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Research Article

SYNTHESIS, SPECTROSCOPIC AND THEORETICAL STUDIES OF SOME ALKYL AND ARYL SUBSTITUTED ACID HYDRAZIDE LIGANDS

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ABSTRACT

Acetoacetic acid hydrazide (AAAH), butyrylacetic acid (BUTAH) and benzoylacetic acid (BENZAH) hydrazides were prepared and characterized using elemental analysis, infrared and electronic spectra, mass spectra and ^{1}HNMR and the quantum chemical calculations of these determined. The microanalyses gave satisfactory results that agreed fairly well with the calculated values. The infrared spectra of the hydrazides gave the amide I band at 1612cm^{-1}, 1618 cm^{-1} and 1600cm^{-1}respectively for AAAH, BUTAH and BENZAH experimentally. The ν(N-H) stretching frequencies for the amino group were observed at 3539cm^{-1}, 3460cm^{-1} and 3452cm^{-1} respectively for these compounds. The DFT studies were consistent with experimental values. The fragmentation patterns in the mass spectra for these compounds were in agreement with the calculated values. The ^{1}HNMR of the hydrazides both experimentally and theoretically determined corroborated each other.

INTRODUCTION

Hydrazine derivatives have been investigated due to their coordinative and biological abilities as well as their use in analytical chemistry as metal-extracting agents (Ying- Xia Zhhou *et al.*, 2012). Acid hydrazides and their condensation products have been reported for their potential as tuberculostats and also a wide range of remarkable biological properties which include bactericidal, anti-malaria, anti-cancer, anti-depressant, anti-HIV and vasodilator activities (Ying- Xia Zhhou *et al.*, 2012; Salawu and Abdulsalam, 2011; Sahebalzamani *et al.*, 2010; Rajaei *et al.*, 2010; Sechi *et al.*, 2008; Milway *et al.*, 2003). These hydrazides have been successfully studied to create self-assembled square grid structures with novel structural and magnetic properties (Sechi *et al.*, 2008). These hydrazides based on –CONHNH$_2$ and their derivatives contain trigonal N- and O- donors which make them potential chelating ligands (Ying- Xia Zhhou *et al.*, 2012). The ligands and their complexes have supramolecular interactions because they include hydrogen – bonding donors (amino-groups) and acceptors (carbonyl) and thus hydrogen-bonding play an important role in extending and stabilizing the structures of the resultant complexes (Ying- Xia Zhhou *et al.*, 2012). These ligand complexes serve as models for biological important species and find applications in biomimetic catalytic reactions (Sahebalzamani *et al.*, 2010). Thus, there is continued interest in these hydrazide ligands, their derivatives and complexes. We had previously reported the synthesis and infrared spectra of the ligands. In this work, we provide the mass spectra, NMR and compare these experimental results with calculated values. DFT was also used to calculate the dipole moment, and the HOMO-LUMO energy band gaps.

MATERIALS AND METHODS

Reagent grade ethylacetoacetate, ethylbutyrylacetate, ethylbenzoylacetate, hydrazine hydrate, ethanol, deionized water, calcium chloride were purchased from the British Drug House Chemicals (BDH) and Aldrich Chemicals Co., and were used without further purification.Preparation of the Hydrazides Synthesis of the Acetoacetic acid hydrazide (AAAH) (Adekunle *et al.*, 2010a). Hydrazine hydrate (19.40mL, 400mmoles) transferred to a 250mL quick-fit conical flask fitted with a reflux condenser was stirred with gentle heating while 51mL (400mmoles) ethylacetoacetate was added portion wise. The orange coloured suspension obtained was refluxed for 15min, after which 170mL ethanol was added to a clear yellow solution. The resultant solution was refluxed for an additional 4hrs. The ethanol was distilled off and the remaining solution was transferred into a beaker and left overnight at room temperature. The precipitates obtained were filtered by suction, washed with deionized water, and dried over calcium chloride in a dessicator. Yield: 17.2g, (37%) $CH_3COCH_2CONHNH_2$, creamish white crystalline material. Anal. Cal. $C_4H_8N_2O_2$ (M.M: 116.12): C, 41.37; H, 6.94; N, 24.13. Found: C, 41.22; H, 6.86; N, 23.68.ESI-MS (MeOH) : 99.08 {100%: $CH_3COCH_2CON^+$}, 100.05 (7.5% {$CH_3COCH_2CONH^+$}. ^1H NMR: δ/ppm: 2.06(s, 2H, amino group), 2.49(3H, methyl group), 3.33(2H, methylene group), 10.25(1H, amide group).Preparation of Butyrylacetic acid hydrazide (BUTAH) (Adekunle *et al.,* 2010a). 9mL (9.33g, 190mmoles) hydrazine hydrate was transferred to a 250mL quick –fit conical flask fitted with a reflux condenser. Ethylbutyrylacetate (29.5 g, 190 mmoles) was added portion wise. On addition of about 20mL of the ester, an off-white coloured paste was observed. The remaining 10mL was added and the mixture heated under reflux for 15min, after which 140mL ethanol was added, which dissolved the paste and gave a faint yellow solution. The refluxing continued for an additional 4hrs after which the ethanol was distilled off. The remaining peached coloured suspension was transferred to a 250mL beaker where on cooling, formed crystalline cream precipitates. The precipitates were filtered by suction, washed with deionized water and dried in a dessicator over calcium chloride. Yield: 16.6g (62%) $CH_3CH_2CH_2COCH_2CONHNH_2$, creamish white crystalline material. Anal. Cal. $C_6H_{12}N_2O_2$ (M.M: 144.18): C, 49.99; H, 8.39; N, 19.43. Found: C, 49.66; H, 8.32; N, 19.31.ESI-MS (MeOH): 127.11 (100%: {$CH_3CH_2CH_2COCH_2CON^+$}, 128.11 {10% $CH_3CH_2CH_2COCH_2CONH^+$}. ^1H NMR: δ/ppm: 0.89(3H, methyl group), 1.58(2H, methylene after CH_3), 2.48(2H, of CH_2-CO) 3.33(2H, methylene group of CO-CH_2-CO), 10.40(1H, amide group).Preparation of benzoylacetic acid hydrazide (BENZAH) (Adekunle *et al.,* 2010a). Ethylbenzoylacetate (33.3g, 170mL) solution in ethanol (30mL) was added portion wise to 8mL (8.67g, 170mL) hydrazine hydrate in a 250mL quick-fit conical flask. The light peach solution obtained was refluxed with gentle heating for 15min, after which 150mL ethanol was added and refluxing continued for additional 4hrs. The ethanol was distilled off and the remaining solution was transferred to a 250mL beaker where it was left overnight. The cream coloured crystalline precipitates of the benzoylacetic acid hydrazide formed were filtered by suction, washed with deionized water and then dried in a dessicator over calcium chloride. Yield: 21.5g (70%) $C_6H_5COCH_2CONHNH_2$, white crystalline material. Anal. Cal. $C_9H_{10}N_2O_2$ (M.M: 178.19): C, 60.66; H, 5.66; N, 15.72. Found: C, 60.44; H, 5.62; N, 15.66.ESI-MS (MeOH) 161.05 (100%: {$C_6H_5COCH_2CON^+$}, 162.05 {12% $C_6H_5COCH_2CONH^+$}. ^1H NMR: δ/ppm: 2.08(2H, amino group), 3.33(2H, methylene group of CO-CH_2-CO), 7.37(1H, meta-position), 7.45(1H,para-position), 7.86(1H, ortho-position), 7.82(1H, amide group).

