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Standard enthalpies of formation of dicyclopropyldinitromethane and tricyclopropylmethane

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ABSTRACT

The energies of combustion of liquid dicyclopropyldinitromethane and liquid tricyclopropylmethane were determined by calorimetry of combustion at $T = 298.15$ K. The enthalpies of vaporization were estimated on the basis of electrostatic potential model. The formation enthalpies of the compounds in liquid and gas states were obtained from these data. The gas enthalpies of formation were also calculated by methods of the group additivity and isodesmic reactions. The obtained experimental and calculation values were compared.

1. Introduction

Cyclic compounds are of interest in several major respects. Firstly, cyclization of hydrocarbons usually accompanies by considerable changes in their geometry, which lead to appearance of strain in the molecules and change in their enthalpies of formation. Therefore, polycyclic compounds containing cyclopropane fragments constitute the promising substances for study correlations between energetic parameters and molecular geometry [1–4]. Secondly, the strain in three-membered rings leads to the appearance of a high and peculiar reactivity of these compounds, which manifests itself in numerous reactions of opening of small cycle, specific rearrangements and isomerizations. This allows to perform syntheses of complex molecules with a specified combination of functional groups [5,6], in particular, drugs antitumor [7] and antibacterial [8,9]. Thirdly, three-membered cycles are found in the structures of a number of natural compounds [10,11]. Cyclopropanes are interesting in the formation of conformationally rigid amino acids and peptides [12,13].

In this work, enthalpies of formation at $T = 298.15$ K for two compounds containing cyclopropane fragments: dicyclopropyldinitromethane (DCPDNM) and tricyclopropylmethane (TCPM) in liquid and ideal gas states were obtained.

2. Experimental and results

2.1. Samples

The samples of dicyclopropyldinitromethane ($C_7H_{10}N_2O_4$(liq), DCPDNM) and tricyclopropylmethane ($C_{10}H_{16}$(liq), TCPM) (Fig. 1) were synthesized in the laboratory of organic synthesis of Chemical Department of Lomonosov Moscow State University. The substances were purified by distillation and preparative g.l.c. (Table 1). In the TCPM, traces of water were found; its amounts were determined by the analysis by the Fisher method and taken into account in the calculations of combustion energy. Purity of studied samples was confirmed by the analysis of the gaseous products of combustion on content of CO_2(g). The molar mass of DCPDNM (186.165 g·mol^{-1}) and of TCPM (136.234 g·mol^{-1}) were calculated based on relative atomic masses recommended in [14]. The density, ρ, of the DCPDNM equals $\rho = 1.2397$ g·cm^{-3} and the density of TCPM equals $\rho = 0.8500$ g·cm^{-3} at $T = 298.15$ K. The densities were determined by pycnometric method. The combined expanded uncertainty was $U_c(\rho) = 0.001$ g·cm^{-3} (Table S1 of Supplementary data). The boiling temperatures, T_{boil}, of the DCPDNM and TCPM were determined by micromethod of Sviblov-Emikh [15]. They are equal to 563 K and 433 K, respectively, with standard uncertainty of 1 K at a pressure of 101.3 kPa.

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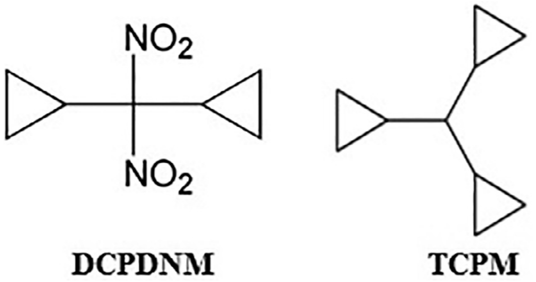

Fig. 1. Structures of dicyclopropyldinitromethane ($C_7H_{10}N_2O_4$, DCPDNM) and tricyclopropylmethane ($C_{10}H_{16}$, TCPM).

2.2. Combustion calorimetry

Detailed description of configuration of the static-bomb isoperibolic calorimeter was reported in [16,17]. The increase of the temperature was measured by means of copper resistance thermometer ($R_{298} \sim 50\ \Omega$) using bridge circuit [18]. The sensitivity of the temperature measurements was about 5×10^{-5} K.

The energy equivalent of the calorimetric system, ε(Calor.), was determined with thermochemical standard benzoic acid (K-1 brand, D.I. Mendeleev Research Institute of Metrology) using the energy of combustion in certified conditions $\Delta_b u = (-26432.5)$ $J{\cdot}g^{-1}$ at $T = 298.15$ K (combined expanded uncertainty of $\Delta_b u$ is $U_c(\Delta_b u) = 1.9\ J{\cdot}g^{-1}$; standard uncertainty of T is $u(T) = 0.05$ K). The correction for small deviations from these conditions was calculated according to Jessup's formula [19]. The mean values obtained for the energy equivalents were $\varepsilon(\text{Calor.}) = 62089.0\ J{\cdot}\Omega^{-1}$ with an empty bomb (Table 2). Combined expanded uncertainty is $U_c(\varepsilon$ (Calor.)) = $6.2\ J{\cdot}\Omega^{-1}$ (0.95 level of confidence).

