JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Heat Capacity and Thermodynamic Functions of Diphenylacetylene

Ekaterina S. Tkachenko, Raisa M. Varushchenko,* Anna I. Druzhinina, Marina D. Reshetova, and Nataliya E. Borisova

Chemistry Department, Moscow State University, 119992, Moscow, Russia

Supporting Information

ABSTRACT: The heat capacity of diphenylacetylene was measured by vacuum adiabatic calorimetry over the temperature range from (8 to 371) K. The temperature and the enthalpy and entropy of fusion have been determined. The standard thermodynamic functions (changes of the entropy, enthalpy, and Gibbs free energy) were obtained for the crystal and liquid states in the temperature interval studied and for the ideal gas state at $T = 298.15$ K. The ideal gas entropies in wide temperature range were also calculated by the principle of additivity and statistical thermodynamics using molecular constants determined by the density functional theory (DFT) method on the level B3LYP/cc-pVTZ. The $S^0_m(g)(298.15K)$ values derived from the experimental and calculated data agree within (0.3 to 0.2) % which confirms their reliability. The data on thermodynamic properties of diphenylacetylene studied earlier and in this work were critically analyzed for verification of their reliability and mutual consistency.

INTRODUCTION

Materials founded on diphenylacetylene (DPhA) and its derivatives have a wide range of applications. They are used as building blocks of polymer synthesis,[1,2] components of liquid crystal materials,[3,4] and organic semiconductors.[5,6] The application of DPhA in molecular electronics favored the development of new technologies, such as the synthesis of a prototype single-molecule diode.[7] DPhA has also obtained an increasing attention in optoelectronics (e.g., organic light emitting diodes, OLED).[8] Due to various applications of DPhA and its derivatives, much attention was focused on the thermodynamic investigation of these compounds.

The thermodynamic properties of DPhA were widely studied by experimental methods. Data on the saturation vapor pressures and enthalpies of sublimation and vaporization were published in refs 9 to 15. A reliable value of $\Delta_{sub}H^0_m = (95.1 \pm 1.1)\ \mathrm{kJ\cdot mol^{-1}}$ was obtained on the basis of saturation vapor pressure measured by the Knudsen method and the heat capacity of crystal DPhA determined by differential scanning calorimetry (DSC) in the temperature range from (298.273 to 316.153) K.[14] The saturation vapor pressure of liquid DPhA was determined by comparative ebulliometry in the temperature range from (439.627 to 517.206) K.[15] Obtained pT data were approximated by the Wagner equation[16,17] using the calculated values of the critical parameters:

$$\ln(p/p_c) = (1/T_r)[AY + BY^{1.5} + CY^{2.5} + DY^5] \qquad (1)$$

where $T_r = T/T_c$, $Y = 1 - T_r$, $T_c = 860$ K, and $p_c = 4.2$ MPa .

The enthalpy of vaporization $\Delta^g_l H_m(298K) = (75.9 \pm 3.1)\ \mathrm{kJ\cdot mol^{-1}}$ were derived from eq 1 using the Clapeyron equation:

$$dp/dT = \Delta^g_l H_m/(T\Delta^g_l V_m) \qquad (2)$$

where $\Delta^g_l V_m$ is the difference between molar volumes of the liquid and real vapor.

The enthalpy of sublimation of DPhA calculated on the basis of $\Delta_{vap}H^0_m$ and $\Delta_{fus}H^0_m$ values of ref 15, $\Delta_{sub}H^0_m(298K) = (95.7 \pm 3.1)\ \mathrm{kJ\cdot mol^{-1}}$, agrees within the error limits with the experimental value in ref 14.

The low-temperature heat capacity, C_p, of crystal DPhA was measured by adiabatic calorimetry in the temperature region from (9 to 303) K by Saito et al.[18] The authors presented the smoothed C_p values and derived main thermodynamic functions in the crystal state. The heat capacities were extrapolated to $T \rightarrow 0$ K by the Debye rule. An accuracy of heat capacity measurement and a purity of the substance were not evaluated. The heat capacity of DPhA was also determined by Steele et al.,[15] Kurbatov,[19] and Smith and Andrews[20] using DSC, mixing, and conduction calorimetry in the temperature intervals from (303 to 500) K, (338 to 576) K, and (101.9 to 322.6) K, respectively. The heat capacities of DPhA in refs 15 and 18 to 20 disagree within (4 to 0.4) % at $T = 298.15$ K. At the same time, discrepancies between C_p values at low temperatures of (120 and 200) K are (1 and 1.7) %, according to the data of refs 18 and 20.

The experimental heat combustion of crystal DPhA and derived enthalpy of formation $\Delta_f H^0_m(\mathrm{cr}) = (312.40 \pm 1.1)\ \mathrm{kJ\cdot mol^{-1}}$ at $T = 298.15$ K were determined by Coops et al.[21] The data on the ideal gas enthalpy of formation obtained by experimental and calculation methods disagree from (385 to 427.96) $\mathrm{kJ\cdot mol^{-1}}$.[14,22−25] The enthalpy of formation $\Delta_f H^0_m(g)(\mathrm{exp}) = (407.5 \pm 1.6)\ \mathrm{kJ\cdot mol^{-1}}$ was appreciated in ref 14 as a reliable quantity calculated from $\Delta_f H^0_m(\mathrm{cr})$[21] and $\Delta_{sub}H^0_m$[14] values at $T = 298.15$ K. Using the AM1 semiempirical method, Palafox[25] computed the enthalpy of formation $\Delta_f H^0_m(g)(\mathrm{calc}) = 409.5\ \mathrm{kJ\cdot mol^{-1}}$, which agreed with the experimental value[14] in the

Special Issue: Kenneth N. Marsh Festschrift

Received: July 5, 2011
Accepted: September 8, 2011
Published: September 30, 2011

best way. In ref 25 the ideal gas absolute entropy was calculated by the same method, $S^0_m(g)(298K) = 452.0\,J\cdot K^{-1}\cdot mol^{-1}$. According to evaluation by Dorofeeva,[26] this value can be overestimated from (15 to 30) $J\cdot K^{-1}\cdot mol^{-1}$ relatively to the entropy calculated by additive difference method using a system of isodesmic thermochemical equations.

This paper deals with the new determination of the heat capacity of DPhA by adiabatic calorimetry because the literature C_p values at low temperatures, $T \leq 200$ K, are not accurate enough. The heat capacity measurements in this work are carried out in a wider temperature range from (8 to 371) K compared with ref 18, and the determinations of the fusion characteristics and the purity of the substance are included. The main thermodynamic functions were derived: the absolute entropy by the third law of thermodynamics and changes of H and G functions in condensed and ideal gas states including the free Gibbs energy of formation, $\Delta_f G^0_m$. For verification of reliability and thermodynamic consistency of the experimental data, the ideal gas entropy and heat capacity were computed by the additive principle and statistical thermodynamic method coupled with quantum mechanical calculations on the level B3LYP/cc-pVTZ of the DFT theory. Experimental and calculation values were discussed and used for the prognosis of some thermodynamic data.

■ EXPERIMENTAL SECTION

Materials. DPhA (Tolan; benzene, 1,1′-(1,2-ethynediyl)bis-; 2-(phenylethynyl)benzene; $C_6H_5—C{\equiv}C—C_6H_5$, CAS Registry No. 501-65-5) was purchased from Acros Organics. According to the certificate, the purity of a sample determined by the gas–liquid chromatography (GLC) was >0.985 mass fraction which was in agreement with that determined by a calorimetric melting study, 0.9845 mole fraction in this work. A recrystallization of the sample from methanol followed by solvent removal just below the melting point of DPhA resulted in enhancing the mole fraction of the main compound to 0.9994 in accordance with the calorimetric melting study. The DPhA was the crystal powder of the white color.

