

MOLECULAR STRUCTURE AND VIBRATIONAL FREQUENCIES OF
N-AMINOPHTHALIMIDE

Fatih UCUN* and Adnan SAĞLAM

Department of Physics, Faculty of Arts and Sciences, Süleyman Demirel University,
Isparta, Turkey, e-mail: fucun@fef.sdu.edu.tr

Received: 14 August 2006, Accepted: 26 September 2006

Abstract: The molecular structure, vibrational frequencies and the corresponding assignments of N-aminophthalimide (NAPH) in the ground state have been calculated using the Hartree-Fock (HF) and density functional methods (B3LYP) with 6-31G (d, p) basis set. The calculations were utilized in the C_s symmetry of NAPH. The obtained vibrational frequencies and optimized geometric parameters (bond lengths and bond angles) were seen to be in good agreement with the experimental data. The comparison of the observed and calculated results showed that B3LYP is superior to the scaled HF method. Theoretical infrared intensities and Raman activities were also reported.

Key words: N-aminophthalimide; vibrations; IR spectra; Raman spectra; HF; DFT

N-AMİNOFİTALOMİD'İN MOLEKÜLER YAPISI VE TİTREŞİM
FREKANSLARI

Özet: Temel haldeki N-aminofitalamidin (NAPH) moleküler yapısı, titreşim frekansları ve uygun mod tanımlamaları, 6-31 G (d, p) temel setli Hartree-Fock (HF) ve yoğunluk fonksiyonu metodları (B3LYP) kullanılarak hesaplandı. Hesaplamalar, NAPH'ın C_s simetrisine uyarlandı. Elde edilen titreşim frekansları ve optimize geometrik parametreleri (bağ uzunlukları ve bağ açıları), deneysel değerlerle iyi bir uyum içinde olduğu görüldü. Deneysel ve teorik sonuçların karşılaştırılması, B3LYP'nin HF metodundan daha üstün olduğunu gösterdi. Ayrıca teorik infrared şiddetleri ve Raman aktiviteleri verildi.

Anahtar Kelimeler: N-aminofitalamidin; titreşimler; IR spektrumu; Raman Spektrumu; HF; DFT

INTRODUCTION

N-aminophthalimide ($C_8H_6N_2O_2$) consists of one benzene ring and one heterocyclic ring fused together. The molecule is in solid form at room temperature and it has a melting point around 162 °C. NAPH is useful for the preparation of phenolphthalein fluoresce in dyes and plastics (FINAR 1985), and it is a basic compound for many organic molecules. NAPH derivatives are seen to be acidic partners the presence of phthaloyl group increasing the acidity of the sole proton and concomitantly reducing strict hindrance (BROSSE et. all 2003). Because this compound also had the potential of forming an N-N-hydrogen-bonded chain it takes interest in authors as a part of studies of organic compound (HEARN & LECERO 1982, COOGAN et. all 2002). The studies also have shown that the oxidation of NAPH with lead tetra acetate in the presence of subtracts containing an olafenic double bond provides a general method for

the synthesis of the N-aminoaziridines (KUZNETSOV et. all 2001, ATKINSON et. all 1998, JONESÞTON-PETT 1995, ATKINSON&BARHER 1995).

In the present study we wish to report the assignments of complete vibration (IR and R) spectrum and structure parameters of NAPH supported by the Hartree-Fock (HF) and density functional theory (B3LYP) methods.

CALCULATIONS

The molecular structure of NAPH in the ground state is optimized by HF and B3LYP with 6-31G (d, p) basis set. Two sets are scaled by 0.8929 and 0.9613, respectively (FORESMAN & FRISH 1996). The computations were performed by using Gauss-View molecular visualization program (FRISH et. all 2001) and Gaussian 03 program package on personal computer (FRISH et. all 2002).