Physical Measurements

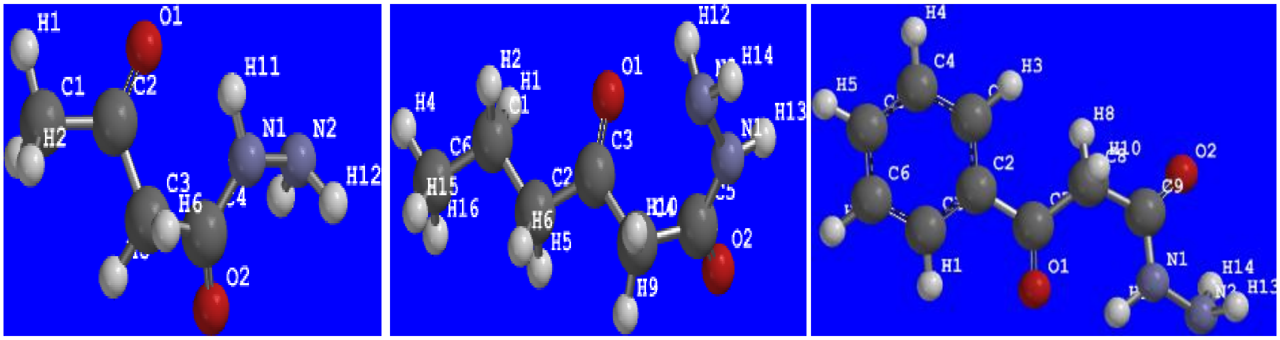
Elemental analyses were performed using a Perkin-Elmer 240C elemental analyser. The infrared spectra were recorded on a Nicolet Avater 330FT- IR spectrophotometer using KBr discs. Genesys 10 scanning spectrophotometer (Thermo Electron Corporation) was used to record the electronic reflectance spectra of the ligand. ESI mass spectra on a water Qtof Micro YA263 spectrometer and 300MHz NMR spectra on a Bruker DPX300 spectrometer in deuterated methanol (MeOH-d_4).

Computational Method: Quantum chemical calculations for AAAH, BUTAH and BENZAH were done byemployingDFT, B3LYP using Spartan 10 program package. The B3LYP methods which uses the exchange functional proposed by Becke and the correlation functional given by Lee, Yang and Parr (Becke, 1993; Lee *et al.,* 1988; Hehre *et al.,* 1986; Parr and Yang, 1989; Cramer, 2002; Young, 2002; Lewars, 2003; Jensen 2007). The 6-31(D) basis set has been used in conjunction with DFT method. This basis set has the advantage of being flexible enough to guarantee reliable theoretical results and being small enough for rapid calculations. All geometries were pre-optimized by molecular mechanics and then fully optimized by DFT method. It represents an excellent compromise between completeness and economy.

Table 1: Key infrared frequencies and electronic spectra transitions for the compounds (cm^{-1})

Compounds	Amide I	Amide II	$\nu(NH_2)$	ν (C=O)	ν (C-H)	Electronic bands($\times10^3$)[nm]
AAAH	1612(m)	1544(w)	3539(w)	1782(m)	2939(w)	51,282[195], 37,175[269]
BUTAH	1618(m)	1592(w)	3460(m)	1727(w)	2974(m), 2872(w)	45,045[222]
BENZAH	1626(m)	1600(s)	3452(w)	1740(m)	3120(m)	49,751[201], 41,494[241]

Theoretical Studies



AAAH **BUTAH** **BENZAH**

Figure 1: Optimized Structure of the Ligands

The molecular geometry was fully optimized without any constraint using analytical gradient procedure implemented within the program. A restricted HF-DFT self-consistent field calculation was carried out using Pulay DIIS and Geometry direct minimization implemented within the program. The calculated quantities include the geometrical parameters, total energy, dipole moment and molecular orbital energies.

