Supplementary Material for

The Intramolecular Hydrogen Bond N-H…S in 2,2′-Diaminodiphenyl Disulfide, Experimental and Computational Thermochemistry

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S1. Fusion experiments

$m_{\text{sample}a}$	purity	$T_{\rm fus}$	$\Delta^{\rm l}_{\rm cr} H^{\circ}_{\rm m}(T_{\rm fus})$
mg	mole fraction	K	kJ·mol ⁻¹
	DPDS		
9.5105	0.9998	331.7	27.40
8.7146	0.9999	331.8	27.30
10.5244	0.9999	331.9	28.76
8.9098	0.9999	332.0	28.5
	0.9999 ± 0.0001^b	331.9 ± 0.4^{b}	27.99 ± 1.19^{b}
	2ADPD	os	
5.5903	0.9990	364.4	31.86
5.8847	0.9991	364.5	31.38
5.0539	0.9989	364.5	31.71
4.6746	0.9987	364.7	31.11
	$0.9989 \pm 0.0003~^b$	$364.5 \pm 0.4^{\ b}$	31.52 ± 0.54 ^b
	4ADPD	os	
2.6469	0.9993	349.3	25.73
2.0434	0.9989	349.5	26.87
3.1601	0.9993	349.3	25.08
3.3203	0.9994	349.2	25.38
	0.9992 ± 0.0004 b	349.3 ± 0.4 ^b	25.77 ± 1.25^{b}

Table S1. Purities, fusion temperatures and enthalpies of the diphenyldisulfide (DPDS), 2-aminodiphenyl disulfide (2ADPDS) and 4-aminodiphenyl disulfide (4ADPDS) from DSC determinations, at $p^{\circ}=0.1$ MPa

^aStandard uncertainties $u(m_{\text{sample}})=0.0001$ mg. bExperimental values, uncertainties corresponds to expanded one, which include the contributions from the calibration, was calculated with a coverage factor k=1.96 and confidence level of 0.95, for two tailed normal distribution.

S2. Heat capacity of solid, liquid and gas phases

Ľ	OPDS (cr)]	DPDS (l)	DPDS (g)		
Т	$C_{\rm p}$ (cr) ^a	Т	$C_{\rm p}$ (l) ^a	Т	$C_{\rm p}({\rm g})$	
K	J·mol ⁻¹ ·K ⁻¹	K	J·mol ⁻¹ ·K ⁻¹	K	$\overline{J \cdot mol^{-1} \cdot K^{-1}}$	
258.15	202.8	338.15	333.9	298.15	205.94	
263.15	207.9	343.15	342.3	300.15	207.21	
268.15	212.4	348.15	342.7	310.15	213.52	
273.15	217.5	353.15	343.3	320.15	219.77	
278.15	221.6	358.15	344.1	330.15	225.96	
283.15	226.6	363.15	344.8	340.15	232.07	
288.15	231.2	368.15	346.1	350.15	238.11	
293.15	235.4	373.15	347.2	360.15	244.05	
298.15	241.7	378.15	347.6	370.15	249.90	
303.15	246.9	383.15	348.9	380.15	255.66	
308.15	253.9	388.15	350.3	390.15	261.31	
313.15	260.0	393.15	352.7	400.15	266.86	
318.15	266.2	398.15	355.1	410.15	272.29	
				420.15	277.63	
				430.15	282.85	
				440.15	287.96	
				450.15	292.96	
				460.15	297.85	
$C_{\rm p}({\rm DPDS, cr})/{\rm J}\cdot{\rm mo}$	$h^{-1} \cdot K^{-1} = 243.416 \cdot 1.117 T/K$	$C_{\rm p}({\rm DPDS, l})/{\rm J}\cdot{\rm mo}$	$I^{-1} \cdot K^{-1} = 690.827 \cdot 2.079 \ T/K$	$C_{\rm p}({\rm DPDS, g})/{\rm J}\cdot{\rm m}$	$101^{-1} \cdot K^{-1} = -30.088 + 0.936$	
$+3.735 \cdot 10^{-3} (T/K)^2$; $r^2 = 0.9992$	$+ 3.100 \cdot 10^{-3} (T/K)^2$	$r^2 = 0.9982$	$T/K - 0.484 \cdot 10^{-3}$ (2)	$T/K)^2$; $r^2=1.0$	
24	DPDS (cr)	2		24		
<i>T</i>	$C(cr)^{a}$	T	C (l) ^a	ZA	C(q)	
1		1 1	$C_p(l)$	1 77	$\frac{C_p(g)}{T_{r_p}(g)}$	
<u>K</u>	J·mol ⁻¹ ·K ⁻¹	<u>K</u>	J·mol ⁻¹ ·K ⁻¹	<u>K</u>	J·mol ⁻¹ ·K ⁻¹	
258.15	202.2	3/1.15	430.3	298.15	254.62	
263.15	204.2	3/3.15	431.1	300.15	256.07	
268.15	206.1	3/8.15	431.9	310.15	263.29	
2/3.13	209.1	383.13 200.15	434.0	520.15	270.40	
2/8.15	211.4	388.15 202.15	430.5	550.15 240.15	277.40	
283.13	214.1	393.13	438.4	340.15	284.29	
288.15	217.0	398.15	440.8	350.15	291.07	
293.15	220.3	403.15	442.9	360.15	297.72	

Table S2. Heat capacity values of the solid and liquid phases as a temperature function determined by dsc and estimated by computational calculations B3LYP/cc-pVTZ level..