Apparatus and Procedure. The heat capacity of DPhA was measured in a setup consisting of a vacuum adiabatic calorimeter, a data acquisition and control system, and a personal computer. The volume of a titanium container was $\sim(1\cdot 10^{-6})$ m^3. The temperature of the calorimeter was measured with the accuracy $\pm$ $(5\cdot 10^{-3})$ K by a (rhodium + iron) resistance thermometer ($R_0 \sim 50\ \Omega$) calibrated on the International Temperature Scale of 1990 (ITS-90). The construction of the calorimeter and the technique were described in refs 27 and 28. The metrological characteristics of the calorimeter were tested by measuring the heat capacity of the standard specimen of high pure copper, having the mass fraction of 0.99995. The C_p values agree with precise literature data[29−31] within (1.4 to 1.1) % between temperatures of (8 and 20) K, from (0.4 to 0.3) % within the temperature range from (20 to 80) K, and from (0.3 to 0.2) % above 80 K.

For measuring the heat capacity, the DPhA sample was pressed into a tablet and divided into several pieces for filling the calorimeter container. The latter was sealed vacuum-tight by means of a bronze brass lid and indium gasket, then was pumped out, and was filled with the helium heat-exchange gas up to $p \sim 24$ kPa.

The heat capacity of DPhA was measured at the saturated vapor pressure, $C_{s,m}$, over the temperature ranges from (8 to 371) K using liquid helium and nitrogen as refrigerants. Experimental $C_{s,m}$ values in 508 experiments with the temperature step $\Delta T \sim 1$ K were tabulated in the Supporting Information. The values of the heat capacities obtained repeatedly at the same temperature from (80 to 85) K by using helium or nitrogen refrigerants agreed within errors ≤ 0.3 %, which proves the reliability of the modified procedure[28] used for keeping the adiabatic conditions in the calorimeter. A difference $(C_{p,m} - C_{s,m}) = T(\partial V/\partial T)_p(\partial p/\partial T)_s$, evaluated at $T = 298.15$ K, was smaller than uncertainties of $C_{s,m}$ for DPhA and was not taken into account.

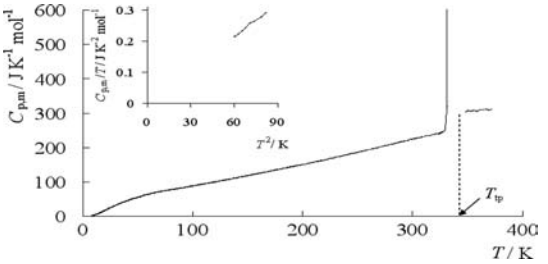

Figure 1. Plot of molar heat capacity, $C_{p,m}$, of DPhA as a function of temperature, T, where T_{tp} denotes the temperature of triple point. In the inset, the dependence of $C_{p,m}/T$ on T^2 is given for the helium range of the temperatures studied.

Heat Capacity. The heat capacity curve reveals a fusion at $T_{tp} = 332.02$ K (Figure 1).

The triple-point temperature and the purity of DPhA were obtained by the calorimetric method of the fractional melting study of the sample.[32] Four series of experiments were made for the determination of the dependence between reciprocal fraction of the sample melted, $1/F_i$, and equilibrium fusion temperatures, T_i (Table 1). The first experiment revealed the linear dependence $T_i = f(1/F_i)$ and the correlation coefficient, R^2, being equal to 0.9995. According to ref 32, the data on T_i at the $1/F_i$ values could be fitted by an equation:

$$T_i = (T_1 - T_{tp})(1/F_i) + T_{tp} \tag{3}$$

Here, $T_{tp} = 332.00$ K is the triple-point temperature of the pure sample, $(T_1 - T_{tp}) = -0.011$ is a depression of the T_{tp} value, and T_1 denotes the triple point temperature of the completely melted sample ($F_i = 1$).

The mole fraction of impurities, N_2, in this experiment was calculated from the formula:[32]

$$N_2 = \{\Delta_{fus}H_m(T_1 - T_{tp})\}/(R\cdot T_{tp}{}^2) \tag{4}$$

where $R = 8.314472\ J\cdot K^{-1}\cdot mol^{-1}$ and $\Delta_{fus}H_m$ is the enthalpy of fusion of DPhA.

Experiments 2 to 4 exhibit $T_i = f(1/F_i)$ concave dependences, the coefficients R^2 of appropriate linear dependences being equal to 0.98. It is doubtful whether these dependences can be explained by the formation of the solid solution because of the high purity of the sample, 0.9994 mole fraction (Table 2). Nevertheless, for the determination of the impurity content, a treatment of these experiments were carried out by the Smit–Aleksandrov method[35,36] which was applicable for the case of solid solution formation between the main compound and impurities. The T_{tp} temperatures in these experiments were calculated by the Mastrangelo–Dornte[33] method. In the latter, a dependence of T_i upon $1/F_i$ was expressed through the k coefficient, equal to a ratio of the impurity content in the solid phase to that of a liquid one. At the same time, the k value, being situated in the

Table 1. Experiments 1 to 4 on the Dependence of the Equilibrium Melting Temperatures T_i, from the Reciprocal Fraction of the Sample Melted, $1/F_i$, and the Triple Point Temperatures, T_{tp}, Calculated by Rossini et al.[32] (Exp. 1) and Mastrangelo−Dornte[33] (Exp. 2 to 4) Methods for DPhA

exp. 1				exp. 3			
T_i/K	q_i/J	$1/F_i$	T_{tp}/K	T_i/K	q_i/J	$1/F_i$	T_{tp}/K
331.91[a]	3.764	8.00	332.00	331.94	3.764	7.00	332.03
331.95[a]	3.764	4.00		331.96	3.774	3.50	
331.97[a]	3.764	2.67		331.97	3.764	2.33	
331.97[a]	3.775	2.00		331.98	3.764	1.75	
331.98[a]	3.764	1.60		331.98	3.763	1.40	
331.99[a]	3.764	1.33		331.98	3.764	1.17	
331.99	3.764	1.14		331.99	3.764	1.00	
332.00	3.764	1					

exp. 2				exp. 4			
T_i/K	q_i/J	$1/F_i$	T_{tp}/K	T_i/K	q_i/J	$1/F_i$	T_{tp}/K
331.93	3.764	7.00	332.03	331.92	5.015	8.00	332.03
331.95	3.764	3.50		331.94	5.015	4.00	
331.97	3.764	2.33		331.95	5.015	2.67	
331.97	3.775	1.75		331.96	5.015	2.00	
331.98	3.764	1.40		331.97	5.027	1.60	
331.98	3.764	1.17		331.97	5.016	1.33	
331.99	3.764	1.00		331.97	5.015	1.14	
				331.98	5.015	1.00	

[a] The T_i and $1/F_i$ values were used for the calculation of N_2 and T_{tp} in the range of $1/F_i$ from (1.3 to 10) according to the Aleksandrov recommendation.[34]

Table 2. Comparison of the Triple-Point Temperature, T_{tp}, and the Purity, N_1, of DPhA Obtained by Different Methods

method	T_{tp}/K	purity mole fraction
Rossini et al.[32]	332.0 ± 0.01	0.9998 ± 0.0001
Smit−Aleksandrov[35,36]		0.9999 ± 0.0003
Mastrangelo−Dornte[33]	332.03 ± 0.01	0.9986 ± 0.0001
recommended	332.02 ± 0.02	mean 0.9994 ± 0.0004

limits $0 < k < 1$, shows that impurities are near by nature to the main component of the sample under study.

The N_2 and T_{tp} values were calculated by the Mastrangelo−Dornte method from the equations:

$$T_0 = T_{1.0} + (T_{1.0} - T_{0.5})\frac{1 + k}{1 + k} \qquad (5)$$

$$N_2 = \frac{\Delta_{fus}H_m}{RT_0^2}(T_{1.0} - T_{0.5})\frac{1 + k}{(1 - k)^2} \qquad (6)$$

$$\text{where} \quad k = \frac{2}{3}\left(\frac{T_{1.0} - T_{0.5}}{T_{0.5} - T_{0.25}} - \frac{1}{2}\right) \qquad (7)$$

where temperatures $T_{1.0}$, $T_{0.5}$, and $T_{0.25}$, appropriate to reciprocal values of $1/F_i$, equal 1, 2, and 4, respectively. The k coefficient, obtained in three experiments, equals 0.33, which shows the impurities are near by nature to the DPhA.