Geometric Parameters

The optimized structures of these compounds under study adopt a C1 symmetry. The geometrical parameters were obtained after total optimization of the equilibrum geometries by DFT , Bond length, bond angles and dihedral angles which contributed to the internal energies were measured and recorded (See Table 1). The effects of the substituent ethyl and benzyl group on the AAAH is clearly noticeable.For instance, the bond length of C_1-C_2 in the AAAH is 1.513Å this bond increased to 1.520Å when one hydrogen is replaced by a ethyl group. C_2-C_3 bond length is also 1.528Å also increased to 1.533Å. There are significant increasein the value of bond angles and dihedral angles from AAAH to BENZAHas revealed in Table 1.

Uv-visible spectra studies: The ultra-violet spectra of these species were studied with Density function theory (DFT). The results in Table 1 show the first five electronic transition states in nanometer (nm), the oscillation strength (f) that can give an idea of intensity of the transition, in the ultraviolet region, The calculated uv absorption bands within the range 185-277.1nm for AAAH and BUTAH indicating an electronic transition from n→π* of the carbonyl moiety while the transitions in BENZAH can be ascribed to both n→π* within the carbonyl and the π→π* of the benzene ring.

Table 2: Geometrical parameter for the hydrazide ligands

Bond distance/Ǻ

Bond	**AAAH**	**BUTAH**	**BENZAH**
C1-C2	1.513	1.520	-
C2-C3	1.528	1.533	1.527
C3-C4	1.536	1.522	1.536
C4-N1	1.362	1.373	1.359
N1-N2	1.414	1.404	1.414
C2-O1	1.220	1.218	1.227
C4-O2	1.225	1.222	1.227
C2-C5	-	1.529	-
C5-C6	-	1.532	-
Ar-C2	-	-	1.497

Bond angle in degrees

Bond Angle/º	**AAAH**	**BUTAH**	**BENZAH**
C1-C2-O1	121.56	122.39	-
C1-C2-C3	116.20	115.92	-
O1-C2-C3	122.22	121.69	121.82
C3-C4-O2	121.13	122.56	119.03
C4-N1-N2	120.60	121.39	120.41
C1-C5-C6	-	112.48	-
BEN-C2-O1	-	-	119.80
BEN-C2-C3	-	-	118.36

Dihedral Angle in degrees

Dihedral Angle	**AAAH**	**BUTAH**	**BENZAH**
C1-C2-C3-C4	144.58	146.32	-
C2-C3-C4-N1	43.42	83.45	-31.66
C3-C4-N1-N2	-173.82	-9.58	174.65
O2-C4-N1-N2	8.92	169.61	-8.61
O1-C2-C3-C4	-36.68	-34.11	19.35
C2-C3-C4-O2	-139.25	-95.73	151.49
BEN-C2-C3-C4	-	-	-162.30

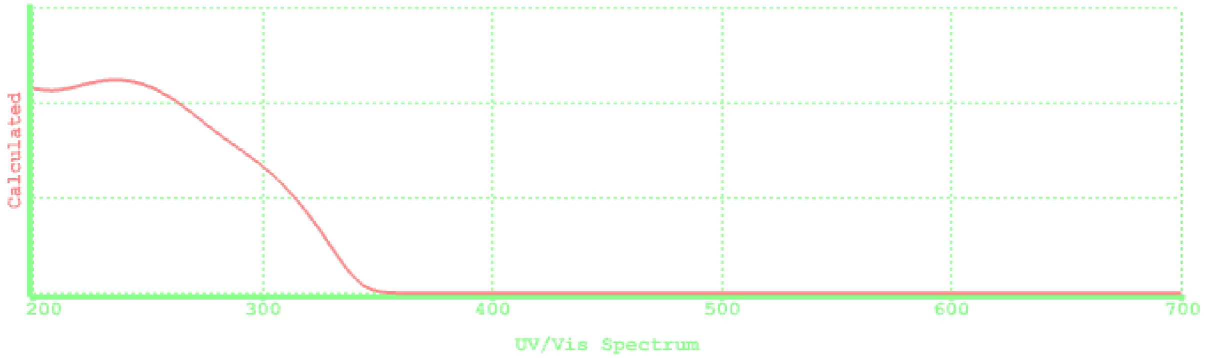
Table 3: Uv-visible spectra data for the hydrazide Ligands

Compound	Wavelength/nm	intensity
AAAH	184.9	0.0235
	208.5	0.00053
	215.8	0.0017
	235.7	0.0263
	245.5	0.0037
	277.1	0.001
BUTAH	187.2	0.0413
	191.0	0.0038
	219.0	0.0015
	227.7	0.00023
	233.3	0.0018
	274.1	0.0004
BENZAH	229.7	0.354
	246.4	0.0015
	261.1	0.0213
	285.2	0.017
	297.4	0.0037
	326.42	0.0024

