DFT, FT-IR, FT-Raman and NMR studies of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles

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ABSTRACT

We present a detailed analysis of the structural and vibrational spectra of some novel azo dyes. 2-(Substituted phenylazo)malononitriles were synthesized by the coupling reaction of the diazonium salts, which were prepared with the use of various aniline derivatives with malononitrile, and then 4-(substituted phenylazo)-3,5-diamino-1H-pyrazole azo dyes were obtained via the ring closure of the azo compounds with hydrazine monohydrate. The experimental and theoretical vibrational spectra of azo dyes were studied. The structural and spectroscopic analysis of the molecules were carried out by using Becke's three-parameters hybrid functional (B3LYP) and density functional harmonic calculations. The ^{1}H nuclear magnetic resonance (NMR) chemical shifts of the azo dye molecules were calculated using the gauge-invariant-atomic orbital (GIAO) method. The calculated vibrational wavenumbers and chemical shifts were compared with the experimental data of the molecules.

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1. Introduction

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastics, biological and medical studies, and advanced application in organic synthesis [1–3]. Especially, pyrazoles are important compounds that have many derivatives with wide range properties, such as biological and pharmacological activities [4–7].

Several studies, such as synthesis [4,8–10], absorption spectra [10,11], and solvatochromic behavior [12] have been published of azo dyes. But, a few theoretical studies have been reported for the molecular structure and vibrational spectra of azo dyes [13–15].

In this study, some novel 4-(substituted phenylazo)-3,5-diamino-1H-pyrazole azo dyes were synthesized and calculated geometric structure, vibrational spectra and chemical shift. The calculated vibrational wavenumbers and chemical shifts were compared with the experimental data of the molecules. Furthermore, we interpreted the calculated spectra in terms of total energy distributions (TED).

2. Experimental

2.1. General

All chemicals used for synthesis of the azo dyes were purchased from Aldrich without further purification. The solvents used were of spectroscopic grade.

Fourier Transform Infrared (FT-IR) spectra of the 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles were carried out using a Thermo Nicolet 6700 spectrometer with Smart Orbit attenuated total reflection attachment. The FT-Raman spectrums of the samples were recorded between 50 and 3500 cm^{-1} region on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd: YAG laser. The detector is a liquid nitrogen cooled Ge detector. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker-Spectrospin Avance DPX 400 Ultra-Shield in deuterated chloroform (CDCl$_3$-d$_1$) using tetramethylsilane (TMS) as the internal reference; chemical shifts were (δ) given in ppm. Melting points were determined on an Barnstead Electrothermal 9200.

2.2. Synthesis of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles

2-(Substituted phenylazo)malononitriles and 4-(substituted phenylazo)-3,5-diamino-1H-pyrazoles were prepared according to the literature procedures [16–21]. A general preparative proce-

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dure was described for the preparation of azo dyes 4-(phenylazo)-3,5-diacetamido-1H-pyrazole (PDP) and 4-(4-methylphenylazo)-3,5-diacetamido-1H-pyrazole (4m-PDP) by Elnagdi and co-workers [21]. 4-(2-methylphenylazo)-3,5-diacetamido-1H-pyrazole (2m-PDP) and 4-(3-methylphenylazo)-3,5-diacetamido-1H-pyrazole (3m-PDP) were prepared in similar manner. The synthesis of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles are shown in Scheme 1. The color, yield and melting point of azo dyes are given in Table 1.
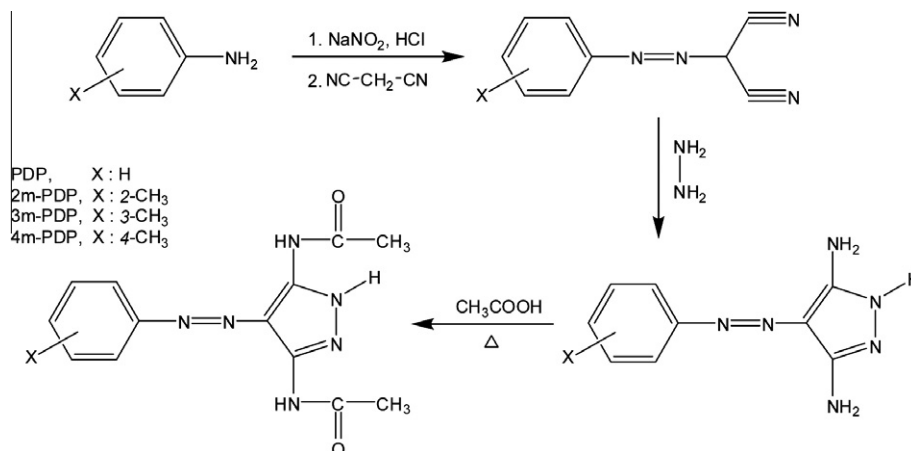
3. Computational details

