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Top-Down and Bottom-Up evaluation of thermochemistry of α,ω-alkanediols

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ABSTRACT

At vapor-liquid equilibrium, the thermodynamic properties of the liquid and vapor phases are intrinsically linked through the thermodynamics of vaporization. However, the standard enthalpies of formation and vaporization of α,ω-alkanediols reported in the literature to date are inconsistent with this fundamental thermodynamic relationship. The aim of this work is to evaluate the existing data and provide recommendations for standard enthalpies of formation and standard enthalpies of vaporization for technical applications. For this purpose, available data are critically analyzed using a "top-down/bottom-up" approach based on gas-phase properties and a bottom-up approach starting from the liquid phase. For those α,ω-alkanediols where discrepancies remain, the relevant thermodynamic properties were re-determined with a combination of combustion calorimetry, vapor pressure measurements and quantum chemical calculations. Based on the comprehensive evaluation, it was shown that the thermodynamic properties of α,ω-alkanediols deviate from the regular trends typically expected for homologous series. Due to the significant contribution of intramolecular hydrogen bond conformers in the gas-phase population, the properties of 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol exhibit distinct particularities compared to long-chained α,ω-alkanediols. Starting from 1,5-pentanediol, the enthalpies of vaporization and the standard enthalpies of formation in the gas phase follow a regular linear trend, attributed to the predominance of conformers without intramolecular hydrogen bonding. The recommended accurate thermodynamic data provide the basis for the development of technical processes utilizing diols from renewable sources in future work.

Keywords: structure-property relationships, diols; enthalpies of phase transitions; vapor pressure; enthalpies of formation, quantum chemical calculations

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1. Introduction

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α,ω-Alkanediols (such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, *etc*.) are a fascinating class of organic compounds because their OH groups exhibit interesting physicochemical and thermochemical properties in the liquid and gas phases due to the interplay of inter- and intramolecular hydrogen bonds. These properties are of interest for the development of biofuels, polymer precursors and environmentally friendly solvents.

Renewable diols production can reduce dependence on fossil fuels, lower carbon emissions, and promote greener manufacturing processes. Methods like microbial fermentation and catalytic conversion of plant-derived sugars enable the sustainable production of diols like ethylene glycol, propylene glycol, and 1,4-butanediol [1]. These bio-based diols help drive the transition toward more environmentally friendly materials and circular economy principles. Long-chain diols (C6-C10) are valuable intermediates in the production of high-performance polyesters, polyurethanes, lubricants, and surfactants. Their longer carbon chains provide enhanced hydrophobicity, flexibility, and durability in materials, making them essential for applications in coatings, adhesives, and biomedical materials. Producing these diols from renewable raw materials, such as plant oils, lignocellulosic biomass, and microbial fermentation, offers a sustainable alternative to petroleum-based sources. Biotechnological processes, including engineered microbial fermentation and enzymatic conversion, enable the efficient synthesis of long-chain diols from fatty acids or sugars. This renewable approach reduces environmental impact, supports the bioeconomy, and promotes greener manufacturing in various industries.

A newly emerging and promising area for the utilisation of renewable diols is their use as Liquid Organic Hydrogen Carriers (LOHCs). LOHC systems are an attractive option for the long-term storage of hydrogen in unsaturated organic molecules, such as, *e.g.*, benzyltoluenes [2], alkyl carbazoles [3]. These molecules have a similar physical state to conventional diesel fractions, can be transported over long distances and, if necessary, catalytically dehydrogenated to produce molecular hydrogen.

The major drawbacks of these conventional LOHC systems are:
a) the use of petroleum-based LOHC compounds,
b) the need to operate at high temperatures for hydrogen release,
c) the use of noble metal-based catalysts.

A recently published novel strategy appears to overcome all three drawbacks [4,5]. It involves diols such as 1,2-propanediol [1,6] or 1,4-butanediol [7], two bio-based molecules, as new hydrogen-rich LOHC compounds. For example, the reversible catalytic cyclisation of 1,4-butanediol to γ-butyrolactone releases two moles of hydrogen and can be seen as a very attractive biobased LOHC

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system [7]. Knowledge of the thermodynamic properties of diols and lactones is essential for the technical implementation of such reactions in the context of chemical hydrogen storage technologies.

The focus of this work is the evaluation and revision of the following thermochemical properties of α,ω-alkanediols: standard molar enthalpy of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, standard molar enthalpy of sublimation, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, standard molar enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$, and standard molar enthalpy of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$, in the condensed and gaseous state. These properties are related to each other as follows (referenced to $T = 298.15$ K):

$$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{liq},\ 298.15\ \mathrm{K}) = \Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g},\ 298.15\ \mathrm{K}) - \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) \qquad (1)$$

$$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr},\ 298.15\ \mathrm{K}) = \Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g},\ 298.15\ \mathrm{K}) - \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) \qquad (2)$$

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) + \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) \qquad (3)$$

The experimental thermochemistry of the short-chained α,ω-alkanediols: 1,2-ethanediol [8], 1,3-propanediol [9], and 1,4-butanediol [10] was partially investigated in our earlier studies. In the course of these studies, we found that the experimental thermochemistry of α,ω-alkanediols with a chain length of C6 to C10 is rather confusing. In fact, most of the thermochemical data on the long-chain alkanediols have been reported only in a few publications by the Sabbah group [11–14] and the Della Gatta group [15,16]. A brief summary of the experimental enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, and enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(liq or cr), of α,ω-alkanediols available in the literature is shown in Table 1.

Table 1
Overview of the experimental enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, and enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$ (liq or cr), of α,ω-alkanediols available in the literature (at the reference temperature $T = 298.15$ K, in $\mathrm{kJ \cdot mol^{-1}}$) [a]

Diol	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ [b]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(liq or cr)
1,3-propanediol	-	-458.7±3.0 (liq) [17] to -482.0±2.5 (liq) [9]
1,6-hexanediol	91.6±4.1	-362.2±4.8 (cr) [18] to -583.9± 0.7 (cr) [19]
1,7-heptanediol	97.5±3.2	-574±19 (liq) [12]
1,8-octanenediol	108.7±3.7	-627±10 (cr) [12]
1,9-nonanediol	113.3±7.0	-658±14 (cr) [12]
1,10-decanenediol	111.0±2.0	-678.9±6.5(cr) [12] to -699.9±2.1 (cr) [20]
1,11-undecanediol	128.6±4.0	
1,12-dodecanediol	126.1±5.6	
1,13-tridecanediol	128.2±7.7	
1,14-tetradecanediol	135.4±6.0	
1,15-pentadecanediol	132.0±4.1	
1,16-hexadecanediol	138.8±4.0	

[a] The experimental uncertainties are expressed as two times the standard deviation of the mean value.

[b] Original values from [15,16] were uniformly adjusted to the reference temperature $T = 298.15$ K in our previous work [21]

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The most dramatic situation regarding the consistency of experimental enthalpies of formation is evident for 1,6-hexanediol, where the available values range from -362. 2 to -583.9 kJ·mol^{-1} (Table 1, column 3), and 1,10-decanediol, where the scatter of the available results, at 21 kJ·mol^{-1}, is also too large to consider the quality of the data acceptable.

It should be mentioned that most of the combustion results of diols, which lead to the enthalpies of formation, were measured by Knauth and Sabbah [11,12], using a microbomb rocking calorimeter and samples of 5 to 10 milligrams. The uncertainties of 10 to 19 kJ·mol^{-1} (see Table 1, column 3) show that achieving reproducibility of measurements with micro-bombs is a challenging task. That said, the experimental formation enthalpies of diols compiled in Table 1 must be checked for internal consistency within their homologous family.

The Della Gatta group measured the enthalpies of vaporization of α,ω-alkanediols using a combination of the Knudsen method and the torsion effusion method [15,16]. The experimental enthalpies of vaporization of α,ω-alkanediols measured at T_{av} were adjusted by the authors to the reference temperature T = 298.15 K (see Table 1, column 2). It is apparent that the results of the Della Gatta group are strongly aggravated by large uncertainties of up to 7.7 kJ/mol. These unusually large uncertainties make the interpretation of the trends in the measured enthalpies of vaporization problematic.

For example, the comparison of the vaporization enthalpies in Table 1 for the sequence of the following diols:

1,8-octanediol ($\Delta_l^g H_m^o$(298.15 K) = 108.7 ± 3.7 kJ·mol^{-1}),
1,9-nonanediol ($\Delta_l^g H_m^o$(298.15 K) = 113.3 ± 7.0 kJ·mol^{-1}),
1,10-decanediol ($\Delta_l^g H_m^o$(298.15 K) = 111.0 ± 2.0 kJ·mol^{-1})

make it clear that the uncertainties completely overshadow the usual trend for the homologous series of a monotonic increase in thermochemical properties.

Furthermore, there is no reason or specific interaction that makes the enthalpy of vaporization of 1,9-nonanediol higher than that of 1,10-decanediol, and it is highly unusual that the enthalpies of vaporization of 1,11-undecanediol to 1,15-pentadecanediol are barely distinguishable within the uncertainties attributed to these values.

This unacceptable scatter in the available thermochemical data for each alkanediol has prompted this study, the main aim of which is to evaluate and revise the energetics of the diols using additional experiments, empirical correlations and quantum chemical (QC) calculations, which have now reached a level of accuracy where they can predict enthalpies of formation with the so-called "chemical accuracy" of ~±4 kJ·mol^{-1}. This level of accuracy is achieved by two high-level computational methods, G4 [22] and DLPNO-CCSD(T$_1$)/CBS [23], used in this work. The G4 method was tested on primary alcohols [24] and two diols [26] and showed good results when using atomization

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reactions. However, difficulties with using this approach may arise in accounting for conformational diversity of diol molecules. In order to evaluate the energetics of the conformers more reliably, the high-level DLPNO-CCSD(T$_1$)/CBS method was additionally used in combination with isodesmic reactions. In these reactions, the error associated with the accurate consideration of the conformational equilibrium can be eliminated if the products are to some extent similar in conformation to the reagent structures. These advances make it possible to closely match theoretical predictions with experimental data, making quantum chemistry a powerful tool in thermochemistry and molecular design.

This modern QC calculation development enables us to validate thermochemical data for diols with a "top-down" strategy, where the quantum chemistry should provide a plausible expectation for the gas phase enthalpy of formation, $\Delta_f H^o_m$(g), to evaluate the experiment in the condensed phase (according to Eqs. 1 to 3), *e.g.* in the liquid state, as shown in Fig. 1.