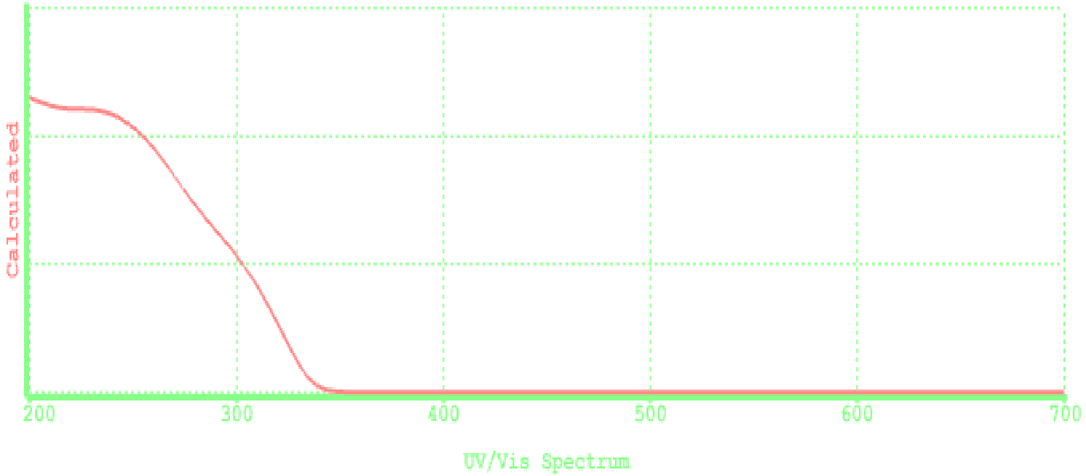
Table 4: NMR Spectroscopic studies

1H/PROTONS	AAAH	BUTAH	BENZAH
CH3	1.78-2.20	0.80-1.15	-
CH2	-	1.55-1.82	-
CH2	-	2.43-2.47	-
CH2	2.97-3.04	2.82-4.08	3.24-3.72
NH	7.48	4.96	8.09
NH2	2.35-3.17	2.52-3.71	2.4-3.31
Ar-H	-	-	7.31-8.28

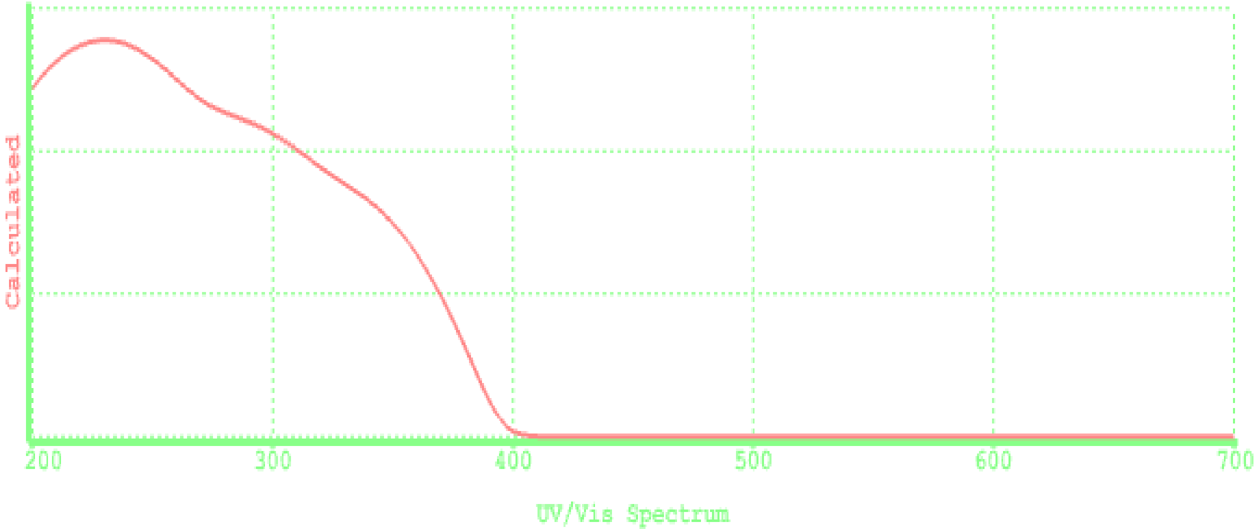
13C	AAAH	BUTAH	BENZAH
C1	30.78	46.80	-
C2	208.64	210.04	199.78
C3	46.65	46.40	41.73
C4	170.06	171.40	171.38
C5	-	18.15	-
C6	-	14.28	-
ArC	-	-	128.15-134.84