The test samples (about 0.2–0.4 g) were placed and sealed into Terylene-film ampoules (ρ of film is 1.38 $g{\cdot}cm^{-3}$ [20]). The burning of both substances was carried out using an auxiliary substance (benzoic acid; ρ of acid is 1.32 $g{\cdot}cm^{-3}$ [19]). The ampoule together with tablet (~0.15–0.30 g) of benzoic acid (for provide a temperature rise ~1 K) were placed into a platinum cup. Weighing was carried out with a precision of $\pm 2{\cdot}10^{-2}$ mg on Mettler balance (Type 100 A5M, Max. Bel. 100 g.). The bomb, with 1 ml of distilled water added, was charged with purified oxygen to a pressure 3.04–4.05 MPa (Table 2). The initial temperature did not differ from 298.15 K by more than 0.03 K. Ignition of the substance was carried out by heating the wire with a discharge of the capacitor. Iron wire (0.1 mm in diameter) was used in experiments 4–7; in other experiments platinum wire (0.1 mm in diameter) was used. The ignition energy in the experiments with DCPDNM, TCPM and at the calibration of calorimeter by benzoic acid was the same and was not taken into account when calculating $\Delta_c u°$.

The combustion products were analysed for carbon dioxide by the Rossini method [19]. The content of CO_2 in the combustion products of DCPDNM equals to 1.0000 mass fractions. The content of CO_2 in the combustion products of TCPM equals to 0.9983 mass fractions (sample TCPM contained 0.0020 mass fractions H_2O). The combined expanded uncertainty of the analyses of combustion products is U_c (analysis of CO_2(g)) = 0.0002 mass fractions. The results indicate the completeness of combustion and confirm the high purity of the substance studied. Soot was not observed in any combustion experiments. Qualitative tests for CO with indicator tubes (TU. 12.43.20-76) were negative within the limits of their sensitivity $6{\cdot}10^{-6}$ g of CO. The content of HNO_3 in the solution was determined by titration of washing waters by ~0.1 $mol{\cdot}dm^{-3}$ of NaOH (aq).

The results of the determination of specific combustion energy, $\langle -\Delta_c u° \rangle$, of DCPDNM (from seven combustion experiments) and of TCPM (from two combustion experiments, because the substance was available in very limited quantity) are shown in Table 2.

The change of internal energy for the isothermal bomb process $\Delta\ U$(IBP) was calculated in accordance with [19]:

$$-\Delta U(\text{IBP}) = [\varepsilon(\text{Calor.}) + \varepsilon_f(\text{Cont.})] \cdot \Delta R_{\text{corr}} \qquad (1)$$

The value, $(-\Delta_c u°)$, was calculated based on the sample mass using the following formula:

$$(-\Delta_c u°) = \left[-\Delta U(\text{IBP}) - \Delta U(\text{b.a.}) - \Delta U(\text{f}) - \Delta U(\text{HNO}_3) - \Delta U_{\sum}(\text{st})\right] \cdot m^{-1} \qquad (2)$$

The DCPDNM was in sufficient quantity to conduct a series of seven combustion experiments. The combined standard uncertainty of the mean value of the standard energy of combustion, $\langle -\Delta_c u°$ DCPDNM$\rangle$, corresponds to the 95% confidence interval for normal distribution and equals to 12.7 $J{\cdot}g^{-1}$. The combined standard uncertainty of the mean value of the standard energy of combustion of TCPM, $\langle -\Delta_c u°$ TCPM$\rangle$, was evaluated according to work [24]. We believe that the dispersion of the results in the combustion of two preparations DCPDNM and TCPM is characterized by the same variance. This is possible, because both preparations were by the similar in composition and by the same methods of preparation, and were burned in the same device. As a result, the average weighted dispersion of the measurements of two compounds, s_x^2, was determined by the formula:

$$s_x^2 = \left[\Sigma s_i^2 (n_i - 1)\right] / (\Sigma n_i - m); \; s_x^2 = 792.2; \quad s_x = 28.1, \qquad (3)$$

where n_i are the number of experiments; $s_i = [(-\Delta_c u°)_i - \langle -\Delta_c u° \rangle]$ are the variances in the ith series; m are the number of series.

