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Energetics and stability of azulene: From experimental thermochemistry to high-level quantum chemical calculations

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This is paper is dedicated to the memory of late Professor Manuel Ribeiro da Silva.

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ABSTRACT

The standard (p^0 = 0.1 MPa) molar enthalpy of formation for crystalline azulene was derived from the standard molar enthalpy of combustion, in oxygen, at T = 298.15 K, measured in a mini-bomb combustion calorimeter (aneroid isoperibol calorimeter) and the standard molar enthalpy of sublimation, at T = 298.15 K, measured by Calvet microcalorimetry. From these experiments, the standard molar enthalpy of formation of azulene in the gaseous phase at T = 298.15 K was calculated. In addition, very accurate quantum chemical calculations at the G3 and G4 composite levels of calculation were conducted in order to corroborate our experimental findings and further clarify and establish the definitive standard enthalpy of formation of this interesting non-benzenoid hydrocarbon.

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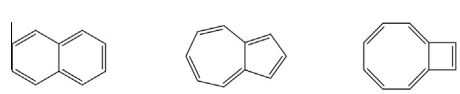
1. Introduction

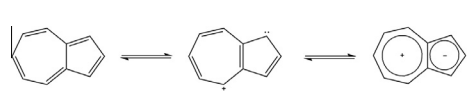
Azulene (bicyclo[5.3.0]decapentaene) (**I**) is one of the few completely conjugated non-benzenoid, non-alternant hydrocarbons that appear to have appreciable aromatic stabilization. The name "azulene" was introduced by the nineteenth century perfumist G.W. Septimus Piesse, who suggested the name for the blue-colored constituent of Chamomile Oil" rather than for its aroma. Azulene is a popular ingredient in beauty, cosmetic, skin, and body care products due to its antioxidant activity preventing skin blemishes and helping stop deterioration of skin cells that leads to wrinkles. However, this compound presents some mutagenic activity when exposed to sunlight. Therefore, extreme care must be taken when introducing azulene into cosmetics [1,2].

Azulene and many of its derivatives have been well characterized and are stable compounds. Consisting of a skeleton of 10 sp^2-hybridized carbon atoms arranged in two cyclic moieties, azulene is a planar molecular system and it contains an electronic system containing 10 π-electrons (in what it conforms to the Hückel 4n + 2 rule) distributed between condensed five and seven membered carbon rings. Azulene is structurally isomeric with some other bicyclic systems and we are tempted to think it to, somehow, represents an 'interpolation' system between naphthalene (bicyclo[4.4.0]decapentaene) (**II**) and bicyclo[6.2.0]decapentaene (**III**); as so, their properties are also likely to interpolate the properties of the above extreme isomers,



(II) (I) (III)

It is possible to write two kekulé-type resonance structures as well as a number of resonance structures with separated charges, *i.e.* with a negative charge in the five membered ring and a positive charge in the 7 membered ring, thus providing each ring by itself a complete Hückel 6-electron π-system, and thus allowing us to anticipate some aromatic stabilization of this system.



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The importance of the contributions from these charged resonance is supported by the high dipole moment [3] (μ = 0.8–1.08 D) observed for azulene, thereby constituting a notorious difference from naphthalene, which has zero dipole moment. It is not surprising that azulene, which is perhaps the oldest and most thoroughly studied of all non-benzenoid aromatic hydrocarbons, continues to be an object of intensive experimental and theoretical research, the molecular structure (**I**) serving as the basic model in all such quantum chemical calculations. Aromatic character is corroborated either by experimental X-ray and electron-diffraction measurements [4] or by quantum chemical calculations, [5] which indicate the peripheral bond lengths in azulene to be in the aromatic range and show no regular alternation. On the other hand, the bond conjoining both rings is significantly longer, indicating dominant single-bond character.

In addition to the above peculiarities of azulene and its homologous parent systems, the large discrepancy evidenced by the available experimental measurements of the enthalpy of formation of azulene, 280.0 kJ · mol^{-1} from the 1957 measurement [6] *vs.* 308 kJ · mol^{-1} in the 1983 experiment [7], prompted us to a new combined experimental and computational study of the energetics of this interesting molecular system.

2. Experimental

2.1. Materials and purity control

Azulene was obtained from Aldrich Chemical Co. and was purified by sublimation. Details of the origin and purification of the samples are presented in table 1. The density of the compound was estimated from the mass and the dimension of pellet of the crystalline compound, as 1.053 g · cm^{-3}.

2.2. Enthalpy of formation in the gas phase

The enthalpy of formation in the gas phase of azulene, $\Delta_f H^0_m(g)$, at T = 298.15 K, was determined from the experimental value of its standard enthalpy of formation in the condensed state, $\Delta_f H^0_m(cr)$, and the standard phase change enthalpy, $\Delta^g_{cr} H^0_m$.

