



# Thermodynamic properties of 2,7-di-*tert*-butylfluorene – An experimental and computational study



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## ABSTRACT

This work presents a comprehensive experimental and computational study of the thermodynamic properties of 2,7-di-*tert*-butylfluorene. The standard ( $p^\circ = 0.1$  MPa) molar enthalpy of formation in the crystalline phase was derived from the standard molar energy of combustion, measured by static bomb combustion calorimetry. The enthalpies and temperatures of transition between condensed phases were determined from DSC experiments. The vapour pressures of the crystalline and liquid phases were measured between (349.14 and 404.04) K, using two different experimental methods. From these results the standard molar enthalpies, entropies and Gibbs energies of sublimation and of vaporization were derived. The enthalpy of sublimation was also determined using Calvet microcalorimetry.

The thermodynamic stability of 2,7-di-*tert*-butylfluorene in the crystalline and gaseous phases was evaluated by the determination of the standard Gibbs energies of formation, at the temperature 298.15 K, and compared with the ones reported in the literature for fluorene.

A computational study at the G3(MP2)//B3LYP and G3 levels has been carried out. A conformational analysis has been performed and the enthalpy of formation of 2,7-di-*tert*-butylfluorene has been calculated, using atomization and isodesmic reactions. The calculated enthalpies of formation have been compared to the experimental values.

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## 1. Introduction

Fluorene has long been known for its fluorescent properties and several compounds with a fluorene core are being tested in electronic devices, like organic light-emitting diodes (OLEDs) and organic photovoltaic cells (OPCs). Part of our scientific activities has been focussed on the characterization of the thermodynamic properties of fluorene [1] and several fluorene derivatives [2–4]. Within the context of the work developed so far, this paper reports an experimental and computational study of the stability and volatility properties of 2,7-di-*tert*-butylfluorene (DTBF) aiming at the evaluation of the effect of the *tert*-butyl substituents on the related thermodynamic properties of fluorene. This effect will be compared with that determined for *tert*-butyl groups in 2,6-di-*tert*-butyl-naphthalene [5].

DTBF (Fig. 1), and several related derivatives, are commonly used as synthetic intermediates in peptide synthesis [6,7], and

are also regularly used in oligomeric and polymeric hybrids with triphenylamine [8] and carbazole [9], designed for white and blue phosphorescent organic light-emitting diodes. Fluorene units add rigidity to some oligomers improving their thermal and morphological stability and consequently their durability. The *tert*-butyl substituents also affect the photophysical properties of these systems and significantly reduce the self-quenching in blue phosphorescent OLEDs containing the hybrids as the host.

## 2. Experimental

### 2.1. Purification and purity control

2,7-Di-*tert*-butylfluorene (CAS 58775-05-6) was purchased from Sigma–Aldrich Chemical Co., with a minimum initial purity of 0.995, and was purified by successive sublimation under reduced pressure. During the purification process, the purity control of the sample was carried out by gas chromatography (GC), performed on an Agilent 4890D Gas Chromatograph, equipped with an HP-5 column (0.05 diphenyl and 0.95 dimethylpolysiloxane by mole fraction) and a flame ionization detector, using

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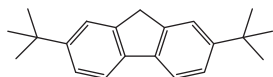


Fig. 1. Structural formula of 2,7-di-*tert*-butylfluorene.

ethanol as solvent and nitrogen as carrier gas (data presented in Table 1).

The relative atomic masses of the elements, calculated as the average of the interval values recommended by the IUPAC Commission in 2013 [10], were used for the calculation of the compound molar mass yielding  $M = 278.4300 \text{ g mol}^{-1}$ .

## 2.2. Differential scanning calorimetry

The temperatures and enthalpies of condensed phase transitions of DTBF were determined calorimetrically, using a power compensated differential scanning calorimeter (PerkinElmer Diamond Pyris 1). The power and temperature scales of the calorimeter were calibrated by measuring the melting temperature of several reference materials [11,12]. Five independent runs were performed on fresh samples of DTBF, sealed in aluminium crucibles, from  $T = 298 \text{ K}$  to about  $20 \text{ K}$  above the temperature of fusion, at a heating rate of  $3.3 \times 10^{-2} \text{ K s}^{-1}$  under a continuous nitrogen flux of  $0.8 \text{ mL s}^{-1}$ .

## 2.3. Vapour pressure measurements

The enthalpy, entropy and Gibbs energies of sublimation and vaporization of the compound were calculated from the dependency of vapour pressure with temperature that was determined using the combination of two independent methods in complementary ranges: a Knudsen mass-loss effusion method was used to measure the crystalline vapour pressures between  $0.1 \text{ Pa}$  and  $1 \text{ Pa}$  from  $T = (349.14 \text{ to } 372.21) \text{ K}$ , and a static method was used to measure crystalline and liquid vapour pressures from  $T = (368.55 \text{ to } 404.04) \text{ K}$ .

The Knudsen effusion experimental apparatus, previously described in detail [13], enables the simultaneous operation of nine effusion cells contained in cylindrical holes inside three aluminium blocks, controlled at different temperatures measured using a platinum resistance thermometer Pt100 (PRTs, class 1/10 DIN in a four-wire connection). Each block contains three cells with effusion orifices made in platinum foil ( $0.0125 \pm 0.0012$ ) mm thickness, (Goodfellow Cambridge Ltd.) with different effusion areas ( $A_0$ ) [14]: series A:  $A_0(A_1) = A_0(A_2) = A_0(A_3) = (0.636 \pm 0.004) \text{ mm}^2$ ; series B:  $A_0(B_1) = A_0(B_2) = A_0(B_3) = (0.785 \pm 0.004) \text{ mm}^2$ ; and series C:  $A_0(C_1) = A_0(C_2) = A_0(C_3) = (0.985 \pm 0.004) \text{ mm}^2$ . The Clausing factors of the effusion orifices were calculated as  $w_0 = [1 + (l/2r)]^{-1}$ , where  $l$  is the thickness of the platinum foil and  $r$  is the radius of the orifices, yielding the results 0.986, 0.988 and 0.989, respectively, for the orifices of series A, B and C. In each effusion experiment, the loss of mass of the samples,  $\Delta m$ , is determined by weighing the effusion cells to  $\pm 0.01 \text{ mg}$ , before and after a convenient effusion time period,  $t$ . At each temperature,  $T$ , the vapour pressure  $p$ , is calculated by means of the Eq. (1):

$$p = (\Delta m / A_0 w_0 t) \cdot (2\pi RT / M)^{1/2} \quad (1)$$

where  $M$  is the molar mass of the effusing vapour (assumed monomeric), and  $R = 8.3144598 \text{ J K}^{-1} \text{ mol}^{-1}$  [15].