In this case, s_x^2 is determined in a series of a sufficiently large number of experiments (more precisely, for a sufficiently large number of degrees of freedom $f = (\sum n_i - m)$), and, therefore, it can be assumed that $s_x^2 \approx \sigma_x^2$, where σ_x is a dispersion of the normal distribution law. The confidence interval with a probability of 95% for the mean value in each series of experiments can be determined from the ratio: $2{\cdot}s_{x(\text{compound})} = 2{\cdot}s_x/\sqrt{n_i}$. For a series of experiments with TCPM it equals $2{\cdot}s_{x\ (\text{TCPM})} = 39.8\ J{\cdot}g^{-1}$.

Table 1
Provenance and purity of liquid samples of DCPDNM and TCPM.

Compound	Source	Purification Method	Method of analysis	Final purity[a] mass fractions
$C_7H_{10}N_2O_4$ (DCPDNM)	Synthesized	distillation and preparative g.l.c.	analytical g.l.c.	0.9999
			analysis CO_2(g)	1.0000
$C_{10}H_{16}$ (TCPM)	Synthesized	distillation and preparative g.l.c.	analytical g.l.c.	0.9999
			analysis CO_2(g)	0.9983
			analysis H_2O(liq)	0.0017

[a] The standard uncertainty, u, is u(g.l.c.) = 0.0002 mass fractions; the combined expanded uncertainties U_c are U_c(analysis CO_2(g)) = 0.0002 mass fractions (0.95 level of confidence) and U_c(analysis H_2O(liq) = 0.0002 mass fractions (0.95 level of confidence).

Table 2
Combustion energy of $C_7H_{10}N_2O_4$(liq) (DCPDNM) (Molar Mass = 186.165 g·mol^{-1}; ρ = 1.2397 g·cm^{-3} [this work])[a]; and $C_{10}H_{16}$(liq) (TCPM) (Molar Mass = 136.234 g·mol^{-1}; ρ = 0.8500 g·cm^{-3} [this work])[a]; p^o = 101.3 kPa at T = 298.15 K[b].

n_i	DCPDNM							TCPM	
	1	2	3	4	5	6	7	8	9
P_{in}, MPa	4.05	4.05	4.05	3.34	3.55	3.04	3.04	3.04	3.04
m/g	0.21026	0.19540	0.17734	0.39216	0.30495	0.27444	0.34997	0.14962$^{*)}$	0.20559$^{*)}$
m(b.a)/g	0.14810	0.18459	0.26083	0.22613	0.16166	0.30192	0.24497	0.19335	–
m(f)/g	0.01035	0.00921	0.00959	0.01237	0.01349	0.01477	0.01727	0.01491	0.03525
$\Delta R_{corr}/\Omega$	0.143790	0.153307	0.179283	0.244871	0.185849	0.234961	0.239212	0.213262	0.178309
ε_f(Cont.)/J·Ω^{-1}	78.2	78.4	79.0	72.3	73.1	67.7	69.0	67.2	66.6
$-\Delta U$(IBP)/J	8939.0	9530.7	11145.7	15221.5	11552.8	14604.4	14868.9	12460,0	10417.8
ΔU(b.a.)/J	3911.6	4875.4	6889.0	5972.5	4269.8	7974.3	6470.1	5106.8	–
ΔU(Fe)/J	–	–	–	33. 0	33.4	35. 8	35.6	–	–
ΔU(f)/J	237.5	211.3	220.0	283.8	309.5	338.9	396.3	342.1	808.8
$\Delta U(HNO_3)$/J	11.6	8.9	10.0	32.7	23.8	23.8	25.6	1.30	0.7
$\Delta U_{\sum}$/J	7.2	7.9	9.5	11.0	8.7	10.0	10.0	6.0	3.6
$(-\Delta_c u^\circ)$/(J·g^{-1})	22691.4	22657.1	22652.5	22665.5	22651.6	22670.2	22662.8	46811.2	46717.7
Mean $\langle -\Delta_c u^\circ \rangle$/(J·g^{-1})	22664.4[c] ± 12.7							46764.5[d] ± 39.8	
$m(CO_2exp)/m(CO_2theor)$	1.0001	1.0001	1.0001	0.9997	0.9999	1.0003	1.0005	0.9984	0.9982
Mean	1.0000[e] ± 0.0002							0.9983[f] ± 0.0002	