211	DI DD (01)	<u>2</u> 1		211	DI DD (6)
Т	$C_{\rm p} ({\rm cr})^{-a}$	Т	$C_{\rm p}$ (l) ^a	Т	$C_{\rm p}\left({\rm g}\right)$
K	$J \cdot mol^{-1} \cdot K^{-1}$	K	$J \cdot mol^{-1} \cdot K^{-1}$	K	J·mol ⁻¹ ·K ⁻¹
258.15	202.2	371.15	430.3	298.15	254.62
263.15	204.2	373.15	431.1	300.15	256.07
268.15	206.1	378.15	431.9	310.15	263.29
273.15	209.1	383.15	434.0	320.15	270.40
278.15	211.4	388.15	436.5	330.15	277.40
283.15	214.1	393.15	438.4	340.15	284.29
288.15	217.6	398.15	440.8	350.15	291.07
293.15	220.3	403.15	442.9	360.15	297.72
298.15	223.8	408.15	444.9	370.15	304.25
303.15	227.0	413.15	447.7	380.15	310.66
308.15	231.5	418.15	450.0	390.15	316.94
313.15	235.9	423.15	452.1	400.15	323.09
318.15	240.7			410.15	329.12
323.15	245.9			420.15	335.02
328.15	250.9			430.15	340.79
333.15	255.1			440.15	346.43
338.15	260.0			450.15	351.95
343.15	265.8			460.15	357.35
348.15	270.7				

 $C_{\rm p}(2\text{ADPDS, cr})/ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}=426.360-2.080$ $T/\text{K} + 4.702\cdot10^{-3} (T/\text{K})^2; r^2=0.9995$ $C_{\rm p}(\text{2ADPDS, l})/\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ = 521.478-0.840 T/K + 1.599·10⁻³ (T/K)²; r²=0.9985 $C_{p}(\text{2ADPDS, g}) / J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -$ 19.112+1.102 *T*/K - 0.616 · 10⁻³ (*T*/K)²; r²=1

4A	DPDS (cr)	44	ADPDS (1)	4A	DPDS (g)
Т	$C_{\rm p} ({\rm cr})^{-a}$	Т	$C_{\rm p}$ (l) ^a	Т	$C_{\rm p}({\rm g})$
K	J·mol ⁻¹ ·K ⁻¹	K	$J \cdot mol^{-1} \cdot K^{-1}$	K	J·mol ⁻¹ ·K ⁻¹
258.15	253.5	355.15	419.3	298.15	256.94
263.15	259.8	358.15	420.9	300.15	258.37
268.15	264.5	363.15	423.1	310.15	265.49
273.15	270.9	368.15	425.8	320.15	272.50
278.15	274.6	373.15	428.3	330.15	279.41
283.15	280.1	378.15	429.7	340.15	286.21
288.15	285.1	383.15	432.2	350.15	292.90
293.15	289.0	388.15	435.0	360.15	299.47
298.15	294.0	393.15	437.0	370.15	305.92
303.15	300.2	398.15	440.2	380.15	312.25
308.15	305.5	403.15	442.3	390.15	318.46
313.15	310.3	408.15	444.4	400.15	324.54
318.15	313.9	413.15	447.4	410.15	330.50

323.15	318.2	418.15	450.0	420.15	336.34
328.15	323.9	423.15	452.6	430.15	342.05
333.15	327.4	428.15	453.7	440.15	347.63
		433.15	456.0	450.15	353.10
		438.15	459.0	460.15	358.44
		448.15	463.6		
		453.15	465.4		
		458.15	468.8		
$C_{\rm p}(4\text{ADPDS, cr})/J \cdot T/K - 1.123 \cdot 10^{-3} (T/$	$mol^{-1} \cdot K^{-1} = -96.703 + 1.649$ $K)^2$; $r^2 = 0.9993$	$C_{\rm p}(4{\rm ADPDS}, 1)/{\rm J\cdot m}$ $T/{\rm K} - 0.385 \cdot 10^{-4} (T/{\rm K})^{-1}$	$\text{mol}^{-1} \cdot \text{K}^{-1} = 244.015 + 0.507$ (K) ² ; r ² =0.9992	C _p (4ADPDS, g)/ J· 12.212+1.081 <i>T</i> /K r ² =1	$mol^{-1} \cdot K^{-1} = -$ - 0.599 \cdot 10^{-3} (T/K)^2;

^{*a*} For compounds in solid and liquid phase, the uncertainty corresponds to the expanded uncertainty which include the contribution of the calibration and was calculated with a coverage factor k=2.36 and confidence level of 0.95, for two tailed normal distribution. For solids and liquids uncertainty is $U(C_p, \text{DPDS}, \text{cr})= 0.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $U(C_p, \text{DPDS}, \text{cr})= 0.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $U(C_p, \text{2ADPDS}, \text{cr})= 0.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $U(C_p, \text{4ADPDS}, \text{cr})= 0.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $U(C_p, \text{4ADPDS}, \text{cr})= 0.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $U(C_p, \text{4ADPDS}, \text{cr})= 0.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

S3. Combustion calorimetry

The combustion experiments were performed with an isoperibolic calorimeter of rotary bomb wich has a Parr 1004 C bomb with an internal platinum coating and an internal volume of 0.348 dm³. This equipment was calibrated with benzoic acid (SRM 39 j) supplied by National Institute of Standards & Technology, which has a massic energy of combustion of $(-26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$, eight experiments were performed obtaining a ε (calor) = $(14362.7 \pm 2.2) \text{ J} \cdot \text{K}^{-1}$, where the associated uncertainty corresponds to the standard deviation of the mean which was recently reported.¹