The apparatus used for the static method was previously described in detail [16], and can be equipped with two MKS Baratron diaphragm capacitance gauges [16,17]. The model used in this work (631A01TBEH) is suitable for measuring pressures in the range  $(0.5\text{--}1.3 \cdot 10^2) \text{ Pa}$  and operates at a constant self-controlled temperature ( $T_{\text{gauge}} = 423 \text{ K}$ ). Before initiating the vapour pressure measurements, the samples are conveniently outgassed until repeated measurements at a selected temperature deliver consistent pressure results. To avoid condensation of the vapour, the temperature of the tubing is kept at a temperature slightly higher than that of the sample cell. The typical standard uncertainty of the temperature measurements is  $u(T/\text{K}) = \pm 0.01$  and the standard uncertainties of the pressure measurements are  $u(p/\text{Pa}) = \pm 0.01$  using the Knudsen method, and  $u(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa})$  using the static method.

## 2.4. Calvet microcalorimetry

The enthalpy of sublimation of DTBF was also determined calorimetrically using a high temperature Calvet Microcalorimeter (Setaram HT1000D), applying the vacuum sublimation drop microcalorimetric technique proposed by Skinner et al. for the study of solid samples [18]. The details of the apparatus and the technique were previously described in the literature [19]. In a typical experiment, a capillary tube containing a sample of the crystalline compound (about 2–3 mg) and a blank capillary tube, both very close in mass and accurately weighed ( $\pm 1 \cdot 10^{-6} \text{ g}$ ), were simultaneously dropped at the temperature  $298.15 \text{ K}$  into separate reaction vessels inside the calorimeter held at a predefined temperature (in this work  $T = 406.57 \text{ K}$ ). After the tubes reach thermal stability, the sample is removed from the hot-zone of the calorimeter by vacuum sublimation. The variation of the enthalpy of the process occurring in the capillary tube with sample relatively to that occurring in the empty capillary tube,  $\Delta_{\text{cr}, 298.15 \text{ K}}^{406.57 \text{ K}} H_{\text{m}}^{\circ}$ , was used to derive the standard molar enthalpy of sublimation of the sample at  $T = 298.15 \text{ K}$  using the gas enthalpy difference  $\Delta_{\text{g}, 298.15 \text{ K}}^{406.57 \text{ K}} H_{\text{m}}^{\circ}$ , according to Eq. (2).

$$\Delta_{\text{cr}, 298.15 \text{ K}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}, 298.15 \text{ K}}^{\text{g}, 406.57 \text{ K}} H_{\text{m}}^{\circ} - \Delta_{\text{g}, 298.15 \text{ K}}^{\text{g}, 406.57 \text{ K}} H_{\text{m}}^{\circ} \quad (2)$$

The thermal corrections related to the difference in mass of both capillary tubes were derived from individual blank correction experiments [19]. The microcalorimeter was calibrated *in situ* with anthracene (purity mass fraction 0.9999), using the same experimental conditions and temperature. The calibration constant of the calorimeter,  $k_{\text{cal}} = (1.0557 \pm 0.0022)$ , was calculated as the average of six independent sublimation experiments, where the quoted uncertainty is the standard deviation of the mean, using the reported standard molar enthalpy of sublimation  $\Delta_{\text{cr}, 298.15 \text{ K}}^{\text{g}} H_{\text{m}}^{\circ}(298.15 \text{ K}) = (100.4 \pm 0.4) \text{ kJ mol}^{-1}$  [13]. The system was also tested at the same temperature by determining the enthalpy of sublimation of pyrene (purity mass fraction 0.9989), yielding the

Table 1

Source, purification and analysis details of the compound studied.

Chemical name	Supplier	Minimal initial purity <sup>a</sup>	Purification method	Final mass fraction purity <sup>b</sup>
2,7-Di- <i>tert</i> -butylfluorene	Aldrich	0.995	Sublimation	0.9996

<sup>a</sup> Values referred to HPLC analysis, as stated in the certificate of analysis of the supplier.

<sup>b</sup> Determined in the present work using GC.

result  $\Delta_{\text{cr}}^{\circ}H_{\text{m}}^{\circ}(298.15\text{ K}) = (100.3 \pm 1.3)\text{ kJ mol}^{-1}$ , which is in excellent agreement with the value recently reported in the literature [11].

### 2.5. Static bomb combustion calorimetry

The standard ( $p^{\circ} = 0.1\text{ MPa}$ ) molar enthalpy of combustion of DTBF was derived from the respective energy of combustion determined by static bomb combustion calorimetry. The combustion experiments were performed in an isoperibol static bomb calorimetric system, equipped with a stainless steel twin valve combustion bomb with an internal volume  $0.290\text{ dm}^3$ . Both the apparatus and the operating technique have been previously described in detail [20–22]. The energy equivalent of the calorimeter was determined by the combustion of benzoic acid NIST Standard Reference Material (39j,  $\Delta_{\text{c}}u = -(26434 \pm 3)\text{ J g}^{-1}$  under bomb conditions [23]), following the procedure described by Coops et al. [24]. The energy equivalent of the calorimeter  $\varepsilon(\text{calor}) = (15551.7 \pm 1.6)\text{ J K}^{-1}$  (quoted uncertainty refers to the standard deviation of the mean), was determined as a mean of eight calibration experiments, for an average mass of  $2900.0\text{ g}$  of water used as calorimetric fluid.