P_{in} is an initial pressure of purified oxygen in the bomb.
m is mass of the samples in the vacuum; $^{*)}$ mass of the sample TCPM was calculated from the results of CO_2 analysis; m(b.a) is mass of benzoic acid in the vacuum, ρ = 1.32 g·cm^{-3} [19]; m(f) is mass of Terylene-film in the vacuum, ρ = 1.38 g·cm^{-3} [20]; all masses were determination with a precision of ±5·10^{-5} on a Mettler balance (Type 100 A5M, Max. Bel. 100 g.); ΔR_{corr} is the increase of the thermometer resistance corrected for heat exchange; standard uncertainty $u(\Delta R_{corr})$ = 1·10^{-5} Ω; ε_f(Cont.) is the energy equivalent of contents in the final state; combined expanded uncertainty is $U_c(\varepsilon_f$(Cont.)) = 0.1 J·Ω^{-1} (0.95 level of confidence); $-\Delta U$(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions ε(Calor.) = 62089.0 J·Ω^{-1}; the combined expanded uncertainty is $U_c(\Delta U$ (IBP) = 6.2 J(0.95 level of confidence); ΔU (b.a.) is the correction for the energy combustion of the benzoic acid. It is calculated using value $\Delta_c u^\circ$ = (−26412.0 ± 1.9) J·g^{-1}, which is obtained from certificate value in certified conditions $\Delta_b u$ = (−26432.5) J·g^{-1} by introducing amendment for reduction to the standard state [19]; the combined expanded uncertainty U_c is $U_c(\Delta U$(b.a.)) = 0.3 J (0.95 level of confidence); ΔU(Fe) is the correction for the energy combustion Fe,$\Delta_c u^\circ$ = (−823.3 ± 6.0) J·g^{-1} [21], the combined expanded uncertainty U_c is $U_c(\Delta U$(Fe)) = 0.05 J (0.95 level of confidence); ΔU(f) is the correction for the energy combustion of film. The energy of combustion of Terylene-film is $\Delta_c u^\circ$ = (−22927.9 ± 6.3) J·g^{-1} [22]; the combined expanded uncertainty is $U_c(\Delta U$(f)) = 0.1 J (0.95 level of confidence); $\Delta U(HNO_3)$is the correction for the energy formation of solution HNO_3(aq) from N_2(g), O_2(g) and H_2O(liq) (based on −59.5 kJ·mol^{-1} the molar energy of formation of aqueous nitric acid [21,23]); the combined expanded uncertainty is $U_c(\Delta U(HNO_3))$ = 0.002 J (0.95 level of confidence); $\Delta U_{\sum}$ is the correction to standard state [19]; the standard uncertainty is $u(\Delta U_{\sum})$ = 0.08 J; $(-\Delta_c u^\circ)$ is the standard specific energy of combustion.

[a] Standard uncertainties u(Molar Mass) = 0.002 g·mol^{-1}; the densities of the substances are determined in this work by pycnometric, the combined expanded uncertainty is $U_c(\rho)$ = 0.0002 g·cm^{-3}.

[b] Standard uncertainties u are u(T) = 0.01 K, $u(p^o)$ = 0.5 kPa.

[c] $(-\Delta_c u^o$ DCPDNM, liq) is the mean value of standard specific energy of combustion of DCPDNM; the combined expanded uncertainty is $U_c(-\Delta_c u^\circ$DCPDNM, liq) = 12.7 J·g–1 (0.95 level of confidence).

[d] $(-\Delta_c u^\circ$ TCPM, liq) is the mean value of standard specific energy of combustion of TCPM; the combined expanded uncertainty is $U_c(-\Delta_c u^\circ$TCPM, liq) = 39.8 J·g–1 (0.95 level of confidence); $(mCO_2exp)/(mCO_2theor)$ is the ratio of the mass of CO_2 determined experimentally to that calculated theoretically; the combined expanded uncertainty is $U_c((mCO_2exp)/(mCO_2theor))$ = 2·10^{-4}g (0.95 level of confidence).

[e] $(mCO_2exp)/(mCO_2theor)$ is the mean value for the DCPDNM.

[f] $(mCO_2exp)/(mCO_2theor)$ is the mean value for the TCPM.

2.3. Energy, $\Delta_c U^o_m$, and enthalpy of combustion, $\Delta_c H^o_m$, and formation, $\Delta_f H^o_m$, of DCPDNM and TCPM in liquid state at T = 298.15 K

The standard molar energy of combustion, $\Delta_c U^o_m$, of DCPDNM and TCPM corresponds to reactions:

$$C_7H_{10}N_2O_4(liq) + 7.5O_2(g) = 7\ CO_2(g) + 5\ H_2O(liq) + N_2(g) \qquad (4)$$

$$C_{10}H_{16}(liq) + 14O_2(g) = 10\ CO_2(g) + 8\ H_2O(liq) \qquad (5)$$

The standard molar energies of combustion, $\Delta_c U^o_m$, enthalpies of combustion, $\Delta_c H^o_m$, were calculated using the data of Table 2 and values of $\Delta n \cdot R \cdot T$, which are equal for DCPDNM (+1.24) kJ·mol^{-1} and for TCPM (−9.9) kJ·mol^{-1}. The standard molar enthalpies of formation, $\Delta_f H^o_m$, of DCPDNM and TCPM in liquid state at T = 298.15 K were calculated using the standard molar enthalpies of formation of $\Delta_f H^o_m CO_2$(g) = (−393.51 ± 0.13) kJ·mol^{-1} and $\Delta_f H^o_m H_2O$(liq) = (−285.83 ± 0.04) kJ·mol^{-1} recommended by CODATA [23] (Table 3).

