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Thermal Study of Two Benzotriazole Derivatives

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Abstract

An experimental study based on the thermal analysis of 5-methyl-1*H*-benzotriazole and 5,6-dimethyl-1*H*-benzotriazole was developed, by using differential scanning calorimetry. Additionally, a summary of the experimental techniques and computational methodology being performed, in order to complement the energetic study of both compounds, is described. The knowledge of the thermochemical, thermophysical and structural properties of functionalized benzotriazoles is relevant for the evaluation of their chemical behaviour, as well as in the prediction of the reactivity of similar compounds that have not been thermodynamically characterized.

Author Keywords. Benzotriazole Derivatives, Differential Scanning Calorimetry, Thermal Analysis, Enthalpy of Fusion, Temperature of Fusion, Thermophysical Study.

Type: Research Article

1. Introduction

Benzotriazole is a heterocyclic compound formed by the fusion of the benzene ring with the 4,5-positions of 1,2,3-triazole (Ram et al. 2019). It is also known as 1*H*-benzo[d]-1,2,3-triazole and exists in 1*H*- and 2*H*- tautomeric forms, being the 1*H*- form predominant over the 2*H*-form at room temperature (Figure 1) in both gas and solution phases (Ueno et al. 2003). As a heterocyclic polyfunctional compound, benzotriazole and its derivatives are well known for their versatile biological properties, such as antifungal (Lv et al. 2018) antimicrobial (Briguglio et al. 2015), antiviral (Loddo et al. 2015) and even antitumor agents (Li et al. 2020). Also, these compounds are used in industrial applications due to their corrosion inhibiting capability in several metals (Finšgar and Milošev 2010), in which the knowledge of the corresponding stability is relevant for further studies.

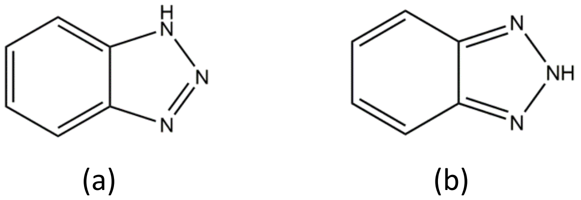

Figure 1: Tautomeric forms of benzotriazole: (a) 1*H*-benzotriazole and (b) 2*H*-benzotriazole

The thermodynamic properties of these type of compounds are not well established and our research group is involved in a systematic study of heterocyclic organic compounds, in which the determination of the thermochemical and thermophysical properties of functionalized benzotriazoles is one of the main goals.

In this context, it is essential to assess the energy associated with structural characteristics and reactivity of the compounds, through the determination of some relevant thermodynamic parameters, in particular the enthalpy of formation. The direct determination of this thermodynamic property in the condensed phase is derived from calorimetric measurements (generally energies of combustion); on the other hand, the enthalpy of formation of the gaseous may be obtained from the enthalpy of formation in the condensed phase combined with the corresponding enthalpy of phase transition (vaporization or sublimation). These data in the gas phase allow the knowledge of the intramolecular interactions without the influence of the neighbouring molecules, which enables the evaluation of the enthalpic effects promoted by the presence of different substituent groups, when compared with homologous structural molecules. Therefore, the gas phase enthalpic data are used for the establishing of relationships structure/energy/reactivity (Freitas and Ribeiro da Silva 2017).

The present work focuses on a thermophysical study of two benzotriazoles derivatives, 5-methyl-1*H*-benzotriazole and 5,6-dimethyl-1*H*-benzotriazole (Figure 2). In order to understand the thermal behaviour of each derivative, it has been developed a differential scanning calorimetry study, to determine the respective enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\circ}$, and temperature of fusion, T_{fus}.

Additionally, an ongoing experimental energetic study based on Knudsen effusion method, on combustion calorimetry and on high temperature Calvet microcalorimetry will be also briefly described, as well as, a computational study.

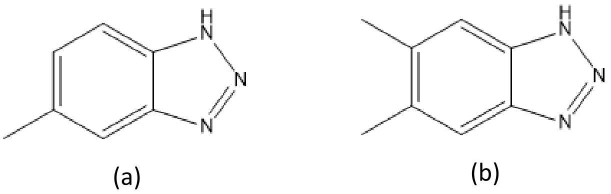

Figure 2: Structural formula of the studied compounds: (a) 5-methyl-1*H*-benzotriazole and (b) 5,6-dimethyl-1*H*-benzotriazole

2. Materials and Methods

2.1. Materials and purification methods

The compounds studied were obtained commercially from TCI Europe with the minimum assured mole fraction purity of 0.9999. Being the initial degree of purity enough for performing calorimetric measurements, neither of them, were subjected to any type of purification method. Other details about the purity analysis and provenience of the studied compounds are summarized in Table 1. The purity was analysed with an Agilent 4890D gas chromatography–flame ionization detector (GC–FID) apparatus, equipped with a HP-5 column. The relative atomic masses recommended by the IUPAC Commission in 2013 were used in the calculation of the molar quantities (Meija et al. 2016).