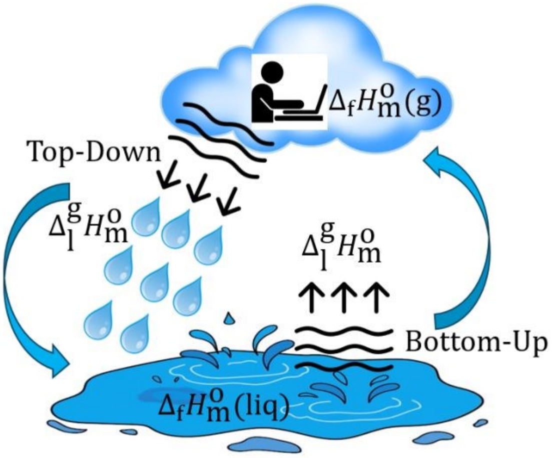

Fig. 1 Visualization of the "Top-Down" and "Bottom-Up" strategies for evaluation of thermochemistry of α,ω-alkanediols via vaporization enthalpy according to Eq. (1).

The $\Delta_l^g H^o_m$(298.15 K)-values required by Eq. (1) for the "drop" from "top" (quantum chemically calculated enthalpies of formation) to the liquid phase formation enthalpies of the short-chain diols have just been ascertained in our work [21] and can be used in this study to evaluate the thermochemistry of α,ω-alkanediols.

α,ω-Alkanediols are flexible molecules with three and more internal rotational degrees of freedom that lead to the existence in the gas-phase an equilibrium mixture with of a large number of conformers with significantly different energetics. Determining the most stable conformer required to calculate the $\Delta_f H^o_m$(g) values and is a challenging task for these compounds. At present, the most complete information on conformational equilibrium has been obtained for the two simplest α,ω-alkanediols – 1,2-ethanediol and 1,3-propanediol. Both experimental and theoretical studies including statistical thermodynamics population analysis [25–27] show that the most stable conformers of these molecules are stabilized by an intramolecular O–H···O–H hydrogen bond between the hydroxyl

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groups. However, a rather ambiguous interpretation of conformational equilibrium is given for 1,4-butanediol. The results of gas-phase electron diffraction [28] and microwave spectroscopy [29] studies were interpreted as strong evidence for the mixture of two hydrogen-bonded conformers (denoted as HB here), whereas the analysis of vibrational spectra in the vapor phase [25,26,30–34] showed the presence of both HB conformers and those with free hydroxyl groups (denoted as F conformers here). Some studies have found that experimental spectra show good agreement with theoretical spectra with a predominant contribution from HB conformers [25,32,33] but others have noted the need to include higher energy F conformers to reproduce the experimental data [26,30,31,34]. Previously reported theoretical calculations [26,32–35], also do not provide complete clarity on the stability of the various 1,4-butanediol conformers. And this is due not only to insufficiently high level of the calculation methods used and the problem of accounting for the large anharmonicity induced by low-frequency torsional motions in 1,4-butanediol, which is neglected in the calculation of the zero-point vibrational energy (ZPE), enthalpic correction ($H_{298.15} - H_0$) and entropy, but also to the approach used to determine the most stable conformers.

The differences in electronic energy of conformers (ΔE_e), ground-state energy (ΔE_0, where $E_0 = E_e$ + ZPE), enthalpy (ΔH, where $H = E_e$ + ZPE + ($H_{298.15} - H_0$)) and Gibbs free energy (ΔG, where $G = H - TS$) are used in QC calculations to estimate the conformer population and determine the most stable conformer. In many cases, all these quantities enable correct identification of the most stable conformer. The conformer population is quite often defined based on the ΔH values. This can be justified if the entropies of conformers are approximately the same and then $\Delta H \approx \Delta G$. To determine the values of ΔG, it is necessary to calculate the entropy of all conformers, but sometimes this is replaced by accounting for the structural degeneracy of each conformer, which depends on its symmetry [26,33,34]. This assumption can be applied when the conformers are spatially similar, however, this is not the case for 1,4-butanediol: the HB conformers have a boat-like arrangement with the internal hydrogen bond closing the ring, whereas the F conformers have the extended open-chain structures. These structural features lead to significantly larger values of the product of moments of inertia of F conformers compared to the HB conformers and, as a rule, smaller values of low-lying vibrational frequencies. Therefore, for an accurate calculation of the Gibbs free energies, it is necessary to take into account all molecular parameters of conformers when calculating entropy using the statistical thermodynamics method. However, such calculations have not been performed for 1,4-butanediol in the past [26,32–35], which may be the reason for the discrepancies in the interpretation of the experimental results.

Benchmark relative energies, ΔE_e, for 65 conformers of 1,4-butanediol calculated at the CCSD(T)-F12b/cc-pVTZ-F12 level [35] have shown that the group of HB conformers is more stable than the F conformers. This result is consistent with a 89% population of HB conformers determined

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according to the Boltzmann distribution based on the ΔE_0 energies of 11 low-energy conformers of 1,4-butanediol calculated at the B3LYP/6-311++G(d,p) level and taking into account the structural degeneracy of each conformer [32]. However, a similar calculation for 65 conformers using the ΔE_0 values calculated by the MP2/6-311++G(d,p) method [33] resulted in a significantly lower value of 46% for the HB conformer population. A similar result, with relative population of 47% for HB conformers, was obtained from MP2/6-311G(d,p) calculations for the 10 lowest-energy conformers [26]. Among other long chain α,ω-alkanediols, the relative population of conformers was determined for 1,5-pentanediol and 1,6-hexanediol using MP2 and DFT electronic energies and corrections necessary to estimate the Gibbs free energies [36,37]. For these two diols, the extended F conformers were found to be the most abundant.

In the present work, before proceeding to the conformational analysis of long chain diols, it was decided to perform a new calculation of the relative population of 1,4-butanediol conformers based on a more accurate estimation of the Gibbs free energy. This enables us to develop an approach to find the most stable conformers of the remaining diols for which a complete conformational analysis is not possible with our computing capacities. The entropy, ZPE and enthalpic corrections were estimated within the rigid rotor−harmonic oscillator approximation (RRHO), since accounting for the internal rotation in such large flexible molecules still presents great difficulty. Another approximation used in our work is the calculation of the enthalpy of formation only for the most stable conformer. As mentioned above, this is common practice when using isodesmic reactions, but the $\Delta_f H^o_m$(g) values calculated from the atomization reaction are often corrected for the conformer population. We abandoned this correction because it was previously shown that it can significantly overestimate the calculated values [27,38]. In this context, the highly flexible α,ω-alkanediols selected for experimental and computational studies in this work could either support the validity of the approximations used here, or our study could reveal and quantify the necessary corrections to achieve agreement between experiment and calculations. This means that in the case of α,ω-alkanediols, the alternative "bottom-up" strategy (see Fig. 1) should be applied, where the available experimental enthalpies of formation of the condensed phase need to be critically evaluated using new combustion experiments and structure-property correlations, and the consistent experimental $\Delta_f H^o_m$(cr or liq) values in conjunction with the new experimental vaporization (or sublimation) enthalpies of alkanediols can help to address the deficiencies of the QC calculations with the flexible molecules, which exhibit considerable conformational diversity. The combination of "top-down" and "bottom-up" strategies therefore makes it possible to integrate theoretical expectations ("top-down") with measurements and empirical observations ("bottom-up") in order to evaluate the available experimental data and recommend reliable thermochemical properties for α,ω-alkanediols.

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2 Experimental and theoretical methods

2.1 Thermochemical methods

Commercially available samples of α,ω-alkanediols were used. Their origin and purity are listed in Table S1 in the electronic supporting information (ESI). A self-built high-precision calorimeter with a static bomb [39] was used to measure the standard molar energy of combustion of 1,8-octanediol. The absolute vapor pressures of 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol were measured using the transpiration method [40]. The standard molar enthalpies of vaporization and the standard molar enthalpies of sublimation as well as the standard molar entropies of vaporization and the standard molar entropies of sublimation were derived from the temperature dependence of the absolute vapor pressures.

2.2 Quantum chemical calculations

Conformational analysis was performed with MMFF94 force field using GMMX conformational searching methodology implemented in the GaussView 6 computational molecular chemistry application [41]. The geometry of 10 (1,2-ethanediol) to 1000 (1,10-decanediol) generated structures was further optimized at the B3LYP/6-31G(d,p) level. From these conformers, the group of low-energy conformers was selected for each diol to calculate the Gibbs free energy using the G4 [22] and DLPNO−CCSD(T_1) [23] methods. The Gaussian 16 software [42] and ORCA 5.0.3 program release [43] were used in these QC calculations. The results of the calculations are shown in Tables S2 to S5.

The single-point DLPNO-CCSD(T_1)/CBS energies (E_e) were determined using the extrapolation to the basis set limit procedure implemented in the ORCA and the geometries optimized at the B3LYP-D3(BJ)/def2-TZVPP level. The entropy, ZPE and enthalpic corrections were calculated within the RRHO approximation using the rotational constants, vibrational frequencies and symmetry determined from the B3LYP-D3(BJ)/def2-TZVPP calculations. The vibrational frequencies were scaled by a factor of 0.9657 when calculating entropy and by a factor of 0.9883 when calculating the ZPE and enthalpic corrections [44]. The Gibbs free energies of the conformers were calculated using the equation $G = H - TS$, where $H = E_e + \text{ZPE} + (H_T - H_0)$, $T = 298.15$ K and S is the entropy calculated applying the formulas of statistical thermodynamics. The conformer with the lowest G value was chosen as the most stable, and the enthalpy of formation was calculated for it. The DLPNO-CCSD(T_1)/CBS and G4 calculations predicted the same most stable conformers for all diols except 1,4-butanediol, therefore only the results obtained using the DLPNO-CCSD(T_1)/CBS method are discussed in more detail below.

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The G4 enthalpies of formation were calculated from atomization reaction, whereas 8 isodesmic-type reactions (see Table S5) were used to determine the $\Delta_f H^o_m$(g) values by DLPNO-CCSD(T$_1$)/CBS method. The accurate $\Delta_f H^o_m$(g) values for small reference species used in these reactions were taken from the Active Thermochemical Tables (ATcT) [45]. For three reference molecules (1,2-ethanediol, 1,2- and 1,3-propanediol), the experimental data from this work and Ref. [46] were used and their accuracy was confirmed by preliminary QC calculations.

3. Top-Down strategy: gas-phase enthalpies of formation from quantum chemical calculations

3.1 Conformational analysis and identification of most stable conformers

Relative enthalpies (Δ*H*), Gibbs free energies (Δ*G*) and conformer populations (p_i) of C_2-C_{10} diols determined in this work are presented in Table S2, as well as quantities used to calculate them. The Cartesian coordinates of most stable HB and F conformers are given in Table S3.