Table 3
Standard energy of combustion, $\Delta_c U^o_m$, and enthalpy of combustion, $\Delta_c H^o_m$, and formation, $\Delta_f H^o_m$, of DCPDNM and TCPM in liquid state at T = 298.15 K.

Substance[a]	$\Delta_c U^o_m$/kJ·mol^{-1}	$\Delta_c H^o_m$/kJ·mol^{-1}	$\Delta_f H^o_m$/kJ·mol^{-1}
DCPDNM	−4219.3 ± 2.4	−4218.1 ± 2.8	34.4 ± 2.9
TCPM	−6370.9 ± 5.4	−6380.8 ± 5.5	159.1 ± 5.6

[a] The uncertainties of all thermodynamic quantities of investigated substances are combined expanded uncertainties U_c (0.95 level of confidence).

2.4. Quantum chemical calculations

The experimental measurements were supplemented by quantum chemical calculations. Preliminary geometry optimization, vibrational frequency calculation, and conformational analysis were carried out at the B3LYP/6-31G(d,p) density functional level. The optimized geometries of the most stable conformers were used as inputs for further G4 calculations [25]. The standard enthalpies of formation were calculated using both the atomization [26] and isodesmic reaction [27] procedures. All quantum chemical calculations were performed using the Gaussian 16 package of programs [28].

Politzer et al. [29,30] have shown that a number of physical properties can been expressed quantitatively in terms of molecular descriptors defined from the molecular electrostatic potential (MEP). In particular, the following correlation was established for the enthalpy of vaporization [30]:

$$\Delta^g_{liq} H^\circ_m = a\sqrt{A_S} + b\sqrt{\sigma^2_{tot}\nu} + c \qquad (6)$$

where A_S is the surface area, σ^2_{tot} indicates the variability of the potential on the molecular surface, and ν is the degree of the balance between positive and negative regions. In this work, we propose the modified MEP model which includes additional molecular descriptors D (the density), V_S (the average value of the potential on the surface), and Π (the measure of local polarity):

$$\Delta^g_{\text{liq}}H^\circ_m = aD + bA_S + cV_S + d(\sigma^2_{\text{tot}}\upsilon) + e\Pi + f \qquad (7)$$

Compared to Eq. (6), the linear dependence on A_S and $\sigma^2_{\text{tot}}\upsilon$ is considered in Eq. (7). Note, that the linear dependence of sublimation enthalpy on A_S was suggested earlier by Mathieu and Bougrat [31]. For the selected 40 molecules (Table S2 of Supplementary data) the $\Delta^g_{\text{liq}}H_m$ values predicted using the Eq. (7) produce an rms error of 2.3 kJ•mol^{-1} with a maximum error of 5.8 kJ•mol^{-1}, compared to 7.0 and 24.1 kJ•mol^{-1} for the same molecules using the Eq. (6).

The DFT/B3LYP/6–311++G(3df,2p) method was used to optimize geometries and determine the densities for generating the electrostatic potentials. All descriptors in Eq. (7) were calculated using the program Multiwfn [32]. The electrostatic potentials were calculated on the molecular surface, taking this to be the 0.001 a.u. contour of the electronic density [30]. The computed values of the descriptors involved in Eq. (7) are given in Table S2 of Supplementary data. The coefficients a, b, c, d, e, and f were determined from least-squares fitting to reliable experimental values of enthalpies of vaporization of 40 compounds. Comparison between the experimental and calculated enthalpies of vaporization is given in Table S2 of Supplementary data; the uncertainty of $\Delta^g_{\text{liq}}H^\circ_m$ values predicted by Eq. (7) is defined as two times the root-mean-square deviation (±5 kJ•mol^{-1}).

2.5. Theoretical enthalpies of vaporization

The enthalpies of vaporization of TCPM, DCPDNM, and other cyclopropane derivatives calculated according Eq. (7) are given in Table 4. Since we could not find in the literature the experimental enthalpies of vaporization for these compounds (with the exception of bicyclopropyl), the comparison was made for the liquid-phase enthalpies of formation. Table 4 includes the $\Delta_f H^\circ_m(g)$ values calculated by G4 method, theoretical enthalpies of vaporization, and the $\Delta_f H^\circ_m(liq)$ values calculated on their basis. Together with experimental liquid-phase enthalpies of formation, the enthalpies of vaporization estimated by empirical equations are also given in Table 4.