To ensure complete combustion of the samples studied here, it was necessary to use benzoic acid (NIST SRM 39j) as auxiliary material. For each combustion experiment the sample of the diphenyl disulfides in the pellet form was surrounded by benzoic acid and then compressed in such a way that only a pellet of about 1 g was made. A scheme of the distribution of diphenyl disulfides and benzoic acid in the pellet is shown in figure 1. This pellets were placed in a platinum crucible, and to close the electric circuit, a platinum wire and a cotton thread were used. The specific energy of the cotton is $\Delta_c u^\circ = -(16.9452 \pm 0.0042) \text{ kJ} \cdot \text{g}^{-1}$ and has an empirical formula of $\text{CH}_{1.742}\text{O}_{0.921}$.^{2, 3} The masses of the platinum and cotton threads, the crucible and the samples were measured on a Sartorius ME 215S balance (sensitivity, $\pm 10^{-5}$ g) and the apparent mass to mass correction was applied.

All experiments were carried out in an atmosphere of 3.04 MPa of high purity oxygen (mass fraction = 0.99999) and in the presence of 10 cm³ of deionized water. The air contained in the combustion bomb was not evacuated, as is usually the case in combustion experiments of sulfur compounds. The combustion bomb was placed in the calorimeter's cuvette, which contained 2700 g of distilled water, which was weighted on a Sartorius BP 12000-S balance (sensitivity of $\pm 10^{-1}$ g). The starting temperature of the experiments was selected in such a way that the final temperature was as close as possible to 298.15 K, and the energy required to start the combustion reaction was supplied by a Parr 2901 ignition unit. To measure temperature changes during the combustion experiments, a Hard Scientific 5610 thermistor (calibrated over a temperature range of (273.15 to 373.15) K was placed inside the calorimeter's cuvette. The thermistor was coupled to an HP 34420 A digital multimeter (sensitivity, 10^{-6} k Ω). Resistance values were transformed to temperature values using an adjustment equation. The rotation of the combustion bomb was started 4 minutes after ignition and continued for the remainder of the experiment. In this manner, the heat generated by the rotation of the bomb was included in the correction for agitation and thermal leakage of the calorimeter.²⁰ The acid solution produced after the combustion experiment was transferred to a flask together with the rinsing water and afored with distilled water to a volume of 100 cm³. From this solution, aliquots were taken and titrated with a standard sodium hydroxide solution. The acid concentration obtained with these experiments corresponds to the total acidity. The amount of sulfuric acid is calculated from the stoichiometry of the reaction and the initial mass of the compound, considering the fact that 99.5 to 100 percent of the sulfur converts to sulfuric acid.⁴ The amount of nitric acid is calculated as the difference between the values of the total acidity and the amount of sulfuric acid calculated by stoichiometry. This procedure has already been used in previous work and its validity has been proven.^{1,5}

The corrected temperature increase obtained during the experiments was calculated by the Regnault-Pfaundler method.⁶ For these calculations the specific energy pressure coefficient, $(\partial u/\partial p)_T$ a T = 298.15 K, was assumed to be $-0.2 \text{ J} \cdot \text{g}^{-1} \cdot \text{MPa}^{-1}$, which is a typical value for most organic compounds.⁷ The correction for nitric acid was taken to be $-59.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the standard molar energy of 0.1 mol·dm⁻³ of aqueous HNO₃ from O₂ (g), N₂ (g) and H₂O (l).⁸

The calculation of the specific combustion energy and the reduction to the standard state was performed for each experiment as described by Hubbard et al.⁹ with a Computer program developed in our laboratory, which has been used previously.¹ The apparent mass correction for the effect of air buoyancy was applied.

The results of the combustion experiments for the three compounds studied are shown in the tables S3, S4 and S5.

The internal energy associated to the isothermal bomb process $\Delta_{IBP}U$ was calculated as:

$$\Delta_{\text{IBP}}U = \varepsilon(\text{calor})(T_i - T_f + \Delta T_{\text{corr}}) + \varepsilon^1(\text{cont})(T_i - 298.15) + \varepsilon^1(\text{cont})(298.15 - T_f + \Delta T_{\text{corr}}) + \Delta_{\text{ign}}U$$
(1)

Where $T_i ext{ y } T_f$ are initial and final temperature of principal period respectively, ΔT_{corr} , correction term, $\varepsilon^{i}(\text{cont})$ and $\varepsilon^{f}(\text{cont})$ are initial and final energy equivalent of the bomb respectively and $\Delta_{\text{ing}}U$ is ignition energy.

And mass combustion energy of the compound was calculated as:

 $\Delta_{c}u^{\circ}(\text{compound}) = [\Delta_{\text{IBP}}U + \Delta_{\text{dec}}U(\text{HNO}_{3}) + \Delta_{\Sigma}U - m\Delta_{c}u^{\circ}(\text{cotton}) - m\Delta_{c}u^{\circ}(\text{benzoic acid})]/m(\text{compound}).$ (2)

Where $\Delta U(\text{HNO}_3)$ is the decomposition energy of nitric acid; $\Delta_{\Sigma} U$ is the correction to the standard states, which includes the dilution energy of sulfuric acid and *m*(compound) is the mass of compound.