The combustion experiments of both the calibration and compound samples were carried under identical conditions: burnt in pellet form, ignited at  $T = (298.150 \pm 0.001)\text{ K}$ , in the presence of oxygen ( $x_{\text{O}_2} \geq 0.99995$ ,  $p = 3.04\text{ MPa}$ ) and  $1.00\text{ cm}^3$  of deionized water. To guarantee the complete combustion of DTBF, two combustion aids were tested to prevent the formation of carbon soot residue. In some of the combustion experiments, the sample pellet was enclosed in Melinex<sup>®</sup> bags, using the technique described by Skinner and Snelson [25]. The use of this combustion aid, however, did not prove successful and *n*-hexadecane (Aldrich Gold Label, mass fraction  $>0.999$ ) was tested with better results. The energies of combustion of Melinex<sup>®</sup> and *n*-hexadecane in each experiment, were calculated using the respective massic energies of combustion,  $\Delta_{\text{c}}u^{\circ}(\text{melinex}) = -(22902 \pm 5)\text{ J g}^{-1}$  [25] and  $\Delta_{\text{c}}u^{\circ}(\textit{n-hex}) = -(47161.9 \pm 1.3)\text{ J g}^{-1}$ , where the quoted uncertainties are standard deviations of the mean of individual results. The latter one was determined in our laboratory and is in good agreement with that reported in the literature [26].

Details about calorimetric temperature measurements, electrical energy for ignition, cotton thread fuse, formation of carbon soot and the energetic effect for the amount of nitric acid produced in the combustion are described in previous work [2,3]. An estimated pressure coefficient of specific energy,  $(\partial u/\partial p)_T = -0.2\text{ J g}^{-1}\text{ MPa}^{-1}$  at  $T = 298.15\text{ K}$  [27], a typical value for most organic compounds, was assumed. Corrections to the standard state,  $\Delta U_{\Sigma}$ , used for the calculation of the standard massic energy of combustion,  $\Delta_{\text{c}}u^{\circ}$ , were calculated by the procedure given by Hubbard et al. [28].

The mass of compound,  $m(\text{cpd})$ , used in each experiment, and on which the energy of combustion was based, was determined from the mass of carbon dioxide ( $\text{CO}_2$ ) produced, after allowance for that formed from the combustion of the cotton thread and the combustion aids, and corrected from the apparent mass in air using the density value  $\rho = 0.988\text{ g cm}^{-3}$  [29].

### 3. Computational details

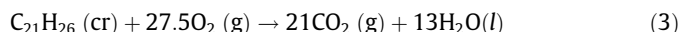
Standard *ab initio* molecular orbital calculations [30] were performed with the Gaussian09 series of programs [31]. Energies of the different conformers of 2,7-di-*tert*-butylfluorene were obtained using the Gaussian-3 theory at the G3(MP2)//B3LYP [32] level. For the most stable conformer, a calculation at the G3 [33] level has also been carried out. G3(MP2)//B3LYP- and G3-calculated energies, at 0 K, and enthalpies, at 298 K, are presented in Table S1 of the Supporting information. Heat capacities,  $C_v(\text{g})$ ,

and of entropies,  $S(\text{g})$ , for 2,7-di-*tert*-butylfluorene have been calculated at the B3LYP/6-31G(2df,p) level in the range (200–500) K and are reported in Table S2 of Supporting information.

## 4. Results and discussion

### 4.1. Enthalpies of formation in the crystalline phase

The standard ( $p^{\circ} = 0.1\text{ MPa}$ ) massic energy of combustion of DTBF,  $\Delta_{\text{c}}u^{\circ}(\text{cr})$ , measured by static bomb combustion calorimetry, allowed the derivation of the respective standard molar enthalpy of formation, in the crystalline phase,  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$ . The respective combustion reaction is represented by the following equation:



The internal energy for the isothermal bomb process,  $\Delta U(\text{IBP})$ , was calculated according to Eq. (4), in which  $c_p(\text{H}_2\text{O}, \text{l})$  is the massic heat capacity of liquid water at constant pressure,  $\Delta m(\text{H}_2\text{O})$  is the water mass variation between that added to the calorimeter and the reference value of  $2900.0\text{ g}$  assigned to the energy equivalent of the calorimeter,  $\varepsilon_{\text{f}}$  is the energy equivalent of the bomb content in the final state,  $\Delta T_{\text{ad}}$  is the calorimeter temperature change corrected for the heat exchange and the work of stirring, and  $\Delta U(\text{ign})$  is the electrical energy of ignition.

$$\Delta U(\text{IBP}) = -\{\varepsilon(\text{calor}) + c_p(\text{H}_2\text{O}, \text{l}) \cdot \Delta m(\text{H}_2\text{O}) + \varepsilon_{\text{f}}\} \Delta T_{\text{ad}} + \Delta U(\text{ign}) \quad (4)$$

Detailed results of six individual combustion experiments are presented in Table S3 (Supporting information), yielding the mean value of the standard massic energy of combustion  $\langle \Delta_{\text{c}}u^{\circ} \rangle = -(42458.5 \pm 8.5)\text{ J g}^{-1}$ . In order to derive the standard molar enthalpy of formation in the crystalline phase,  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$ , from the standard molar enthalpy of combustion,  $\Delta_{\text{c}}H_{\text{m}}^{\circ}$ , the standard molar enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$  at  $T = 298.15\text{ K}$ ,  $-(285.830 \pm 0.042)\text{ kJ mol}^{-1}$  and  $-(393.51 \pm 0.13)\text{ kJ mol}^{-1}$ , respectively, were used [34]. The standard massic energy of combustion and the derived values of standard molar energy and enthalpy of combustion, respectively  $\Delta_{\text{c}}U_{\text{m}}^{\circ}(\text{cr})$  and  $\Delta_{\text{c}}H_{\text{m}}^{\circ}(\text{cr})$ , as well as the standard molar enthalpy of formation of the compound in the crystalline phase,  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$ , at  $T = 298.15\text{ K}$  are presented in Table 2. The uncertainties ascribed to the standard molar energies of combustion are twice the overall standard deviation of the mean and include the contributions from the calibration with benzoic acid and those from the auxiliary quantities used.