First of all, it is noteworthy that all empirically estimated enthalpies of vaporization are in good agreement with the values predicted by MEP model. Therefore, the largest discrepancy between experimental and calculated $\Delta_f H^\circ_m(liq)$ values observed for 1,1-dinitrocyclopropane (18) seems to be due to inaccuracy of experimental measurements. The difference between experimental and theoretical values does not exceed 6.3 kJ·mol^{-1} for the half of the species (1, 2, 5–9, 15–17, 20) and so theoretical calculations confirm the experimental data for these compounds.

2.6. Gas-phase enthalpies of formation of DCPDNM and TCPM obtained by the method of isodesmic reactions

The reliable result for DCPDNM can be obtained only using isodesmic reactions, because in our previous works [41,42], it was revealed that the G4 method, when applied to atomization reactions, underestimates the $\Delta_f H^\circ_m(g)$ values for most nitro compounds by up to 20 kJ·mol^{-1}.

Dicyclopropylmethane derivatives would be the best choice as a reference species in these reactions. However, the experimental enthalpy of formation is determined only for dicyclopropyl, and with large uncertainty. The isodesmic reactions for DCPDNM (Table 5) were constructed using monocyclopropane compounds (reactions (1)–(5)) and compounds containing three cyclopropane

Table 4
Comparison between experimental liquid-phase enthalpies of formation of some alkyl and nitro cyclopropanes and theoretical values estimated in this work.

	Compound	Calculation, this work			Experiment		Reference	Experiment – Calculation
		$\Delta_f H^\circ_m(g)$[a]/ kJ·mol^{-1}	$\Delta^g_{\text{liq}}H^\circ_m$[b]/ kJ·mol^{-1}	$\Delta_f H^\circ_m(\text{liq})$/ kJ·mol^{-1}	$\Delta^g_{\text{liq}}H^\circ_m$[b]/ kJ·mol^{-1}	$\Delta_f H^\circ_m(\text{liq})$/ kJ·mol^{-1}		$\Delta_f H^\circ_m(\text{liq})^{\text{exp}} - \Delta_f H^\circ_m(\text{liq})^{calc}$/ kJ·mol^{-1}
1	*cis*-1,2-Dimethylcyclopropane	2.2	27.7	−25.5		−26.3 ± 0.7	[33]	−0.8
2	*trans*-1,2-Dimethylcyclopropane	−3.5	28.2	−31.7		−30.7 ± 0.8	[33]	1.0
3	1,1,2-Trimethylcyclopropane	−34.0	32.7	−66.7		−96.2 ± 0.8	[33]	−29.5
4	1,1,2,2-Tetramethylcyclopropane	−60.9	36.8	−97.7		−119.8 ± 0.9	[33]	−22.1
5	Ethylcyclopropane	4.0	28.2	−24.2		−24.8 ± 0.8	[33]	−0.6
6	1,1-Dimethyl-2-ethylcyclopropane	−57.0	37.5	−94.5		−90.2 ± 0.9	[34]	4.3
7	*cis*-1,2-Diethylcyclopropane	−42.3	37.4	−79.7	35.4[c]	−80.0 ± 1.4	[35]	−0.3
8	*trans*-1,2-Diethylcyclopropane	−48.9	38.1	−87.0	34.3[c]	−83.4 ± 1.6	[35]	3.6
9	1,1-Dimethyl-2-propylcyclopropane	−78.9	42.3	−121.2		−116.0 ± 1.7	[36]	5.2
10	Bicyclopropyl	135.2	30.9	104.3	33.5[c] 31.7 ± 0.5	96.0 ± 3.8	[37] [38]	−8.3
11	Phenylcyclopropane	155.8	39.0	116.8		100.3 ± 0.9	[39]	−16.5
12	1,1-Diphenylcyclopropane	254.4	55.8	198.6		185.5 ± 3.3	[39]	−13.1
13	*cis*-1,2-Diphenylcyclopropane	257.3	54.7	202.6		178.8 ± 0.9	[39]	−23.8
14	*trans*-1,2-Diphenylcyclopropane	253.2	58.0	195.2		166.2 ± 2.5	[39]	−29.0
15	*cis*-1-Methyl-1,2-dicyclopropylcyclopropane	177.6	47.0	130.6	46.9[c]	134.1 ± 1.2	[39]	3.5
16	*trans*-1-Methyl-1,2-dicyclopropylcyclopropane	177.7	46.8	130.9	47.3[c]	131.9 ± 1.2	[40]	1.0
17	Nitrocyclopropane	26.7[d]	45.6	−18.9	44.7[c]	−17.4 ± 3.1	[2]	1.5
18	1,1-Dinitrocyclopropane	51.0[d]	63.2	−12.2	63.2[c]	34.7 ± 8.3	[3]	46.9
19	Nitrospiropentane	155.9[d]	51.0	104.9	47.7[c]	126.9 ± 4.4	[2]	22.0
20	1-Nitrospiro[2.3]hexane	94.5[d]	54.6	39.9	49.7[c]	46.2 ± 5.7	[3]	6.3
21	Tricyclopropylmethane (TCPM)	191.9[d]	46.6	145.3		159.1 ± 6.3	This work	13.8
22	Dinitrodicyclopropylmethane (DCPDNM)	83.6[d]	66.3	17.3		33.6 ± 3.9	This work	16.3

[a] Value calculated from atomization is given, unless otherwise indicated.
[b] Predicted using MEP model.
[c] Estimated by empirical equation.
[d] Calculated from isodesmic reactions.