RESULTS AND DISCUSSION

NAPH has $P2_12_12_1$ space group and orthorhombic crystal system ($a = 20.472 \text{ \AA}$, $b = 6.672 \text{ \AA}$, $c = 5.254 \text{ \AA}$ and $V = 714.5 \text{ \AA}^3$) (PUVIARASAN et. all 2002). It has 18 atoms and the symmetry C_s . The three Cartesian displacements of the 18 atoms provide 54 internal modes namely:

$$\Gamma_{\text{inter.}} = 36A' + 18A''$$

From the character table for the C_s since $\Gamma_{\text{trans.}} = A' + 2A''$ and $\Gamma_{\text{rot.}} = 2A' + A''$, we find

$$\Gamma_{\text{vib.}} = \Gamma_{\text{inter.}} - \Gamma_{\text{trans.}} - \Gamma_{\text{rot.}} = 33A' + 15A''$$

vibration modes. All vibrations are active in both infrared (IR) and Raman (R). For a molecule containing N atom, $2N - 3$ of all vibrations is in plane the other $N - 3$ is out of plane (WILSON et. all 1980). Thus, for NAPH molecule, the 33 of all vibrations are in plane and 15 are out of plane. Since the molecule is in the C_s group the vibrations being anti-symmetric through the mirror plane σ_h will belong to the species A'' and the ones being symmetric through σ_h to the species A' . Thus, the vibrations of the A' species will be in plane and the others of the A'' species are out of plane.

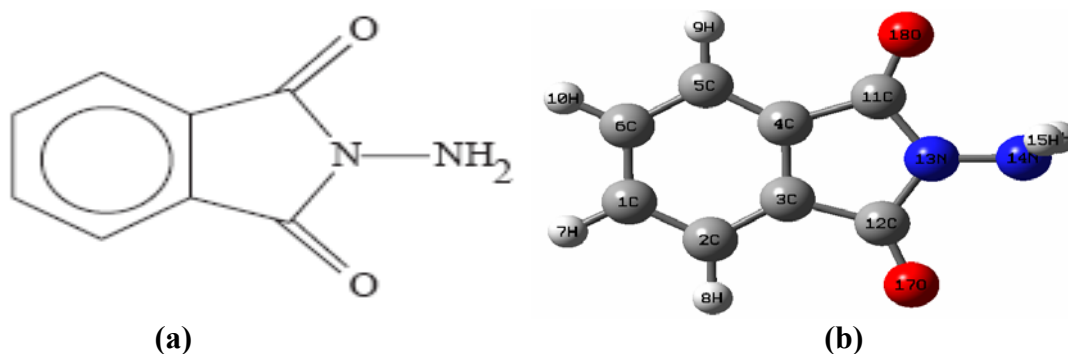


Figure 1. (a) The experimental and (b) theoretical geometric structures, of NAPH in the ground state.

The experimental and ab initio optimization structures of NAPH are illustrated in Fig. 1. The resulting vibrational frequencies with together IR intensities and Raman activities and the proposed assignments for the optimized geometry are given in Table 1. The vibrations in the table were scaled using 0.8929 and 0.9613 for HF and B3LYP with 6-31G (d, p) basis set, respectively (FORESMAN & FRISH 1996). The table also consists of experimental results for comparison. As seen, the experimental and theoretical vibration values are in good agreement with each other. The correlation graphics between them are shown in Fig.2. The correlation values for HF and B3LYP are 0.9980 and 0.9989, respectively. These values also show their suitable agreements. But, in addition we can say B3LYP have a better correlation than HF.

Table 1. Experimental and calculated vibrational frequencies of NAPH.