The population of 1,2-ethanediol conformers was determined taking into account all 10 possible conformations of this molecule. The HB conformer was found to be the most stable and its overall prevalence compared to F conformers was estimated at 95%. This result agrees with predominance of HB conformers predicted earlier by G4 method (93% of HB conformers) [27] using the same approach for Gibbs free energy calculation as in the present work.

A previous population analysis of 1,3-propanediol was performed using the G4 method for 20 conformers whose energy calculated at the B3LYP/6-31G(d,p) level did not exceed 15 kJ·mol^{-1} [27]. Like for 1,2-ethanediol, the most stable conformer of 1,3-propanediol is HB, but these conformers contribute almost two times less to the total population (51%) compared to 1,2-ethanediol. In this work, we reduced the number of conformers to 11 to see how this would affect the result. In the simplified model, all four HB conformers were detected, but their contribution to the total population, as expected, increased to 70% due to the exclusion of more than half of the higher-energy F conformers. Thus, most likely, the simplified conformer selection of diols based on their relative B3LYP/6-31G(d,p) energies will not miss the most stable conformer.

Conformer population analysis of 1,4-butanediol (Table S2) was performed for all 65 possible conformers detemined using GMMX conformational searching. Cartesian coordinates of these conformers are given in Table S4. The identified conformers agree with those obtained by manual conformational scanning [35] with the exception of three conformers (pairs of conformers (30, 31), (45,46) and (49,50) in Ref [35] have the same structure). As can be seen in Table S2, the relative population of HB conformers (29%) is significatly smaller than that obtained previously using a more approximate estimate of the entropy contribution to the Gibbs free energy (about 47% [26,33]).

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It should be noted that in the group of F conformers, a subgroup of 26 conformers is distinguished that have a linear carbon backbone (denoted as F-lin conformers here). These straight chain diols are characterized by a continuous linear arrangement of carbon atoms with C–C–C–C angles from 172.5 to 180.0° and an average value of 178.3°. F-lin conformers contribute 50 % to the total population of 1,4-butanediol conformers. As can be seen in Fig. 2, the difference between the calculated ΔG values for the lowest-lying HB and F-lin conformers is within the limits of their uncertainties, so it can be assumed that taking into account the anharmonicity of the vibrations may result in the F-lin conformer becoming the most stable (see Section 3.2).

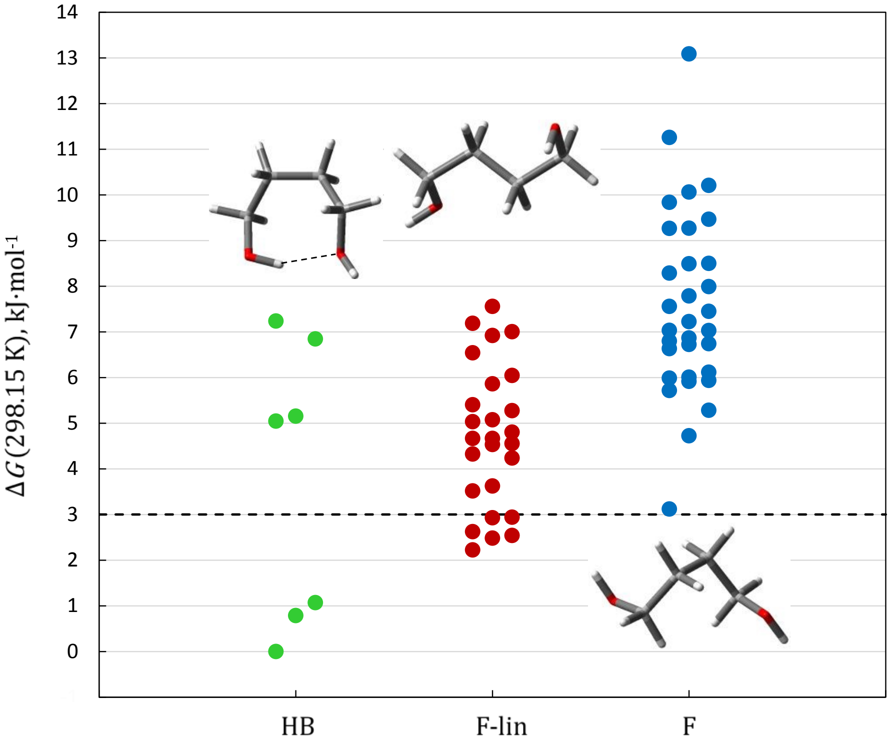

Fig. 2. Relative Gibbs energies of 1,4-butanediol conformers calculated at DLPNO-CCSD(T_1)/CBS//B3LYP-D3/def2-TZVPP level. HB are the O–H···O–H hydrogen bonded conformers, F-lin are the conformers with free hydroxyl groups and linear carbon backbone with φ_{av}(C–C–C–C) = 178.3° and F are the remaining conformers with free hydroxyl groups. The dashed line is the accuracy of calculated values.

The most stable conformers from all three groups were also revealed when considering only the 20 lowest-energy B3LYP/6-31G(d,p) conformers of 1,4-butanediol, but the population of HB conformers became predominant (50% HB and 43% F-lin). Similar simplified models were used in the present work for the remaining C_5-C_{10} diols. Since F-lin was found to be the most stable conformer in all of these diols, F-lin and F conformers were added to the initially selected 20 conformers. Analysis of the results for C_5-C_7 diols showed that F-lin conformers dominate among the low-lying conformers of these molecules (Table S2) and therefore, when determining the most stable conformers of C_8-C_{10} diols, the F conformers were not taken into account.

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3.2 Approximate treatment of vibrational anharmonicity

Based on the calculated ΔG values (Table 2), it can be concluded that the most stable conformers of C_2-C_4 diols should be the HB conformers, whereas, starting from 1,5-pentanediol, the F-lin conformations become the most stable. Since for most molecules the calculated ΔG values are within the accuracy of their determination, it is interesting to evaluate how a more accurate calculation accounting for the anharmonicity of vibrations can affect their values. The simplest approaches were used here for such approximate evaluation.

Table 2

Enthalpies of formations of most stable HB and F conformers of α,ω–alkanediols and difference in their enthalpies and Gibbs free energies calculated using DLPNO-CCSD(T_1)/CBS and G4 methods at $T = 298.15$ K (in kJ·mol^{-1})[a]

Molecule	Method	$\Delta_\mathrm{f}H^\circ_\mathrm{m}$ HB conformer	$\Delta_\mathrm{f}H^\circ_\mathrm{m}$ F-lin (F) conformer[b]	ΔH [c]	ΔG [c]
1,2-ethanediol	DLPNO	**-390.0 ± 2.3**	-379.3 ± 2.3	10.7 (10.8)	8.8 (8.9)
	G4	-389.1	-378.4	10.7	8.6
1,3-propanediol	DLPNO	**-412.4 ± 2.3**	-407.5 ± 2.3	4.9 (2.0)	3.4 (1.0)
	G4	-411.5	-407.7	3.8	2.5
1,4-butanediol	DLPNO	-433.4 ± 2.6	**-426.4 ± 2.6**	7.0 (4.2)	2.2 (0.1)
	G4	-433.1	-428.2 F-lin	4.9	1.7
1,5-pentanediol	DLPNO	-449.4 ± 2.4	**-446.6 ± 2.4**	2.8 (1.6)	-2.9 (-3.4)
	G4	-449.9	-447.0	2.9	-2.6
1,6-hexanediol	DLPNO	-469.7 ± 2.1	**-466.7 ± 2.1**	3.0 (1.9)	-6.2 (-5.4)
	G4	-471.4	-467.9 F-lin	3.5	-5.4
1,7-heptanediol	DLPNO	-494.1 ± 2.4	**-487.9 ± 2.4**	6.2 (3.7)	-2.5 (-2.9)
	G4	-495.8	-489.4	6.4	-2.6
1,8-octanediol	DLPNO	-512.9 ± 2.4	**-508.5 ± 2.4**	4.5 (2.0)	-4.2 (-5.3)
	G4	-516.3	-510.7	5.6	-3.4
1,9-nonanediol	DLPNO	-536.7 ± 2.3	**-528.7 ± 2.3**	8.0 (5.8)	-2.1 (-3.5)
	G4	-541.1	-532.0	9.1	-2.6
1,10-decanediol	DLPNO	-555.2 ± 2.4	**-549.5 ± 2.4**	5.7 (3.2)	-5.2 (-4.3)
	G4	-559.0	-553.4	5.7	-7.5

[a] Recommended values are given in bold.

[b] F conformers for 1,2-ethanediol and 1,3-propanediol and F-lin for all others.

[c] The ΔH and ΔG values are the difference in these functions between F-lin and HB conformers; values given in parentheses are those approximately corrected for anharmonicity of vibrational frequencies (see text for details).

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A free rotor approximation proposed by Radom and co-workers [47,48] was used to calculate the ZPEs and enthalpic corrections. This model suggests that for molecules with low-frequency torsional modes, a better result than the RRHO model is achieved by treating frequencies up to 260 cm^{-1} as tending to zero and replacing their contribution to the enthalpy correction by 1/2 *RT*. Errors in entropies, associated with treating low frequencies as harmonic motions, were reduced using Truhlar's approximation [49,50] in which all harmonic frequency values below 100 cm^{-1} were replaced by 100 cm^{-1}.

The ΔG values approximately accounting for vibrational anharmonicity are given in Table 2 in parentheses. It is worth paying attention to 1,4-butanediol, for which the value of $\Delta G = G(\text{F-lin}) - G(\text{HB})$ decreased to 0.1 kJ·mol^{-1}, which does not exclude that the F-lin conformer may be more stable when taking into account anharmonicity using more accurate methods. A comparison of the calculated enthalpies of formation with the experimental valuess can also help to clarify which configuration, HB or F-lin, is the most stable conformer of 1,4-butanediol.

3.3 Calculation of gas phase enthalpies of formation

The $\Delta_f H^o_m(g)$ values for most stable HB and F-lin conformers of α,ω-alkanediols calculated using DLPNO-CCSD(T_1) and G4 methods are summarized in Table 2. The details of the DLPNO-CCSD(T_1) calculation using isodesmic-type reactions are given in Table S5. As can be seen, the results obtained using the two methods are in good agreement: the deviations are not more than 2 kJ·mol^{-1} for C_2-C_7 diols and 4.5 kJ·mol^{-1} for the three largest molecules.