Table 5
Gas-phase enthalpy of formation of dinitrodicyclopropylmethane (DCPDNM) calculated from different working reactions using G4 energies[a].

	Reaction	$\Delta_r H^\circ_m$ /kJ·mol^{-1}	$\Delta_f H^\circ_m$ /kJ·mol^{-1}
	Atomization reaction		68.8
1	DCPDNM + 3 CH_4 → 2 methylcyclopropane + 2 CH_3NO_2	50.5	78.6
2	DCPDNM + 2 CH_4 → 2 methylcyclopropane + $CH_2(NO_2)_2$	79.2	80.0
3	DCPDNM + CH_4 + CH_3CH_3 → 2 methylcyclopropane + $CH_3CH(NO_2)_2$	38.9	79.8
4	DCPDNM + 2 C_6H_6 + CH_4 → 2 methylcyclopropane + 2 $C_6H_5NO_2$	3.0	85.1
5	DCPDNM + CH_3CH_3 → 2 nitrocyclopropane + cyclopropane	112.0	80.1
6	DCPDNM + methylcyclopropane + CH_4 → *cis*-1-methyl-1,2-dicyclopropylcyclopropane + 2 CH_3NO_2	1.5	86.7
7	DCPDNM + methylcyclopropane → *cis*-1-methyl-1,2-dicyclopropylcyclopropane + $CH_2(NO_2)_2$	30.2	88.0
8	DCPDNM + methylcyclopropane + CH_4 → *trans*-1-methyl-1,2-dicyclopropylcyclopropane + 2 CH_3NO_2	1.5	84.9
9	DCPDNM + methylcyclopropane → *trans*-1-methyl-1,2-dicyclopropylcyclopropane + $CH_2(NO_2)_2$	30.2	86.2
10	DCPDNM + cyclopropane + CH_3CH_3 → TCPM + 2 CH_3NO_2	−7.1	86.3
	recommended (average of reactions 1-10):		83.6 ± 7.0[b]

[a] The enthalpies of formations for reference species used in these reactions are given in Table S4 of Supplementary data.

[b] The uncertainty is defined as two times the root-mean-square deviation of calculated values from the average of reactions (1)–(10).

rings (reactions (6)–(10)). As can be seen from the Table 5, reactions (1)–(5) provide the $\Delta_f H^\circ_m(g)$ values about 6 kJ·mol^{-1} less than those from reactions (6)–(10). Since it cannot be ruled out that the first reactions underestimate the interaction of cyclopropane rings in DCPDNM, and the second overestimate it, the average of all 10 reactions, (83.6 ± 7.0) kJ·mol^{-1}, is accepted for the gas-phase enthalpy of formation of DCPDNM.

The gas-phase enthalpies of formation of TCPM calculated from different working reactions are given in Table 6. It is seen that the values obtained from reactions with cyclopropane and methylcyclopropane are substantially lower than those from reactions with structurally similar tricyclopropyl species. A similar pattern is observed for biphenyl (Table S3 of Supplementary data) and adamantane [42]: the use of benzene and cyclohexane molecules in isodesmic reactions leads to the underestimated $\Delta_f H^\circ_m(g)$ values in comparison with the results obtained when the biphenyl derivatives and adamantane derivatives are used as the reference species. The interaction of strained cyclopropane rings is taken into account in the reactions (3) and (4) (Table 6), and because of this, the average value obtained from these reactions, (191.9 ± 4.0) kJ·mol^{-1}, is accepted for the gas-phase enthalpy of formation of TCPM. Note that the G4 enthalpies of formation obtained from the atomization reaction are usually close to the experimental values for hydrocarbons except for large polycyclic and cage molecules. Since our estimated value is also close to the value obtained from atomization reaction (189.4 kJ·mol^{-1}), its uncertainty is evaluated to be no more than 4.0 kJ·mol^{-1}.

Table 6
Gas-phase enthalpy of formation of tricyclopropylmethane (TCPM) calculated from different working reactions using G4 energies.[a]

	Reaction	$\Delta_r H^\circ_m$/ kJ·mol^{-1}	$\Delta_f H^\circ_m$/ kJ·mol^{-1}
	Atomization reaction		189.4
1	TCPM + 5 CH_4 → 3 cyclopropane + 3 CH_3CH_3	98.5	183.3
2	TCPM + 2 CH_4 → 3 methylcyclopropane	37.2	184.7
3	TCPM → *cis*-1-methyl-1,2-dicyclopropylcyclopropane	−11.8	192.8
4	TCPM → *trans*-1-methyl-1,2-dicyclopropylcyclopropane	−11.7	190.9
	recommended (average of reactions (3) and (4)):		191.9 ± 4.0[b]

[a] The enthalpies of formations for reference species used in these reactions are given in Table S4 of Supplementary data.