The mole fraction of impurities, N_2, was also calculated by the Smit−Aleksandrov method using an equation for fusion equilibrium in the binary system:[36]

$$\ln\left(-\frac{dT_i}{d(1/F_i)}\right) = \ln\left\{\frac{N_2}{A_{cr}}(1 - k)^2\right\} - k\ln(1/F_i) \qquad (8)$$

where A_{cr} is a cryoscopic constant and k denotes the coefficient of the impurity distribution. Equation 8 makes it possible to determine k directly from the experimental dependences $T_i = f(1/F_i)$ without resorting to additional independent experiments. By treating T_i and $1/F_i$ data of experiments 2 to 4 by the least-squares method (LSM) using the linear dependence of $\ln[-(dT_i)/(d(1/F_i))]$ on $\ln(1/F_i)$ ($R^2 = 0.9$), the values of $k = -1.3643$ and $\ln\{(N_2/A_{cr})(1 - k)^2\} = -3.6319$ were calculated on the basis of cryoscopic constant $A_{cr} = (2.2953 \pm 0.0092) \cdot 10^{-2}\ K^{-1}$, estimated by Rossini, the mole fraction value of impurities was calculated from eq 4, $N_2 = 0.0001$. The uncertainty of the N_2 calculation is ∼30 %.

Table 2 summarizes the triple-point temperatures, T_{tp}, and the purity of the DPhA sample, N_1, determined by three methods and appropriate recommended values.

As is seen from Table 2, the data on the triple point temperature and purity of the sample agree within ± 0.02 K and ± 0.0004 mole fraction, respectively, that is within error limits for the three considered methods. We cannot explain the smaller N_1 value of the Mastrangelo−Dornte method in comparison with other two methods. The latter gave coincidental N_1 values within errors that verified the Smit−Aleksandrov method. The concave $T_i = f(1/F_i)$ dependence of the latter can be explained by unsettled thermodynamic equilibriums between solid and liquid phases in the calorimeter container.

The enthalpy of fusion, $\Delta_{fus}H_m$, of DPhA was determined calorimetrically based on the total enthalpy absorbed during the fusion with corrections for hypothetic normal heat capacities of the crystal and liquid which the substance could be had in the fusion region and the heat capacity of empty container. The $\Delta_{fus}H_m$ value was calculated from the equation:

$$\Delta_{fus}H_m = \Delta_{tot}H - \Delta H_1 - \Delta H_2 - \Delta H_{emp} \qquad (9)$$

where $\Delta_{tot}H$ is the total enthalpy absorbed in heating the calorimeter from initial temperature $T_1 < T_{tp}$ to final temperature $T_2 > T_{tp}$, ΔH_1 and ΔH_2 are the heating enthalpies calculated by extending the normal heat capacities of the crystal and liquid in the temperature intervals from T_1 to T_{tp} and from T_{tp} to T_2, respectively, and ΔH_{emp} is the enthalpy contribution needed for heating the empty container from T_1 to T_2. The enthalpy of fusion of DPhA is listed in Table 3.

Thermodynamic properties of fusion determined in this work and literature data are listed in Table 4. The T_{fus} temperature determined by DSC in ref 14 is close to the T_{tp} value of adiabatic calorimetry. But the appropriate T_{fus} value of ref 15 deviates from the latter by (3 to 3.5) K. This can be explained by defining the T_{fus} value as the temperature appropriated to a maximum of the heat capacity peak instead of to the onset of the fusion.

Thermodynamic Functions of DPhA in Solid and Liquid States. The heat capacity of DPhA was extrapolated to $T \rightarrow 0$ with the equation:

$$C_{p,m} = A_D \cdot T^3 \qquad (10)$$

Table 3. Molar Enthalpy of Fusion, $\Delta_{fus}H_m$, of DPhA Calculated by Equation 9[a]

	T_1	T_2	$\Delta_{tot}H$	ΔH_1	ΔH_2	ΔH_{emp}	$\Delta_{fus}H_m$
n[b]	K	K	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$
1	302.99	358.96	83789	6930	8269	47538	21053
2	307.74	363.23	83778	5836	9596	47310	21036
3	304.81	360.61	83787	6512	8781	47463	21030
							mean 21040 ± 100[c]

[a] Meanings of the symbols T_1, T_2, $\Delta_{tot}H$, ΔH_{emp}, ΔH_1, and ΔH_2 are given in the text under eq 9. [b] n is the number of the experiment. [c] The uncertainties of the fusion enthalpies are appropriate to the 95 % confidence interval.

Table 4. Triple-Point, T_{tp}, and Fusion, T_{fus}, Temperatures, Enthalpy and Entropy of Fusion, $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$, Cryoscopic Constants, A_{cr} and B_{cr}, and Purity, N_1, of DPhA Determined by Adiabatic Calorimetry, AC, and DSC

property	AC	DSC
$T_{tp(fus)}/K$	332.02 ± 0.02	331.5 ± 0.2[14] 335.0[15]
$\Delta_{fus}H_m/kJ\cdot mol^{-1}$	21.04 ± 0.10	20.0 ± 0.1[14] 20.5[10] 21.5 ± 0.5[15]
$\Delta_{fus}H_m(298K)^a/kJ\cdot mol^{-1}$	20.07 ± 0.20	
$\Delta_{fus}S_m/J\cdot K^{-1}\cdot mol^{-1}$	63.37 ± 0.24	
$A_{cr}\cdot 10^2/K^{-1}$	2.296 ± 0.023	
$B_{cr}\cdot 10^3/K^{-1}$	1.71 ± 0.02	
N_1/mole fraction	0.9994 ± 0.0004	0.99[14] 0.998[15]

[a] A fusion enthalpy, $\Delta_{fus}H_m(298K)$, was calculated by Kirchhoff's law on the basis of the $\Delta_{fus}H_m(T_{tp})$ value and heat capacity differences of liquid and crystal at the temperatures 298.15 K and T_{tp}, the $C_{p,m}(l)(298K)$ value evaluated by the Chickos and Acree[37] method.

The coefficient $A_D = (3.569 \pm 0.031)\cdot 10^{-3}\ J\cdot K^{-4}\cdot mol^{-1}$ was calculated by the LSM from $C_{p,m}$ data in the temperature interval from (7.76 to 9.02) K. The root-mean-square (rms) deviation between the calculated and the experimental $C_{p,m}$ values (± 1 %) lies within the limits of experimental errors. The linear regression coefficient equals $R^2 = 0.990$. Thus, the temperature dependence $C_{p,m}(T)$ obeys the Debye cube's law, and $C_{p,m}(T)$ and $S_m^0(T)$ functions equal zero at $T \to 0$ K. The characteristic temperature, $\Theta_D = 79.0$ K, was calculated from the Debye equation

$$C_{p,m} = 3\cdot D(\Theta_D/T) \tag{11}$$

The experimental heat capacities, divided into several intervals, were fitted with polynomials of the following form:

$$C_{p,m} = \sum A_i\left(\frac{T - A_k}{B_k}\right)^i \tag{12}$$

where $(T - A_k)/B_k$ is the normalizing term and i denotes the degree of the polynomial.

The main thermodynamic functions were calculated by integration of the dependences $C_{p,m} = f(T)$ obtained from eqs 10 and 12 for the crystal and liquid states and summing up the values of the enthalpy and entropy changes in the range of fusion.