All calculations were performed using the Gaussian 09 program package [22] and Gauss-View molecular visualization program [23]. The molecular structures of azo dyes were optimized by DFT/B3LYP level with the 6-31G(d) basis set [24]. The optimized structural were used in the vibrational wavenumber calculation. The total energy distribution (TED) was calculated by using the scaled quantum mechanics (SQM) program. ^{1}H NMR chemical shift values were calculated by the gauge-including atomic orbital (GIAO)-DFT method at 6-31G(d) level.

4. Result and discussion

4.1. Molecular geometry

The optimized structural parameters of azo dyes calculated by DFT/B3LYP level with the 6-31G(d) basis set. The calculated parameters of azo dyes (PDP, 2m-PDP, 3m-PDP, 4m-PDP) are given in Table 2 and the optimized structures with numbering of the atoms of azo dyes are shown in Fig. 1. The molecules of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazole consist of two ring (phenyl and pyrazole) systems and connected to each other by the azo group (N=N). The distance of the N_{14}–N_{15} bond in PDP, 2m-PDP, 3m-PDP and 4m-PDP is 1.2777, 1.2783, 1.2779, and 1.2778 Å, respectively. Average length of the N_{14}–N_{15} bond in 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazole molecules increases by 0.0259 Å, as compared to diazene (HN=NH) (1.252 Å) [25]. The lengthened N_{14}–N_{15} distance of azo dyes is also caused by the conjugation with pyrazole ring. The length of the N_{14}–N_{15} bonds in 2m-PDP, 3m-PDP and 4m-PDP is longer than N_{14}–N_{15} bonds in PDP because of steric incidence. As shown in Table 2, the N=N bond distance decreases from 1.2783 to 1.2778 with substitute number of azo dye increases from 2 to 4.

Table 1
The color, yield and melting point of azo dyes.

Azo dyes	Color	Yield (%)	Melting point (°C)
PDP	Yellow	95	218–219
2m-PDP	Dark green	90	163–165
3m-PDP	Yellow	85	203–204
4m-PDP	Yellow	65	245–246

Table 2
Selected bond distances (Å) and bond angles (°) of azo dyes.

Parameters	B3LYP			
	PDP	2m-PDP	3m-PDP	4m-PDP
Bond Lengths (Å)				
C_1–N_{14}	1.4137	1.4135	1.4137	1.4120
C_7–N_{15}	1.3652	1.3650	1.3659	1.3662
C_7–C_8	1.4092	1.4092	1.4089	1.4086
C_7–C_9	1.4365	1.4365	1.4361	1.4359
C_9–N_{18}	1.3868	1.3867	1.3871	1.3871
C_8–N_{19}	1.3777	1.378	1.3778	1.3782
N_{14}–N_{15}	1.2777	1.2783	1.2779	1.2778
N_{16}–N_{17}	1.3788	1.3786	1.3786	1.3784
N_{16}–H_{29}	1.0115	1.0114	1.0115	1.0114
C_2–C_{22}	–	1.5104	–	–
C_3–C_{23}	–	–	1.5118	–
C_4–C_{24}	–	–	–	1.5097
Bond Angles (°)				
C_2–C_1–N_{14}	120.0043	119.9972	119.9972	120.0043
C_6–C_1–N_{14}	119.9972	120.0043	120.0043	119.9972
C_7–C_8–N_{16}	107.9735	107.9735	107.9735	107.9735
C_7–C_9–N_{17}	107.9403	107.9403	107.9403	107.9403
C_8–C_7–N_{15}	110.5339	110.5339	110.5339	110.5339
C_8–N_{16}–H_{29}	124.8757	126.0204	124.8616	126.0204
C_8–N_{16}–N_{17}	113.7664	107.9592	113.7628	107.9592
C_8–N_{19}–C_{12}	124.2846	110.3651	124.3002	110.3651
C_9–C_7–N_{15}	110.5067	110.5067	110.5067	110.5067
C_9–N_{17}–N_{16}	103.875	107.9138	103.8638	107.9138
C_9–N_{18}–C_{10}	128.2119	110.3651	128.2578	110.3651
C_{11}–C_{10}–O_{20}	123.0916	124.1968	123.049	124.1968
C_{13}–C_{12}–O_{21}	124.1968	124.1968	124.1968	124.1968
C_1–C_2–C_{22}	–	119.9808	–	–
C_3–C_2–C_{22}	–	120.0106	–	–
C_2–C_3–C_{23}	–	–	120.9886	–
C_4–C_3–C_{23}	–	–	120.3004	–
C_3–C_4–C_{24}	–	–	–	120.0249
C_5–C_4–C_{24}	–	–	–	119.9811