### 4.2. Thermodynamic properties of phase transitions

The thermograms of DTBF, obtained during the DSC analysis (example shown in Fig. S1 of the Supporting information), revealed the existence of a crystalline transition at  $T_{\text{crII-crI}} = (367.0 \pm 0.2)\text{ K}$ , before the fusion transition at  $T_{\text{fus}} = (395.9 \pm 0.1)\text{ K}$ . The crystalline transition is thermodynamically reversible, yielding the same values of temperature and enthalpy either using fresh samples or

**Table 2**

Derived standard ( $p^{\circ} = 0.1\text{ MPa}$ ) molar formation values in the crystalline phase, at  $T = 298.15\text{ K}$ .

$-\langle \Delta_{\text{c}}u^{\circ}(\text{cr}) \rangle$ $\text{J g}^{-1}$	$-\Delta_{\text{c}}U_{\text{m}}^{\circ}(\text{cr})$ $\text{kJ mol}^{-1}$	$-\Delta_{\text{c}}H_{\text{m}}^{\circ}(\text{cr})$ $\text{kJ mol}^{-1}$	$-\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr})$ $\text{kJ mol}^{-1}$
$42458.5 \pm 8.5^{\text{a}}$	$11821.7 \pm 5.9^{\text{b}}$	$11837.8 \pm 5.9^{\text{b}}$	$141.7 \pm 6.5^{\text{b}}$

<sup>a</sup> Uncertainty is the standard deviation of the mean of the individual values (Table S3, Supporting information).

<sup>b</sup> Uncertainties are expanded uncertainties of the mean (0.95 level of confidence,  $k = 2$ ), and include the contributions from the calibration with benzoic acid and from the combustion auxiliaries used.

**Table 3**  
Temperatures, molar enthalpies and entropies of condensed phase transitions.

Phase transition	$T_{\text{trans}}/\text{K}$	$\frac{\Delta_{\text{trans}}H_m^0(T)}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{trans}}S_m^0(T)}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	Method	$\frac{T_{\text{crI-liq}}(\text{lit.})}{\text{K}}$
cr II–cr I	$367.0 \pm 0.2^{\text{a,b}}$	$10.00 \pm 0.07^{\text{b}}$	$27.2 \pm 0.2^{\text{c}}$	DSC	$394\text{--}397^{\text{d}}$
cr II–cr I	$366.8^{\text{e}}$	$12.7 \pm 0.4^{\text{c,f}}$	$34.6 \pm 1.1^{\text{c}}$	VP	$396.1\text{--}396.6$ [35]
cr I–liq	$395.9 \pm 0.2^{\text{a,b}}$	$15.6 \pm 0.3^{\text{b}}$	$39.4 \pm 0.8^{\text{c}}$	DSC	$401.6\text{--}403.1$ [36]
cr I–liq	$394.8^{\text{e}}$	$14.5 \pm 0.3^{\text{c,f}}$	$36.6 \pm 0.8^{\text{c}}$	VP	$393\text{--}395$ [6,37,38] $395$ [39] $393.2\text{--}393.7$ [40] $389.2$ [41]

<sup>a</sup> DSC onset temperatures.

<sup>b</sup> Results derived from five DSC independent runs; uncertainties are twice the standard deviation of the mean of the individual results.

<sup>c</sup> Uncertainties calculated through the Root Sum Square (RSS) method.

<sup>d</sup> Sigma Aldrich, MSDS.

<sup>e</sup> Estimation of triple point temperatures from vapour pressure results.

<sup>f</sup> Results derived indirectly from vapour pressure measurements.

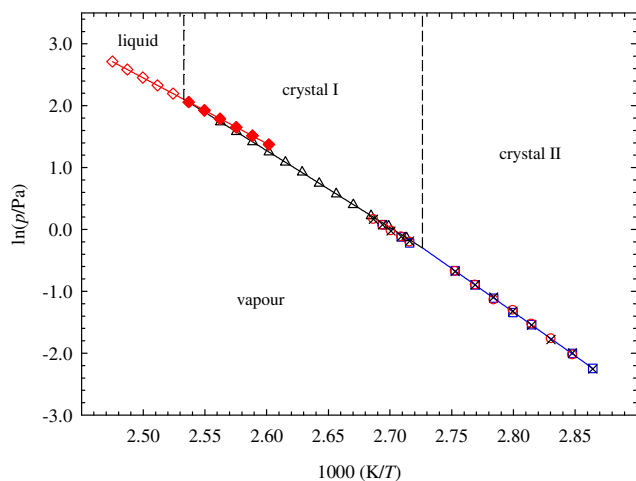
**Table 4**  
Experimental values of vapour pressure.<sup>a</sup>

$T/\text{K}$	$p/\text{Pa}$	$100\Delta p/p^{\text{b}}$	$T/\text{K}$	$p/\text{Pa}$	$100\Delta p/p^{\text{b}}$	$T/\text{K}$	$p/\text{Pa}$	$100\Delta p/p^{\text{b}}$
<i>Crystalline phase II, effusion method</i>								
349.14	0.106	0	355.28	0.215	0.5	361.14	0.409	0.2
351.14	0.134	0	357.20	0.266	0.4	363.27	0.510	−0.4
353.30	0.170	−0.6	359.19	0.329	−0.3			
<i>Crystalline phase I, effusion method</i>								
368.20	0.816	0.2	370.26	0.977	−0.8	372.21	1.179	0.2
369.13	0.888	0.1	371.21	1.077	0.3			
<i>Crystalline phase I, static method</i>								
368.55	0.873	−0.1	376.45	1.778	0	384.34	3.492	−0.2
370.54	1.055	0.6	378.41	2.106	−0.2	386.30	4.126	0.1
372.50	1.246	−0.5	380.40	2.524	0.7	388.27	4.862	0.3
374.50	1.492	−0.3	382.38	2.965	−0.1	390.24	5.670	−0.4
<i>Liquid phase<sup>c</sup>, static method</i>								
384.34	3.946	0.3	392.22	6.859	−0.2	400.05	11.64	0.1
386.32	4.548	0.2	394.20	7.843	−0.3	402.07	13.27	0.1
388.28	5.217	0	396.17	8.987	0	404.04	15.08	0.2
390.28	5.976	−0.5	398.15	10.26	0			

<sup>a</sup> The standard uncertainty of the temperature is  $u(T/\text{K}) = 0.01$  and standard uncertainties of the vapour pressure measurements are, respectively,  $u(p/\text{Pa}) = 0.01$  for the Knudsen method and  $u(p/\text{Pa}) = 0.01 + 0.0025(p/\text{Pa})$  for the static method.