AAAH

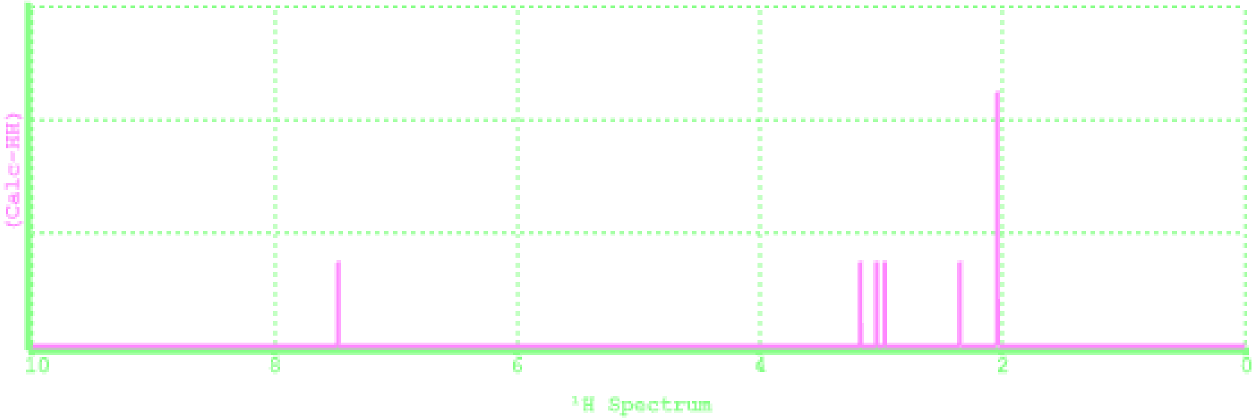


BUTAH

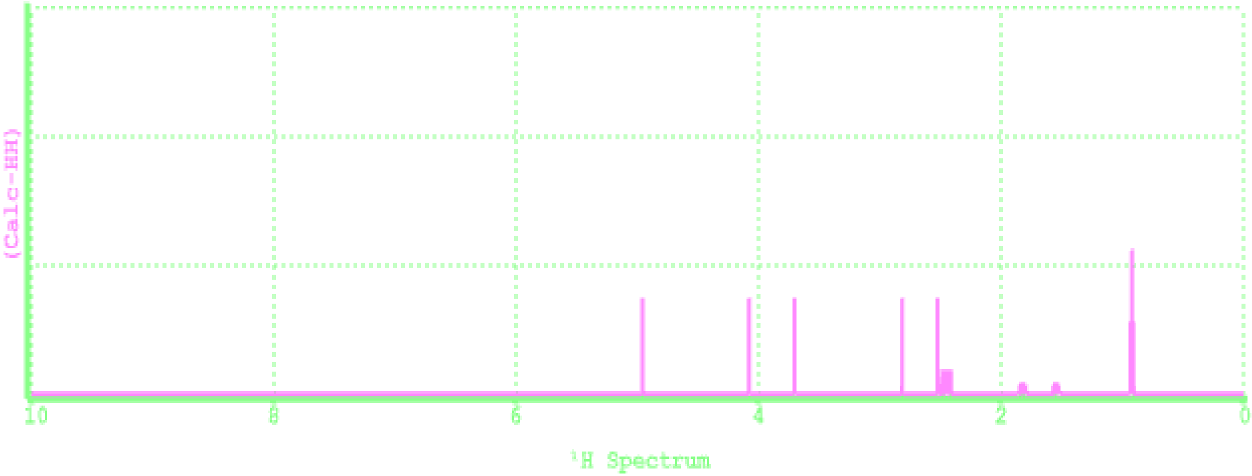


BENZAH

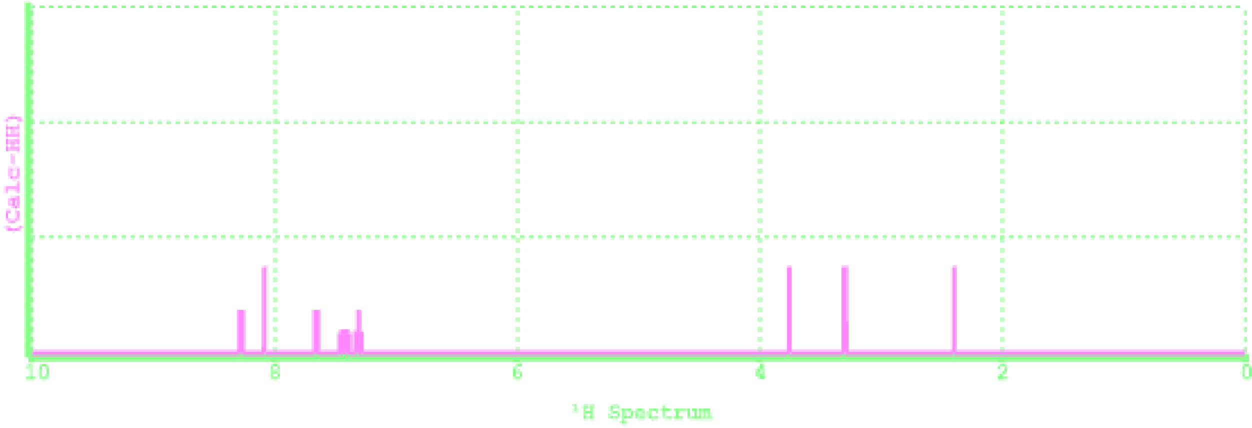
Figure 1: Uv-visible spectra of AAAH, BUTAH and BENZAH