The values of the enthalpies of formation recommended in Table 2 (marked in bold) were obtained for conformers with lower values of Gibbs free energy: for C_2 and C_3 diols these are HB conformers, and for C_5-C_{10} these are F-lin conformers. The only exception is 1,4-butanediol, for which the enthalpy of formation is recommended for the F-lin conformer, despite its *G* value is higher than that of the HB conformer (see Section 7.6).

The QC gas-phase enthalpies of formation of α,ω-alkanediols shown in Table 2 can be considered as the starting point for the "top-down" evaluation strategy. However, as can be seen in Fig. 1, the enthalpies of vaporization are equally required to descend to the liquid phase thermochemistry or to ascend from the liquid phase to the gas phase. The next section deals with this "intermediate" thermochemical property.

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4. Enthalpy of vaporization as an intermediate between Top-Down and Bottom-Up strategies

4.1 Absolute vapor pressures of α,ω-alkanediols measured using the transpiration method

The vapor enthalpies, which are used in the general Eq. (1) to derive the enthalpies of formation of the liquid phase, should be of impeccable quality in order to obtain a reliable validation of the thermochemistry of the diols using the “top-down” strategy. Surprisingly, in contrast to the intensive investigations of the short-chain C2 to C4 diols, only very few vapor pressure measurements of the long-chain C5 to C10 alkanediols were found in the literature. The unusual trends in the enthalpies of vaporization shown in Table 1 also prompted the investigation of 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol using the transpiration method [40]. The essential advantage of this method is that the vapor pressure measurements are carried out at temperatures that are as close as possible to the reference temperature T = 298.15 K, so that the enthalpies of vaporization derived from such measurements are relatively less affected by the adjustment to this temperature compared to many other conventional methods.

The experimental absolute vapor pressure-temperature dependencies measured in this work using the transpiration method for 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol are summarised in Table S6. They were approximated using a three-parametric equation, as presented in detail in ESI, and used to calculate the enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$, or enthalpies of sublimation $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$, according to Kirchhoff's rule, using the heat capacity differences developed in our previous work [21] (see Table S7) The final results at the reference temperature T = 298.15 K, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$, are summarised in Table 3 and compared with the enthalpies of vaporization measured by other methods.

Table 3. Compilation of standard molar enthalpies of vaporization of α,ω-alkanediols (in kJ·mol^{-1})

Diol	Method [a]	T-Range/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}/T_{\mathrm{av}}$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$/298.15 K [b]	Ref.
1,2-ethanediol				**65.7±0.2**	[21]
1,3-propanediol				**71.5±0.3**	[21]
1,4-butanediol				**79.0±0.7**	[21]
1,5-pentanediol	E	391.9-480.1	73.2±0.9	85.9±2.7	[51]
	E	446.0-514.5	64.9±0.4	82.1±3.5	[52]
	n/a	391-479	73.4±1.0	85.9±2.8	[53]
	C	298.15		86.8±1.0	[14]
	BP	352-516	73.5±1.5	85.5±2.8	Table S8
	T	303.4-351.2	84.4±0.4	87.1±0.5	Table S6
				86.6±0.6 [c]	average
1,6-hexanediol			87.0±4.0	**90.7±0.4**	[21]
1,7-heptanediol	C	323	93.8±1.0	96.8±1.2	[13]
	TE	321-361	92.4±3.0	97.5±3.2	[16]
	CGC	298.15		95.9±0.6	[21,54]
	BP	375-535	77.2±1.2	95.5±3.9	[21]
	T	336.2-373.2	87.7±0.3	94.4±0.4	Table S6
				94.8±0.4 [c]	average

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1,8-octanediol	TE	340-372	101.1±3.4	(108.7±3.7)	[15]
	CGC	298.15		98.7±0.2	[21,54]
	BP	374-549	80.7±1.8	98.9±4.1	[21]
	T	343.2-379.3	91.0±0.8	99.2±1.0	Table S6
				98.7±0.3 [c]	average
1,9-nonanediol	TE	347-373	104.4±6.8	(113.3±7.0)	[16]
	C	323	110.0±2.0	(113.6±2.1)	[13]
	CGC	298.15		102.7±0.2	[21,54]
	BP	392-562	78.5±3.8	102.5±5.2	[21]
	T	343.2-379.2	93.9±0.8	103.0±1.0	Table S6
				102.7±0.3	average [c]
1,10-decanediol	TE	351-377	112.4±4.6	(122.6±5.0)	[15]
	E	457.0-566.3	73.6±1.1	106.6±6.7	[16]
	CGC	298.15		106.7±0.2	[21,54]
	BP	405-578	76.8±2.1	106.2±6.2	[21]
	T	346.3-370.5	97.3±1.2	106.6±1.3	[21]
				106.7±0.3 [c]	average

[a] Methods: E = ebulliometry; C = calorimetry; n/a = method is not available; T = transpiration method; BP = estimated from boiling points at different pressures (see Table S8); TE = torsion-effusion method; CGC = correlation gas-chromatography.

[b] Vapor pressures treated using Eqs. (S2) and (S3) with help of heat capacity differences from Table S7 to calculate the enthalpies of vaporization at 298.15 K. Uncertainties of the vaporization enthalpies $U(\Delta_l^g H_m^o)$ are the expanded uncertainties (0.95 level of confidence). They include uncertainties from the fitting equation and uncertainties from temperature adjustment to T = 298.15 K as described elsewhere [55]. Uncertainties in the temperature adjustment of the literature data on vaporization enthalpies to the reference temperature T= 298.15 K are estimated to account with 20% to the total adjustment.

[c] Weighted mean value (uncertainties were taken as the weighting factor). Values given in bold are recommended for further thermochemical calculations. Data in parentheses were not involved in the evaluation.

It is important to emphasise that the vapor pressures and enthalpies of vaporization of alkanediols available in the literature were treated in the same way as our new transpiration results (using the heat capacity differences evaluated in Table S7) and adjusted to T = 298.15 K. Only such uniform data treatment allowed a correct comparison of $\Delta_l^g H_m^o$(298.15 K)-values (see Table 3). As a result, a very consistent set of vaporization values for 1,5-pentanediol, 1,7-heptanediol and 1,10-decanediol was compiled. For each of these diols, the weighted average values were estimated and recommended for the thermochemical calculations (bold values in Table 3). The results for 1,8-octanediol and 1,9-nonanediol summarised in Table 3 are fewer in number, but for each of the two diols at least three entries were averaged and considered reliable. It should be recognised that our new transpiration results were extremely helpful in making the selection of reliable results for the long-chain C8 to C10 alkanediols, where the scatter of available vaporization enthalpies of 10-17 kJ·mol^{-1} made the final selection decision much more difficult. Although our selection of the reliable level for the enthalpies of vaporization of α,ω-alkanediols seems reasonable, the large scatter in the data makes additional validation of this selection necessary. The various methods used to validate the results are described in the following section.

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4.2 Validation of the vaporization enthalpies by structure-property correlations

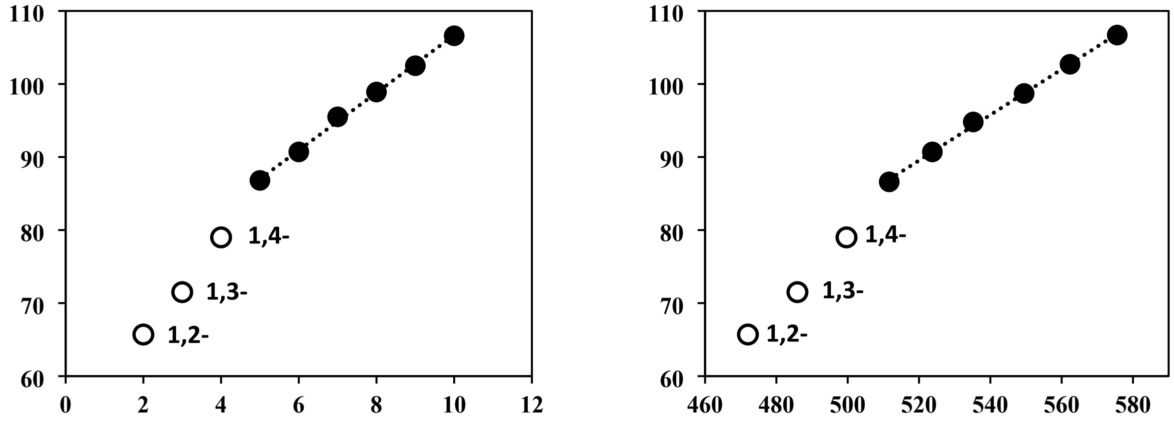
The structure-property correlations form the core of physical-organic chemistry, because new experimental results are integrated into the network of already known and reliable data. If the new results are consistent with the trends already known from the available results, they can be recommended for thermochemical calculations. Otherwise, the unusual structural effects must be explained or the experiments repeated to avoid confusion.

The simplest types of such correlations are relationships between a property of interest and a chain length (N_C), or between a property of interest and the normal boiling temperature (T_b), or between a property of interest and the chromatographic retention index (J_x).

The latter two types are more specific to the enthalpies of vaporization. However, the use of all three types is most successful for the homologous series where a specific contribution for the CH_2 fragment is expected. Therefore, the series of α,ω-alkanediols, which is the focus of this work, is predestined for the use of these correlations to validate the experimental thermochemical properties of interest in this study.

4.2.1 Empirical relationship: enthalpies of vaporization versus chain length N_C.

The relationship between $\Delta_l^g H_m^o$(298.15 K) and the number of carbon atoms in the alkyl chain, N_C, for the α,ω-alkanediol series with our choice of vaporization enthalpies (highlighted in bold in Table 3, column 5) is shown in Fig. 3 (left).



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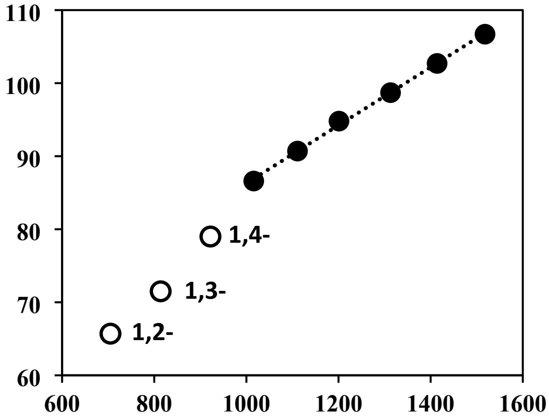

Fig. 3. Structure-property correlations with enthalpies of vaporization, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ K)$ for the data evaluated in Table 3 for α,ω-alkanediols.
Left: chain length dependence with the N_{C}. The numerical data are given in Table S9.
Right: with the normal boiling temperatures, T_b, from the literature [56]. The numerical data are given in Table S10.
Below: with the Kovats indices (J_x) from the literature [57]. The numerical data are given in Table S11.