<sup>b</sup>  $\Delta p = p - p_{\text{calc}}$ , where  $p_{\text{calc}}$  is calculated from the Clarke and Glew equation with parameters given in Table 5.

<sup>c</sup> Including supercooled liquid.



**Fig. 2.** 2,7-Di-tert-butylfluorene phase diagram. Effusion solid vapour pressures: □, small orifices; ○, medium orifices; ×, large orifices; Static vapour pressures: △, solid vapour pressures; ◇, liquid vapour pressures; ◆, supercooled liquid vapour pressures.

recrystallized *in situ*. Table S4 of the Supporting information reports the detailed temperatures of these phase transitions, observed at the onset of the calorimetric peaks, the molar enthalpies of the observed crystal–crystal transition,  $\Delta_{\text{crII-crI}}^{\text{crI}}H_m^0(T_{\text{crII-crI}})$ ,

and the molar enthalpies of fusion,  $\Delta_{\text{crI-liq}}^{\text{liq}}H_m^0(T_{\text{fus}})$ , for each independent run.

In Table 3 are compiled the values of enthalpy, entropy and temperatures of crII–crI and crI–liq phase transitions derived from DSC analysis, as well as the estimation of the temperature of the two triple points and the enthalpies and entropies of those phase transitions, derived indirectly from vapour pressure measurements. The melting temperatures found in the literature [6,35–41] are also listed in this table, and are in good agreement with the present experimental results, with the exception of the results reported by Kaplan and Roberts [36] and Wang et al. [41]. The calorimetric values of the temperature of the phase transitions crII–crI and crI–liq differ from the estimated triple point temperatures by only 0.2 K and 1.1 K, respectively, and the respective calorimetric phase transition enthalpies differ by  $-2.7 \text{ kJ mol}^{-1}$  and  $1.1 \text{ kJ mol}^{-1}$  from the ones derived from vapour pressures measurements.

The crystal and liquid vapour pressures measured using the effusion and static methods, listed in Table 4, were plotted as a function of temperature to build the phase diagram shown in Fig. 2. The reported effusion vapour pressures refer to each crystalline phase and are the mean of the values measured using the different effusion orifices at each temperature (given in detail in Table S5 of the Supporting information). Using the static method, the vapour pressures measured refer to the crystalline phase I

**Table 5**Standard ( $p^\circ = 0.1$  MPa) molar properties of sublimation and vaporization derived from the fitting of the Clarke and Glew equation to the ( $p, T$ ) data.

$\frac{\Delta T}{K}$	$\theta/K$	$\frac{\Delta_{cr,liq}^g C_m^o(\theta)_a}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{cr,liq}^g H_m^o(\theta)_a}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{cr,liq}^g S_m^o(\theta)_b}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{p(\theta)}{\text{Pa}}$	$R^2$	$\frac{\Delta_{cr,liq}^g C_{p,m}^o}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$ c	$s^d$
<i>Crystalline phase II, effusion method</i>								
349.14–363.27	298.15	$51.57 \pm 0.06$	$121.1 \pm 0.4$	$233.2 \pm 1.4$	$9.2 \cdot 10^{-5}$	0.9999	63.0	0.005
	356.21 <sup>e</sup>	$38.36 \pm 0.01$	$117.5 \pm 0.4$	$222.2 \pm 1.1$				
	366.8 <sup>f</sup>	$36.02 \pm 0.01$	$116.8 \pm 0.4$	$220.2 \pm 1.1$				
<i>Crystalline phase I, effusion method</i>								
368.20–372.21	298.15	$49.45 \pm 0.36$	$109.3 \pm 1.8$	$200.7 \pm 6.2$	$2.2 \cdot 10^{-4}$	0.9991	63.0	0.005
	370.21 <sup>e</sup>	$35.50 \pm 0.01$	$104.7 \pm 1.8$	$186.9 \pm 4.9$				
<i>Crystalline phase I, static method</i>								
368.55–390.24	298.15	$49.19 \pm 0.04$	$108.4 \pm 0.2$	$198.6 \pm 0.7$	$2.1 \cdot 10^{-4}$	1.0000	63.0	0.004
	379.40 <sup>e</sup>	$33.69 \pm 0.01$	$103.3 \pm 0.2$	$183.5 \pm 0.5$				
	366.8 <sup>f</sup>	$36.02 \pm 0.01$	$104.1 \pm 0.2$	$185.6 \pm 0.5$				
	394.8 <sup>g</sup>	$30.89 \pm 0.01$	$102.3 \pm 0.2$	$180.9 \pm 0.5$				
<i>Liquid phase, static method<sup>h</sup></i>								
384.34–404.04	298.15	$46.61 \pm 0.04$	$101.2 \pm 0.2$	$183.1 \pm 0.7$	$6.8 \cdot 10^{-4}$	1.0000	137.7	0.002
	394.19 <sup>e</sup>	$30.97 \pm 0.01$	$87.93 \pm 0.15$	$144.5 \pm 0.4$				
	394.8 <sup>g</sup>	$30.89 \pm 0.01$	$87.85 \pm 0.15$	$144.3 \pm 0.4$				

<sup>a</sup> Uncertainties are standard deviations of the least squares regressions.<sup>b</sup> Calculated as  $\{[\Delta_{cr,liq}^g H_m^o(\theta) - \Delta_{cr,liq}^g C_m^o(\theta)]/\theta\}$ ; uncertainties calculated through the RSS method.<sup>c</sup> Estimated values.<sup>d</sup>  $s$  is the standard deviation of the fit defined as  $s = [(\sum_{i=1}^n (\ln p - \ln p_{\text{calc}})^2)/(n - m)]^{1/2}$ , where  $n$  is the number of experimental points used in the fit and  $m$  is the number of adjustable parameters in the Clarke and Glew equation.<sup>e</sup> Mean temperature.<sup>f</sup> Estimated temperature of triple point (crII, crI, g).<sup>g</sup> Estimated temperature of the triple point (crI, liq, g).<sup>h</sup> Including supercooled liquid.**Table 6**Standard ( $p^\circ = 0.1$  MPa) molar enthalpy of sublimation, at  $T = 298.15$  K, determined by Calvet microcalorimetry.