AAAH



BUTAH



BENZAH

Figure 2:^{1}H NMR spectra

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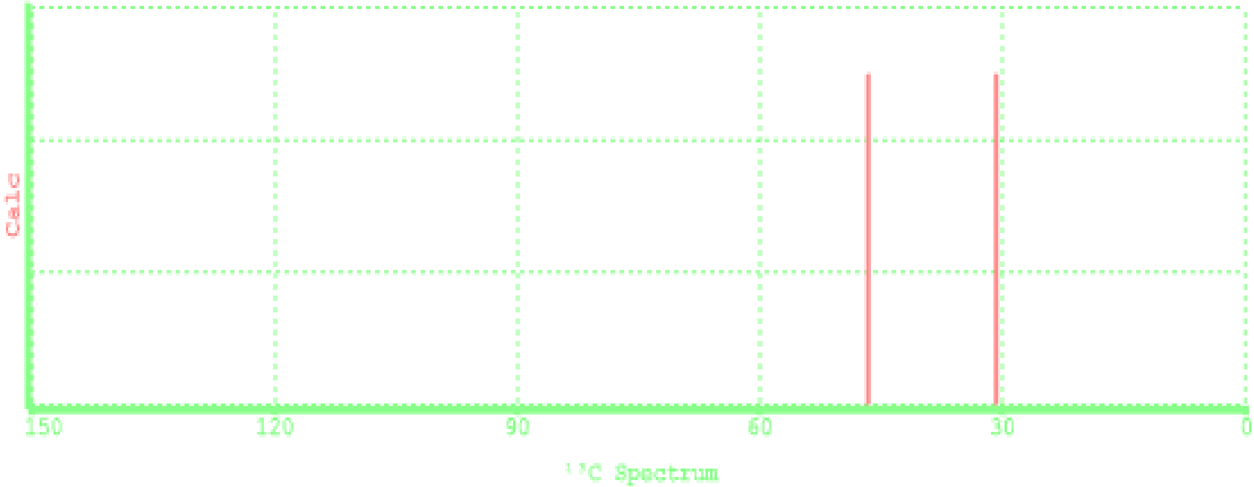
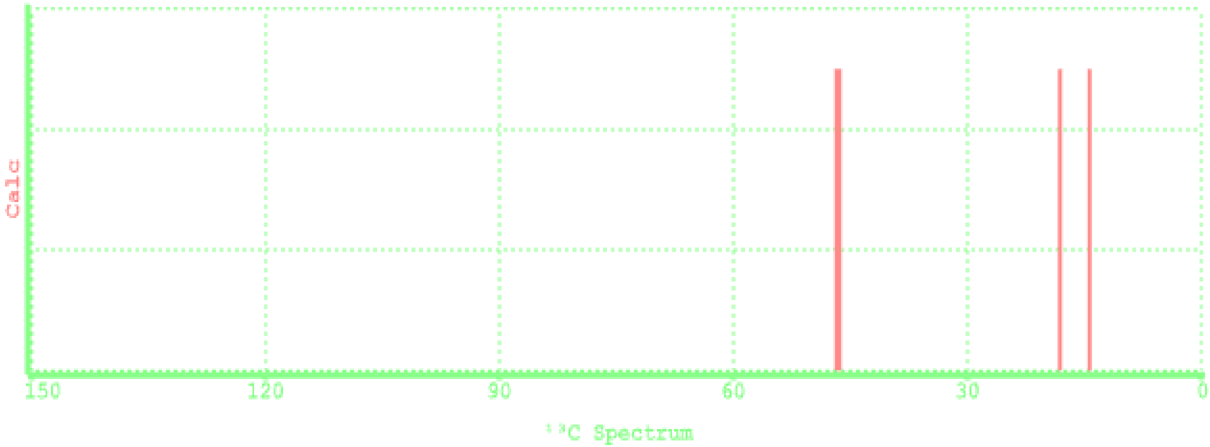
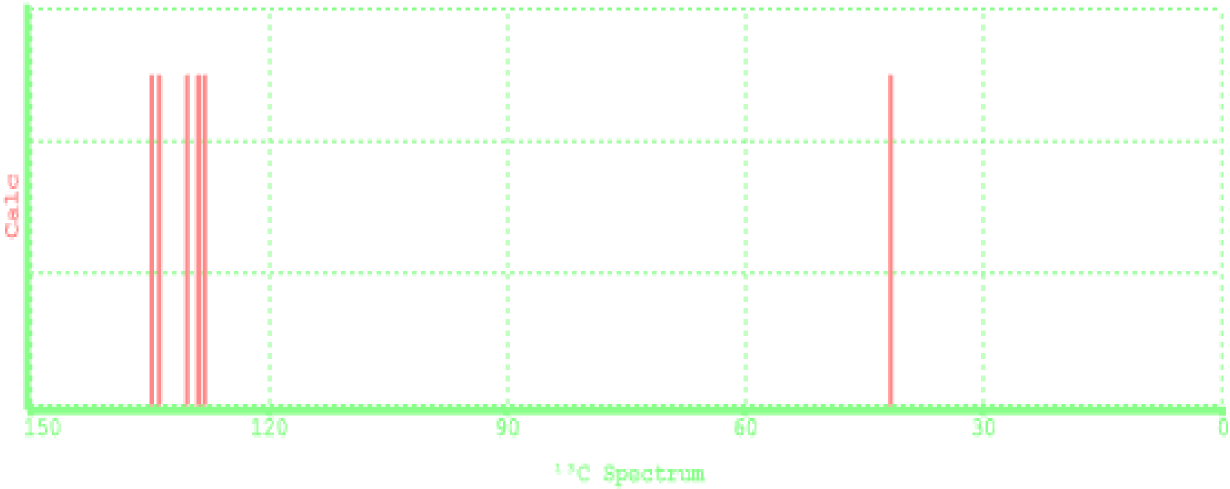


AAAH



BUTAH



BENZAH

Figure 3:^{13}C NMR spectra

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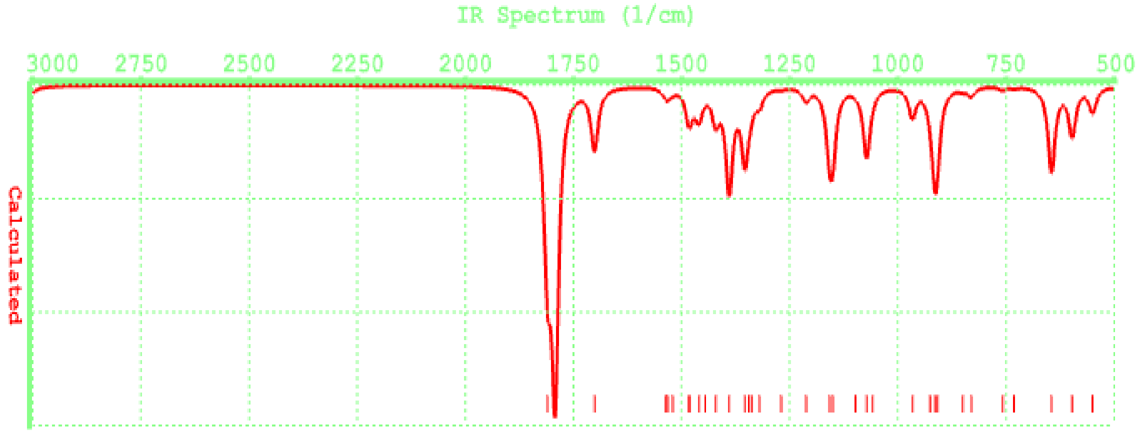
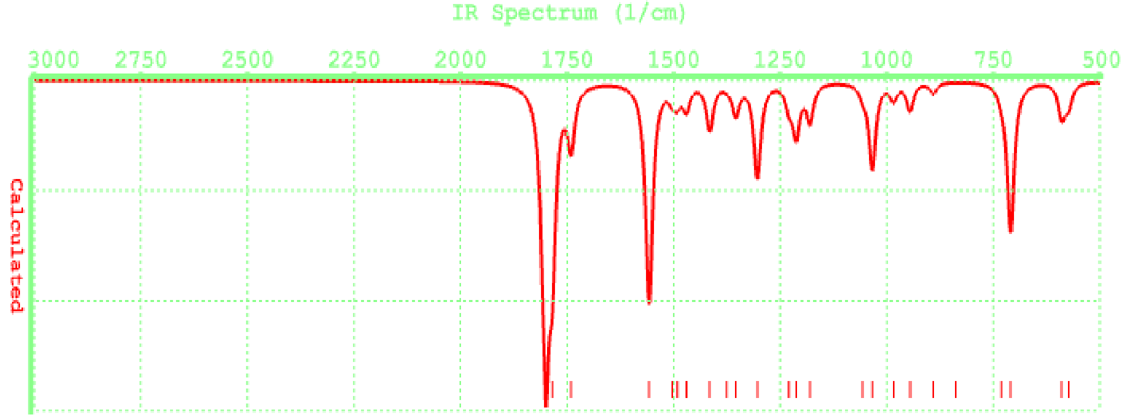
Vibrational Spectra