[b] See text for details.

2.7. Gas-phase enthalpies of formation of DCPDNM and TCPM obtained by the method of group contributions

The ideal gas enthalpies of formation of the compounds under study were also calculated by the principle of additivity. The values of group contributions obtained by Poling et al. [43], Domalski et al. [44] and Cohen [45] were used. The coverage of organic compounds in [45] includes hydrocarbons containing the cyclopropane ring, but does not contain contributions with nitro group. Value for NO_2-group is taken from Domalski et al. [44]. In [43] and [44] additive contributions for the ideal gas state to the NO_2-group are given. The value $\Delta_f H^o_m(g)$ (Table 7) was obtained only from the data of [43] and [44].

Table 7
The standards enthalpies of formation, $\Delta_f H^o_m$, of DCPDNM and TCPM in liquid and gaseous states at T = 298.15 K (kJ·mol^{-1})[a].

	$\Delta_f H^o_m$(liq) Experiment	$\Delta_f H^o_m$(liq) Calculation	$\Delta^g_{liq} H^o_m$ Calculation (Table 4)	$\Delta_f H^o_m$(g) Experiment	$\Delta_f H^o_m$(g) Calculation
DCPDNM	33.6 ± 2.9	33.5 Domalski [44] 17.3 ± 7.0 (Table 4)	66.3 ± 5.0	99.9 ± 5.8	99.8 Domalski [44][b] 116.9 Domalski [44] 99.7 Cohen [45][c] 98.3 Poling [43] 83.6 ± 7.0 (Table 5)
TCPM	159.1 ± 5.6	161.3 Domalski [44] 149.2 Cohen [45] 145.3 ± 7.0 (Table 4)	46.6 ± 5.0	205.7 ± 7.5	207.9 Domalski [44][d] 191.0 Poling [43] 195.8 Cohen [45][e] 182.9 Cohen [45] 191.9 ± 4.0 (Table 6)

[a] The combined expanded uncertainties, U_c: for DCPDNM are $U_c(\Delta_f H^o_m$, liq) = 2.9 kJ·mol^{-1}; U_c ($\Delta^g_{liq} H^o_m$) = 5.0 kJ·mol^{-1}; and $U_c(\Delta_f H^o_m$, g) = 5.8 kJ·mol^{-1} (0.95 level of confidence); for TCPM are $U_c(\Delta_f H^o_m$, liq) = 5.6 kJ·mol^{-1}; U_c ($\Delta^g_{liq} H^o_m$) = 5.0 kJ·mol^{-1}; and $U_c(\Delta_f H^o_m$, g) = 7.5 kJ·mol^{-1} (0.95 level of confidence).

[b] $\Delta_f H^o_m$(liq) + $\Delta^g_{liq} H^o_m$(this work) = (33.5 + 66.3) kJ·mol^{-1}.

[c] Values for groups containing NO_2 are taken from Domalski [44].

[d] $\Delta_f H^o_m$(liq) + $\Delta^g_{liq} H^o_m$(this work) = (161.3 + 46.6) kJ·mol^{-1}.

The results obtained by the additive method (Table 7) for DCPDNM are consistent with the experimental values within the error of the determination, differences for TCPM are larger. The calculation of $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{g})$ for TCPM, which was carried out according to the schemes Domalski [44] and Cohen [45] with the use of contributions for the liquid phase and taking into account the estimated in this work enthalpy of vaporization (footnote *d* and *e*, Table 7), gives the enthalpy of formation in the gas phase closer to the experimental one.

The values of $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{g})$ for both compounds obtained by the method of isodesmic reactions are very different from the experimental values. However, it should be noted that compounds containing in their structure a cyclopropane ring pose a challenging problem for both group additivity and isodesmic reaction calculations.

3. Conclusions

The experimental determination of the formation enthalpies of the DCPDNM and TCPM in the liquid state by the method of bomb calorimetry was supplemented by calculating the formation enthalpies in the gaseous state, using the isodesmic reactions and estimating the enthalpies of vaporization by the molecular electrostatic potential method (MEP), which predicts well the enthalpies of vaporization (Table 4). The values of the formation enthalpies obtained by the calculation methods (Table 7) indicate that further accumulation of the experimental material is necessary, which will allow more accurate consideration of various interactions in molecules of similar structure and improve the calculation schemes.

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Appendix A. Supplementary data

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