Table S3. Experiments of combustion of diphenyl disulfide DPDS at $p^{\circ} = 0.1$ MPa y T = 298.15 K

<i>m</i> (compound)/g	0.44105	0.47087	0.49986	0.48224	0.43449	0.49028	0.55882	0.55300
<i>m</i> (benzoic acid)/g	0.36282	0.35590	0.37331	0.35877	0.34539	0.36277	0.42454	0.40832
<i>m</i> (cotton)/g	0.01997	0.01633	0.01264	0.01199	0.01263	0.01407	0.01531	0.01595
<i>m</i> (platinum)/g	6.15994	6.14704	6.15209	6.15291	6.13769	6.13618	6.15917	6.15381
T_i/K	296.0134	296.2078	296.2085	296.2070	296.2085	296.2074	295.8172	295.8179
$T_{\rm f}/{ m K}$	297.7764	298.0212	298.1156	298.0499	297.9146	298.0797	297.9706	297.9234
$\Delta T_{\rm corr}/{ m K}$	0.0224	0.0168	0.0149	0.0187	0.0208	0.0188	0.0194	0.0205
$\Delta T_{\rm c}/{\rm K}$	1.7406	1.7966	1.8922	1.8242	1.6853	1.8535	2.1340	2.0850
ϵ^{i} (cont.)/kJ·K ⁻¹	0.0534	0.0535	0.0535	0.0535	0.0534	0.0535	0.0536	0.0536
ϵ^{f} (cont.)/kJ·K ⁻¹	0.0539	0.0539	0.0540	0.0539	0.0538	0.0539	0.0541	0.0542
$(-\Delta_{\rm IBP}U)/{\rm kJ}$	25.0883	25.8959	27.2741	26.2938	24.2912	26.7162	30.7601	30.0536
$\Delta U(\text{HNO}_3)/\text{kJ}$	0.0344	0.0711	0.0566	0.0696	0.0461	0.0718	0.1125	0.0334
$\Delta_{ m ing}U/ m kJ$	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042
$\Delta_{\Sigma} U/kJ$	0.0241	0.0247	0.0258	0.0249	0.0233	0.0253	0.0292	0.0282
$(-m\Delta_{\rm c}u^{\circ})$ (cotton)/kJ	0.3384	0.2767	0.2141	0.2031	0.2140	0.2384	0.2594	0.2702
$(-m\Delta_c u^\circ)$ (benzoic acid)/kJ	9.5836	9.4007	9.8606	9.4766	9.1232	9.5823	11.2138	10.7854
$(-\Delta_c u^\circ)$ (compound)/kJ·g ⁻¹	34.2542	34.2402	34.2436	34.2560	34.2576	34.2629	34.2600	34.2430
	<-	$-\Delta_{\rm c} u^{\circ}$ (298.1)	5 K)/kJ \cdot g ⁻¹	$= 34.2522 \pm 0$	0.0031			

m (compound), mass of compound; *m* (benzoic acid), mass of benzoic acid; *m* (cotton), mass of cotton thread; *m* (platinum), mass of platinum; T_i and T_f initial and final temperature of principal period respectively; ΔT_{corr} , correction term; ΔT_c , corrected temperature rise; ε^i (cont) and ε^f (cont) initial and final energy equivalent of the bomb respectively; $-\Delta_{IBP}U$, energy of the isothermal bomb process; $\Delta_{ing}U$, ignition energy; ΔU (HNO₃), decomposition energy of nitric acid; $\Delta_{\Sigma}U$, correction to the standard states, which includes the dilution energy of sulfuric acid and $\Delta_c u^{\circ}$ (compound), mass combustion energy of the compound.

The uncertainties associated with each average value of specific combustion energy is the standard uncertainty for eight experiments for DPDS.

Table S4. Experi	mental results of	f combustion	of 2ADPDS	at $p^{\circ} = 0.1 \text{ M}$	IPa y T = 298	3.15 K.			
<i>m</i> (compound)/g	0.36865	0.36536	0.36008	0.36645	0.35919	0.35647	0.35333		
<i>m</i> (benzoic acid)/g	0.60213	0.60611	0.60215	0.6041	0.61228	0.60617	0.60579		
<i>m</i> (cotton)/g	0.01293	0.01311	0.0123	0.01343	0.01321	0.01222	0.01195		
<i>m</i> (platinum)/g	6.13071	6.1355	6.13227	6.13762	6.13788	6.15278	6.14102		
$T_{\rm i}/{ m K}$	296.2037	296.2067	296.2039	296.2024	296.2053	296.2044	296.2139		
$T_{\rm f}/{ m K}$	298.1394	298.1443	298.1222	298.1381	298.141	298.1221	298.1249		
$\Delta T_{ m corr}/ m K$	0.0143	0.0148	0.0144	0.014	0.016	0.015	0.0164		
$\Delta T_{\rm c}/{\rm K}$	1.9214	1.9228	1.9039	1.9217	1.9197	1.9027	1.8946		
ϵ^{i} (cont.)/kJ·K ⁻¹	0.0535	0.0535	0.0535	0.0535	0.0535	0.0535	0.0535		
ϵ^{f} (cont.)/kJ·K ⁻¹	0.0544	0.0544	0.0543	0.0543	0.0543	0.0543	0.0543		
$(-\Delta_{IBP}U)/kJ$	27.6951	27.7153	27.4428	27.6994	27.6706	27.4255	27.3087		
$\Delta U(\text{HNO}_3)/\text{kJ}$	0.0524	0.0605	0.0753	0.0645	0.0613	0.0637	0.0666		
$\Delta_{ m ing} U / m kJ$	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042		
$\Delta_{\Sigma} U/kJ$	0.0301	0.0303	0.0301	0.0303	0.0304	0.0302	0.0301		
$(-m\Delta_c u^\circ)$ (cotton)/kJ	0.219	0.2221	0.2084	0.2275	0.2238	0.207	0.2024		
$(-m\Delta_c u^\circ)$ (benzoic acid)/kJ	15.9048	16.0097	15.9053	15.9566	16.1728	16.0113	16.0012		
$(-\Delta_c u^\circ)$ (compound)/kJ·g ⁻¹	31.1645	31.1821	31.17	31.1652	31.132	31.176	31.1561		
	$\langle -\Delta_c u^{\circ} (298.15 \text{ K})/\text{kJ} \cdot \text{g}^{-1} \rangle = 31.1637 \pm 0.0062$								

