_{w5}	C_8-C_4-C_2	92000	[20]	72	$H_{\beta 5}$	O_{21}-C_{15}-C_{14}	105.00	[21]*
56	$H_{\gamma 5}$	C_2-C_4-H_9	50800	[20]	73	$H_{\beta 4}$	C_{17}-C_{15}-O_{21}	108800	[21]*
57	$H_{\mu 5}$	C_8-C_4-H_9	50800	[20]	74	$H_{\beta 2}$	C_{22}-C_{16}-C_{14}	90800	[21]*
58	H_{w3}	C_3-C_6-C_8	92000	[20]	75	$H_{\beta 3}$	O_{39}-C_{16}-C_{14}	100800	[21]
59	$H_{\mu 3}$	C_3-C_6-H_{10}	50800	[22]*	76	$H_{\beta 1}$	C_{22}-C_{16}-O_{39}	100800	[21]
60	$H_{\gamma 3}$	C_8-C_6-H_{10}	50800	[20]	77	$H_{\Delta 2}$	C_{15}-H_{18}-C_{17}	60600	[21]*
61	$H_{\mu 4}$	N_{11}-C_8-C_6	105000	[21]*	78	$H_{\Delta 1}$	C_{15}-C_{17}-H_{19}	60600	[25]*

Appendix D Cont.

Force const.		Internal coordinate	Force const. ^{b}	Ref.^{c}	Force const.		Internal coordinate	Force const. ^{b}	Ref.^{c}
No	Sym.^{a}				No	Sym.^{a}			
79	$H_{\Delta 3}$	C_{15}-H_{20}-C_{17}	60600	[25]*	96	$H_{\theta 11}$	C_{32}-C_{26}-C_{24}	64200	[20]*
80	$H_{\alpha 2}$	C_{17}-H_{18}-H_{19}	54100	[25]	97	$H_{\theta 12}$	C_{31}-C_{26}-C_{24}	62900	[20]
81	$H_{\alpha 1}$	C_{17}-H_{18}-H_{20}	54100	[25]	98	$H_{\theta 6}$	C_{32}- C_{27}-C_{22}	97900	[20]
82	$H_{\alpha 3}$	C_{17}-H_{19}-H_{20}	54100	[25]	99	$H_{\chi 6}$	C_{22}-C_{27}-H_{33}	49400	[20]
83	$H_{\Omega 1}$	C_{27}-C_{22}-C_{16}	86800	[22]	100	$H_{\varepsilon 6}$	C_{32}-C_{27}-H_{33}	49400	[20]
84	$H_{\Omega 2}$	C_{23}-C_{22}-C_{16}	86800	[22]	101	$H_{\theta 2}$	C_{34}-C_{29}-C_{25}	97900	[20]
85	$H_{\theta 8}$	C_{24}-C_{23}-C_{22}	97900	[20]	102	$H_{\varepsilon 2}$	C_{29}-H_{35}-C_{25}	48400	[20]*
86	$H_{\sigma 1}$	C_{25}-C_{23}-C_{24}	88000	[20]	103	$H_{\chi 2}$	C_{34}-C_{29}-H_{35}	49400	[20]
87	$H_{\theta 10}$	C_{25}-C_{24}-C_{26}	62900	[20]	104	$H_{\theta 4}$	C_{34}-C_{31}-C_{26}	97900	[20]
88	$H_{\theta 9}$	C_{26}- C_{24}-C_{23}	62900	[20]	105	$H_{\chi 4}$	C_{26}-C_{31}-H_{36}	51400	[20]*
89	$H_{\theta 7}$	C_{27}- C_{22}-C_{23}	97900	[20]*	106	$H_{\varepsilon 4}$	C_{34}-C_{31}-H_{36}	51400	[20]*
90	$H_{\chi 7}$	C_{24}-C_{23}-H_{28}	49400	[22]*	107	$H_{\theta 5}$	C_{26}-C_{32}-C_{27}	97900	[20]
91	$H_{\varepsilon 7}$	C_{22}-C_{23}-H_{28}	49900	[22]*	108	$H_{\varepsilon 5}$	C_{26}-C_{32}-H_{37}	51400	[20]
92	$H_{\theta 1}$	C_{29}-C_{25}-C_{24}	97900	[20]	109	$H_{\chi 5}$	C_{27}-C_{32}-H_{37}	51400	[20]
93	$H_{\varepsilon 1}$	C_{24}-C_{25}-H_{30}	51400	[20]*	110	$H_{\theta 3}$	C_{29}-C_{34}-C_{31}	97900	[20]
94	$H_{\chi 1}$	C_{29}-C_{25}-H_{30}	51400	[20]*	111	$H_{\chi 3}$	C_{31}-C_{34}-H_{38}	48400	[20]*
95	$H_{\sigma 1}$	C_{31}-C_{26}-C_{32}	51400	[20]*	112	$H_{\varepsilon 3}$	C_{29}-C_{34}-H_{38}	49400	[20]

Appendix D Cont.