Symmetry	Assignments	Calculated Frequencies (cm ⁻¹)							
		Experimental ^a Frequencies (cm ⁻¹)		HF 6-31G (d,p)		B3LYP 6-31G (d,p)			
		IR	R	IR inten. (km / mol)	R activity (Å ⁴ / amu)	IR inten. (km / mol)	R activity (Å ⁴ / amu)		
A'	NH ₂ asym. stretch.	3482w		3432	12	64	3417	4	82
A'	NH ₂ sym. stretch.	3340m	3343vw	3347	7	120	3338	2	179
A'	C-H stretch.	3092vw	3095w	3025	9	222	3094	10	261
A'	C-H stretch.		3085w	3022	6	22	3092	5	24
A'	C-H stretch.	3067vw	3069w	3008	12	116	3080	8	120
A'	C-H stretch.	3033vw		2994	3	61	3068	2	63
A'	C=O stretch. + NH ₂ bend. + C-C-N bend.	1784s	1784m	1855	157	74	1795	97	96
A'	C=O stretch.+ NH ₂ bend. + C-C-N bend.	1720vs	1717vw	1797	897	12	1750	554	20
A'	NH ₂ bend.		1615m	1646	18	10	1635	9	18
A'	C=C stretch. + CH bend.	1604s	1602vw	1622	5	35	1600	10	31
A'	C=C stretch. + CH bend.	1520vw		1608	2	8	1593	3	5
A'	CH bend.	1498w		1462	7	1	1449	7	3
A'	CH bend.	1466m	1467vw	1456	15	1	1445	1	1
A'	N-N stretch. + NH ₂ bend. + C-N-C bend. + CH bend.	1408s	1406vw	1430	304	2	1378	208	28
A'	CH bend. + C=C stretch.	1350w	1345vw	1305	4	4	1347	3	3
A'	CH bend. + C=C stretch.	1292w		1276	10	3	1297	3	6
A''	NH ₂ rock.	1198m		1268	23	14	1262	1	~0
A'	CH scissor. + C-C stretch.	1184w	1198m	1175	58	16	1184	55	62
A'	CH scissor. + C-C stretch	1174w	1173vw	1160	47	23	1147	4	7
A'	CH bend.	1145m	1154vw	1139	7	3	1140	7	6
A'	Ring bend.+ C-N-N bend.	1091w		1096	~0	9	1118	35	6
A'	Ring bend.	1074w		1032	6	1	1058	8	1
A'	CH out of plane bend.	1022m		1016	~0	~0	1005	8	14
A''	CH out of plane bend.	995m	996w	996	25	12	977	30	12
A'	CH scissor.	967w		982	1	1	970	~0	~0
A''	Ring breath. + N-N stretch. + C-C=O bend.	920m		976	23	19	936	1	1
A''	CH out of plane bend.	908m		909	170	3	893	132	3
A'	Ring bend. + O=C-N bend.	876m	874vw	906	~0	2	876	~0	4
A''	CH wag.			850	42	2	841	40	2
A''	C-C=C bend.	799m	798vw	793	5	~0	768	11	~0
A'	CH wag.+ O=C-N out of plane bend.	715vs		786	~0	~0	761	1	~0
A''	Ring torsion. + NH ₂ wag.		709m	715	125	3	691	3	16
A'	Ring bend. NH ₂ wag.			690	3	15	686	63	3
A''	Ring out of plane bend.+ O=C-N out of plane bend.	671w		687	4	~0	686	5	1

Table 1 Continued

A'	NH ₂ wag.	608w	606w	663	1	1	655	1	~0
A'	NH ₂ wag. + Ring torsion.			588	2	4	584	1	8
A'	Ring rock.	528m		513	11	1	509	10	1
A'	Ring scissor.	472w	474vw	459	10	7	460	5	7
A''	Ring stretch.			456	~0	1	450	~0	1
A''	Ring out of plane bend.	434w		407	~0	~0	399	~0	~0
	Ring stretch. + O=C-N								
A'	bend.		325vw	338	20	3	331	13	2
A'	NH ₂ wag. + C-N-N bend.			289	15	2	279	14	3
A''	NH ₂ torsion.			231	1	1	229	1	1
A'	NH ₂ torsion.		252vw	226	14	3	226	4	3
A''	Ring rock. + NH ₂ rock.			200	38	2	141	~0	~0
A''	Ring wag. + O=C-N-N out								
	of plane bend.		173w	138	6	1	136	~0	3
A''	Ring out of plane rock.			135	~0	2	111	9	1
A''	NH ₂ wag. + Ring wag.			108	5	1	87	49	3

^a Taken from Ref. (PUVIARASAN et al 2002).

Table 2. Experimental and theoretical optimized structure parameters of NAPH in the ground state.