2.2. Coulometric Karl Fischer Titration

The water content of both benzotriazole derivatives was analyzed by Karl Fischer coulometric titration (oven method), using a Metrohm 831 KF coulometer with a generator electrode without diaphragm. The reagent used as anolyte was Hydranal-Coulomat AG Oven. The results obtained confirmed the existence of water for both compounds studied, according to the registered in Table 1. The assigned uncertainties are the standard deviation of the mean of four experiments.

Compound	CAS No.	Supplier	Purification method	Final mass fraction purity	Water Content (%)
5-methyl-1*H*-benzotriazole	136-85-6	TCI Europe, 99%	–	0.9999	(0.265 ± 0.002)
5,6-dimethyl-1*H*-benzotriazole	4184-79-6	TCI Europe, 99%	–	0.9999	(10.669 ± 0.277)

Table 1: Purification and provenance details of the studied compounds

2.3. Differential scanning calorimetry

A heat-flux DSC calorimeter (Hitachi-DSC7020) was used to study the thermal behaviour of the samples of each benzotriazole derivative, as well as to determine the respective T_{fus} and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\circ}$. The calibration of the calorimeter was performed using three high purity reference materials: indium, tin and benzoic acid (Della Gatta et al. 2006).

The experiments were performed using samples with masses within the range of (1 to 2) mg and were hermetically sealed in aluminium crucibles. Four different samples of each compound were analysed over the temperature range from T = 298 K to 20 K above the melting temperature of 5-methyl-1*H*-benzotriazole and 5,6-dimethyl-1*H*-benzotriazole, at a heating rate of 0.033 $\mathrm{K\cdot s^{-1}}$.

2.4. Combustion calorimetry

Static bomb combustion calorimetry experiments enable the determination of the standard massic energies of combustion of the compounds (containing C, H, O and/or N) and the respective enthalpies of formation, in the crystalline phase, at T = 298.15 K. The generic combustion reaction for this type of compounds is presented in Equation (1). The calorimetric apparatus and the experimental procedure have been previously described in the literature (Ribeiro da Silva, Ribeiro da Silva, and Pilcher 1984). The calorimetric system is calibrated using benzoic acid Standard Reference Material 39j obtained from the National Institute of Standards & Technology (NIST 1995). The quantity of compound burnt in each experiment is determined using a gravimetric analysis of the total mass of carbon dioxide formed. The standard massic energy of combustion for each compound is calculated by the procedure given by (Hubbard, Scott, and Waddington 1956; Paulechka et al. 2021).

$$C_aH_bO_cN_d\,(\mathrm{cr\ or\ l}) + [a + (b/4) - (c/2)]O_2\,(g) \rightarrow aCO_2(g) + (b/2)H_2O\,(l) + (d/2)N_2(g) \qquad (1)$$

2.5. Calvet microcalorimetry

High-temperature Calvet microcalorimetry enable the determination of the standard molar enthalpies of sublimation of both studied compounds. The apparatus and the technique are described in detail in the literature by Santos et al. (2004).

Samples between the range of (4 to 10) mg are dropped with the corresponding blank capillary tube, at room temperature (T = 298.15 K), into the calorimeter block. After the capillary tubes reach thermostability, the sublimation of the samples are made by vacuum. For minimizing thermal corrections related to the mass difference of the dropping capillary tubes, nearly equal masses are used.

The microcalorimeter is calibrated with a standard reference material, according to the temperature selected in the measurements (Sabbah et al. 1999).

2.6. Vapour pressures measurements

Knudsen effusion method enable the determination of vapour pressures at different temperatures, within the range of (0.1 to 1.0) Pa. The technique and the method are previously published in the literature (Ribeiro da Silva, Monte, and Santos 2006). The apparatus allows the operation of nine effusion cells simultaneously at three different temperatures and each effusion cell is inside an aluminium block. Each block is kept at a controlled constant temperature different from the other blocks.

The sublimated mass, *m*, of the compounds is determined by weighing the effusion cells, before and after the estimated effusion time, *t*. The vapour pressure of each effusion cell, *p*, is calculated by the Equation (2), where A_0 is the area of the effusion orifice, *R* is the gas constant (R = 8.3144621 J·K^{-1}·mol^{-1}), *M* is the molar mass of the each compound and w_0 is the Clausing factor.

$$p = (m/A_0 w_0 t)\,(2\pi RT/M)^{1/2} \tag{2}$$

2.7. Theoretical study

The computational approach to determine the gas-phase enthalpy of formation of both compounds is based on gas-phase hypothetical chemical equations. The number of possible equations depends on the availability of the experimental thermochemical data of the auxiliary species. The theoretical calculations are performed with the Gaussian-09 software, using the composite method G3(MP2)//B3LYP (Curtiss et al. 1998). If the experimental results are in good agreement with the estimated values, the computational methodology developed is validated.

3. Results and Discussion

The mean values of the onset temperature and enthalpy of fusion obtained from the DSC study for the benzotriazole derivatives studied are presented in Table 2. The assigned uncertainties are twice the standard error of the mean of four independent runs and include the standard uncertainties associated to the calibration results.