Table 5. Smoothed Molar Thermodynamic Functions[a] of DPhA

T	$C_{p,m}$	$H_m^0(T) - H_m^0(0)$	$S_m^0(T)$	$-\{G_m^0(T) - H_m^0(T)\}$
K	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
		Crystal		
5	0.44613	0.0005577	0.14871	0.0001859
10	3.3905	0.008200	1.0236	0.002036
20	17.459	0.1081	7.3855	0.03962
25	25.265	0.2147	12.112	0.08808
30	32.682	0.3597	17.379	0.1616
35	39.592	0.5410	22.954	0.2624
40	45.415	0.7538	28.629	0.3913
45	50.829	0.9946	34.295	0.5487
50	55.371	1.261	39.895	0.7342
55	60.865	1.551	45.418	0.9475
60	65.091	1.866	50.911	1.188
65	69.081	2.202	56.283	1.456
70	72.217	2.555	61.516	1.751
75	75.154	2.923	66.597	2.071
80	77.649	3.305	71.522	2.417
85	80.258	3.637	75.533	2.783
90	82.961	4.045	80.196	3.172
95	85.787	4.467	84.757	3.585
100	88.697	4.903	89.231	4.020
110	94.562	5.820	97.960	4.956
120	100.39	6.794	106.44	5.978
130	106.33	7.828	114.71	7.084
140	112.50	8.922	122.81	8.272
150	118.79	10.08	130.79	9.540
160	125.14	11.30	138.66	10.89
170	131.53	12.58	146.43	12.31
180	138.00	13.93	154.13	13.82
190	144.57	15.34	161.77	15.40
200	151.06	16.82	169.36	17.05
210	157.57	18.36	176.88	18.78
220	164.63	19.97	184.37	20.59
230	171.85	21.66	191.85	22.47
240	179.11	23.41	199.32	24.43
250	186.45	25.24	206.78	26.46
260	193.93	27.14	214.23	28.56
270	201.56	29.12	221.70	30.74
280	209.29	31.17	229.17	32.99
290	216.99	33.30	236.64	35.32
298.15	223.14 ± 0.45	35.10 ± 0.12	242.74 ± 0.97	37.28 ± 0.45
300	224.51	35.51	244.13	37.73
310	231.76	37.79	251.61	40.21
320	238.87	40.15	259.08	42.76
330	245.96	42.57	266.54	45.39
332.03	247.40	43.07	268.05	45.93
		Liquid		
332.03	302.00	64.11	331.42	45.93
340	303.79	66.52	338.61	48.60
350	306.04	69.57	347.44	52.03

Table 5. Continued

T	$C_{p,\mathrm{m}}$	$H^0_\mathrm{m}(T) - H^0_\mathrm{m}(0)$	$S^0_\mathrm{m}(T)$	$-\{G^0_\mathrm{m}(T) - H^0_\mathrm{m}(T)\}$
K	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\mathrm{kJ\cdot mol^{-1}}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$\mathrm{kJ\cdot mol^{-1}}$
360	308.41	72.65	356.10	55.55
370	309.93	75.74	364.57	59.15

[a] The uncertainties of the experimental heat capacities correspond to the 95 % confidence interval (Supporting Information).

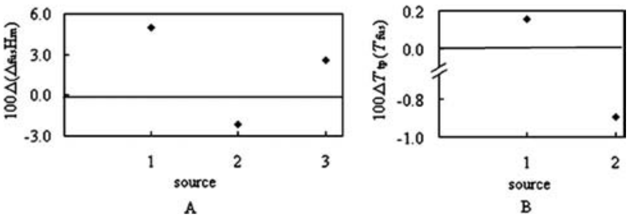

Figure 2. Relative deviations of fusion enthalpy (A) and triple point and fusion temperatures (B) of DPhA, investigated in this work from appropriate literature data of: 1, Diogo et al.;[14] 2, Steele et al.;[15] 3, Chickos et al.[10]

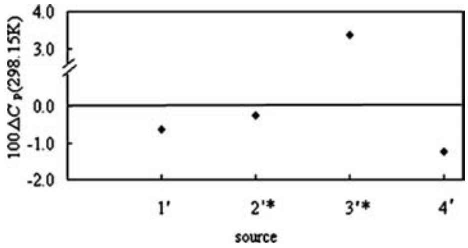

Figure 3. Relative deviations of the heat capacity of crystalline DPhA at 298.15 K from literature data: 1′, Saito et al.;[18] 2′, Steele et al.;[15] 3′, Kurbatov;[19] 4′, Smith and Andrews.[20] *Values of $C_{p,\mathrm{m}}$(298.15K) were evaluated by extending experimental heat capacities to T = 298.15 K.

Smoothed values of $C_{p,\mathrm{m}}(T)$ and thermodynamic functions $H^0_\mathrm{m}(T) - H^0_\mathrm{m}(0)$, $S^0_\mathrm{m}(T)$, and $\{G^0_\mathrm{m}(T) - H^0_\mathrm{m}(T)\}$are listed in Table 5 for the whole temperature interval studied.

■ THERMODYNAMIC CALCULATION AND DISCUSSION

Comparison with Literature Values. The literature data on the enthalpy of fusion at T = 298.15 K, the triple-point or fusion temperatures, and heat capacity of DPhA are compared with appropriate values of this work. Relative deviations of fusion enthalpy, $\Delta(\Delta_\mathrm{fus}H_\mathrm{m})$, temperatures, $\Delta T_\mathrm{tp}(T_\mathrm{fus})$, and heat capacity, ΔC_p(298.15K), of DPhA at T = 298.15 K from literature data are presented in Figures 2 and 3, respectively.

The zero lines in all of the graphs are attributed to our data. The main part of the literature data $C_{p,m}$, T_fus, and $\Delta_\mathrm{fus}H_\mathrm{m}$ values were obtained by the DSC method. As is seen from Figure 3, the heat capacity of DPhA measured in ref 15 agrees within error limits with the $C_{p,\mathrm{m}}$ values of this work. The fusion temperature from ref 14 is lower than our T_tp value by 0.16 % (0.52 K) which is beyond the experimental error limits. Deviations of thermodynamic values of refs 10, 14, 15, and 18 to 20 from our data and those ones between the literature data themselves are great. This can be explained by less accuracy of experimental techniques in references under consideration compared with adiabatic calorimetry in this work.

The absolute entropy of DPhA S^0_m(298.15K) = 245.07 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ obtained by Saito et al.[18] is by 2.3 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (1 %) higher than our value (Table 5), which can be explained by not having a sufficient degree of crystallinity for the sample in ref 18.

Table 6. Enthalpy and Entropy of Sublimation, Entropy of Ideal Gas Compression, R ln{p(298.15 K)/101.325}, the Ideal Gas Entropy, Changes of Enthalpy, and Gibbs Free Energy of DPhA at T = 298.15 K

property	values
$\Delta_\mathrm{sub}H_\mathrm{m}(T)/\mathrm{kJ\cdot mol^{-1}}$	$95.1 \pm 1.1^{a,13}$ 95.7 ± 3.1^{14}
$\Delta_\mathrm{sub}S_\mathrm{m}(T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$319 \pm 3.7^{a,13}$
$R\ln\{p(298.15\ \mathrm{K})/101.325\}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	−114.5
$S^0_\mathrm{m}(T)(\mathrm{g})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	447.3 ± 4
$H^0_\mathrm{m}(T) - H^0_\mathrm{m}(0)(\mathrm{g})/\mathrm{kJ\cdot mol^{-1}}$	130.2 ± 1.6
$-\{G^0_\mathrm{m}(T) - H^0_\mathrm{m}(T)\}(\mathrm{g})/\mathrm{kJ\cdot mol^{-1}}$	3.16 ± 0.14

[a] The $\Delta_\mathrm{sub}H_\mathrm{m}$ and $\Delta_\mathrm{sub}S_\mathrm{m}$ values having less uncertainties were used for the calculation of main thermodynamic functions.

Calculation of the Ideal Gas Thermodynamic Functions. Changes of the ideal gas entropy, enthalpy, and Gibbs energy at T = 298.15 K were obtained on the basis of appropriate functions in condensed states (Table 5), literature data on the enthalpy and entropy of sublimation[14] (Table 6), and the entropy of ideal gas compression from {p(298.15 K) to 101.325} kPa, R ln{p(298.15 K)/101.325}. The compression entropy (Table 6) was calculated by the use of the p(298.27 K) = $0.1056\cdot 10^{-3}$ kPa value evaluated as an average from three experiments for the vapor-pressure measurements over the crystal in ref 14.