Parameters	Calculated 6-31G (d, p)			Parameters	Calculated 6-31G (d, p)		
	Experimental ^a	HF	B3LYP		Experimental ^a	HF	B3LYP
Bond lengths (Å)				Bond angles (°)			
C(1)-C(2)	1.400	1.390	1.401	C(1)-C(2)-C(3)	117.1	117.2	117.5
C(2)-C(3)	1.377	1.377	1.385	C(3)-C(2)-H(8)	-	121.1	120.7
C(3)-C(4)	1.387	1.382	1.398	C(4)-C(5)-C(6)	116.9	117.2	117.4
C(4)-C(5)	1.382	1.376	1.387	C(4)-C(5)-H(9)	-	121.2	121.6
C(5)-C(6)	1.384	1.390	1.400	C(5)-C(6)-C(1)	121.8	121.1	121.1
C(1)-C(6)	1.383	1.390	1.400	C(5)-C(6)-H(10)	-	119.6	119.3
C(1)-H(7)	0.950	1.075	1.086	C(6)-C(1)-C(2)	120.9	121.2	121.1
C(2)-H(8)	0.950	1.074	1.085	C(2)-C(1)-H(7)	-	119.2	119.5
C(5)-H(9)	0.950	1.074	1.085	C(3)-C(4)-C(5)	121.7	121.8	121.5
C(6)-H(10)	0.950	1.075	1.086	C(3)-C(4)-C(11)	108.2	108.0	108.3
C(4)-C(11)	1.479	1.489	1.490	C(5)-C(4)-C(11)	130.1	130.2	130.2
C(3)-C(12)	1.490	1.495	1.496	C(2)-C(3)-C(4)	121.5	121.3	121.5
C(12)-N(13)	1.398	1.394	1.414	C(2)-C(3)-C(12)	108.5	108.7	109.0
C(11)-N(13)	1.389	1.386	1.407	C(4)-C(3)-C(12)	130.0	130.0	129.5
N(13)-N(14)	1.409	1.380	1.397	C(4)-C(11)-N(13)	105.7	105.3	105.3
N(14)-H(15)	0.950	1.000	1.019	C(4)-C(11)-O(18)	129.6	129.7	130.3
N(14)-H(16)	0.940	1.000	1.019	O(18)-C(11)-N(13)	124.6	125.0	124.4
C(12)-O(17)	1.200	1.189	1.209	C(3)-C(12)-N(13)	104.6	104.5	104.3
C(11)-O(18)	1.210	1.189	1.215	C(11)-N(13)-C(12)	112.8	113.3	113.0
				C(11)-N(13)-N(14)	125.6	123.9	124.0
				C(12)-N(13)-N(14)	121.6	122.8	123.0
				N(13)-N(14)-H(15)	108.0	109.2	107.9
				N(13)-N(14)-H(16)	108.0	109.2	107.9
				H(15)-N(14)-H(16)	-	108.8	106.8

^a Taken from Ref. (LOEHLIN 1985).

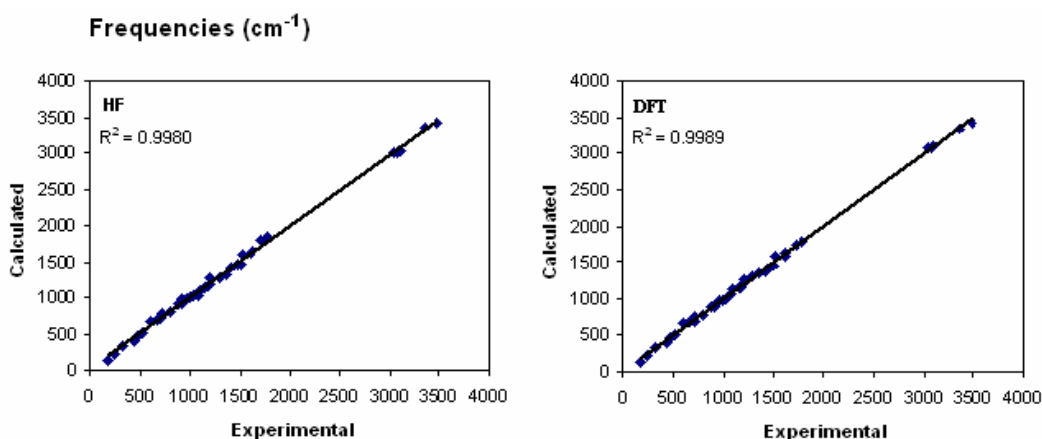


Figure 2. Correlation graphics between the experimental and calculated frequencies for NAPH.