4.2. Vibrational analysis

Vibrational spectral assignments were performed on the recorded FT-IR and FT-Raman spectra based on the theoretically pre-
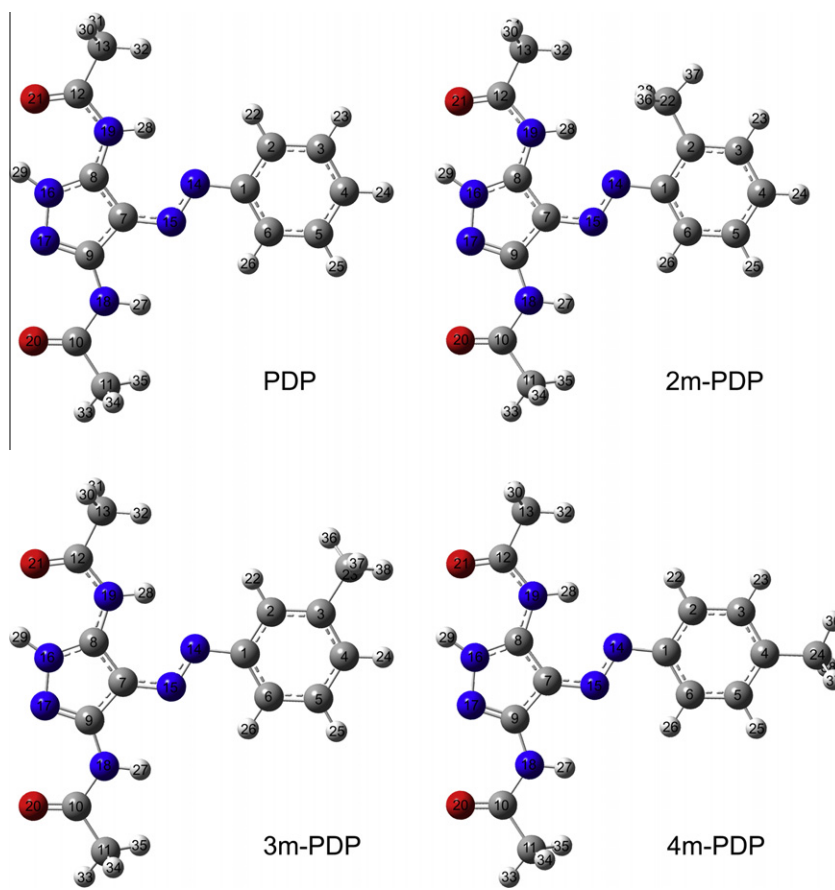

Scheme 1. Synthesis of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles.