It is obvious that the expected homologous linear behaviour starts first from the C5 diol and the following equation approximates the dependence of the vaporization enthalpies on the chain length:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15)/\ \mathrm{kJ\ mol^{-1}} = 4.01 \times N_{\mathrm{C}} + 66.6 \text{ with } R^2 = 0.9999 \qquad (\text{for } C \geq 5) \qquad (4),$$

The reason why the 1,2-, 1,3- and 1,4-diols do not belong to this line is the intra-molecular hydrogen bonding known from the spectroscopic studies [58], which was also observed in the conformers of these diols (see Table S2). Nevertheless, the definite linear increase of the vaporization enthalpies starting from the C5 diol should be considered as evidence for the internal consistency of the values selected in Table 3.

4.2.2 Empirical relationship: enthalpies of vaporization versus T_b.

The purely empirical correlations relating vaporization enthalpy to normal boiling temperatures (T_b) or to molecular weight are well established in the literature [59]. Here, too, a linear relationship between T_b. and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values is expected for the homologous series such as the alkanediols, as shown in Fig. 3 (top right). However, similar to the relationship with chain length (see Fig. 3, top left), the linear part starts with the C5 diol:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\ /(\mathrm{kJ{\cdot}mol^{-1}}) = 0.3117 \times T_b - 72.6 \text{ with } R^2 = 0.9985\ (\text{for } C \geq 5) \qquad (5),$$

as the C2, C3 and C4 diol homologues have strong intra-molecular hydrogen bonds that force the vaporization enthalpies of these three species to leave the line. The high correlation coefficient of Eq. (5) gives confidence that the straight line is also valid for the long-chain diols.

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4.2.3 *Empirical relationship: enthalpies of vaporization versus the Kovats indices J_x.*

A chromatographic Kovats retention index, J_x, is commonly used to identify the composition of reaction mixtures [[60]. The retention index represents the intensity of the interaction of a solute with the coating of the column. The J_x-values have been shown to be linked to the $\Delta_l^g H_m^o$(298.15 K)-values [61]. The Kovats indices of α,ω-alkanediols on a non-polar column DB-1 (see Tables S11) were taken from the literature [57] and correlated with the selection of $\Delta_l^g H_m^o$(298.15 K)-values evaluated in Table 3. A very good linear correlation with the corresponding J_x-values

$$\Delta_l^g H_m^o(298.15\ \text{K})\ /(\text{kJ}\cdot\text{mol}^{-1}) = 46.6 + 0.0397 \times J_x \text{ with } R^2 = 0.9985 \text{ (for C} \geq 5) \qquad (6)$$

can be seen in Fig. 3 (below).

The high correlation coefficients of Eqs. (4 to 6) confirm the internal consistency of the $\Delta_l^g H_m^o$ (298.15 K)-data used in the correlations. Tables S9 to S11 show that the differences between the experimental values and the calculated values calculated are well below than 0.5 kJ·mol^{-1}. Therefore, these correlations were used to extrapolate the $\Delta_l^g H_m^o$(298.15 K)-values for C11 to C16 alkanediols (see Tables S9 to S11).

4.2.4 *Summary of the empirical correlations of the vaporization enthalpies*

Admittedly, the enthalpy of vaporization, $\Delta_l^g H_m^o$(298.15 K), is very well adapted as a thermochemical property for different types of structural relationships. Table 4 contains a comparison of the experimental vaporization enthalpies of α,ω-alkanediols from Table 3 with the values derived from empirical correlations according to Eqs. (4 to 6).

Table 4
A summary of the experimental enthalpies of vaporization, $\Delta_l^g H_m^o$, of α,ω-alkanediols and enthalpies of vaporization enthalpies derived using different types of structure-property correlations (at T = 298.15 K, in kJ·mol^{-1}).

Diol	$\Delta_l^g H_m^o$ (exp) [a] (Table 3)	$\Delta_l^g H_m^o$ vs N_C (Table S9)	$\Delta_l^g H_m^o$ vs T_b (Table S10)	$\Delta_l^g H_m^o$ vs J_x (Table S11)
1,5-pentanediol	86.6±0.6	86.7	86.9	86.9
1,6-hexanediol	90.7±0.4	90.7	90.7	90.7
1,7-heptanediol	94.8±0.4	94.7	94.2	94.3
1,8-octanenediol	98.7±0.3	98.7	98.7	98.7
1,9-nonanediol	102.7±0.3	102.7	102.7	102.7
1,10-decanenediol	106.7±0.3	106.7	106.8	106.9

[a] The experimental uncertainties are expressed as two times the standard deviation of the mean value.

It can be seen from this table that the experimental and empirical results for α,ω-alkanediols are hardly distinguishable, and this fact provides full confidence in the reliability of these values, which

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is why the experimental vaporization enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), evaluated in Table 3 (values in bold) can be safely recommended for thermochemical calculations.

5. Enthalpy of sublimation as an intermediate between Top-Down and Bottom-Up strategies

In fact, long-chain α,ω-alkanediols, starting from 1,6-hexanediol, are solid at room temperature (with the exception of 1,7-heptanediol). In this case, reliable data on the sublimation enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K), are necessary to reconcile the QC gas-phase enthalpies of formation and the crystal-phase enthalpies of formation according to the top-down strategy (see Fig. 4).

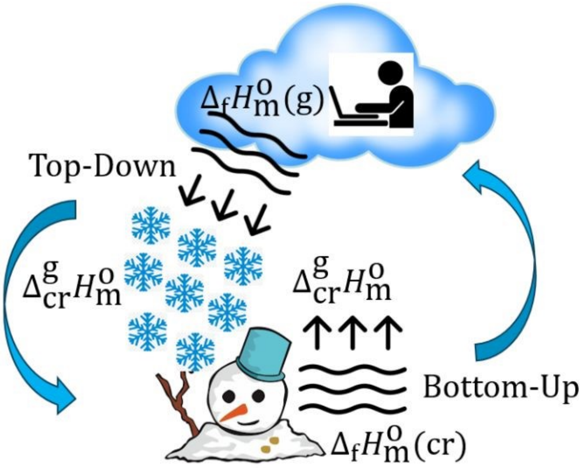

Fig. 4 Top-Down and Bottom-Up strategies for evaluation of thermochemistry of α,ω-alkanediols via sublimation enthalpies

The data available in the literature is of very questionable quality, therefore, a critical evaluation using all available methods is necessary, as described in the following sections.

5.1 Experimental sublimation enthalpies from vapor pressure measurements

Surprisingly, no systematic vapor pressure studies on the solid sample for diols with *Nc* > 6 can be found in the literature. Only the sublimation enthalpies of 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol were measured directly by calorimetry by Knaut and Sabbah [13].

In this work, for the first time, the vapor pressure-temperature dependences over the solid samples of 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol were measured using the transpiration method (see Table S6) and the corresponding sublimation enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{av}})$, were derived (see details in ESI). Our new results and the available results from Ref. [13] were treated consistently in this work to calculate and compare the $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values. The compilation and comparison of the standard molar sublimation enthalpies of α,ω–alkanediols are listed in Table 5.

Table 5
Compilation of the standard molar enthalpies of sublimation of α,ω-alkanediols (in kJ·mol^{-1})

Diol	Method [a]	T-Range	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}/T_{\mathrm{av}}$	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$/298.15 K [b]	Ref.
1,6-hexanediol (cr)	C	298.15		112.0±0.8	13
	T	290.4-314.2	111.8±0.6	111.9±0.7	Table S6
	PhT			112.2±0.7	Table S15
				112.1±0.4 [c]	average
1,8-octanediol (cr)	C	323.0	138.3±1.6	(140.6±1.7)	13
	T	304.4-331.2	132.1±1.4	132.9±1.6	Table S6
	PhT			131.8±1.1	Table S15
				132.1±0.9 [c]	average
1,9-nonanediol (cr)	C			(148.1±2.2) [d]	13
	T	298.2-318.7	137.2±2.0	137.6±2.2	Table S6
	PhT			137.2±0.8	Table S15
				137.3±0.8 [c]	average
1,10-decanediol (cr)	C	342.0	149.8±1.2	(151.7±1.3)	13
	T	315.5-343.7	145.8±1.0	147.2±1.2	Table S6
	PhT			146.8±1.5	Table S15
				147.0±0.9 [c]	average

[a] Methods: C = calorimetry; T = transpiration method; PhT = from consistency of phase transition enthalpies (see Table S15).

[b] Vapor pressures from Table S6 were treated using Eqs. (S2) and (S3) with help of heat capacity differences from Table S7 to calculate the enthalpies of sublimation at 298.15 K. Uncertainties of the sublimation enthalpies $U(\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}})$ are the expanded uncertainties (0.95 level of confidence) calculated as described elsewhere [55]. They include uncertainties from the fitting equation and uncertainties from temperature adjustment to T = 298.15 K. The uncertainties in the temperature adjustment of the literature data on sublimation enthalpies to the reference temperature T= 298.15 K are estimated to account with 20% to the total adjustment.

[c] Weighted average (uncertainties were taken into account as weighting factors). The values in bold are recommended for further thermochemical calculations.

[d] Sum of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15) = (113.6±2.1) kJ·mol^{-1} [Table 3] and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = (34.5±0.7) from Table 6.

The analysis of the very few available data on the sublimation enthalpies for α,ω-alkanediols revealed a strong ambiguity in these results. While the new and old sublimation enthalpies for 1,6-hexanediol are largely in agreement, the discrepancies of 5 to 7 kJ·mol^{-1} for 1,8-octanediol and 1,10-decanediol are considerable and require explanation or validation.

5.2 Step-by-step validation of sublimation enthalpies

It is also known that the sublimation enthalpy as a thermochemical property hardly obeys the additivity rules, in contrast to the vaporization enthalpy. The reason for this can be seen from Eq. (3). The sublimation enthalpy, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, contains not only the additive contribution of the vaporization enthalpy, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$, but also the high proportion of intermolecular interactions, which are captured by the fusion enthalpy, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$. Nevertheless, a validation of the experimental sublimation enthalpies is required, even if no direct empirical relationships can be applied. Fortunately, the same Eq. (3) suggests a straightforward way to accomplish the required validation as shown in Fig. 5.