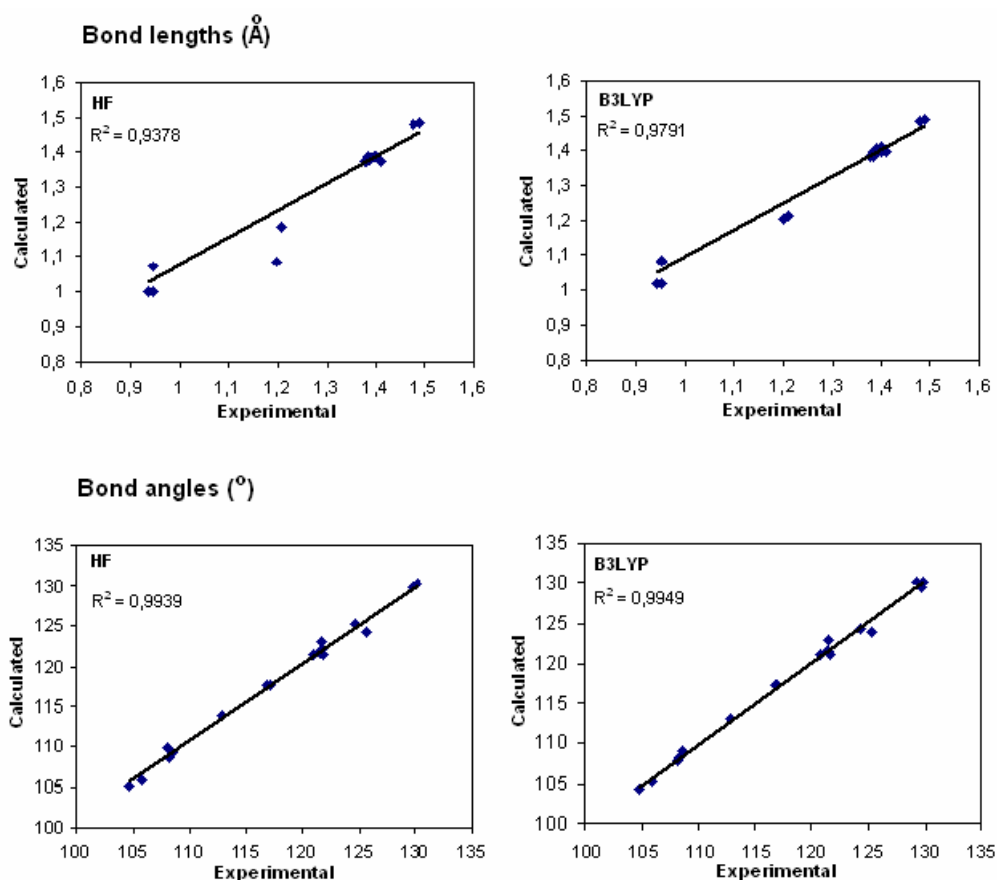


Figure 3. Correlation graphics of NAPH in the ground state between the experimental and calculated geometric parameters for a) bond lengths and b) bond angles.

The species of all the vibrations are given in the first column of Table 1. As we say before, the vibrations in plane belong to the A' species the others-out of plane- to the A'' species. Namely, 33 are in plane and 15 out of plane. This is indeed what we have observed by means of visual inspection of the vibrations.

Table 2 shows the experimental and theoretical optimized structure parameters (bond lengths and angles). As seen from the table, the parameters are very close each other. The correlation graphics are shown in Fig.3. The correlation values in the figure show more appropriate of B3LYP than HF as for vibrations.