Fig. 1. The calculated optimized structures of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles.

dicted wavenumbers by density functional B3LYP/6-31G(d) method with scaling factor of 0.9613 [24] and are collected in Tables S1–S4 (Supporting information). The FT-IR spectra of PDP, 2m-PDP, 3m-PDP and 4m-PDP showed a band at 3450–3200 cm^{-1}, which was assigned to the N–H stretching. The calculated wavenumbers of the N–H stretching are shown at 3500–3300 cm^{-1}. The experimental FT-IR spectrum of the azo dyes show a significant difference in the region of the N–H stretching at 3450–3200 cm^{-1}, compared with the theoretical FT-IR spectrums. In addition, the experimental wavenumber observed in the FT-IR spectrums at 1702–1684 cm^{-1} are assigned to C=O stretching vibration, which show small differences with that obtained with the theoretical FT-IR spectrums. The band of C=O stretching appeared at 1702–1684 cm^{-1} was observed in all the experimental spectra of the azo dyes and the band shifted to a lower frequency range compared theoretical FT-IR spectrums. These differences supports the stronger intermolecular hydrogen bonding interaction between NH and C=O groups. For all aromatic C–H stretching vibrations are observed in the region 3100–3000 cm^{-1}. The phenyl ring vibrations assigned to the aromatic C–H stretch computed in the range 3100–3000 cm^{-1} shows good agreement with the recorded FT-IR.

PDP, 2m-PDP, 3m-PDP and 4m-PDP azo dyes are compounds that contain azo groups linked to phenyl and pyrazole "C" atoms. It is well known that N=N stretching vibration gives strong Raman band and that these are quite weak in FT-IR [25,26]. The bands observed at 1391–1370 cm^{-1} in the FT-IR (Fig. 2) and at 1402–1380 cm^{-1} (Fig. 3) in the Raman spectrums are attributed to the azo stretching vibration of the azo dyes. In theoretical calculation, corresponding wavenumbers of azo dyes are assigned to 1450–1428 cm^{-1}. Similarly, azo stretching vibration shifted to a lower

wavenumbers depending on the neighboring group and intermolecular hydrogen bonding.

The vibrational assignments of most of the fundamental vibration of the studied molecules were straightforward on the basis of their calculated total energy distribution (TED) values (Tables S1–S4). In the high wavenumber region, TED calculations show that all the C–H and N–H stretching vibrations are pure modes. Similar comparative analyses have been made for the other type of bands. As seen in tables for TED values, the calculated modes are mixed with other group modes in different proportions.

4.3. NMR spectra

The molecular structure of azo dyes were optimized, and then gauge-including atomic orbital (GIAO) ^{1}H NMR chemical shifts calculations of the title compound were carried out by using B3LYP functional with 6-31G(d) basis sets. Experimental and calculated chemical shifts of azo dyes are presented in Table 3. The ^{1}H NMR spectra of PDP, 2m-PDP, 3m-PDP and 4m-PDP measured in $CDCl_3$-d_1. The ^{1}H NMR spectra of PDP showed three broad N–H peaks at 11.3, 10.8, 9.3 ppm. The ^{1}H NMR spectra of 2m-PDP and 3m-PDP showed two board peaks at 11.3 and 9.4 for N–H proton. Similarly, the ^{1}H NMR spectra of 4m-PDP showed two board N–H peak at 11.2 and 9.4.