Vibrational spectrum of AAAH consists of 16 atoms, and therefore contains 42 normal modes of vibrations. To aid in the assignments of modes, the study is based on the direct comparison between experimental and calculated spectra by considering both the frequency sequence and the intensity pattern. The IR signature contains the bands which are due to the stretching vibrations of the carbonyl, CH and NH bonds.



AAAH



BUTAH

BENZAH

Figure 4: Infrared spectra

Electronic Properties

The HOMO of these hydrazides is centrally located around the hydrazide moiety while the LUMO exist inthe acetyl, butyl and benzyl group. Experimentally, the HOMO and the LUMO energies were obtained from an empirical formula based on the onset of oxidation-red uction of peaks measured by cyclic voltametry. Theoretically, the HOMO and LUMO energies are calculated using DFT. Electrons move from the hydrazide moiety (HOMO) to the acetyl, Butyl and the Benzyl group (LUMO). The calculated electronic properties (energy band gap, LUMO-HOMO) of these compounds were found to be within 4.70 – 6.16eV, the highest being BUTAH. The calculated values are shown in Table 2 while the LUMO-HOMO structures are shown in Figure 3. There is a significant change in the values.

RESULTS AND DISCUSSION

Preparation of the Compounds

The acetoacetic acid hydrazide, butyrylacetic acid hydrazide and benzoylacetic acid hydrazide were prepared from the ethyl ester according to literature procedure (Adekunle *et al.*, 2010a).

The ligands were obtained in satisfactory yield by refluxing equimolar amount of the respective ethyl esters with hydrazine hydrate except for the acetoacetic acid hydrazide which had a low yield.

$RCOCH_2COOC_2H_5 + NH_2NH_2 \rightarrow RCOCH_2CONHNH_2 + C_2H_5OH$

$R = CH_3$-, $CH_3CH_2CH_2$- C_6H_5-

The acid hydrazides displayed varying degree of solubilities. They were all soluble in ethanol and methanol. The ligands were white, non - hygroscopic and are melted at varying temperatures with the benzoylacetic acid hydrazide having the relatively lowest value of 156 – 158^{o}C, followed by the acetoacetic acid hydrazide melting between 217 – 219 ^{o}C and the butyrylacetic acid hydrazide melted at 218 - 220 ^{o}C. The microanalyses data gave satisfactory result.

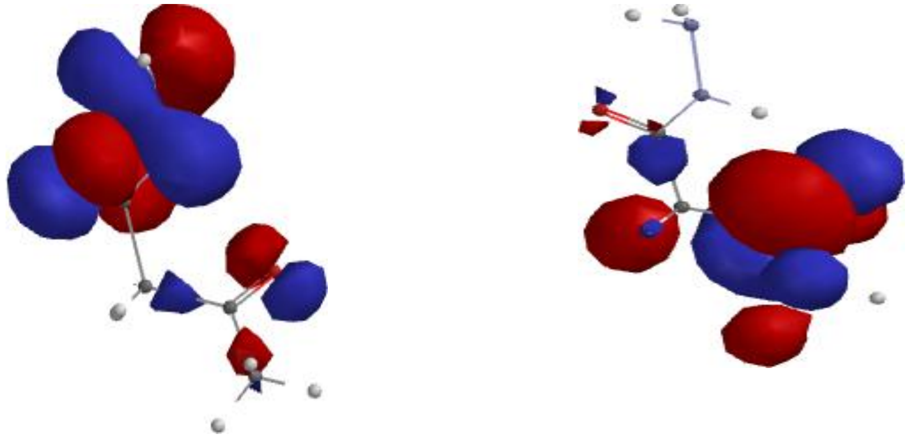
In the infrared spectra of the ligands, the acetoacetic acid hydrazide showed the amide I and amide II bands respectively at 1612 cm^{-1} and 1544 cm^{-1} while the ν (NH_2) was observedat 3539 cm^{-1}. In the theoretical studies, the amide I appeared at 1785cm^{-1}while the ν (NH_2) was observed at 3501cm^{-1}. The butyrylacetic acid hydrazide had the amide I and amide II bands at 1618 cm^{-1}and 1592 cm^{-1}respectively as against the theoretical of 1701cm^{-1} for the amide I .The ν (NH_2) for this hydrazide was found at 3460 cm^{-1} experimentally while theoretical value was at 3465cm^{-1}. The amide I and amide II bands of the benzoylacetic acid hydrazide were observed at 1626cm^{-1}and 1600cm^{-1}respectively while the ν (NH_2) appeared at 3452cm^{-}1 (Adekunle *et al.*, 2010b; Adekunle *et al.*, 2010c; Odunola *et al.*, 2002; David *et al.*, 1999). The calculated amide I and ν (NH_2) were observed respectively at 1748cm^{-1} and 3426cm^{-1}.