CONCLUSION

The vibrational frequencies, optimised structure parameters and the corresponding vibrational assignments of NAPH have been calculated by using HF and B3LYP methods at 6-31G (d, p) basis set level. As seen from Tables 1-2, the experimental and calculated vibration frequencies and geometry parameters correspond well to each other. The used scale factors seem to cause gained vibrations to be in good agreement with the experimental data. Taking into account that the molecular geometry in the vapour phase may be different from in the solid phase owing to extended hydrogen bonding and stacking interactions there is reasonable agreement between the calculated and experimental geometric parameters. The largest differences of the calculated geometries from the experimental ones are 0.075 \AA (HF), 0.136 \AA (B3LYP) for the bond lengths and 1.7° (HF), 1.6° (B3LYP) for the bond angles. From the correlation values in Fig 2-3, it has been seen that the scaled B3LYP method has better fits than HF for both the vibrational frequencies and geometric parameters.

REFERENCES

- ATKINSON RS, BARHER E, 1995, *Chemical Communications*, 819.
- ATKINSON RS, GRIMSHIRE MJ, KELLY BJ, 1998, *Tetrahedron* 45, 2875.
- BROSSE N, PINTO M-F, JAMART-GREGOIRE B, 2003, *European Journal of Organic Chemistry*, 4757.
- COOGAN MP, PLATTS JA, HAIGH RG, 2002, *Sulfur Letters*, 25, 251.
- FRISH A, NIELSEN AB, HOLDER AJ, 2001, *Gauss View User Manual*, Gaussian Inc. Pittsburg, PA.
- FRISH MJ, TRUCKS GW, SCHEGEL HB, SCUSERIA GE, ROBB MA, CHEESEMAN JR, MONTGOMERY JA, VREVEN Jr. T, KUDIN KN, BURANT JC, MILLAM JM, IYENGAR SS, TOMASAI J, BARONE V, MENNUCCI B, COSSI M, SCALMANI G, REGA N, PETERSSON GA, NAKATSUJI H, HADA M, EHARA M, TOYOTA K, FUKUDA R, HASEGAWA J, ISHIDA M, NAKAJIMA T, HONDA Y, KITAO O, NAKAI H, KLENE M, LI X, KNOX JE, HRATCHIAN HP, CROSS JB, ADAMO C, JARAMILLO J, GOMPERS R, STRATMANN RE, YAZYEV O, AUSTIN AJ, CAMMI R, POMELLI C, OCHTERSKI JW, AYALA PY, MOROKUMA K, VOTH GA, SALVADOR P, DANNENBERG JJ, ZAKRZEWSKI VG, DAPPRICH S, DANIELS AD, STRAIN MC, FARKAS O, MALICK DK, RABUCK AD, RAGHAVACHARI K, FORESMAN JB, ORTIZ JV, CUI Q, BABOUL AG, CLIFFORD S, CIOSLOWSKI J, STEFANOV BB, LIU G, LIASHENKO A, PISKORZ P, KOMAROMI I, MARTIN RL, FOX DJ, KEITH T, AL-LAHAM MA, PENG CY, NANAYAKKARA A, CHALLACOMBE M, GILL PMW, JOHNSON B, CHEN W, WONG MW, GONZALEZ C, POPLE JA, 2003, *Gaussian 03 Revision C.02 (or D.01)*, Gaussian, Inc., Pittsburgh, PA.

- FINAR LL, 1995. *Organic Chemistry* Vol-1, Longman, England.
- FORESMAN JB, FRISH A, 1996, *Expoloring Chemistry with Electronic Structure Methods*, 2. Ed., Gaussian, Inc. Pittsburgh, PA.
- HEARN MJ, LECERO ER, 1982, *J. Heterocycl Chemistry*, 19, 1587.
- JONES DW, THORNTON-PETT M, 1995, *Journal of the Chemical Society, Perkin Transactions*, 1, 809.
- KUZNETSOV MA, KUZNETSOVA LM, SCHANTL JG, WURST K, 2001, *European Journal of Organic Chemistry*, 1309.
- LOEHLIN JH, 1985, *Acta Crysatallographia*, C 41, 210.
- PUVIARASAN N, ARJUNAN V, MOHAN S, 2002, *Turkish Journal of Chemistry*, 26, 323.
- WILSON EB, DECIUS JC, CROSS PC, 2002, *Molecular Vibrations*, Dover Pub. Inc., New York.