Theoretical Calculations. Verification of the reliability of the ideal gas absolute entropy obtained by the third law of thermodynamics and determination of the ideal gas heat capacity in dependence on temperature were carried out by the additive principle[38,39] and statistical thermodynamic method coupled with quantum mechanical calculations using density functional theory (DFT) on the B3LYP/cc-pVTZ level.

Theoretical calculation of the entropy requires the calculation of the corrections for the symmetry and optical isomerism of the molecule because these parameters can alter with changing the structure of the molecules in the series of compounds. Therefore, the calculation of the absolute entropy, S^0_m, started with the determination of so-called intrinsic entropy, $S^0_\mathrm{m,int}$, which made it possible to exclude an influence of the rotary components, depending on the symmetry and optical activity of the molecule:

$$S^0_\mathrm{m,\,int} = S^0_\mathrm{m} + R\ln(\sigma_\mathrm{tot}/n) \tag{13}$$

where σ_tot and n denote a total number of the symmetry and a number of the optical isomers. The total symmetry of the molecule DPhA was calculated as $\sigma_\mathrm{tot} = \sigma_\mathrm{ex}\cdot\sigma_\mathrm{in}$, where σ_ex = 4 denotes the number of symmetry of the external rotation of the molecule, as a whole, and σ_in is the number of the internal rotation for two phenyl groups, $\sigma_\mathrm{tot} = 4\cdot 4 = 16$. The entropy at T = 298.15 K, S^0_m = 448.09 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, was calculated from eq 13 using the $S^0_\mathrm{m,int}$ = 471.14 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ value obtained by summing up the appropriate group values[38] and the $R\ln(\sigma_\mathrm{tot}/n)$ = 23.05 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ correction. But using the group values of

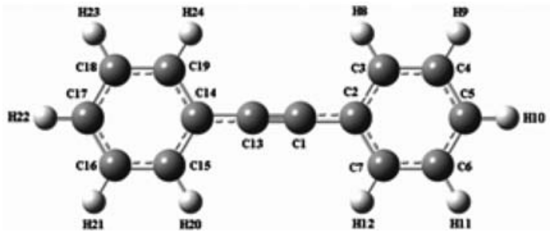

Figure 4. Labeling of the atoms for DPhA.

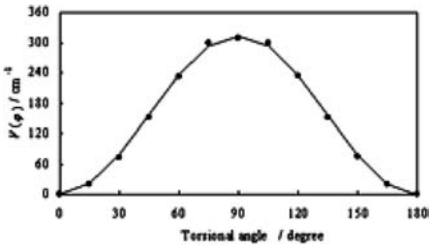

Figure 5. Torsional potential function of DPhA plotted against the angle φ(C3−C2−C14−C15) of reorientation of the phenyl rings relative to the C≡C triple bond. Points are energy values calculated at the B3LYP/cc-pVTZ level of DFT; the solid line is an approximation of these points by the potential of eq 14.

Saabe et al.[39] gives the understated value $S_m^0 = 438.09\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ that can be explained by incorrect contributions of $C_t-(C_B)$ and $C_B-(C_t)$ groups in ref 36 for the C_t-atom, connected with the C_B-atom of the benzyl ring and the 3-fold bond and the C_B-atom connected with the C_t-atom.

Thermodynamic functions $S_m^0(g)(T)$ and $C_{p,m}{}^0(g)(T)$ were calculated by standard formulas of statistical thermodynamics within the framework of the rigid-rotor harmonic-oscillator (RRHO). The DFT calculations of the molecular constants (structural parameters, vibrational frequencies, and potential function of internal rotation) were performed by the Gaussian 03 software package.[40] The conformation of DPhA was determined as a result of complete optimization of the molecule geometry by the B3LYP/cc-pVTZ method. One-dimensional scanning was performed for the potential surface depending on a torsional angle φ(C3−C2−C14−C15) (Figure 4) characterizing internal reorientation of phenyl rings relative to the 3-fold C≡C bond of a stable conformer having the coplanar configuration of D_{2h} symmetry. In doing so, changes of the potential energy were determined for the torsional angle from 0° to 180° at 30° increments and allowing all other structural parameters to be optimized.

The calculated energy values, V_n, were fitted to the torsional potential of a cosine-based Fourier function:

$$V(\varphi) = \frac{1}{2}\sum_n V_n(1 - \cos n) \qquad (14)$$

where φ is the torsional angle.

Figure 5 represents a line of potential energy as a function of the torsional angle φ(C3−C2−C14−C15). The minimum of a potential curve appropriates to the stable conformer. A rather long distance between two phenyl rings promotes considerable decrease of a steric repulsing between ortho hydrogen atoms of phenyl rings and the 3-fold bond of the central carbon atoms. This results in a very plain potential curve. A torsional barrier caused reorientation of phenyl rings relative to the C≡C bond is equal to $(309\cdot 10^2)\ \mathrm{m^{-1}}$.

A spectroscopic and quantum mechanical study of the torsional motion in DPhA was carried out in refs 41 and 42. The torsional barrier was found to equal (202 to 301) $10^2\ \mathrm{m^{-1}}$, but the thermodynamic functions in these references were not calculated.

Theoretical values of vibrational frequencies were scaled by using a 0.965 coefficient according to the recommendation in ref 43 for all modes. Vibrational frequencies and moments of inertia are listed in Table 7.

The $S_m^0(g)(T)$ and $C_m^0(g)(T)$ functions of DPhA were obtained by an RRHO approximation for all rotation and vibration modes except for pseudointernal reorientation of phenyl rings relative to the C≡C bond. The contributions due to the pseudointernal mode were taken into account by using coefficients ($V_1 = -2.1\cdot 10^2$ and $V_2 = 314.6\cdot 10^2$) $\mathrm{m^{-1}}$ of eq 14 instead of low-frequency $\nu = (21\cdot 10^2)\ \mathrm{m^{-1}}$. According to software GaussView 4.1, the low frequencies, $(44 \text{ and } 49)\cdot 10^2\ \mathrm{m^{-1}}$, are responsible for large amplitudes of internal reorientations of phenyl rings in plane and out-of-plane relative to the 3-fold C≡C bond, respectively, but a technique of their account was not elaborated to the best of our knowledge. Table 8 lists the ideal gas absolute entropies and heat capacities computed by statistical thermodynamics on the basis of DFT calculations and by the additive Benson's method[38] and the entropies obtained by the third law of thermodynamics.

The $S_m^0(g)(298\mathrm{K})$ values obtained by DFT calculation both with and without taking into consideration the pseudointernal reorientation are close to each other. Thus, the absolute entropies at $T = 298.15$ K determined by three independent methods agree within error limits that confirms their reliability. The $S_m^0(g)(298\mathrm{K})$ value of ref 25 obtained by the AM1 method conforms to the DFT value of this work within 1.2 %. The $S_m^0(g)$ values at $T > 300$ K are larger than those at $T = 298.15$ K, resulting in a disagreement in values. This can be explained by larger uncertainties of the $\Delta_{\mathrm{vap}}S$ value and the entropy of compression due to the wide extrapolation interval of the vapor pressure over liquid from the initial temperature of 439.6 K of pT parameters[14] to the temperatures (332.02 and 350) K. The ideal gas heat capacities obtained by DFT and additive methods systematically disagree within ~3.5 %. But a choice of reliable $C_{p,m}(g)(T)$ values is significant for many thermodynamic calculations. In particular the ideal gas heat capacities were employed in a series of our papers[44−46] for extending the precise vapor-pressure data of the moderate region (1 to 2) ≤ (p/kPa) ≤ (100 to 200) toward the triple-point temperatures, where experimental determinations are very seldom carried out because of methodical difficulties. Below, this technique will be used for DPhA.