4.4. Azo-hydrazo tautomerism

4-(Substituted phenylazo)-3,5-diacetamido-1H-pyrazole azo dyes can exist two possible tautomeric forms, namely the azo (A) and the hydrazo (B) forms as shown in Scheme 2. The FT-IR and
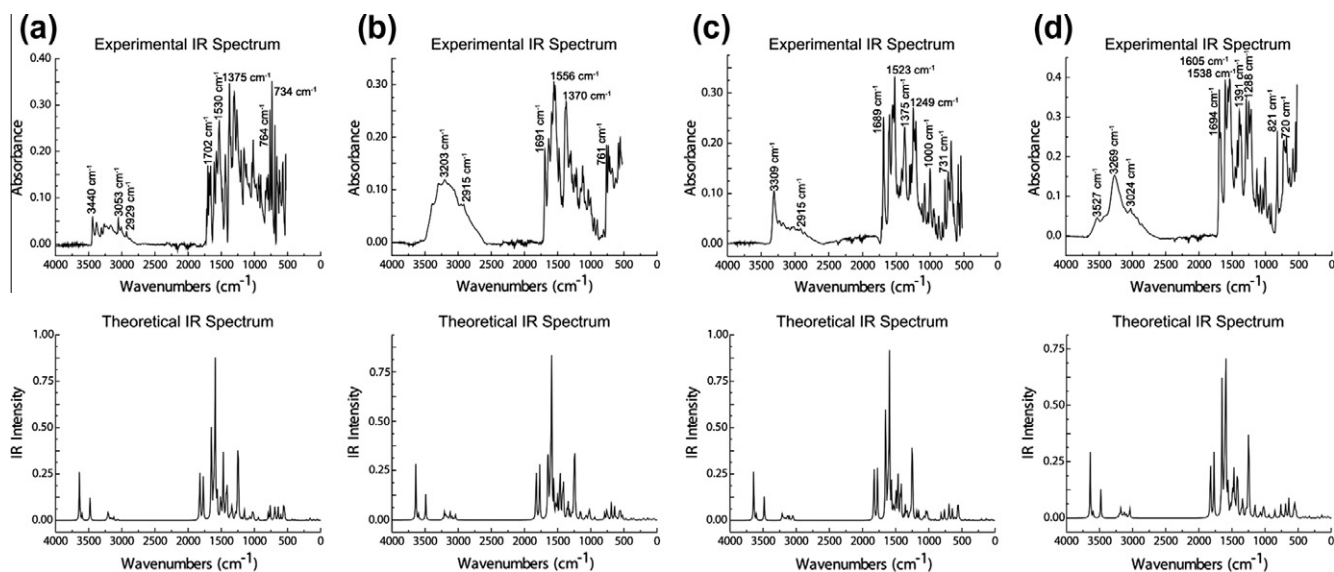
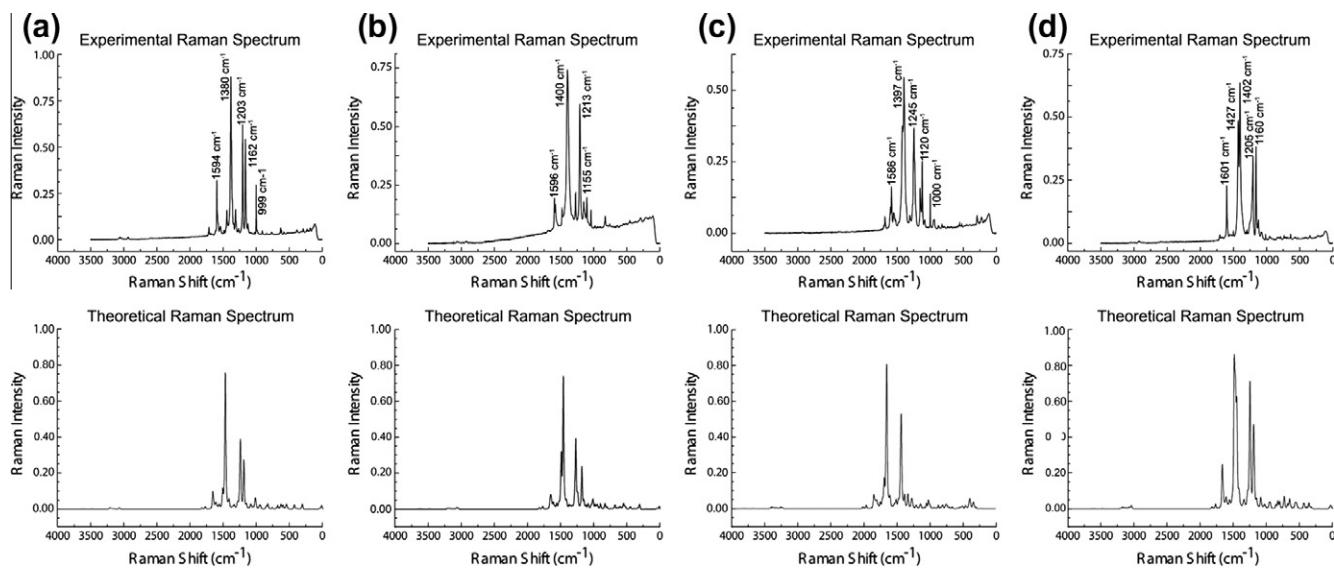**Fig. 2.** The recorded and simulated FT-IR spectrums of PDP (a), 2m-PDP (b), 3m-PDP (c) and 4m-PDP (d).