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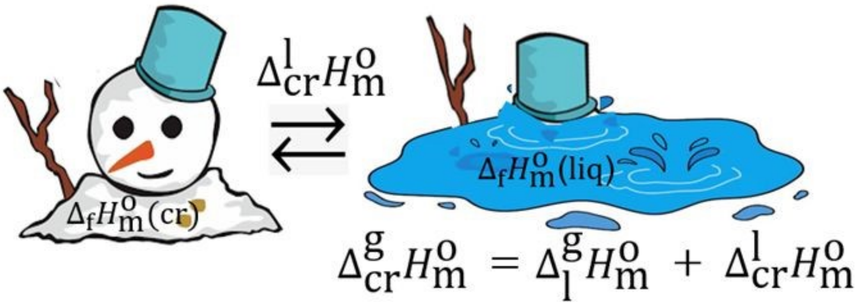

Fig. 5 Relationship between enthalpies of phase transition: crystal-gas, liquid-gas and crystal-liquid determined according to Eq. (3).

The reliable vaporization enthalpies, $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}$(298.15 K), that contribute to Eq. (3), have just been validated in Tables 3 and 4. This is the first step in validating the experimental sublimation enthalpies.

What about the fusion enthalpy, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}$ (298.15 K), which makes the second contribution to Eq. (3)? There has been no lack of experimental studies on the melting of α,ω-alkanediols in the literature (see Table S12). Provided that the literature values for fusion enthalpies measured at T_{fus} are correctly adjusted from T_{fus} to the reference temperature T = 298.15 K, the second step in the required validation of sublimation enthalpies is complete, and the result from the summation of $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}$(298.15 K) and $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}$(298.15 K) gives the empirically expected level to support our new sublimation enthalpy measurements. The evaluation of the available data for $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(T_{\text{fus}})$ and their adjustment to T = 298.15 K is the subject of the following section.

5.2.1 *Step I: Evaluation and analysis of the available fusion enthalpies of α,ω*-alkanediols

The α,ω-alkanediols belong to the organic phase change materials (PCMs), which are widely used in thermal energy storage systems due to their high enthalpies and controllable phase change temperatures [62,63]. Therefore, their thermal behaviour, including melting points and fusion enthalpies, has been intensively studied in recent literature using differential scanning calorimetry (DSC) (see Table S12).

The experimental data summarised in this table show significant but acceptable variations in the melting parameters for each diol. These variations are natural, as the melting temperatures and phase transition enthalpies are sensitive to the purity of the sample analysed as well as the heating/cooling rates applied during the DSC studies. However, apart from some obvious outliers, at least two matching experimental results were found in the literature for most alkanediols and averaged (see Table S12) for the evaluation and discussion in this section.

The DSC measurements revealed an interesting systematic change in the melting points for α,ω-alkanediols [64]. It was observed that the odd-numbered members (hereinafter referred to as "*odd*")

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in this homologous series are less well packed than the even-numbered members (hereinafter referred to as "even") [64]. The plot of the averaged $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ against T_{fus} also showed that the energetics of the solid-liquid phase transitions for α,ω-alkanediols are specific to the *odd* and *even* members, as shown in Fig. 6.

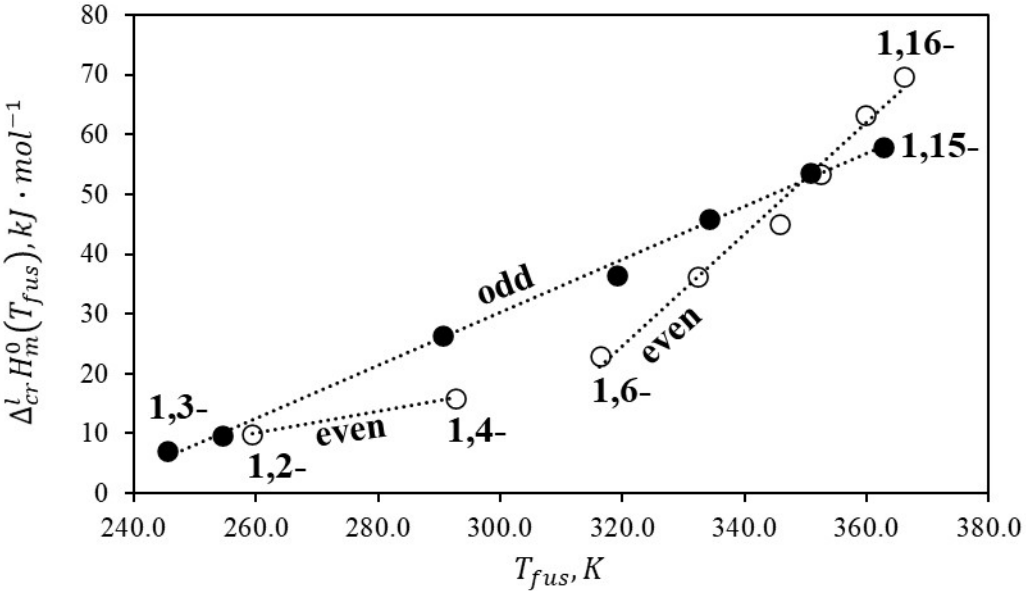

Fig. 6. Relationship between the fusion enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ and the fusion temperatures, T_{fus}, for the data evaluated in Table S12 for α,ω-alkanediols.
● - the *odd* members of the series, the numerical data are given in Table S13.
○ - the *even* members of the series, the numerical data are given in Table S14.

The fusion enthalpies for C3 to C16 diols are divided into two groups for the *even* and *odd* members of the homologous family. Both groups showed their own linear dependence, which was approximated by the following equations:

odd diols: $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = 0.4416\times J_x - 102.2$ with $R^2 = 0.9967$ (7)
even diols: $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})\ /(\mathrm{kJ\cdot mol^{-1}}) = 0.9365\times J_x - 275.0$ with $R^2 = 0.9835$ (8)

The X-ray data collected by Thalladi *et al.* [64] showed that the *even*-numbered diols form a layer-like network and the *odd*-numbered members form a three-dimensional structure. As a result, the *odd*-numbered members in both series are less tightly packed than the *even*-numbered members. This quantitative finding is now supported by the collection of fusion enthalpies of α,ω-alkanediols evaluated in Tables S12 to S14.

It is worth noting that two compounds, 1,2-ethanediol and 1,4-butanediol, completely fall out of the correlation according to Eqs. (7) and (8). The obvious explanation for these outliers is that the competition between the strong intramolecular hydrogen bonding and the strong intermolecular hydrogen bonding in both species influences the formation of the crystal lattice. However, it cannot be completely ruled out that the deviation is partly due to the considerable variation (from 4 - 7 kJ·mol^{-1}) in the fusion enthalpies for 1,2-ethanediol and 1,4-butanediol reported in the literature

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(see Table S12). The very high correlation coefficients R^2 obtained for both linear dependencies can be regarded as evidence of good consistency of the fusion parameters within each group and indirectly support the selection of the experimental values for 1,5-pentanediol and 1,7-heptanediol, where the discrepancy between the available data precluded the use of a mean value.

The temperature adjustment of the fusion enthalpies from T_{fus} to $T = 298.15$ K was carried out according to the following equation:

$$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})/(\mathrm{J{\cdot}mol^{-1}}) = \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}}/\mathrm{K}) - (\Delta_{\mathrm{cr}}^{\mathrm{l}}C_{\mathrm{p,m}}^{\mathrm{o}})\times[(T_{\mathrm{fus}}/\mathrm{K}) - 298.15\ \mathrm{K}] \qquad (9)$$

The differences in heat capacity between the crystalline and liquid phases, $\Delta_{\mathrm{cr}}^{\mathrm{l}}C_{\mathrm{p,m}}^{\mathrm{o}}$, were determined in our recent work [21] and are listed in Table S7. The summary of the $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values adjusted to the reference temperature is listed in Table 6, column 6.

Table 6
The adjustment of the experimental enthalpies of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$, of α,ω-alkanediols from melting points (T_{fus}) to $T = 298.15$ K[a]

	T_{fus} [b]	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ [b]	$\Delta_{\mathrm{cr}}^{\mathrm{l}}C_{\mathrm{p,m}}^{\mathrm{o}}$ [c]	(T_{fus} – 298.15)	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) [d]
Diols	K	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	K	kJ·mol^{-1}
1	2	3	4	5	6
Even					
1,6-	316.3	22.9±0.2	-77.5	18.2	21.5±0.5
1,8-	332.2	36.2±0.2	-91.0	34.1	33.1±1.0
1,10-	345.7	45.1±0.2	-104.5	47.6	40.1±1.5
1,12-	352.5	53.5±0.6	-118.0	54.4	47.1±2.0
1,14-	359.8	63.4±0.4	-131.5	61.7	55.3±2.5
1,16-	366.0	69.8±0.4	-145.0	67.9	60.0±3.0
Odd					
1,7-	290.5	26.3±0.6	-84.3	-7.6	26.9±0.6
1,9-	319.1	36.5±0.4	-97.8	21.0	34.5±0.7
1,11-	334.1	45.9±0.5	-111.3	36.0	41.9±1.3
1,13-	350.7	53.7±0.7	-124.8	52.6	47.1±2.1
1,15-	362.7	58.0±0.5	-138.3	64.6	49.1±2.7

[a] Uncertainties are presented as expanded uncertainties (0.95 level of confidence with k=2).
[b] Averaged experimental values from Table S12.
[c] The heat capacity differences from Table S7.
[d] The experimental enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$ measured at T_{fus} (see Table S12) were adjusted to $T = 298.15$ K according to Eq. (9)

These values can now be combined with the vaporization enthalpies $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) evaluated in Table 3 to verify the experimental sublimation enthalpies of the solid α,ω-alkanediols measured in this work using the transpiration method (see Table 6), as shown in the next section.

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5.2.2 Step II: Consistency of phase change enthalpies of α,ω-alkanediols

The consistency of the energetics of the liquid-gas, crystal-liquid and crystal-gas phase transitions can be evaluated according to Eq. (3), as shown in Fig. 5. The required enthalpies of vaporization (Table 3) and fusion enthalpies (Table 6) for the solid C6-C10 diols were evaluated in the previous sections. The results of the calculations of the empirical $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values according to Eq. (3) are given in Table 5 (with the notation “from phase transition (PhT)”) and compared there with the experimental sublimation enthalpies.

As can be seen from Table 5, the sublimation enthalpies $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) of 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol, calculated according to Eq. (3), do not agree in all cases (with the exception of 1,6-hexanediol) with the calorimetric results of Knaut and Sabbah [13], whereas they agree very well with our new experimental values measured using transpiration (see Table S6) for all four diols. This agreement was considered to be the reason for excluding the calorimetric sublimation enthalpies from Ref. [13] from the calculation of the average values in Table 5. The weighted average $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values for 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol are given in bold in Table 5 and were recommended for thermochemical calculations according to the "top-down" and "bottom-up" strategies.

