



Thermochemical study of the isomeric compounds: 3-acetylbenzotrile and benzoylacetonitrile



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ABSTRACT

The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 3-acetylbenzotrile and benzoylacetonitrile, in the crystalline phase, were derived from the respective standard massic energies of combustion measured by static bomb combustion calorimetry, in oxygen, at $T = 298.15$ K. The standard molar enthalpies of sublimation, at $T = 298.15$ K, were measured by Calvet microcalorimetry. From the above experimentally determined enthalpic parameters, the standard molar enthalpies of formation in the gaseous phase, at $T = 298.15$ K, are found to be: $(52.4 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ and $(74.8 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ for 3-acetylbenzotrile and benzoylacetonitrile, respectively.

Molecular structures were computed using highly accurate *ab initio* techniques. Standard molar enthalpies of formation of the experimentally studied compounds were derived using an appropriate set of working reactions. Very good agreement between the calculated and the experimental values was obtained, so the calculations were extended to the estimates of the standard molar enthalpies of formation of 2- and 4-acetylbenzotrioles whose study was not performed experimentally.

Our results were further interpreted and rationalized in terms of the enthalpic stability and compared to other relevant disubstituted benzenes.

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1. Introduction

Benzotrile is widely used as an extraction solvent, a chemical intermediate for the synthesis of pharmaceuticals, agrochemicals, dyestuffs and rubber chemicals and a versatile precursor to many species used in the manufacture of polymers and anhydrous metallic salts [1,2]. Benzotrile derivatives are used in dye industry for making aniline blue and also for preserving food products [3]. Organic molecules which are able to manipulate photonic signals efficiently are of outmost importance in technologies such as optical communication, optical computing and dynamic image processing [4,5]. Due to the importance of cyano-substituted aromatic compounds in molecular electronic devices and new kinds of mesogenic materials the interest in their chemical and electronic properties has been renewed [6]. Acetylbenzotrile isomers are frequently used in synthetic

organic and pharmaceutical industry [2], thus justifying the relevance of the knowledge of their thermodynamic and reactivity parameters. Experimental and theoretical vibrational spectra and electronic structure properties of 4-acetylbenzotrile have been studied [1–7].

As a continuation of the systematic work that we have been carrying out in our group concerning the thermodynamic parameters of acetylbenzene derivatives [8–13] the present study provides results on the standard molar energies of combustion, standard molar enthalpies of sublimation, and standard molar enthalpies of formation in both crystalline and gaseous states, at $T = 298.15$ K, for the title compounds. The standard ($p^\circ = 0.1$ MPa) molar enthalpies of formation of 3-acetylbenzotrile and benzoylacetonitrile, in the crystalline state, at $T = 298.15$ K, were derived from the measurements, by static bomb combustion calorimetry, of its standard massic energies of combustion. The standard molar enthalpies of sublimation were measured by Calvet microcalorimetry.

Standard *ab initio* molecular calculations, at the G3 level, were performed and the gas-phase standard molar enthalpies of formation for 2-, 3- 4-acetylbenzotrioles and for benzoylacetonitrile were estimated.

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2. Experimental

2.1. Materials and purity control

The compounds, 3-acetylbenzotrile [CAS 6136-68-1] and benzoylacetone [CAS 614-16-4], were obtained commercially from Aldrich Chemical Co., with assessed mass fraction purities of 0.97 and 0.99, respectively. The compounds were purified by successive sublimations under reduced pressure. The purity of the compounds was checked by gas-liquid chromatography (GLC, Agilent 4890D) and from the average ratios of the mass of carbon dioxide recovered from the combustion to that calculated from the mass of sample as: 0.9997 for 3-acetylbenzotrile and 0.9998 for benzoylacetone. Table 1 contains the list of the origin and purification details as well as the final purities of the samples studied here.

2.2. Combustion calorimetry

The enthalpies of combustion of 3-acetylbenzotrile and benzoylacetone were measured in an isoperibol calorimetric system equipped with a twin valve bomb made of stainless steel and with an internal volume of 0.340 dm³ [14,15].

Combustion of certified benzoic acid NBS Standard Reference Material, Sample 39j, was used for calibration of the bomb. Its massic energy of combustion is $-(26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$, under certificate conditions [16]. The calibration results were corrected to give the energy equivalent, ε_{cal} , corresponding to the average mass of water added to the calorimeter: 3119.6 g. One set of six calibration experiments was performed leading to the value of the energy equivalent of the calorimeter, $\varepsilon_{\text{cal}} = (15905.0 \pm 0.8) \text{ J} \cdot \text{K}^{-1}$, where the uncertainty quoted is the standard deviation of the mean.