2.2.1. Combustion calorimetry

Combustion experiments were performed in a mini-bomb combustion calorimeter (aneroid isoperibol calorimeter). A detailed description of the calorimetric system is found in the literature [8] so, only a brief description of the main components and procedure will be given. The mini-bomb is made of stainless steel with 18.185 cm^3 internal volume and electrodes and crucible support of platinum. The compounds were burned in a pellet form. The platinum crucible containing the pellet and auxiliary material were placed in its support in the head of the mini-bomb with a 20 mm long platinum wire attached to each electrode terminal for electrical discharge and sample ignition. A platinum sheet was placed with an inverted "U shape" above the crucible to promote complete combustion. 0.050 cm^3 of water were placed inside the body of the mini-bomb and the head with a Viton O-ring was then tightly adjusted to it by means of a stainless steel screw-ring. The bomb was filled three-times with ultra-pure oxygen and purged before being filled up to 3.04 MPa. Afterwards, the bomb was introduced in a cylindrical copper block. The block was sealed, evacuated and filled with ultra-pure helium up to 0.2 MPa. This copper block is confined in a cylindrical cavity surrounded by a 9 dm^3 thermostatic water bath, regulated at constant temperature T = (298.420 ± 0.001) K by a TRONAC temperature controller (model PTC-40). A multimeter (Keithley, model 2000) interfaced to a PC was used for data acquisition containing a bean type thermistor (R = 4 kΩ at T = 298.15 K) for temperature measurement. The charging, firing circuit and voltage measurement across the 2000 l F discharger condenser were done automatically by means of a set of Advantech acquisition/automation modulus, series 4000. At the end of the combustion experiment, the bomb was depressurized and the amount of carbon soot, when formed, was determined by gravimetry. The electrical energy for ignition, ΔU_{ign}, was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. As samples were ignited at T = 298.15 K,

$$\Delta U(\mathrm{IBP}) = -\varepsilon_{cal} \cdot \Delta T_{ad} + \varepsilon_i \cdot (T_i - 298.15) + \varepsilon_f \cdot (298.15 - \Delta T_{ad} - T_i) + \Delta U_{ign}, \quad (1)$$

where ΔU(IBP) is the energy associated to the isothermal bomb process, ε_i and ε_f are the energy of the bomb contents before and after ignition, respectively and ΔT_{ad} the adiabatic temperature obtained by application of the Regnault–Pfaundler method in a modified version of the LABTERMO software [9].

The energy equivalent of the mini-bomb combustion calorimeter, ε_{cal} = (1946.71 ± 0.84) J · K^{-1}, was obtained from the calibration experiments, made with benzoic acid (NIST SRM 39j) with a certified massic energy of combustion of −(26434 ± 3) J · g^{-1} under bomb conditions. The atomic weights of the elements were those recommended by the IUPAC Commission in 2011 [10].

2.2.2. Microcalorimetry Calvet

The standard molar enthalpy of sublimation of azulene was measured using the "vacuum sublimation" drop microcalorimetric technique [11,12]. The apparatus and technique have been described [12]. Samples about (3–8) mg in thin glass capillary tubes sealed at one end, were dropped, at room temperature, into the hot vessel in a high-temperature Calvet microcalorimeter held at T = 401 K and then removed from the hot zone by vacuum sublimation. 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 into each of the twin calorimeter cells. The microcalorimeter (Calvet High Temperature Microcalorimeter, SETARAM HT 1000) was calibrated *in situ* for these measurements using the reported standard molar enthalpies of sublimation of naphthalene [13].

From six independent experiments we have obtained a mean value for the observed standard molar enthalpy of sublimation, $\Delta^{g,T}_{cr,298.15\,K} H^0_m$, which was then corrected to T = 298.15 K, $\Delta^T_{298.15\,K} H^0_m(g)$, using the equation:

$$\Delta^T_{298.15\,K} H^0_m(g) = \int_{298.15\,K}^{T} C^0_{p,m}(g)dT, \quad (2)$$

where T is the temperature of the hot reaction vessel, $C^0_{p,m}(g)$ is the molar heat capacity of the compound in the gas phase and was obtained from statistical thermodynamics using the vibrational frequencies obtained from the DFT calculations with the B3LYP functional and the 6-31G(d) basis set.

TABLE 1
Provenience and purity of azulene.

Chemical name	CAS	Provenance	Initial mole fraction purity	Purification method	Final mole fraction purity	Analysis method
Azulene	275-51-4	Aldrich chemical Co.	0.98	Sublimation	0.9994	GC–MS

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