An interesting additional option for validating the $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values for α,ω-alkanediols resulted from a correlation with the fusion enthalpies $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ evaluated in Table S12. The reason for this surprisingly good correlation is that both thermochemical properties are closely related to the lattice energy, which increased simultaneously with the growing chain length in the properties involved in the correlation. A good linear correlation (see Table S16):

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})/\ \mathrm{kJ{\cdot}mol^{-1}} = 1.67 \times \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}}) + 74.9 \text{ with } R^2 = 0.9899 \text{ (for C6-C16)} \qquad (10)$$

can be regarded as an additional indicator of the good consistency of both data sets evaluated in this work.

6. Top-down strategy: What $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(liq or cr)-values can finally be expected for *α,ω*-alkanediols?

The careful evaluation and revision of the experimental vaporization and sublimation enthalpies of α,ω-alkanediols, which was carried out in sections 4 and 5, ultimately paves the way for the realization of the "top-down" strategy and the assessment of the expected "theoretical" condensed-phase enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$(liq or cr), from the combination of the QC gas phase formation enthalpies (Table 7, column 2) and the vaporization/sublimation enthalpies evaluated in this work (see Table 7, columns 3 and 4).

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Table 7

Calculation of the "theoretical" condensed-phase enthalpies of formation, $\Delta_f H_m^o$(liq or cr), from the compilation of the quantum chemical gas-phase enthalpies of formation of α,ω-alkanediols, $\Delta_f H_m^o$(QC), and the vaporization/sublimation enthalpies evaluated in this work (at T = 298.15 K in kJ·mol^{-1}).

Diol	$\Delta_f H_m^o$(QC) [a]	$\Delta_l^g H_m^o$ [b]	$\Delta_{cr}^g H_m^o$ [c]	$\Delta_f H_m^o$ (liq or cr) [d]	$\Delta_f H_m^o$ (liq or cr) [e]	Δ [f]
1	2	3	4	5	6	7
1,2-ethanediol (liq)	-390.0 ± 2.3	65.7±0.2		-455.7±2.3	-455.9±0.6	-0.2±2.4
1,3-propanediol (liq)	-412.4 ± 2.3	71.5±0.3		-483.9±2.3	-482.8±1.6	1.1±2.8
1,4-butanediol (liq)	-426.4 ± 2.6	79.0±0.7		-505.4±2.7	-504.7±1.7	0.7±3.2
1,5-pentanediol (liq)	-446.6 ± 2.4	86.6±0.6		-533.2±2.5	-530.2±2.5	3.0±3.5
1,6-hexanediol (cr)	-466.7 ± 2.1		112.1±0.4	-578.8±2.1	-579.8±2.5	-1.0±3.3
1,7-heptanediol (liq)	-487.9 ± 2.4	94.8±0.4		-582.7±2.4	(-574±19)	8.7±19
1,8-octanenediol (cr)	-508.5 ± 2.4		132.1±0.9	-640.6±2.6	-642.0±1.4 [g]	-1.4±3.0
1,9-nonanediol (cr)	-528.7 ± 2.3		137.3±0.8	-666.0±2.4	(-658±15)	8.0±15
1,10-decanenediol (cr)	-549.5 ± 2.4		147.0±0.9	-696.5±2.6	-698.8±1.0	-2.3±2.9

[a] DLPNO values from Table 2. The uncertainties were defined as $s_d \times t$, where s_d is the standard deviation from the weighted average value and t is Student's coefficient for the 95% confidence level. The values from this column plotted versus chain-length N_C provide the straight line):
$\Delta_f H_m^o$(g, 298.15 K)/(kJ·mol^{-1}) = -343.5 – 20.6×N_C with R^2 = 0.9999 (for C ≥ 5).

[b] From Table 3.

[c] From Table 5.

[d] "Theoretical" values calculated using Eq. (1) and Eq. (2) and data from columns 2 and 3 or 4.

[e] Experimental values from Table 8.

[f] Difference between column 6 and 5.

[g] Measured in this work, see Table 8.

The $\Delta_f H_m^o$(liq or cr) values given in Table 5, column 5, provide a valuable guideline for evaluating the scattering experimental results found in the literature (see Table 1) as shown in the next section.

7. Bottom-Up strategy: Condensed-phase enthalpies of formation from combustion calorimetry

7.1. Review and revision of the condensed-phase enthalpies of formation of α,ω-alkanediols

The history of combustion experiments with α,ω-alkanediols began in 1936 [65] with measurements on 1,2-ethanediol, and surprisingly, these early results (albeit with a high degree of uncertainty) still agree with later studies. Table 8 summarizes the available experimental results from combustion calorimetry.

Table 8

Compilation of experimental results from combustion calorimetry of α,ω-alkanediols at T = 298.15 K ($p°$ = 0.1 MPa).

Diol	$\Delta_c u^o$(liq or cr)/ [a] J·g^{-1}	$\Delta_c H_m^o$(liq or cr)/ [b] kJ·mol^{-1}	$\Delta_f H_m^o$(liq or cr) [b] kJ·mol^{-1}	Purity, [c] mol fraction
1,2-ethanediol (liq)	-19176±43 [66]	-1191.4±7.1	-453.1±7.1	0.99

	-19356±48 [67]	-1202.6±6.0	(-441.9±6.1)	-
	-19147±40 [68]	-1189.6±5.0	-454.9±5.1	-
	-19137±48 [69]	-1189.0±6.0	-455.9±0.9	-
	n/a [52]	-1188.8±0.7	-455.6±0.8	0.999
	-19066±46 [11]	-1184.6±5.7	-459.9±5.7	0.9913
		-	-458.2±2.5 [e]	
			-455.9±0.6 [d]	
1,3-propanediol (liq)	n/a [52]	-1859.0±2.3	(-464.8±2.5)	0.999
	-24187±67 [11]	-1843±10	-480.8±10.3	0.9923
	-24478±18 [17]	-1865.1±3.0	(-458.7±3.0)	-
			-483.6±2.2 [e]	-
	-24171.9±16.0 [9]	-1841.8±2.5	-482.0±2.5	
			-482.8±1.6 [d]	
1,4-butanediol (liq)	-27688±24 [52]	-2499.1±2.9	-504.2±3.0	0.998
	-27698±17 [52]	-2499.9±2.0	-503.3±2.1	0.998
	-27650±63 [11]	-2496±12	-508±12	0.9939
	-27679.0±9.0 [70]	-2498.2± 1.9	-505.0±2.0	-
			-504.7±1.7 [d]	
1,5-pentanediol (liq)	n/a [65]	-3156±5.0	-526.5±5.2	-
	n/a [52]	-3151.1±2.8	-531.4±2.9	0.998
	-30234±55 [11]	-3154±12	-529±12	0.9919
			-530.2±2.5 [d]	
1,6-hexanediol (cr)	n/a [52]	-3791.9±4.8	-569.9±5.0	0.998
	n/a [18]	-3999.8±4.6	(-362.2±4.8)	0.99
	-32000±37 [12]	-3787.7±9.2	-574.1±9.2	0.9938
	-31916.7±1.6 [19]	-3778.0±2.0	-583.9±3.0 **-579.8±2.5** [d]	0.9999
1,7-heptanediol (liq)	-33734±70 [12]	-4467±19	(-574±19) **-582.7±1.5** [f]	0.9920
1,8-octanenediol (cr)	-34778±33 [12]	-5094 ± 10	(-627±10)	0.9991
	-34671.2±1.6 [Table S19]	-5078.6± 0.9	**-642.0±1.4**	0.9996
1,9-nonanediol (cr)	-35771±44 [12]	-5742±15	(-658±15) **-668.3±1.7** [g]	0.9981
1,10-decanenediol (cr)	36585.3±7.3 [71]	-6387.3±3.7	-692.0±3.9	-
	-36660±13 [12]	-6400.3± 6.4	-678.9±6.5	0.9933
	-36540.0±1.5 [20]	-6379.4± 0.9	-699.7±1.0	0.9999
			-698.8±1.3 [d]	

[a] Original experimental values from the literature (n/a = not available). Uncertainties correspond to standard uncertainties of the mean.

[b] Results were recalculated in this work according to modern requirements for combustion calorimetry [72]. Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence).

[c] Purity level given in the original literature.

[d] The weighted mean value (uncertainties were taken as the weighing factor), values in parentheses were not involved in the averaging.

[e] From equilibrium studies (see for details Section 7.3).

[f] From chain-length dependence (Table S22).

[g] From (Table S21).

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The treatment of the primary results of combustion experiments involves numerous important details, references and steps, which were ultimately standardised in the IUPAC compilation published by Sunner and Mansson in 1979 [72]. For this reason, we have used the standard molar energies of combustion, $\Delta_\mathrm{c}u^\mathrm{o}$, given in the original literature (see Table 7, column 2) and converted them uniformly to the final condensed standard molar enthalpies of formation, $\Delta_\mathrm{f}H^\mathrm{o}_\mathrm{m}$(liq or cr), according to the procedure recommended in the IUPAC book [72] (see Table 8, column 4).

Most combustion experiments with α,ω-alkanediols were conducted by Knauth and Sabbah [11,12] using a rocking calorimeter with a stainless steel micro bomb. Since the standard molar enthalpies of formation of α,ω-alkanediols derived from combustion experiments by Knauth and Sabbah [11,12] are subject to considerable uncertainty, the necessary experimental details of their study must be briefly summarised in order to discuss possible sources of error.

First of all, the purity of the samples used for combustion calorimetry is crucial for the reliability of the formation enthalpies derived using this method. Conventionally, the typical purity of samples is between 0.9995 and 0.9999, expressed in terms of molar fraction. Particularly restricted are quantities of low-molecular impurities such as traces of water or solvents (acetone, methanol, methylene chloride, *etc.*) as a rule used for recrystallization of samples for combustion experiments. The commercial samples, used by Knauth and Sabbah [11,12], were purified by rectification using a rotary band column with 30 theoretical plates (for liquids) and by sublimation at 313 K under a reduced pressure of approximately 1 Pa (for solids). The sample of 1,6-hexanediol (99+%, "Gold Label", Aldrich) was used without further purification. The purity of the samples was determined by by low-temperature differential thermal analysis using the freezing-point method. Despite additional purification, the samples used by Knauth and Sabbah [11,12] were significantly below the conventional requirements for combustion calorimetry (see Table 2).