The symbol have the same meaning as in table S3. The uncertainty associated with each average of specific combustion energy is the standard deviation of the mean, which implies a standard uncertainty for seven experiments.

	Table S5. Experimental results	of combustion	n of 4ADPDS	at $p^{\circ} = 0.1 \text{ MI}$	Pa y $T = 298.1$	5 K	
<i>m</i> (compound)/g	0.49496	0.49813	0.50082	0.49241	0.49261	0.50486	0.50124
<i>m</i> (benzoic acid)/g	0.36682	0.40159	0.39817	0.39292	0.40482	0.40232	0.40158
<i>m</i> (cotton)/g	0.01310	0.01308	0.0125	0.01289	0.01323	0.01279	0.01215
<i>m</i> (platinum)/g	6.13157	6.13898	6.13619	6.1388	6.14736	6.14223	6.13832
$T_{\rm i}/{ m K}$	296.2070	296.1081	296.2064	296.2032	296.2071	296.205	296.2081
$T_{\rm f}/{ m K}$	297.9908	297.9604	298.0562	298.0262	298.0519	298.0683	298.0654
$\Delta T_{\rm corr}/{ m K}$	0.0196	0.0189	0.0171	0.0165	0.0164	0.0157	0.0169
$\Delta T_{\rm c}/{ m K}$	1.7642	1.8334	1.8327	1.8065	1.8284	1.8476	1.8404
ϵ^{i} (cont.)/kJ·K ⁻¹	0.0537	0.0537	0.0537	0.0537	0.0537	0.0538	0.0537
ϵ^{f} (cont.)/kJ·K ⁻¹	0.0540	0.0541	0.0541	0.0541	0.0541	0.0541	0.0540
$(-\Delta_{IBP}U)/kJ$	25.4292	26.4267	26.4167	26.039	26.3547	26.6317	26.5277
$\Delta U(\mathrm{HNO}_3)/\mathrm{kJ}$	0.0685	0.061	0.0532	0.0661	0.0662	0.0336	0.0820
$\Delta_{ m ing} U/ m kJ$	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042
$\Delta_{\Sigma} U/kJ$	0.0238	0.0251	0.025	0.0247	0.0251	0.0251	0.0252
$(-m\Delta_c u^\circ)$ (cotton)/kJ	0.2219	0.2216	0.2117	0.2184	0.2241	0.2167	0.2058
$(-m\Delta_c u^\circ)$ (benzoic ac	eid)/kJ 9.6891	10.6075	10.5174	10.3786	10.6929	10.6268	10.6072
$(-\Delta_{\rm c} u^{\circ})$ (compound)/	$kJ \cdot g^{-1}$ 31.1660	31.1395	31.1677	31.1756	31.1532	31.1562	31.1378
			-1) 21.150	C + 0 0054			

 $\langle -\Delta_c u^{\circ} (298.15 \text{ K})/\text{kJ} \cdot \text{g}^{-1} \rangle = 31.1566 \pm 0.0054$

The symbol have the same meaning than table S3. The uncertainty associated with average result of specific combustion energy is the standard deviation of mean, which implies a standard uncertainty for seven experiments.

The preparation of the disulfide pellet with benzoic acid is described below:

The disulfide powder was placed in a pellet press of Parr Instrument Company and compressed in order to obtain a pellet of 4.4 mm diameter and 6.6 mm height, then this pellet was weighed on a Sartorius balance (sensitivity 0.01 mg).

Next, inside another pellet press (something bigger than the first one) a thin layer of benzoic acid was placed and, on this layer, the tablet previously made was placed. More benzoic acid was added around the tablet until it was completely covered. With the help of a press, the interior content was compressed and a new pellet was obtained. The dimensions of this were now approximately 13 mm diameter and 10 mm height, as shown in Figure S1. This new tablet was weighed on a Sartorius balance (sensitivity 0.01 mg) and the total mass was recorded.

The mass of benzoic acid was calculated as the difference between the total mass and the mass of the disulfide pellet.



Figure S1. Distribution of diphenyl disulfides and benzoic acid in the pellet for combustion experiments.

S4. Termogravimetry

Table S6. Experimental data and calculated vaporization enthalpies for DPDS determined by thermogravimetry.