Additionally, the calculated values of the entropy of fusion are also presented in Table 2. The uncertainties are calculated through the root sum square method.

Compound	T_{fus}(exp.)/ K	T_{fus}(lit.)/ K	$\Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}^{\circ}$ (T_{fus}) / kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{l}} S_{\mathrm{m}}^{\circ}$ (T_{fus}) / J·K^{-1}·mol^{-1}
5-methyl-1*H*-benzotriazole	349.93 ± 0.67	357 (0.999) (TCI Europe, n.d.)	14.56 ± 0.63	41.61 ± 0.18
5,6-dimethyl-1*H*-benzotriazole	424.72 ± 1.15	429 (0.999) (TCI Europe, n.d.) 429-430 (Plaut 1954) 429.6-429.8 (Kopańska et al. 2004) 427.5-428 (Märky, Schmid, and Hansen 1979) 424 (Kreutzberger and Wiedemann 1979)	18.85 ± 1.59	44.38 ± 0.37

Table 2: Mean values of the temperature and enthalpy of fusion obtained from the DSC study for the studied compounds

The results obtained for the onset temperature of 5-methyl-1*H*-benzotriazole and 5,6-dimethyl-1*H*-benzotriazole present a considerable difference between the temperatures of fusion, comparing with the available in the literature. Also, no phase transitions were detected in the crystalline phase between *T* = 298 K and the temperature of fusion of each compound (Figure 3 and Figure 4).

The additional substitution on the aromatic ring of a hydrogen by a methyl group seems to promote an increase in the melting temperature of ≈ 75 K, due to an increase in enthalpy of fusion of ≈ 4 kJ·mol^{-1}. Regarding the results of the entropies of fusion, these values are similar, displaying only a variation of 3 J·K $^{-1}$·mol^{-1} from each other, which indicates that the pronounced increase of the melting temperature seems to be also enthalpic driven, as expected.

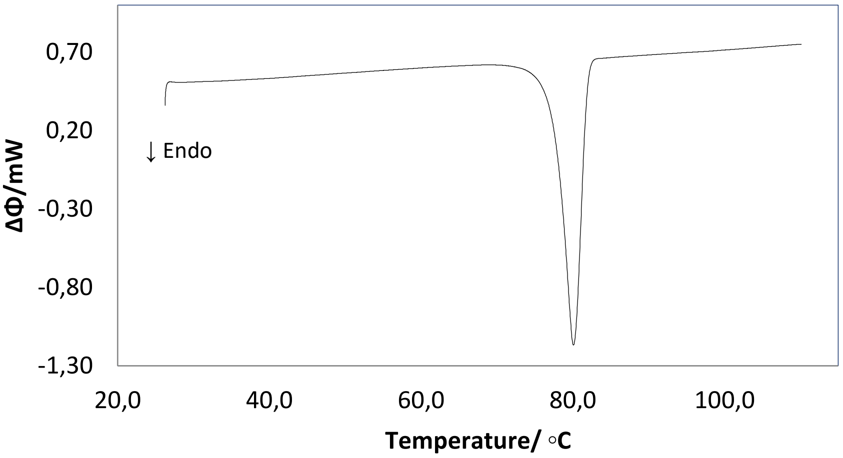

Figure 3: Thermogram obtained of 5-methyl-1*H*-benzotriazole in a thermal analysis by DSC

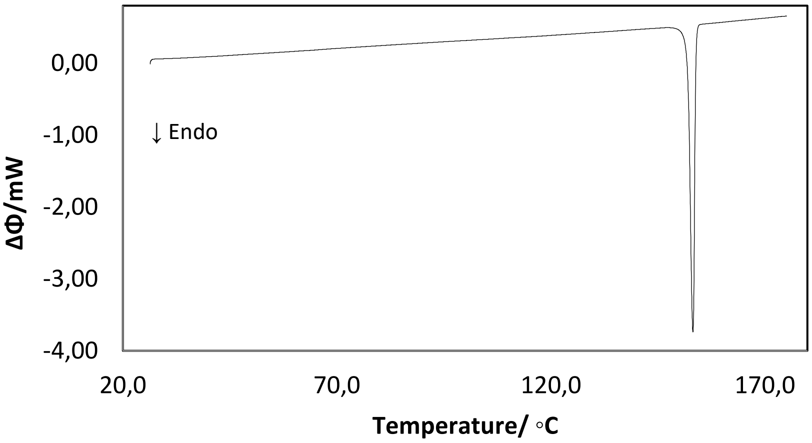

Figure 4: Thermogram obtained of 5,6-dimethyl-1*H*-benzotriazole in a thermal analysis by DSC

4. Conclusions

In this work, the experimental results for the enthalpy of fusion and the temperature of fusion of 5-methyl-1*H*-benzotriazole and 5,6-dimethyl-1*H*-benzotriazole are reported. Additionally, an ongoing calorimetric and computational study for both compounds is briefly described, thus there are still no results to be presented.

Overall, these studies enable the evaluation and understanding of the energetic effect inherent to the presence of methyl groups, in the benzotriazole derivatives studied. Furthermore, energy/structure prediction schemes for homologous molecules can be proposed.

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