In all combustion experiments, 1.00 cm³ of water was introduced into the bomb, which was then closed and purged twice with oxygen, to remove air, before charged with 3.04 MPa of oxygen. The ignition of the samples, in the pellet form, was made at $T = (298.15 \pm 0.001) \text{ K}$, by discharge of a 1400 μF capacitor through a platinum ignition wire, using a cotton thread fuse, with empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, and having a massic energy of combustion, $\Delta_c u^\circ = -16240 \text{ J} \cdot \text{g}^{-1}$ [17]. This value has been previously confirmed in our laboratory.

Calorimeter temperatures were measured to $\pm(1 \cdot 10^{-4}) \text{ K}$, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett–Packard HP 2804A), interfaced to a PC programmed to compute the adiabatic temperature change. At least 100 readings were taken for the main period and for both the fore and after periods. Data acquisition and control of the calorimeter were performed using the LABTERMO program [18,19].

n-Hexadecane (Aldrich Gold Label, mass fraction >0.999), stored under nitrogen, was used as auxiliary combustion for 3-acetylbenzotrile. The massic energy of combustion of the particular sample used was determined in our laboratory as $\Delta_c u^\circ = -(47136.0 \pm 2.3) \text{ J} \cdot \text{g}^{-1}$.

The corrections for nitric acid formation were based on $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ [20], for the molar energy of formation of $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ HNO}_3$ (aq) from N_2 , O_2 , and H_2O (l). An estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$, at $T = 298.15 \text{ K}$, a typical value for most organic

compounds [21] was assumed. For each compound, the massic energy of combustion, $\Delta_c u^\circ$, was calculated by the procedure, given by Hubbard *et al.* [22]. The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after the allowance for that formed from the cotton thread fuse and *n*-hexadecane. The values of the specific densities used for the two compounds, for the cotton thread fuse and for the *n*-hexadecane were, respectively, $\rho = 1.11 \text{ g} \cdot \text{cm}^{-3}$ [23], $\rho = 1.50 \text{ g} \cdot \text{cm}^{-3}$ [22] and $\rho = 0.770 \text{ g} \cdot \text{cm}^{-3}$ [22].

The molecular mass of the compounds was calculated by the conventional procedure [22] using the averaged atomic masses of elements derived from data recommended by the IUPAC Commission in 2011 [24].

2.3. Microcalorimetry Calvet

The standard molar enthalpies of sublimation of the two isomers were measured using the so called “vacuum sublimation drop-microcalorimetric technique” [25,26]. Each sample contained in a small thin glass capillary tube sealed at one end, was dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter (Setaram HT 1000), held at a predefined temperature, and then removed from the hot zone by vacuum sublimation. Simultaneously an empty capillary tube of similar mass was dropped in the reference cell. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were minimized, as far as possible, by dropping tubes of nearly equal mass, to within $\pm 10 \mu\text{g}$, into each of the twin calorimeter cells. The microcalorimeter was calibrated *in situ* using the reported standard molar enthalpy of sublimation of naphthalene, $\Delta_{\text{cr}}^\circ H_m^\circ (T = 298.15 \text{ K}) = (72.6 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ [27].

3. Computational details

The B3LYP method [28,29] together with the 6-31G(d) basis set was used for the optimization of the geometry of all the compounds studied here. Then, for all minima obtained from the previous set of optimization runs, the absolute enthalpies, at $T = 298.15 \text{ K}$, for 2-, 3-, 4-acetylbenzotrile, benzoylacetone and all the other species considered were calculated employing the composite G3 method. Full details and the theoretical basis of the method can be found in Curtiss *et al.* [30], thus a brief description is provided here. In this method, the geometries are obtained from second-order perturbation theory [MP2(FU)/6-31G(d)] and the final accurate molecular electronic energy is computed from a proper composition of the energies obtained from a series of very accurate single-point energy calculations at the second-order Moller–Plesset (MP2), fourth-order Moller–Plesset (MP4) and quadratic configuration interaction [QCISD(T)] levels of theory. The overall result from such calculations uses scaled zero-point energies obtained from Hartree–Fock theory with the 6-31G(d) basis set and, by adopting certain assumptions about additivity of the calculations and including a spin-orbit correction and a higher-level correction, aims to effectively reproduce the results of a calculation at the QCISD(T,FU)/G3 large level. The optimized structures obtained for each of the acetylbenzotrioles are illustrated in figure 1.

TABLE 1

Purification details of 3-acetylbenzotrile and benzoylacetone.

Chemical name	CAS	Provenance	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
3-Acetylbenzotrile	6136-68-1	Sigma-Aldrich®	0.97	Sublimation	0.9997	CO ₂ recovery
Benzoylacetone	614-16-4	Sigma-Aldrich®	0.99	Sublimation	0.9998	CO ₂ recovery

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