Force const.		Internal coordinate	Force const.	Ref.	Force const.		Internal coordinate	Force const.	Ref
No.	Sym.				No	Sym.			
113	$H_{\Delta 8}$	C_1-C_{40}-H_{41}	64220	[22]	135	$P_{(C)}$	P (C_{29})	75800	[20]
114	$H_{\Delta 4}$	C_1-C_{40}-H_{42}	64220	[22]	136	$P_{(C)}$	P (C_{31})	75800	[20]
115	$H_{\Delta 6}$	C_1-C_{40}-H_{43}	64220	[22]	137	$P_{(C)}$	P (C_{32})	27840	[26]
116	$H_{\alpha 4}$	C_{40}-H_{41}-H_{42}	55120	[22]	138	$P_{(C)}$	P (C_{34})	75800	[20]
117	$H_{\alpha 5}$	C_{40}-H_{41}-H_{43}	55120	[22]	139	$T_{(CC)}$	T(C_1-C_2)	27840	[26]
118	$H_{\alpha 6}$	C_{40}-H_{42}-H_{43}	55120	[22]	140	$T_{(CC)}$	T(C_1-C_3)	27840	[26]
119	$P_{(C)}$	P (C_1)	3060	[22]	141	$T_{(CC)}$	T(C_2-C_4)	27840	[26]
120	$P_{(C)}$	P(C_2)	78400	[20]	142	$T_{(CC)}$	T(C_3-C_6)	27840	[26]
121	$P_{(C)}$	P (C_3)	78400	[20]	143	$T_{(CC)}$	T(C_8C_4)	27840	[26]
122	$P_{(C)}$	P (C_4)	78400	[20]	144	$T_{(CC)}$	T(C_6-C_8)	27840	[26]
123	$P_{(C)}$	P (C_6)	78400	[20]	145	$T_{(CN)}$	T(N_{11}-C_8)	1900	[24]
124	$P_{(C)}$	P (C_8)	92380	[23]*	146	$T_{(NN)}$	T(N_{11}-N_{13})	3000	[26]
125	$P_{(N)}$	P (N_{11})	20640	[23]	147	$T_{(CN)}$	T(N_{13}-C_{14})	49100	[28]
126	$P_{(C)}$	P (C_{14})	21700	[21]	148	$T_{(CC)}$	T(C_{15}-C_{14})	5000	[28]
127	$P_{(C)}$	P (C_{15})	70800	[28]	149	$T_{(CC)}$	T(C_{14}-C_{16})	5000	[28]
128	$P_{(C)}$	P (C_{16})	70800	[28]	150	$T_{(CC)}$	T(C_{17}-C_{15})	5000	[28]
129	$P_{(C)}$	P (C_{22})	75800	[20]	151	$T_{(CC)}$	T(C_{16}-C_{22})	5000	[26]
130	$P_{(C)}$	P (C_{23})	47800	[20]	152	$T_{(CC)}$	T(C_{24}-C_{23})	27840	[26]
131	$P_{(C)}$	P (C_{24})	65060	[20]*	153	$T_{(CC)}$	T(C_{22}-C_{23})	27840	[26]
132	$P_{(C)}$	P (C_{25})	114.72	[20]*	154	$T_{(CC)}$	T(C_{24}-C_{25})	27840	[26]
133	$P_{(C)}$	P(C_{26})	75800	[20]	155	$T_{(CC)}$	T(C_{24}-C_{26})	27840	[26]
134	$P_{(C)}$	P (C_{27})	75800	[20]	156	$T_{(CC)}$	T(C_{22}-C_{27})	27840	[26]

Appendix D Cont.

Force const.		Internal coordinate	Force const.	Ref.	Force const.		Internal coordinate	Force const.	Ref
No.	Sym.				No	Sym.			
156	$T_{(CC)}$	$T(C_{22}\text{-}C_{27})$	27840	[26]					
157	$T_{(CC)}$	$T(C_{29}\text{-}C_{25})$	27840	[26]					
158	$T_{(CC)}$	$T(C_{26}\text{-}C_{31})$	27840	[26]					
159	$T_{(CC)}$	$T(C_{32}\text{-}C_{26})$	27840	[26]					
160	$T_{(CC)}$	$T(C_{32}\text{-}C_{27})$	27840	[26]					
161	$T_{(CC)}$	$T(C_{34}\text{-}C_{29})$	27840	[26]					
162	$T_{(CC)}$	$T(C_{34}\text{-}C_{31})$	27840	[26]					
163	$T_{(CC)}$	$T(C_{1}\text{-}C_{40})$	3600	[22]					

[a] K; stretching; H; in-plane; P; out-of-plane bending; T; torsion; and F; is interaction force constants, Sym; symbols, [b] units in N/m for stretching, Nm/rad^2 for bending (H & P) and N⍰m/rad for stretch/Bend interactions, [c]References for the transferred force constants, * refined force constants.