



Study of thermal stability and acoustic fingerprint spectra of phenyl and benzyl triazole derivatives using time resolved pulsed photoacoustic pyro analysis technique



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ABSTRACT

The paper reports the use of pulsed laser based photoacoustic (PA) pyro analysis technique to study the thermal decomposition, stability and acoustic fingerprints of nitro rich phenyl and benzyl triazole derivatives. Two compounds named as 1-(3-methoxy-2,6-dinitrophenyl)-1H-1,2,3-triazole (S_{10}) and 1-(4-methoxy-3,5-dinitrobenzyl)-1H-1,2,3-triazole (S_4) are studied using visible 532 nm and UV 266 nm wavelengths, respectively, obtained from Q-switched Nd:YAG laser of 7 ns pulse duration and repetition rate 10 Hz. These compounds are also subjected to the thermo gravimetric–differential thermal analysis (TG–DTA) technique. The obtained results of pulsed PA and TG–DTA techniques are used to understand the thermal stability and decomposition mechanism of HEMs. We have also evaluated the thermal quality factor 'Q' which plays very important role to test the thermal stability of the S_4 and S_{10} irrespective of incident laser wavelengths.

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1. Introduction

The laser based photoacoustic (PA) effect was first reported by Alexander Graham Bell in 1880 [1]. It has been widely used in various fields such as air pollution monitoring [2,3], combustion process [4], atmospheric sciences [5,6], medical diagnosis [7] and thermal decomposition of high energy materials (HEMs) [8,9]. Some groups also studied the thermal decomposition mechanism and thermal stability of HEMs using TG–DSC/DTA coupled with Fourier transform infrared spectroscopy (FTIR) or gas chromatography–mass spectrometry (GC–MS) and demonstrated that volatile decomposition starts above the melting point. They have identified the NO_2 as an important volatile gas [10–13].

The PA technique works on the principle of detection of acoustic signal produced by different types of solid, gaseous and liquid molecules after absorption of incident radiation of suitable wavelength. Therefore, the resultant time resolved PA signal represents the acoustic fingerprint of the particular type of molecule in terms of their strength and acoustic frequency of the given PA cell. The PA technique offers several advantages such as high sensitivity, selectivity, simplicity and compact size, fast

time-response, non-destructive detection, and is widely recognized for its excellent performance in trace gas detection from ppb to ppt level [14–17]. The NO_2 molecule is found to be one of the principal volatile byproduct gas released by HEMs during the process of thermal decomposition and treated as a thermal marker [8,18]. In addition, series of other intermediate byproduct gaseous such as N_2O , NO , H_2O , CO , CO_2 , H_2 etc. are simultaneously released from HEMs [19,20]. Many of these gaseous molecules have strong absorption in UV 266 nm range [21]. Also, solid HEMs releases several other types of gaseous molecules during pyrolysis process due to thermal decomposition. The released vapor of HEMs molecules subsequently follows the photo dissociation process inside the PA cell when it is excited by UV 266 nm wavelength under the controlled temperature and pressure [22,23]. Generally, the nitrogen and oxygen rich energetic molecules have C– NO_2 or N– NO_2 bonds and the presence of these bonds solely depend on the structure of HEMs. These molecules follow the root of cleavage of C– NO_2 , N– NO_2 bonds during the pyrolysis process which is initiated inside the heating chamber. In the next step, the vapor is allowed into the PA cell and excited by UV 266 nm wavelength. Where it goes for photo dissociation process and produces free NO, NO_2 and other intermediate byproduct gases due to $\pi^* \leftarrow n$ electronic transition [22]. However, NO_2 molecule has strong absorption in visible 532 nm wavelength and excited to ${}^2\text{B}_2$ state, which is responsible for V–T and V–V relaxations [24–26].

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Present study provides significant information about thermal stability and decomposition of HEMs in vapor phase. The PA spectra of 1-(3-methoxy-2,6-dinitrophenyl)-1H-1,2,3-triazole (S_{10}) and 1-(4-methoxy-3,5-dinitrobenzyl)-1H-1,2,3-triazole (S_4) are recorded using the visible 532 nm and UV 266 nm wavelengths, respectively obtained from the Q-switched Nd:YAG laser system of pulse duration 7 ns and repetition rate 10 Hz. In addition, these compounds are also subjected to FTIR spectroscopy to identify the some of the major functional groups. The solid compounds are dissolved in chloroform solution and IR spectra are recorded between 400 and 4000 cm^{-1} range at room temperature. Earlier we have reported the thermal decomposition mechanism of pyrazoles, 1-methyl-2,4,5-trinitroimidazole (MTNI) and potassium nitrite (KNO_2) etc. on the basis of freely released NO_2 which follows the root of multiple step bond breaking mechanism using 532 nm wavelength of Nd:YAG laser. It was observed that the frequency shift in PA spectrum is due to change in the density of gaseous

medium [8,9]. In continuation of our previous work we have now used UV 266 nm to verify the position of acoustic fingerprint spectra of HEMs molecules with respect to temperature and found that there is no shift in the frequency of the PA spectrum of the given samples. The only difference is observed in terms of variation in the strength of PA signals which clearly indicates that the PA signal is generated due to contribution of entire molecule vapor and its byproduct gaseous. Therefore, the obtained PA spectra at UV 266 nm wavelength can be treated as an actual PA fingerprint of HEMs molecules.