$\frac{T}{K}$	m mg	$\frac{(\mathrm{d}m/\mathrm{d}t)\cdot10^9}{\mathrm{kg}\cdot\mathrm{s}^{-1}}$	$\frac{(1/T)\cdot 10^3}{K^{-1}}$	$\ln(dm/dt \cdot T)$	
		Ser	ies 1		
360.0	19.6336	0.6300	2.778	-15.299	
362.0	19.6257	0.7120	2.762	-15.171	
364.0	19.6165	0.8085	2.747	-15.039	
366.0	19.6062	0.9264	2.732	-14.897	
368.0	19.5941	1.0667	2.717	-14.751	
370.0	19.5805	1.1889	2.703	-14.637	

372.0	19.5654	1.3484	2.688	-14.505	
374.0	19.5482	1.5172	2.674	-14.382	
376.0	19.5289	1.6964	2.660	-14.265	
378.0	19.5074	1.9082	2.646	-14.142	
380.0	19.4831	2.1307	2.632	-14.027	
	Series 1 ln(dm/dt T)=9.0-8755.7/ <i>T</i> ; r ² =0.9996; σ	$_{a}=0.2; \sigma_{b}=56.5; \Delta_{l}^{g}H_{m}(370.0 \text{ K})$	$kJ \cdot mol^{-1} = 72.8 \pm 0.5$	
	^	Sei	ries 2		
360.0	26.4358	0.6205	2.778	-15.314	
362.0	26.4277	0.7390	2.762	-15.134	
364.0	26.4186	0.8052	2.747	-15.043	
366.0	26.4082	0.9527	2.732	-14.869	
368.0	26.3958	1.0407	2.717	-14.775	
370.0	26.3825	1.2056	2.703	-14.623	
372.0	26.3669	1.3752	2.688	-14.486	
374.0	26.3497	1.5213	2.674	-14.379	
376.0	26.3301	1.7396	2.660	-14.240	
378.0	26.3080	1.9317	2.646	-14.130	
380.0	26.2836	2.2057	2.632	-13.992	
	Series 2 ln(dm/dt T)=9.4-8897.7/ <i>T</i> ; r ² =0.9987; σ	_a =0.3; σ_b =108.4; $\Delta_l^g H_m$ (370.0 K)	$/kJ \cdot mol^{-1} = 74.0 \pm 0.9$	
		Sei	ries 3		
360.0	20.2872	0.5586	2.778	-15.420	
362.0	20.2799	0.6481	2.762	-15.265	
364.0	20.2716	0.7294	2.747	-15.142	
366.0	20.2621	0.8402	2.732	-14.995	
368.0	20.2514	0.9557	2.717	-14.860	
370.0	20.2392	1.0765	2.703	-14.736	
372.0	20.2254	1.2123	2.688	-14.612	
374.0	20.2099	1.3711	2.674	-14.483	
376.0	20.1924	1.5477	2.660	-14.357	
378.0	20.1728	1.7293	2.646	-14.241	
380.0	20.1508	1.9313	2.632	-14.125	
	Series 3 ln(dm/dt 7)=9.1-8832.0/ <i>T</i> ; r ² =0.9996; c	$\sigma_a=0.2; \ \sigma_b=55.9; \ \Delta_l^g H_m(370.0 \text{ K})$	$kJ \cdot mol^{-1} = 73.4 \pm 0.5$	
		Sei	ries 4		
360.0	19.8155	0.5657	2.778	-15.407	
362.0	19.8082	0.6498	2.762	-15.263	
364.0	19.7998	0.7472	2.747	-15.118	
366.0	19.7903	0.8449	2.732	-14.989	
368.0	19.7794	0.9547	2.717	-14.862	
370.0	19.7672	1.0816	2.703	-14.731	
372.0	19.7533	1.2250	2.688	-14.601	
374.0	19.7376	1.3822	2.674	-14.475	
376.0	19.7200	1.5475	2.660	-14.357	
378.0	19.7001	1.7558	2.646	-14.225	
380.0	19.6779	1.9485	2.632	-14.116	
	Series 4 $\ln(dm/dt T)$	r^{2})=9.1-8816.2/ <i>T</i> ; r^{2} =0.9998; c	$\sigma_a=0.1; \sigma_b=43.1; \Delta_l^g H_m(370.0 \text{ K})$	$kJ \cdot mol^{-1} = 73.3 \pm 0.4$	
		$<\Delta_l^g H_m$ (DPDS, 370.0 H	K)>/kJ·mol ⁻¹ = 73.3 ± 0.3		

Table S7. Experimental data and calculated vaporization enthalpies for 2ADPDS determined by thermogravimetry.								
$\frac{T}{K}$	$\frac{m}{mg}$	$\frac{(\mathrm{d}m/\mathrm{d}t)\cdot10^9}{\mathrm{kg\cdot s}^{-1}}$	$\frac{(1/T)\cdot 10^3}{K^{-1}}$	$\ln(dm/dt \cdot T)$				
Series 1								
400.0	21.7523	0.1492	2.500	-16.634				
402.0	21.7506	0.1625	2.488	-16.544				
404.0	21.7486	0.1793	2.475	-16.440				
406.0	21.7462	0.2086	2.463	-16.284				