Extrapolation of the Vapor Pressure of DPhA to the Triple Point. The Wagner equation[16,17] (eq 1) of the vapor pressure used for fitting the pT parameters of DPhA in the original work[14] is applicable for the entire region of liquid phase from T_{tp} to T_c. The vapor pressure of DPhA at $T_{tp} = 332.02$ K, calculated by eq 1, equals 4.6 Pa. For confirming this value and verifying the reliability of $C_{p,m}{}^0(g) = f(T)$ dependencies obtained by theoretical methods in this work (Table 8), we performed a combined treatment of the vapor pressure and differences of the heat capacities of ideal gas and liquid by a system of two compatible equations:

$$\begin{cases} \ln(p/\langle p\rangle) = A' + B'/T + C'\ln T + D'\cdot T \\ (\Delta C_{p,\mathrm{m}}/2)/R = (1/2)[C_{p,\mathrm{m}}^0(\mathrm{g}) - C_{p,\mathrm{m}}^0(\mathrm{l})]/R = C'/2 + D'\cdot T \end{cases} \qquad (15)$$

Table 7. Symmetry, Products of Moments of Inertia, Vibrational Frequencies of DPhA for the Rigid-Rotor Harmonic-Oscillator Calculation

properties	values
point group	D_{2h}
symmetry number, σ_{ext}	4
number of optical isomers, n	1
products of moments of inertia, $I_A I_B I_C/kg^3 \cdot m^6$	$3599805 \cdot 10^{-138}$
vibration frequencies, $\nu \cdot 10^{-2}/m^{-1}$	21, 44, 49, 136, 150, 252, 276, 394, 398, 399, 462, 510, 531, 549, 555, 615, 620, 684, 685, 692, 752, 753, 827, 828, 829, 906, 907, 954, 954, 974, 974, 982, 983, 1014, 1015, 1064, 1065, 1122, 1144, 1144, 1162, 1164, 1264, 1266, 1293, 1310, 1311, 1426, 1428, 1468, 1485, 1552, 1553, 1580, 1588, 2221, 3056, 3056, 3064, 3064, 3075, 3075, 3082, 3082, 3086, 3086

Table 8. Comparison of the Ideal Gas Entropies $S^0_m(g)(T)$ of DPhA Obtained on the Basis of Experimental Data and by DFT and Additive Calculations and Heat Capacities, $C_{p,m}{}^0(g)(T)$, Computed by Two Last Methods at Different Temperatures

T	$S^0_m(g)(T)/J \cdot K^{-1} \cdot mol^{-1}$			$C_{p,m}{}^0(g)(T)/J \cdot K^{-1} \cdot mol^{-1}$	
K	third law	DFT calculations	additive calculations	DFT calculations	additive calculations
150		349.07		103.47	
200		382.53		131.22	
298.15	447.2 ± 4	446.44	448.09	193.88	187.18
		445.76[a]			
300		447.64		195.07	188.30
332.02	464.6 ± 8	468.46		215.51	207.67
350	476 ± 8	480.11		226.67	218.54
400		512.33		256.09	248.78

[a] Value calculated without taking into account pseudorotation in the molecule.

Table 9. Heat Capacities of DPhA for Liquid and Ideal Gas States in Dependence on the Temperature in Neighborhood of the Triple Point, T_{tp} = 332.02 K

T	$C_{p,m}(l)$	$C_{p,m}{}^0(g)$ [a]	$C_{p,m}{}^0(g)$ [b]
K	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
350.00	305.74	218.54	219.16
351.00	306.06	219.14	219.78
352.00	306.37	219.75	220.41
353.00	306.66	220.35	221.03
354.00	306.95	220.95	221.66
355.00	307.22	221.56	222.28
356.00	307.48	222.16	222.90
357.00	307.73	222.77	223.53
358.00	307.97	223.37	224.15
359.00	308.20	223.98	224.78

[a] The ideal gas heat capacities calculated by the additive Benson's scheme using group additive values of ref 38. [b] The $C_{p,m}{}^0$ values calculated by Benson's scheme with group additive contributions of Saabe et al.[39]

Table 10. Thermodynamic Properties of Vaporization for DPhA: Vapor Pressure at T_{tp} = 332.02 K, $p(T_{tp})$, and Enthalpy of Vaporization, $\Delta_{vap}H^0_m$(298K), Calculated by Equations 1, 2, 15, and 16

properties	equations	
	1, 2	15, 16
$p(T_{tp})$/Pa	4.6	5.0[a] 4.8[b]
$\Delta_{vap}H^0_m(298K)/kJ \cdot mol^{-1}$	75.9 ± 3.1	74.9 ± 1.1[a] 75.3 ± 1.1[b] mean 75.1 ± 1.1

[a] The ideal gas heat capacities used in $p(T_{tp})$ calculation were obtained by the additive Benson's scheme.[38] [b] Appropriate heat capacities were calculated by Benson's scheme using the group additive values obtained by Saabe et al.[39]

where the $\Delta C_{p,m}$ value is the second derivative of the vapor pressure by the temperature, $\langle p \rangle$ is the vapor pressure at the mean temperature $\langle T \rangle$ of the experimental pT interval, and A', B', C', and D' are the coefficients of the combined treatment of the vapor pressure and the heat capacities.

As was shown in refs 44 to 46, this method affords the increase of accuracy of the approximating coefficients of the system in eq 15 by nearly one order. This provides more exact calculations of the vaporization enthalpy when extending the pT parameters to the temperature intervals ≥ 100 K.

Mathematical processing of the pT parameters was conducted by the LSM method using vapor pressures[15] in the temperature range from (439.627 to 508.807) K and the heat capacities of ideal gas calculated by Benson's scheme[38,39] and liquid in the temperature interval from (350 to 359) K (Table 9). Experimental $C_{p,m}(l)$ values were used at the temperatures in the neighborhood of the triple point, where a linear dependence of heat capacity on the temperature took place.

The enthalpy of vaporization was calculated by the formula:[47]

$$\Delta_{vap}H_m/\Delta Z = R\{-B' + CT' + D'T^2\} \qquad (16)$$

where ΔZ is the difference between compression factors of the gas and liquid.

The $p(T_{tp})$ and $\Delta_{vap}H^0_m$(298K) values derived from the system of eqs 15 and 16 are compared in Table 10 with those of Wagner eq 1 and eq 2. A difference between $p(T_{tp})$ values calculated by eqs 1 and 15 Δp = 0.4 Pa is within dispersions, $\sigma = p_{exp} - p_{Wagner}$, making up from (0.3 to 1.1) Pa for DPhA.[15] The values of the enthalpy of vaporization reported by Steele et al.[15]

Table 11. Thermodynamic Functions of Formation for DPhA in the Crystal and Ideal Gas States at T = 298.15 K

$\Delta_f S_m^0(\text{cr})$	$\Delta_f H_m^0(\text{cr})$	$\Delta_f G_m^0(\text{cr})$	$\Delta_f S_m^0(\text{g})$	$\Delta_f H_m^0(\text{g})$	$\Delta_f G_m^0(\text{g})$
$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
−490.3 ± 1.0	312.4 ± 1.1[15]	458.58 ± 1.1	−285.9 ± 4.0	407.5 ± 1.6[13]	492.7 ± 2.0

and calculated from eq 16 of this work are in good agreement, by 1.2 %. But the enthalpy of vaporization, calculated by eq 16 on the basis of $C_{p,m}(\text{g}) = f(T)$ values of the DFT method is less agreeable, $\Delta_{\text{vap}}H_m^0 = 73.6\ \text{kJ}\cdot\text{mol}^{-1}$. Despite that deviations of this value from those given in Table 10 are within error limits, (1.4 to 2.3) $\text{kJ}\cdot\text{mol}^{-1}$, we consider this deviation as indirect confirmation of unreliable $C_{p,m}(\text{g})$ values obtained by the DFT method.

Obtained $\Delta_{\text{vap}}H_m^0(298\text{K}) = (75.1 \pm 1.1)\ \text{kJ}\cdot\text{mol}^{-1}$ and the enthalpy of fusion $\Delta_{\text{fus}}H_m(298\text{K}) = (20.07 \pm 0.20)\ \text{kJ}\cdot\text{mol}^{-1}$ (Table 4) were used for calculation of the enthalpy of sublimation, $\Delta_{\text{sub}}H_m(298\text{K}) = (95.2 \pm 2.4)\ \text{kJ}\cdot\text{mol}^{-1}$ that agrees within errors with the appropriate experimental[14] and calculated[15] values (Table 6).