In addition, we have made an attempt to explain the thermal stability criteria of HEMs on the basis of temperature dependent quality factor (Q) of PA cavity. As the ' Q ' of PA cavity plays very important role to understand the energy storage mechanism with respect to incident laser energy and density of released quantity of gaseous molecules [27–29]. The ' Q ' value of an excited peak and its full width at half maxima ($\Delta\omega_c$) are inversely proportional to each

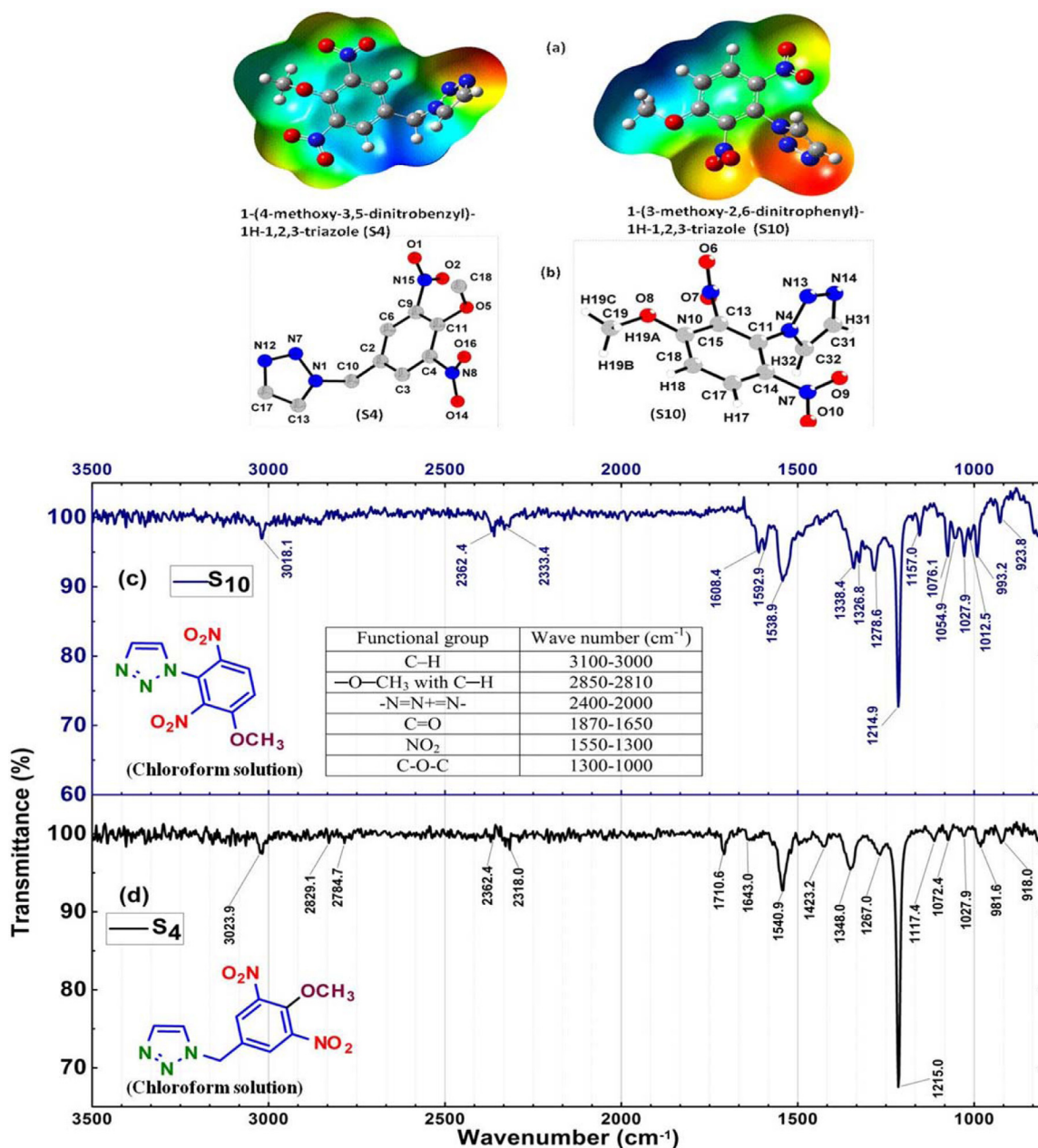


Fig. 1. (a) The electrostatic potential surfaces, (b) X-ray crystallographic structures and FTIR spectra of (c) S_{10} and (d) S_4 .

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