408.0	21.7434	0.2363	2.451	-16.155					
410.0	21.7404	0.2690	2.439	-16.020					
412.0	21.7371	0.3028	2.427	-15.897					
414.0	21.7331	0.3405	2.415	-15.775					
416.0	21.7288	0.3830	2.404	-15.652					
418.0	21.7239	0.4222	2.392	-15.550					
420.0	21.7185	0.4765	2.381	-15.424					
Series 1 ln(dm/dt T)=9.4–10437.5/T; r^2 =0.9985; σ_a =0.3; σ_b =134.4; $\Delta_1^g H_m$ (410.0 K)/kJ·mol ⁻¹ =86.8 ± 1.1									
Series 2									
400.0	21.9005	0.1857	2.500	-16.415					
402.0	21.8983	0.2039	2.488	-16.317					
404.0	21.8957	0.2260	2.475	-16.209					
406.0	21.8928	0.2576	2.463	-16.073					
408.0	21.8895	0.2964	2.451	-15.928					
410.0	21.8858	0.2948	2.439	-15.929					
412.0	21.8816	0.3757	2.427	-15.681					
414.0	21.8767	0.4220	2.415	-15.560					
416.0	21.8715	0.4703	2.404	-15.447					
418.0	21.8654	0.5179	2.392	-15.346					
420.0	21.8587	0.6041	2.381	-15.187					
	Series 2 ln(dm/dt T	^r)=9.5–10371.6/ <i>T</i> ; r ² =0.9910; σ	$_{a}=0.8; \sigma_{b}=329.7; \Delta_{l}^{g}H_{m}(410.01)$	K)/kJ·mol ⁻¹ =86.2 \pm 2.7					
		Ser	ies 3						
400.0	16.9399	0.1557	2.500	-16.591					
402.0	16.9387	0.1730	2.488	-16.481					
404.0	16.9358	0.2059	2.475	-16.302					
406.0	16.9335	0.2224	2.463	-16.220					
408.0	16.9304	0.2615	2.451	-16.053					
410.0	16.9277	0.2982	2.439	-15.917					
412.0	16.9238	0.3188	2.427	-15.845					
414.0	16.9197	0.3688	2.415	-15.695					
416.0	16.9151	0.4103	2.404	-15.583					
418.0	16.9099	0.4483	2.392	-15.490					
420.0	16.9043	0.5140	2.381	-15.349					
	Series 3 ln(dm/dt T)=9.4–10386.1/ <i>T</i> ; r ² =0.9974; o	$a=0.4; \sigma_b=176.5; \Delta_l^g H_m(410.0)$	K)/kJ·mol ⁻¹ =86.4 \pm 1.5					
		Ser	ies 4						
400.0	19.9045	0.1281	2.500	-16.787					
402.0	19.9029	0.1439	2.488	-16.665					
404.0	19.9010	0.1621	2.475	-16.542					
406.0	19.8989	0.1871	2.463	-16.393					
408.0	19.8965	0.2120	2.451	-16.263					
410.0	19.8938	0.2360	2.439	-16.151					
412.0	19.8907	0.2800	2.427	-15.975					
414.0	19.8872	0.3064	2.415	-15.880					
416.0	19.8834	0.3387	2.404	-15.775					
418.0	19.8789	0.3897	2.392	-15.630					
420.0	19.8739	0.4480	2.381	-15.486					
Series 4 $\ln(dm/dt T) = 10.4 - 10887.6/T$; $r^2 = 0.9987$; $\sigma = 0.3$; $\sigma = 1.29.3$; $\Lambda^{g}H$ (410.0 K)/k L mol ⁻¹ =90.5+1.1									
$<\Lambda_{p}^{g}H$ (2ADPDS 410.0 K)>/kLmol ⁻¹ = 88.1 + 0.7									
$<\Delta_{\tilde{l}}H_{\rm m}(2{\rm ADPDS}, 410.0 {\rm K})>/{\rm KJ\cdotmol} = 88.1 \pm 0.7$									

Table S8. Experimental data and calculated vaporization enthalpies for 4ADPDS determined by thermogravimetry.								
Т	m	$(dm/dt) \cdot 10^9$	$(1/T) \cdot 10^3$	$\ln(dm/dt \cdot T)$				
K	mg	kg·s ⁻¹	K-1					
Series 1								
450.0	9.3139	0.1821	2.222	-16.317				
452.0	9.3117	0.1932	2.212	-16.254				