Table 11 lists thermodynamic functions of DPhA formation in the crystal and ideal gas states at T = 298.15 K. The standard Gibbs free energy of formation, $\Delta_f G_m^0$, was calculated from the formula:

$$\Delta_f G_m^0 = \Delta_f H_m^0 - T\cdot\Delta_f S_m^0 \tag{17}$$

using the experimental value of absolute entropy obtained by the third law of thermodynamics (Table 8). The ideal gas enthalpy of formation $\Delta_f H_m^0(\text{g}) = (407.5 \pm 1.6)\ \text{kJ}\cdot\text{mol}^{-1}$ was obtained on the basis of the enthalpy of formation in a solid state, $\Delta_f H_m^0(\text{cr})$,[21] and enthalpy of sublimation of DPhA.[14] The function $\Delta_f S_m^0$ in eq 17 is the difference between the values of absolute entropies of the final and initial products in the reaction:

$$14\text{C}(\text{cr}) + 5\text{H}_2(\text{g}) = \text{C}_{14}\text{H}_{10}(\text{cr}) \tag{18}$$

The absolute entropies of the initial products were taken from CODATA.[48]

A group additivity value $\Delta S(\text{cr})(298\text{K})$ for the calculation of absolute entropy by Benson's scheme[22] was obtained for the C_t-atom, connected with the 3-fold bond and the C_B-atom of benzyl ring, $\text{C}_t-(\text{C}_B)$. The values of $\Delta S(\text{cr})(298\text{K}) = (17.62 \pm 0.20)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was calculated for the first time, to the best of our knowledge, on the basis of the absolute entropy of crystalline DPhA $S(\text{cr})(298\text{K}) = (242.74 \pm 0.97)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (Table 5) and the group additivity contributions $\Delta S'(\text{cr})(298\text{K})$ for $\text{C}_B-(\text{C}_t)-(\text{C}_B)_2$ and $\text{C}_B-(\text{H})-(\text{C}_B)_2$ atoms equal (−10 and 22.75) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively.

CONCLUSION

The low-temperature heat capacity of DPhA was measured in a wide temperature region from (8 to 371) K. The temperature, enthalpy, and entropy of fusion were determined. The purity of the substance obtained by three methods was (0.9994 ± 0.0004) mole fraction. An absolute entropy by the third law of thermodynamics, the changes of the enthalpy, $H_m^0(T) - H_m^0(0)$, and free energy, $\{G_m^0(T) - H_m^0(T)\}$, were derived for condensed states in the temperature interval studied and for the ideal gas at T = 298.15 K.

For verification of the reliability and thermodynamic consistency of the experimental data, the ideal gas entropy and heat capacity were obtained by the additive principle and statistical thermodynamic method coupled with quantum mechanical calculations on the level B3LYP/cc-pVTZ of the DFT theory. The absolute entropies at T = 298.15 K, determined by three independent methods, agree within error limits that confirms the reliability of these values, obtained by experimental and theoretical methods. A systematic deviation within ~3.5 % of the ideal gas heat capacity obtained by the DFT calculation from those ones of the additive principle can be explained by internal reorientations of phenyl rings in-plane and out-of-plane relative to the 3-fold C≡C bond. To the best of our knowledge, an account of the technique of these reorientations is not considered.

The temperature dependence of $C_{p,m}{}^0(\text{g}) = f(T)$ obtained by the additive principle was used for extending the vapor pressure[15] of DPhA determined in the temperature interval $439.6 \le (T/\text{K}) \le 517.2$ toward the triple point T_{tp} = 332.02 K. Extrapolation of the data was performed by combined fitting the pT parameters together with the low-temperature differences $\Delta C_{p,m} = C_{p,m}(\text{g}) - C_{p,m}(\text{l})$. It should be noted that using the $C_{p,m}{}^0(\text{g}) = f(T)$ dependence obtained by the DFT method results in the understated value of $\Delta_{\text{vap}}H_m^0$, which we consider as indirect confirmation of an unreliable $C_{p,m}{}^0(g)$ values of the DFT method.

On the basis of obtained data the important thermodynamic values were derived: the entropy and free Gibbs energy of formation for DPhA in crystal and ideal gas states at T = 298.15 K, and the value $\Delta S(\text{cr})(298\text{K}) = 17.62\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for additive group $\text{C}_t-(\text{C}_B)$ of the C_t-atom, connected with the 3-fold bond and the C_B-atom of benzyl ring. This additive group value is needed for computing the entropy of phenyl derivatives of acetylene by Benson's scheme[22] for the crystal state at T = 298.15 K.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Table of the experimental heat capacities of DPhA. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail address: varusch@thermo.chem.msu.ru. Tel.: 07 (495) 939 53 96. Fax: 07 (495) 932 88 46.

Funding Sources

This work was financially supported by Russian Foundation for Basic Research (Project No. 09-08-00014-a).

ACKNOWLEDGMENT

The authors are grateful to O. V. Dorofeeva for providing the Gaussian programs and assistance in quantum-chemical calculations of ideal gas thermodynamic functions.

REFERENCES

(1) Cook, K. S.; Piers, W. E.; McDonald, R. Synthesis and Chemistry of Zwitterionic Tantala-3-boratacyclopentenes: Olefin-like Reactivity of a Borataalkene Ligand. *J. Am. Chem. Soc.* **2002**, *124*, 5411–5418.

(2) Merlet, S.; Birau, M.; Wang, Z. Y. Synthesis and Characterization of Highly Fluorescent Indenofluorenes. *Org. Lett.* **2002**, *4*, 2157–2159.

(3) Dyer, D. J.; Lee, V. Y.; Twieg, R. J. A New Class of Liquid Crystals: Methylene-1,4-Dihydropyridines. *Liq. Cryst.* **1998**, *24*, 271–281.

(4) Yang, D. D.; Scharrer, E.; Yoa, M. V. Synthesis and Phase Behavior of Liquid Crystalline Diphenylacetylene Derivatives Possessing High Clearing Temperatures. *Mol. Cryst. Liq. Cryst.* **2004**, *408*, 21–31.

(5) Horthholary, C.; Coudret, C. An Approach to Long and Unsubstituted Molecular Wires Synthesis of Redox-Active, Cationic Phenylethynyl Oligomers Designed for Self-Assembled Monolayers. *J. Org. Chem.* **2003**, *68*, 2167–2174.

(6) Hess, C. R.; Juda, G. A.; Dooley, D. M.; Amii, R. N.; Hill, M. G.; Winkler, J. R.; Gray, H. B. Gold Electrodes Wired for Coupling with the Deeply Buried Active Site of Arthrobacter globiformis Amine Oxidase. *J. Am. Chem. Soc.* **2003**, *125*, 7156–7157.

(7) Elbing, M.; Ochs, R.; Koentopp, M.; Fischer, M.; Von Hanisch, C.; Weigend, F.; Evers, F.; Weber, H. B.; Mayor, M. A single-molecule diode. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8815–8820.

(8) Merlet, S.; Birau, M.; Wang, Z. W. Synthesis and Characterization of Highly Fluorescent Indenofluorenes. *Org. Lett.* **2002**, *4*, 2157–2159.

(9) Wolf, K. L.; Weghofer, H. Uber sublimationswarmen. *Z. Phys. Chem.* **1938**, *39*, 194–208.

(10) Chickos, J. S.; Annunziata, R.; Ladon, L. H.; Hyman, A. S.; Liebman, J. F. Estimating Heats of Sublimation of Hydrocarbons. A Semiempirical Approach. *J. Org. Chem.* **1986**, *51*, 4311–4314.

(11) Chickos, J. S. In *Molecular Structure and Energetics*; Liebman, J. F.; Greenberg, A., Eds.; VCH Publishers: New York, 1987; Vol. 2, Chapter 3.