$\frac{T}{K}$	$\frac{\Delta_{cr,298.15 K}^g H_m^o}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{cr,298.15 K}^g H_m^o(\text{g})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{cr}^g H_m^o(298.15 \text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$
$406.57 \pm 0.01^a$	$164.6 \pm 0.4^a$	44.74	$119.9 \pm 0.9^b$

<sup>a</sup> Uncertainties are the standard deviation of the mean of six independent experiments;<sup>b</sup> Uncertainty is the expanded uncertainty of the mean (0.95 level of confidence,  $k = 2$ ), and includes the uncertainty due to the calibration.

and to the liquid phase. The experimental ( $p, T$ ) values were fitted by the truncated form of the Clarke and Glew Eq. (5) [42], in order to determine the thermodynamic properties of sublimation and vaporization at selected reference temperatures.

$$R \ln \left( \frac{p}{p^\circ} \right) = - \frac{\Delta_{cr,liq}^g C_m^o(\theta)}{\theta} + \Delta_{cr,liq}^g H_m^o(\theta) \left( \frac{1}{\theta} - \frac{1}{T} \right) + \Delta_{cr,liq}^g C_{p,m}^o(\theta) \left[ \left( \frac{\theta}{T} \right) - 1 + \ln \left( \frac{T}{\theta} \right) \right] \quad (5)$$

In this equation,  $p$  is the vapour pressure at the temperature  $T$ ,  $p^\circ$  is the reference pressure (in this study,  $p^\circ = 0.1$  MPa),  $\theta$  is a selected reference temperature,  $R$  is the gas constant, and  $\Delta_{cr,liq}^g C_m^o(\theta)$  and  $\Delta_{cr,liq}^g H_m^o(\theta)$  are adjustable values of thermodynamic properties of sublimation or vaporization.

The standard molar Gibbs energy, enthalpy and entropy of sublimation and vaporization of DTBF are reported in Table 5 at different temperatures *viz.* 298.15 K, the mean temperature of the experimental intervals, and the triple point temperatures estimated by the intersection of the  $p, T$  curves related to Eq. (5). The reported uncertainties are standard deviations of the least squares regressions of the fittings. Table 5 also reports the values of the heat capacity differences,  $\Delta_{cr,liq}^g C_{p,m}^o$ , that were inputted into Eq. (5). Those values were estimated through Eqs. (6) and (7), derived by Monte et al. [43] as a rearrangement of those reported by Chickos et al. [44], using the gas phase molar heat capacity, at

298.15 K,  $C_{p,m}^o(\text{g}) = 352.65 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , calculated in this work at the B3LYP/6-31G(2df,p) level of theory. The estimations yielded the values  $\Delta_{cr}^g C_{p,m}^o = -63.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta_{liq}^g C_{p,m}^o = -137.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

$$\Delta_{cr}^g C_{p,m}^o(\theta)/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = -[0.9 + 0.176 C_{p,m}^o(\text{g})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})] \quad (6)$$

$$\Delta_{liq}^g C_{p,m}^o(\theta)/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = -[14.3 + 0.35 C_{p,m}^o(\text{g})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})] \quad (7)$$


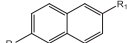
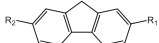
In order to verify the enthalpy of sublimation of the crystalline phase II, that is thermodynamically stable at  $T = 298.15$  K, Calvet microcalorimetry was also used, yielding the results reported in Table 6. Detailed results of the six individual experiments are reported in Table S6 of the Supporting information. The observed enthalpy change  $\Delta_{cr,298.15 K}^g H_m^o = (164.6 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ , corresponding to the mean of six experiments, was then adjusted by means of Eq. (2) in order to derive the enthalpy of sublimation at  $T = 298.15$  K:  $\Delta_{cr}^g H_m^o(298.15 \text{ K}) = (119.9 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$ . The term  $\Delta_{g,298.15 K}^g H_m^o$  was calculated through Eq. (8) from the integration of the fitting of a 3rd degree polynomial (Eq. (9)) to the values of  $C_p(\text{g})$  derived from the  $C_v(\text{g})$  between 200 K and 500 K (Table S2 of the Supporting information).

$$\Delta_{298.15 K}^g H_m^o(\text{g}) = \int_{298.15 \text{ K}}^T C_{p,m}^o(\text{g}) dT \quad (8)$$

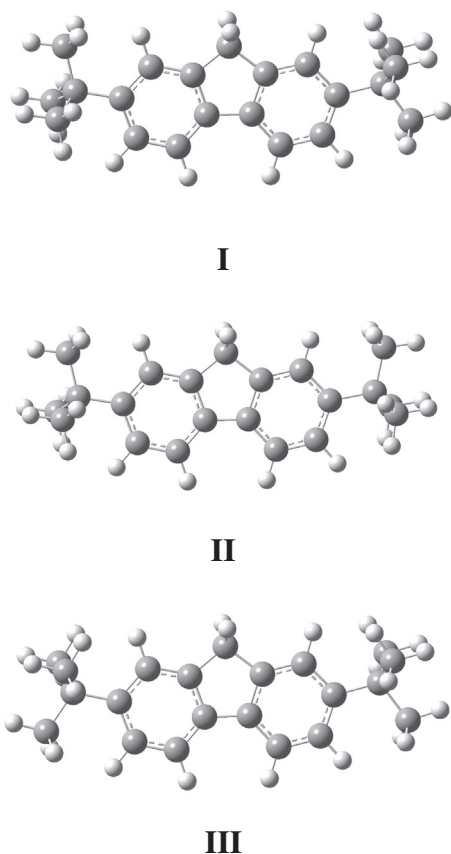
$$C_{p,m}^o(\text{g})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 53.988 + 7.1572 \cdot 10^{-1}(T/\text{K}) + 1.5015 \cdot 10^{-3}(T/\text{K})^2 - 1.8168 \cdot 10^{-6}(T/\text{K})^3 \quad (R^2 = 0.9999) \quad (9)$$

The uncertainty associated to the calorimetric value of  $\Delta_{cr}^g H_m^o(298.15 \text{ K})$  is twice the overall standard deviation of the mean of six independent experiments and includes the uncertainties introduced by the calibration. The calorimetric result agrees within the experimental uncertainty with the value derived by the vapour pressure study.