454.0	9.3090	0.2331	2.203	-16.061					
456.0	9.3062	0.2535	2.193	-15.973					
458.0	9.3030	0.2820	2.183	-15.862					
460.0	9.2995	0.3203	2.174	-15.731					
462.0	9.2954	0.3375	2.165	-15.674					
464.0	9.2910	0.4019	2.155	-15.495					
466.0	9.2859	0.4397	2.146	-15.401					
468.0	9.2803	0.4927	2.137	-15.283					
470.0	9.2740	0.5409	2.128	-15.185					
Series 1 ln(dm/dt T)=10.7-12184.0/T; r^2 =0.9961; σ_a =0.6; σ_b =253.1; $\Delta_l^g H_m$ (460.0 K)/kJ·mol ⁻¹ =101.3 ± 2.1									
Series2									
450.0	12.2829	0.1785	2.222	-16.337					
452.0	12.2806	0.2037	2.212	-16.201					
454.0	12.2781	0.2241	2.203	-16.101					
456.0	12.2752	0.2428	2.193	-16.016					
458.0	12.2720	0.2855	2.183	-15.850					
460.0	12.2684	0.3206	2.174	-15.729					
462.0	12.2644	0.3516	2.165	-15.633					
464.0	12.2599	0.3917	2.155	-15.521					
466.0	12.2550	0.4491	2.146	-15.380					
468.0	12.2493	0.4905	2.137	-15.287					
470.0	12.2431	0.5418	2.128	-15.183					
	Series 2 $\ln(dm/dt T)$)=11.0-12304.9/T; r^2 =0.9983; σ_a	$_{\rm a}=0.4; \ \sigma_{\rm b}=171.0; \ \Delta_{\rm i}^{\rm g}H_{\rm m}(460.0)$	K)/kJ·mol ⁻¹ =102.3 \pm 1.4					
		Ser	ies 3	,					
450.0	8.8630	0.1716	2.222	-16.376					
452.0	8.8609	0.2017	2.212	-16.211					
454.0	8.8584	0.2223	2.203	-16.109					
456.0	8.8556	0.2485	2.193	-15.993					
458.0	8.8524	0.2796	2.183	-15.871					
460.0	8.8489	0.3068	2.174	-15.774					
462.0	8.8449	0.3532	2.165	-15.629					
464.0	8.8404	0.3959	2.155	-15.510					
466.0	8.8354	0.4325	2.146	-15.417					
468.0	8.8299	0.4883	2.137	-15.292					
470.0	8.8237	0.5385	2.128	-15.189					
	Series 3 $\ln(dm/dt T)$	$=11.23-12399.7/T$; $r^{2}=0.9989$; c	$\sigma_{a}=0.3; \sigma_{b}=139.9; \Lambda_{a}^{g}H_{m}(460.0)$	K)/kJ·mol ⁻¹ =103.1+1.2					
		Ser	ies 4	,					
450.0	10.4087	0.1903	2.222	-16.273					
452.0	10.4063	0.1980	2.212	-16.229					
454.0	10.4039	0.2340	2.203	-16.057					
456.0	10.4010	0.2594	2.193	-15.950					
458.0	10.3977	0.2785	2.183	-15.875					
460.0	10.3941	0.3052	2.174	-15.779					
462.0	10.3899	0.3545	2.165	-15.625					
464.0	10.3855	0.4142	2.155	-15.465					
466.0	10.3805	0.4495	2.146	-15.379					
468.0	10.3748	0.4825	2.137	-15.304					
470.0	10.3685	0.5477	2.128	-15.172					
Series 4 $\ln(dm/dt T) = 10.3 - 11979.6/T$; $r^2 = 0.9939$; $\sigma = 0.7$; $\sigma = 312.9$; $\Lambda^g H$ (A60.0 K)/k Lmol ⁻¹ =09.6 + 2.6									
Solies 4 III($um/ut 1$)=10.5=119/9.0/1; r=0.9959, $o_a=0.7$; $\sigma_b=512.9$; $\Delta_1^2 H_m$ (400.0 K)/KJ·mol =99.0 ± 2.0									

 $<\Delta_1^{\rm g} H_{\rm m}$ (4ADPDS, 460.0 K)>/kJ·mol⁻¹= 102.3 ± 0.8

Standard uncertainties u are u(T) = 0.1 K, u(m) = 0.1 µg, and the combined expanded uncertainty U_c is $U_c(dm/dt) = 0.066 \cdot 10^9$ kg·s⁻¹, $U_c(1/T) = 0.001 \times 10^3$ K⁻

¹, $U_c(\ln(dm/dt \cdot T)=0.020; U_c(\ln(dm/dt \cdot T)=0.020)$ (with a coverage factor k=2.45 and confidence level of 0.95 for two tailed normal distribution).

For each experimental series, taking into account the uncertainty of the slope, the uncertainties of temperature and dm/dt, the combined standard uncertainty associated to the enthalpy of phase change, u_{comb} , was obtained. The average of the four experimental series is the weighted average μ , which was calculated as $\mu = \sum (x_i / u_{\text{comb},i}^2) \sum (1/u_{\text{comb},i}^2)$ and its standard deviation corresponds to $u_{\text{comb}}^2 = N \sum (1/u_{\text{comb},i}^2)$, where x_i is each of the N data of phase change enthalpy and, its respective combined standard uncertainty $u_{\text{comb},i}^{.0, 11}$

S5. ¹³C NMR and ¹H NMR Spectrum



Figure S2. ¹H NMR Spectrum (500 MHz) of diphenyl disulfide DPDS (solvent chloform-d).



Figure S3. ¹³C NMR Spectrum (500 MHz) of diphenyl disulfide DPDS (solvent chloform-d).



Figure S4. ¹H NMR Spectrum (500 MHz) of 2-aminodiphenyl disulfide 2ADPDS (solvent chloform-d).



Figure S5. ¹³C NMR Spectrum (500 MHz) of 2-aminodiphenyl disulfide 2ADPDS (solvent chloform-d).



Figure S7. ¹³C NMR Spectrum (500 MHz) of 4-aminodiphenyl disulfide 4ADPDS (solvent chloform-d).

S6. Calculation of the integral of the heat capacity

According to statistical mechanics, given the partition function, Q, the heat capacity can be calculated as:

$$C_p = NkT \frac{\partial^2}{\partial T^2} (T \ln Q) + R \tag{3}$$

Considering only the contributions from translational, rotational, and vibrational motions to the C_{p} , and using the rigid rotor and harmonic oscillator, we have: ¹²

$$C_p = C_{p,tras} + C_{p,rot} + C_{p,vib}$$
(4)

i.e.

$$C_p = \frac{5}{2} R + \frac{3}{2} R + R \sum_{i=1}^{\infty} \left(\frac{h v_i}{k T}\right)^2 \frac{Exp\left(-\frac{h v_i}{k T}\right)}{\left(1 - Exp\left(-\frac{h v_i}{k T}\right)\right)^2}$$
(5)

where the sum in the last term runs over all molecular vibrational frequencies. Using the last expression, the integral:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \tag{6}$$

is straightforwardly evaluated, from which we obtain:

$$\Delta H = 4R(T_2 - T_1) + \frac{R}{2} \sum_{i=1}^{k} \frac{h v_i}{k} \left[\operatorname{coth}\left(\frac{h v_i}{2 k T_2}\right) - \operatorname{coth}\left(\frac{h v_i}{2 k T_1}\right) \right]$$
(7)

S7. References

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