(12) Calhorda, M. J.; Carrondo, M. A. A. F. de C. T.; Dias, A. R.; Galváo, A. M.; Garsia, M. H.; Martins, A. M.; Minas da Piedade, M. E.; Pinheiro, C. I.; Romáo, C. C.; Martinho Simóes, J. A.; Veiros, L. F. Syntheses, Electrochemistry, and Bonding of Bis(cyclopentadieny1)-molybdenum Alkyl Complexes. Molecular Structure of Mo(η^5-C_5H_5)$_2$-(C_4H_9)$_2$. Thermochemistry of Mo(η^5-C_5H_5)$_2$$R_2$, and Mo($\eta^5$-$C_5H_5$)$_2$L (R = CH_3, C_2H_5, C_4H_9; L = Ethylene, Diphenylacetylene). *Organometallics* **1991**, *10*, 483–494.

(13) Minas da Piedade, M. E. Ph.D. Thesis, Instituto Superior Técnico, Lisbon, Portugal, 1988.

(14) Diogo, H. P.; Minas da Piedade, M. E.; Fernandes, A. C.; Martinho Simoes, J. A.; Ribeiro da Silva, M. A. V.; Monte, M. J. S. The enthalpy of sublimation of diphenylacetylene from Knudsen effusion studies. *Thermochim. Acta* **1993**, *228*, 15–22.

(15) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguen, A. Measurements of Vapor Pressure, Heat Capacity, and Density along the Saturation Line for ε-Caprolactam, Pyrazine, 1,2-Propanediol, Triethylene Glycol, Phenyl Acetylene, and Diphenyl Acetylene. *J. Chem. Eng. Data* **2002**, *47*, 689–699.

(16) Wagner, W. New Vapor Pressure Measurements for argon and Nitrogen and a New Method for Establishing Rational Vapor Pressure Equations. *Cryogenics* **1973**, *13*, 470–482.

(17) Ambrose, D.; Walton, J. Vapor Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols. *Pure Appl. Chem.* **1989**, *61*, 1395–1403.

(18) Saito, K.; Asahina, M.; Yamamura, Y.; Ikemoto, I. The search for a possible twist phase transition in a biphenyl analogue: heat capacity of crystalline tolane. *J. Phys.: Condens. Matter* **1995**, *7*, 8919–8926.

(19) Kurbatov, V. Ya. Specific heats of hydrocarbons with several noncondensed rings. *Zh. Obshch. Khim.* **1950**, *20*, 1139–1144.

(20) Smith, R. H.; Andrews, D. H. Thermal energy studies. I. Phenyl derivatives of methane, ethane and some related compounds. *J. Am. Chem. Soc.* **1931**, *53*, 3644–3660.

(21) Coops, J.; Hoijtink, G. J.; Kramer, Th. J. E.; Faber, A. C. Thermochemical investigations on arylethynes I. Heats of combustion of some diarylethynes. *Rec. Trav. Chim.* **1953**, *72*, 781–784.

(22) Domalski, E. S.; Hearing, E. D. Estimation of the Thermodynamic Properties of C-H-N-O-S-Halogen Compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805–1159.

(23) Davis, H. E.; Allinger, N. L.; Rogers, D. W. Enthalpies of Hydrogenation of Phenylalkynes: Indirect Determination of the Enthalpy of Formation of Diphenylcyclopropenone. *J. Org. Chem.* **1985**, *50*, 3601–3604.

(24) Benson, S. W.; Garland, L. J. Thermochemistry of Acetylenes and Polyacetylenes. *J. Phys. Chem.* **1991**, *95*, 4915–4918.

(25) Palafox, M. A. Vibration Spectra and Structure of Diphenylacetylene. *Spectrosc. Lett.* **1996**, *29*, 241–266.

(26) Dorofeeva, O. V. Unpublished results. Thermocenter of Russian Academy of Science, Moscow, 1997. http://webbook.nist.gov

(27) Varushchenko, R. M.; Druzhinina, A. I.; Sorkin, E. L. Low-temperature heat capacity of 1-bromoperfluorooctane. *J. Chem. Thermodyn.* **1997**, *29*, 623–637.

(28) Krol, O. V.; Druzhinina, A. I.; Varushchenko, R. M.; Dorofeeva, O. V.; Reshetova, M. D.; Borisova, N. E. The heat capacities and thermodynamic functions of some derivatives of ferrocene. *J. Chem. Thermodyn.* **2008**, *40*, 549–557.

(29) Furukava, G. T.; Saba, W. G.; Reily, M. L. Critical analysis of the heat capacity data of the literature and evaluation of the thermodynamic properties of copper, silver and gold from 0 to 300 K. *Standard Reference Data Series*; U.S. Government Printing Office: Washington, DC, 1968; Vol. 18.

(30) White, G. K.; Collocott, S. J. Heat capacity of reference materials: Cu and W. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1251–1257.

(31) Stevens, R.; Boerio-Goates, J. Heat capacity of copper on the ITS-90 temperature scale using adiabatic calorimetry. *J. Chem. Thermodyn.* **2004**, *36*, 857–863.

(32) Mair, B. J.; Glasgow, A. R.; Rossini, F. D. Determination of freezing points and amounts of impurity in hydrocarbons from freezing and melting curves. *J. Res. Natl. Bur. Stand. U.S.A.* **1941**, *26*, 591–620.

(33) Mastrangelo, S. V. R.; Dornte, R. W. Solid Solutions Treatment of Calorimetric Purity Data. *J. Am. Chem. Soc.* **1955**, *77*, 6200–6201.

(34) Aleksandrov, Yu. I. *Tochnaya Kriometriya Organicheskih Veshestv* (in Russian); Khimiya: Leningrad, 1975.

(35) Van Wijk, M. F.; Smit, W. M. Impurity determination by thermal analysis. I. The melting curve of gradually frozen sample. *Anal. Chim. Acta* **1960**, *23*, 545–551.

(36) Aleksandrov, Yu. I.; Belyakov, V. I.; Samarina, V. M. Choice of the equations for calculation of the impurity content in the analysis by cryometric method for the binary systems forming solid solutions. *Zh. Anal. Khim.* **1983**, *38*, 1131—1134; In Russian.

(37) Chickos, J. S.; Acree, W. E., Jr. Enthalpies of Vaporization of Oganic and Organometallic Compounds. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519–878.

(38) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(39) Saabe, M. K.; De Vleeschouwer, F.; Reyniers, M. F.; Waroquier, M.; Marin, G. B. First principles based group additive values for the gas phase standard entropy and heat capacity of hydrocarbons and hydrocarbon radicals. *J. Phys. Chem. A* **2008**, *112*, 12235–12251.

(40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.;

Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(41) Okuyama, K.; Hasegawa, T.; Ito, M.; Mikami, N. Electronic spectra of tolane in a supersonic free jet: large-amplitude torsional motion. *J. Phys. Chem.* **1984**, *88*, 1711–1716.

(42) Xu, D.; Cooksy, A. L. Ab initio study of the torsional motional in tolane. *J. Mol. Struct.* **2007**, *815*, 119–125.

(43) Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. Harmonic vibrational frequencies:scaling factors for HF, B3LYP, and MP2 methods in combination with correlation consistent basis sets. *J. Phys. Chem. A* **2004**, *108*, 9213–9217.

(44) Varushchenko, R. M.; Druzhinina, A. I. Low-temperature heat capacity and thermodynamic properties of 1,1,1-trifluoro-2,2-dichloroethane. *Fluid Phase Equilib.* **2002**, *199*, 109–119.

(45) Varushchenko, R. M.; Pashchenko, L. L.; Druzhinina, A. I.; Abramenkov, A. V.; Pimersin, A. A. Thermodynamics of vaporization of some alkyladamantanes. *J. Chem. Thermodyn.* **2001**, *33*, 733–744.

(46) Varushchenko, R. M.; Druzhinina, A. I. Determination of Saturated Vapor Pressure of Organic Substances from the Triple to Critical Point. *High Temp.* **2010**, *48*, 328–335.

(47) Varouchtchenko, R. M.; Droujinina, A. I. Thermodynamics of vaporization of some perfluorotrialkylamines. *J. Chem. Thermodyn.* **1995**, *27*, 355–368.

(48) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

NOTE ADDED AFTER ASAP PUBLICATION

This article posted ASAP on September 30, 2011. Tables 7, 10 and equation 16 have been revised. The correct version posted on October 5, 2011.