**Table 7**  
Gaseous phase increments on enthalpies of formation associated to the insertion of different substituents in benzene, in positions 2,6 of naphthalene and in positions 2,7 of fluorene (all values in  $\text{kJ mol}^{-1}$ ).

Substituent groups							
$R_1$	$R_2$	$\Delta_f H_m^0/\text{kJ mol}^{-1}$	$\Delta H_m^0(\text{inc})/\text{kJ mol}^{-1}$	$\Delta_f H_m^0/\text{kJ mol}^{-1}$	$\Delta H_m^0(\text{inc})/\text{kJ mol}^{-1}$	$\Delta_f H_m^0/\text{kJ mol}^{-1}$	$\Delta H_m^0(\text{inc})/\text{kJ mol}^{-1}$
H	H	$82.9 \pm 0.9$ [45]		$150.6 \pm 1.5$ [45]		$179.4 \pm 3.0$ [1]	
$\text{C}(\text{CH}_3)_3$	H	$-(24.4 \pm 0.8)$ [46]	$-(107.3 \pm 1.2)$				
$\text{C}(\text{CH}_3)_3$	$\text{C}(\text{CH}_3)_3$			$-(63.3 \pm 5.3)$ [5]	$-(107.0 \pm 2.8)^a$	$-(21.2 \pm 6.6)$	$-(100.3 \pm 3.6)^a$
$\text{NH}_2$	H	$87.1 \pm 1.0$ [47]	$4.2 \pm 1.3$			$193.6 \pm 2.7$ [3]	$14.2 \pm 4.0$
$\text{NO}_2$	H	$67.5 \pm 0.6$ [47]	$-(15.4 \pm 1.1)$			$164.4 \pm 3.9$ [3]	$-(15.0 \pm 4.9)$
Br	H	$105.4 \pm 4.1$ [47]	$22.5 \pm 4.2$	$175.6 \pm 2.3$ [48]	$25.0 \pm 2.7$	$208.0 \pm 2.2$ [4]	$28.6 \pm 3.7$
Br	Br					$229.3 \pm 2.5$ [4]	$25.0 \pm 2.0^a$

<sup>a</sup> Mean enthalpic increment per substituent.



**Fig. 3.** B3LYP/6-31G(d) optimized geometries of the three conformers of 2,7-di-*tert*-butylfluorene.

**Table 8**  
Experimental and computationally estimated gas-phase enthalpies of formation of DTBF, at  $T = 298.15$  K (all values in  $\text{kJ mol}^{-1}$ ).

	G3(MP2)//B3LYP/ $\text{kJ mol}^{-1}$	G3/ $\text{kJ mol}^{-1}$
Atomization	$-46.9^a$ ( $-46.6$ ) <sup>b</sup>	$-36.5^b$
Isodesmic reaction (Eq. (10))	$-29.2 \pm 4.0^c$	$-29.9 \pm 4.0^c$
Isodesmic reaction (Eq. (11))	$-32.1 \pm 6.3^c$	$-32.1 \pm 6.3^c$
Experimental	$-21.2 \pm 6.6$	

<sup>a</sup> Value calculated taking into account the Boltzmann weighted populations of the three conformers.

<sup>b</sup> Value calculated for the most stable conformer I (Fig. 3).

<sup>c</sup> Uncertainties calculated through the RSS method using the uncertainties of the reference values of the standard enthalpies of formation of the compounds used in the isodesmic reactions.

### 4.3. Enthalpies of formation in the gaseous phase

#### 4.3.1. Experimental results

The enthalpy of formation of DTBF in the gaseous phase,  $\Delta_f H_m^0(\text{g}) = -(21.2 \pm 6.6) \text{ kJ mol}^{-1}$ , was determined by combining the enthalpy of formation of the crystalline phase II, the thermodynamically stable phase at  $T = 298.15$  K, with the mean of the enthalpies of sublimation of crystalline phase II derived from vapour pressure and calorimetric results,  $\Delta_{\text{cr}}^{\text{g}} H_m^0 = (120.5 \pm 1.0) \text{ kJ mol}^{-1}$ . Table 7 reports the estimated enthalpic increments in the gas phase enthalpies of formation associated with insertion of different substituent groups on benzene [45–47], as well as on positions 2,6 of naphthalene [5,45,48] and on positions 2,7 of fluorene [1,3,4]. The enthalpic increment per *tert*-butyl group in *tert*-butylbenzene ( $\Delta H_{\text{inc}} = -107.3 \text{ kJ mol}^{-1}$ ) is in agreement with the mean enthalpic increment observed in 2,6-di-*tert*-butylnaphthalene ( $\Delta H_{\text{inc}} = -107.0 \text{ kJ mol}^{-1}$ ). For 2,7-di-*tert*-butylfluorene, the mean increment of the *tert*-butyl groups ( $\Delta H_{\text{inc}} = -100.3 \text{ kJ mol}^{-1}$ ) is *ca.*  $7 \text{ kJ mol}^{-1}$  larger than the values referred to above. Larger increments are also observed for fluorene substituted in position 2 with an amine group [3] ( $\Delta H_{\text{inc}} = 14.2 \text{ kJ mol}^{-1}$ ) or a bromine atom [4] ( $\Delta H_{\text{inc}} = 28.6 \text{ kJ mol}^{-1}$ ), when compared to those in benzene ( $\Delta H_{\text{inc}} = 4.2 \text{ kJ mol}^{-1}$  and  $\Delta H_{\text{inc}} = 22.5 \text{ kJ mol}^{-1}$ , respectively). In contrast, the following increments are in close agreement: the mean enthalpic increment for the two bromine atoms in positions 2,7 of fluorene and in positions 2,6 of naphthalene ( $\Delta H_{\text{inc}} = 25.0 \text{ kJ mol}^{-1}$ ); and the increment for the nitro group in benzene and in position 2 of fluorene ( $\Delta H_{\text{inc}} \approx 15 \text{ kJ mol}^{-1}$ ).