Fig. 3. The recorded and simulated FT-Raman spectrums of PDP (a), 2m-PDP (b), 3m-PDP (c) and 4m-PDP (d).

Table 3
Experimental and theoretical ^{1}H NMR data of azo dyes.

Sample	H_{29}	H_{28}	H_{26}	H_{23}	H_{22}	H_{25}	H_{24}	H_{27}	H_{35}	H_{32}	H_{30}	H_{34}	H_{33}	H_{31}	H_{36}	H_{37}	H_{38}
PDP																	
Exp.	11.3	10.8			7.3–7.8			9.3			2.3				–	–	–
Th.	9.9	9.6	7.4	7.4	7.0	9.9	9.6	9.9	2.1	2.0	1.8	1.6	1.5	1.4	–	–	–
2m-PDP																	
Exp.	11.3	9.4			7.2–7.6			9.4			2.2–2.7					2.4	
Th.	10.0	9.2	7.4	7.1	9.4	7.1	7.1	7.1	2.1	1.9	1.9	1.6	1.5	1.3	2.4	1.8	2.4
3m-PDP																	
Exp.	11.3	9.4			7.2–7.5			9.4			2.3					2.4	
Th.	9.9	9.3	7.4	–	9.4	7.0	7.1	7.0	2.0	1.9	1.9	1.6	1.5	1.3	2.2	1.8	2.3
4m-PDP																	
Exp.	11.2	9.4			7.2–7.7			9.4			2.3					2.4	
Th.	9.9	9.5	7.4	7.1	7.0	7.1	–	6.9	2.1	1.9	1.8	1.7	1.4	1.4	2.2	1.7	2.2

FT-Raman spectra of azo dyes showed N=N stretching vibration at 1391–1370 cm^{-1} and at 1402–1380 cm^{-1}, respectively. FT-IR, FT-Raman and ^{1}H NMR results suggest that azo dyes are predominantly in the azo form in CDCl$_3$ and the solid state (Scheme 2A). El-
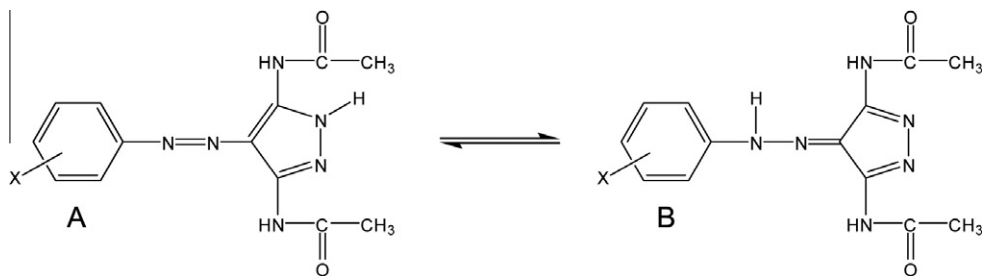
Scheme 2. The azo (A) and hydrazo (B) form of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazoles.

nagdi and co-workers reported that the *p*-substituted diacetyl compounds are present in azo form [21].

5. Conclusion

Theoretical and experimental vibrational, ^{1}H NMR analysis of 4-(substituted phenylazo)-3,5-diacetamido-1H-pyrazole azo dyes, for the first time. A comparison of the result of experimental and theoretical study gave us a full description of the geometry and vibrational properties of this molecule. Based on calculated energy differences, the A conformer is found to be most the stable conformer and the other conformers are predicted the unstable conformer. The calculated geometric parameters and vibrational frequencies obtained with density functional theory calculations (B3LYP/6-31G(d)) method are in good agreement for some bands with the experimental values obtained for the investigated molecules. The differences between the experimental and the theoretical spectrums are due in part to the fact that the theoretical spectrum is obtained in the gas phase, however the experimental spectrums are measured in the solid phase where it may undergo intermolecular interactions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.02.009.

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