The benzoylacetic acid hydrazide had the highest value for the amide I and amide II bands this is due to the fact that the presence of the electron withdrawing inductive effect of the aryl group on the adjacent carbonyl group which is also electron withdrawing.

Table 5: Electronic parameters for this Ligands

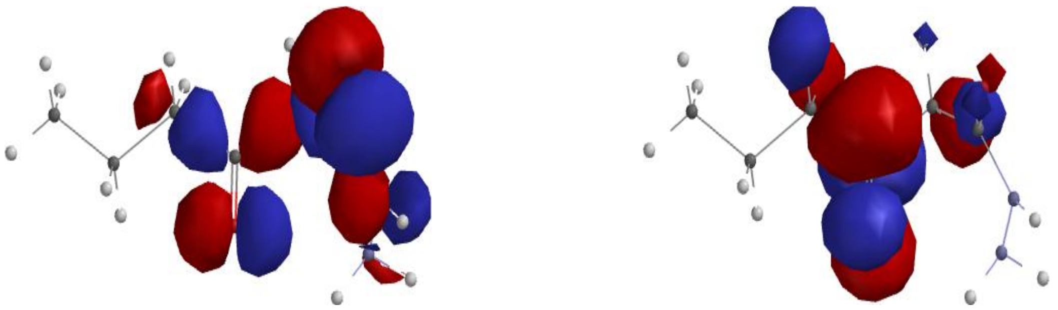
Molecule	Total Energy/a.u	Dipole Moment/D	logP	E_{HOMO}	E_{LUMO}	E_{GAP}	Polarizability
AAAH	-417.17	2.80	-0.97	-6.78	-1.00	5.78	49.40
BUTAH	-495.81	2.98	0.10	-6.62	-0.46	6.16	52.32
BENZAH	-608.91	4.07	0.17	-6.66	-1.96	4.70	54.95

AAAH



HOMO **LUMO**

BUTAH



HOMO **LUMO**

BENZAH

HOMO **LUMO**

Figure 5: HOMO and LUMO energy diagram

The withdrawal of electrons from the group led to the reduction of the electrons available to the –CONHNH$_2$thereby leading to the shortening of the bonds. In contrast, in the theoretical studies the acetoacetic acid hydrazide has the highest for the amide I. The experimental value for the ν (NH$_2$) in the hydrazides showed a similar trend wherein the AAAH has the highest value of 3539cm^{-1}as against the theoretical value of 3501cm^{-1}. The theoretically observed values for BUTAH and BENZAH were 3465cm^{-1} and 3426cm^{-1}respectively whereas the experimental values were 3460cm^{-1} and 3452cm^{-1} respectively for these hydrazides.

The intraligand transitions were observed in the ligands. The $\pi \rightarrow n$ transitions appeared at 37,175cm^{-1}[269 nm]for the acetoacetic acid hydrazide while the $\pi \rightarrow \pi^*$ were observed in both the butyrylacetic acid hydrazide and benzoylacetic acid hydrazide at 45,045cm^{-1}[222 nm] and 49,751cm^{-1}[201 nm] and also at 41,494cm^{-}1 [241 nm] respectively (Daivid *et al.*, 1999; and Odunola *et al.*, 2003). The $n \rightarrow \sigma^*$transition was observed only in the acetoacetic acid hydrazide 51,282cm^{-1} [195 nm] (David *et al.*, 1999; Odunola *et al.*, 2003).

In the theoretical spectra, bands at 185nm and 246 nm assignable to $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ were observed in AAAH, while for the BUTAH hydrazide the prominent observed theoretically calculated electronic transitions were at 187nm and 233nm whereas in the experimental only the band at 222nm was prominent. BENZAH had the bands at 230nm and 261nm were the theoretically prominent bands as against the experimental values of 201nm and 241nm respectively.

In the mass spectra of the acetoacetic acid hydrazide, the fragmentation pattern gave a peak at 99.08 which stand for {$CH_3COCH_2CON^+$} and another at 100.05 assigned to {$CH_3COCH_2CONH^+$}which was just 7.5%. The peaks at 127.11(100%) and 128.11(10%) were observed for the butyrylacetic acid hydrazide and these were found for the {$CH_3CH_2CH_2COCH_2CON^+$} and {$CH_3CH_2CH_2COCH_2CONH^+$} respectively. The benzoylacetic acid hydrazide fragmented to give {$C_6H_5COCH_2CON^+$} and {$C_6H_5COCH_2CONH^+$} at 161.05 and 162.05 respectively.The fragmentation patterns gave molecular weights which were consistent with expected values.

The ^{1}H NMR showed the amino protons between 2.06 and 2.08, while the methyl protons for the alkyl acid hydrazides appeared in the range 0.89 – 2.49. The two protons of the methylene group of -CO-CH_2-CO- was observed at 3.33 for all the hydrazides. The amide group proton was observed at 10.25ppm for AAAH and 10.40ppm BUTAH but was not detected in BENZAH. In the theoretical studies, the highest value observed for this amide group theoretically was at 7.51ppm. The 2H of methylene groups (-CO-CH_2-CO-) in the hydrazides observed experimentally at 3.33ppm appeared at different values theoretically in the range 2.96ppm – 3.04ppm for AAAH, 2.82ppm – 4.10ppm for BUTAH and BENZAH at 3.30ppm – 3.70ppm.

In conclusion, it was observed that the experimentally determined values for the spectra studies are consistent with the theoretical calculations.

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