#### 4.3.2. Computational results

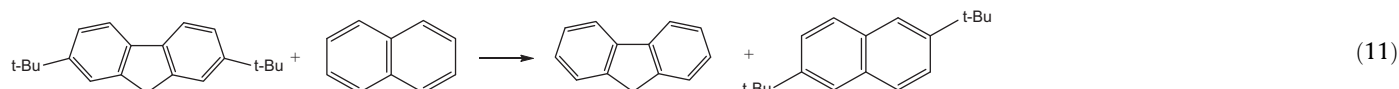
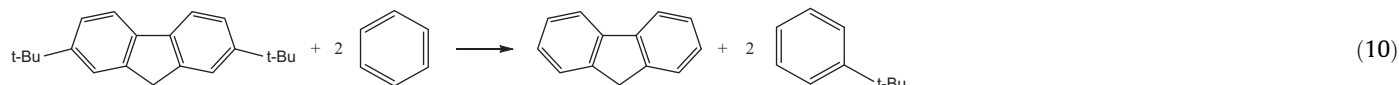
2,7-Di-*tert*-butylfluorene presents three conformers in the gas phase, shown in Fig. 3, depending of the orientation of the two *tert*-butyl groups on the molecule, and the enthalpy difference among the three conformers is very small. The most stable conformer, I, with the two *tert*-butyl groups staggered, is 0.4 and  $0.5 \text{ kJ mol}^{-1}$  more stable than the conformers II and III, respectively, both with the two *tert*-butyl groups eclipsed.

The enthalpy of formation of 2,7-di-*tert*-butylfluorene, calculated through atomization reactions, at the G3(MP2)//B3LYP level of theory taking into account the Boltzmann weighted populations of the three conformers is  $-46.6 \text{ kJ mol}^{-1}$ , the enthalpy of the conformer I being  $-46.9 \text{ kJ mol}^{-1}$ . Due to the size of the molecule, with 21 heavy atoms, G3 calculations are very expensive; they have been carried out only on the most stable conformer I. The G3-calculated enthalpy of formation is  $-36.5 \text{ kJ mol}^{-1}$ .

We have also used two isodesmic reactions, (10) and (11), for calculating the enthalpy of formation of 2,7-di-*tert*-butylfluorene, using benzene and naphthalene as references, respectively.

**Table 9**Standard ( $p^\circ = 0.1$  MPa) molar absolute entropies and standard molar entropies, enthalpies and Gibbs energies of formation, at  $T = 298.15$  K.<sup>a</sup>

Compound	Phase	$\frac{\Delta_f S_m^\circ}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{S_m^\circ}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{-T\Delta_f S_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_f H_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_f G_m^\circ}{\text{kJ}\cdot\text{mol}^{-1}}$
Fluorene [1]	g	179.2 ± 0.9	381.0	103.5	179.4 ± 3.0	282.9 ± 3.0
	cr		201.8 ± 0.9	156.9 ± 0.3	91.6 ± 3.0	248.5 ± 3.0
DTBF	g	233.2 ± 1.4	602.2 <sup>c</sup>	362.9	-21.2 ± 6.6 <sup>d</sup>	341.7 ± 6.6
	crII <sup>b</sup>		369.0 ± 1.4	432.4 ± 0.4	-141.7 ± 6.5	290.7 ± 6.5

<sup>a</sup> Uncertainties calculated through the RSS method.<sup>b</sup> Results of the crystalline phase thermodynamically stable at  $T = 298.15$  K.<sup>c</sup> Calculated at the B3LYP/6-31G(2df,p) level of theory, applying the scale factor 0.9946 in  $S_{\text{vib}}$  [49].<sup>d</sup> Determined from the mean enthalpy of sublimation derived from vapour pressure and calorimetric results.

The values of the enthalpy of formation obtained using isodesmic reactions represented by Eqs. (10) and (11) are collected in Table 8. As it can be observed, all the calculated values are lower than the experimental value, measured in this work; the values obtained using the isodesmic reactions are in reasonable agreement with the experimental one taking into account the reported uncertainties. The mean enthalpic increments for the *tert*-butyl groups, estimated from computational results obtained using Eqs. (10) and (11) ( $\Delta H_{\text{inc}} = -104.5$  kJ mol<sup>-1</sup> and  $\Delta H_{\text{inc}} = -105.8$  kJ mol<sup>-1</sup>, respectively), are also larger than those previously mentioned for benzene and naphthalene, which agrees with what was observed with the experimental results.

#### 4.4. Standard Gibbs energy and thermodynamic stability of the crystalline and gaseous phases

A compound's thermodynamic stability can be evaluated by its standard molar Gibbs energy of formation ( $\Delta_f G_m^\circ$ ). Besides being an important parameter for calculating equilibrium constants of reactions,  $\Delta_f G_m^\circ$  measures the thermodynamic tendency for a compound to decompose into its constituent elements, under standard-state conditions – smaller values indicate larger stability. In order to compare the thermodynamic stability of DTBF with that of fluorene, in either crystalline or gaseous phases, we compared the values of  $\Delta_f G_m^\circ$  (g) and  $\Delta_f G_m^\circ$  (cr) of both. Table 9 presents a compilation of the standard molar absolute entropies and standard molar enthalpies, entropies and Gibbs energies of formation of fluorene [1] and DTBF, in the crystalline and gaseous phases, at  $T = 298.15$  K. The gaseous entropy at 298.15 K was calculated from the value reported in Table S2 of Supporting information, applying the frequency scale factor 0.9946 [49] to the vibrational part of the entropy,  $S_{\text{vib}}$ . The standard molar entropies of formation, in the crystalline and gaseous phases, were calculated considering the respective standard molar absolute entropies and using the following reference standard molar entropy values [50]:  $S_m^\circ$  [C(graphite)] = 5.740 J K<sup>-1</sup> mol<sup>-1</sup>,  $S_m^\circ$  (H<sub>2</sub>, g) = 130.680 J K<sup>-1</sup> mol<sup>-1</sup>. From the values of  $\Delta_f G_m^\circ$  (cr) and  $\Delta_f G_m^\circ$  (g), determined from the standard enthalpies and entropies of formation, it can be seen that DTBF is considerably less stable than the parent compound fluorene, in both crystalline and gaseous phases, probably due to the steric hindrance induced by the bulky *tert*-butyl groups.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2016.05.007>.

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