Diols are known to be highly hygroscopic. To prevent contamination of the hygroscopic diols by atmospheric moisture prior to combustion, the liquid and solid diol samples were sealed in small polyethylene containers [11,12]. Knauth and Sabbah [11,12] used a rocking microcalorimeter calibrated for precise measurements of the combustion energies of small samples (5–10 mg). It is well known [73], that experimental work with a typical microcalorimeter and such small samples is no trivial task [74,75]. Apart from purely technical difficulties in recording the very small temperature rise during the combustion experiment, even the seemingly simple problem of reproducible weighing of the tiny samples arose. Nevertheless, accurate measurements with the microcalorimeter are possible, and the reproducibility of the measurements at a level of 0.01% (based on the combustion energy) is generally proven [74,75], at least for the measurements of the primary standard (benzoic acid) and the secondary standards (salicylic acid and succinic acid).

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Calibration of the microcalorimeter by Knauth and Sabbah [11,12] using benzoic acid yielded a value of 0.025%, which is not perfect but still acceptable. The polyethylene used as a container for the combustion experiments was also measured with the same reproducibility [11,12]. In this context, the very poor reproducibility of the combustion experiments with diols (*e.g.* 0.095% with 1.8-octanediol) does not indicate problems with the equipment, but either problems in the preparation of the samples for the measurements or possibly incomplete combustion of the sample.

It was not possible to verify the completeness of combustion of such tiny samples using conventional methods (*e.g.* visual inspection or CO_2 recovery [76]). However, in our opinion, a possible reason for the low reproducibility of the combustion experiments by Knauth and Sabbah [11,12] could be the partial loss of polyethylene mass during the sealing of the container using the conventional hot wire method (see details in the IUPAC book [72]). From our experience, we know that sometimes, if the polyethylene container is too close to the glowing wire, a very small amount of the polyethylene evaporates, leading to a significant loss of mass (especially for the 5-10 mg sample). With this plausible explanation for the poor reproducibility of the combustion experiments by Knauth and Sabbah [11,12], it should be recognised that for most diols, their average enthalpies of formation are in good agreement with the results obtained with other types of calorimeters and typical sample quantities (from 0.5 to 1.0 g).

Even the uniformly treated, available combustion results for each α,ω-alkanediol summarised in Table 8 showed considerable variation in values, so that only with the help of the "theoretical" enthalpies of formation from Table 7, column 5, an apparent outliers for 1,7-heptanediol, 1,8-octanediol and 1,9-nonanediol measured in Ref. [12] could be safely discarded (see Table 8, column 4). Given the very uncertain enthalpies of formation for 1,7-heptanediol, 1,8-octanediol and 1,9-nonanediol, we decided to repeat the combustion experiments with 1,8-octanediol using a macro-calorimeter with a static bomb (see ESI for necessary details).

7.2. Crystalline-phase enthalpy of formation of 1,8-octanediol from combustion calorimetry

The combustion experiments with 1,8-octanediol refer to the reaction:

$$C_8H_{18}O_2(\mathrm{cr}) + 11.5\ O_2\ (\mathrm{g}) = 8\ CO_2\ (\mathrm{g}) + 9\ H_2O\ (\mathrm{liq}) \qquad (11)$$

The standard specific energy of combustion $\Delta_c u^o(\mathrm{cr})$ of 1,8-octanediol was determined based on five experiments. The latter value was used to calculate the experimental standard molar enthalpy of combustion, $\Delta_c H^o_m(\mathrm{cr})$, which refers to the reaction according to Eq. (11). The $\Delta_c H^o_m$-value was used to obtain the standard molar enthalpy of formation $\Delta_f H^o_m(\mathrm{cr})$ in the crystalline state, applying Hess´s Law to the reaction according Eq. (11), and the standard molar enthalpies of formation of CO_2(g) and

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H_2O(liq) assigned by CODATA [77]. Uncertainties associated with the combustion experiments were estimated according to the procedure recommended by Olofsson [78]. The auxiliary information on the combustion experiments is provided in Tables S17 to S19. The final results of the combustion experiments with 1,8-octanediols are listed in Table 8. It is difficult to judge whether our new result $\Delta_f H_m^o$(cr) = -642.0±1.4 kJ·mol^{-1} is consistent with the previous result $\Delta_f H_m^o$(cr) = -627±10 kJ·mol^{-1} [12], as the latter value is subject to considerable uncertainty. However, the "theoretical" value $\Delta_f H_m^o$(cr) = -640.6±2.6 kJ·mol^{-1} (see Table 7, column 5) from the "top-down" strategy supports our new value.

7.3 Liquid-phase enthalpies of formation of 1,2-ethanediol and 1,3-propanediol from equilibrium studies

A series of equilibrium studies on acetals and ketals synthesis reactions was published by Anteunis *et al.* [79]. Two of these, R1 and R2 are shown in Fig. 5.

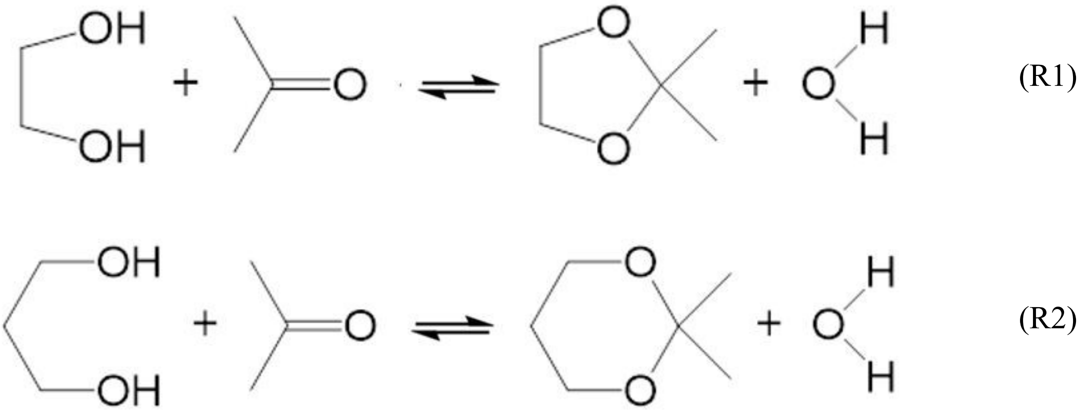

Fig. 7 The equilibrium reactions of ketal synthesis used to validate the liquid-phase enthalpies of formation of 1,2-ethanediol and 1,3-propanediol (see text).

The reaction enthalpies $\Delta_r H_m^o$(liq, 298.15 K) = -(10.0±1.5) kJ·mol^{-1} [79] for R1 and $\Delta_r H_m^o$(liq, 298.15 K) = -(23.0±1.5) kJ·mol^{-1} [79] for R2 measured by NMR-spectroscopy, can be used to independently derive the liquid-phase enthalpies of formation of 1,2-ethanediol and 1,3-propanediol using the Hess´s Law and the known enthalpies of formation of acetone, water, and ketals, which are collected in Table S20. The resulting enthalpies of formation are well comparable with the results of combustion calorimetry (see Table 8), and these independently derived values facilitated the selection of a reliable level, particularly in the case of 1,3-propanediol, where the available results differ by about 20 kJ·mol^{-1} (see Table 8, column 4).

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7.4 Empirical correlation: Liquid phase enthalpies of formation versus Nc

The significant support provided by the "top-down" values for the enthalpies of formation of diols in the condensed phase does not preclude further validation of the experimental combustion results using structure-property correlations, as was already carried out for the vaporization enthalpies in Section 4. From the fusion enthalpies of the solid diols evaluated in Table 6, the set of enthalpies of formation in the liquid phase, $\Delta_f H^o_m$(liq, 298.15 K), can be derived for the C6 to C10 diols according to Eq. (12):

$$\Delta_f H^o_m(\text{liq, 298.15 K}) = \Delta_f H^o_m(\text{cr, 298.15 K}) - \Delta^l_{cr} H^o_m(\text{298.15 K}) \qquad (12)$$

These values are given in Table S21 and can be used, for example, for chain length correlation. The correlation of the experimental $\Delta_f H^o_m$(liq, 298.15 K) values with the number of carbon atoms in the alkyl chain of diols showed a linear dependence (see Table S22):

$$\Delta_f H^o_m(\text{liq, 298.15 K})/(\text{kJ·mol}^{-1}) = -403.6 - 25.58 \times N_C \text{ with } R^2 = 0.9996 \text{ (for C} \geq 5) \qquad (13)$$

with a very high correlation coefficient, which convincingly demonstrates the internal consistency of the experimental data set for α,ω-alkanediols evaluated in Table 8.

7.5 Empirical correlation: Thermochemical properties from group-additivity

Group additivity (GA) is a well-established empirical method that is commonly used either to predict thermochemical properties or to validate experimental results [80]. For molecules that are not too large, have a hydrocarbon skeleton (possibly with a low degree of branching) and only a few functional groups, the GA method provides reliable estimates for unknown properties [81]. For the chemical family of alkanols, reliable GA contributions have been developed after careful revision and validation of experimental thermochemical data $\Delta^g_l H^o_m$(298.15 K) and $\Delta_f H^o_m$(liq or g, 298.15 K) for alkanes and alkanols [82]). A summary of the GA values required for working with diols is listed in Table S23 together with an example of the estimation. A comparison of the experimental and group-additivity-estimated thermochemical properties of α,ω-alkanediols is presented in Table 9.

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Table 9
Comparison of experimental and estimated using group-additivity thermochemical properties of α,ω-alkanediols, in kJ·mol^{-1} at T = 298.15 K ($p°$ = 0.1 MPa).

	$\Delta_f H^o_m$ (liq)$_{exp}$[a]	$\Delta_f H^o_m$ (liq)$_{add}$[b]	Δ [c]	$\Delta^g_l H^o_m$ (exp)[d]	$\Delta^g_l H^o_m$ (add)[e]	Δ [f]	$\Delta_f H^o_m$ (g)$_{exp}$[g]	$\Delta_f H^o_m$ (g)$_{add}$[h]	Δ [i]
1	2	3	4	5	6	7	8	9	10
1,2	-455.9	-445.3	*-10.6*	65.7	77.4	*-11.7*	-390.2	-375.3	-14.9
1,3	-482.8	-474.2	*-8.6*	71.5	81.9	*-10.7*	-411.3	-399.1	-12.2
1,4	-504.7	-502.2	*-2.5*	79.0	81.6	*-2.6*	-425.7	-422.8	-2.9
1,5	-530.2	-530.4	0.2	86.6	86.2	0.4	-443.6	-444.5	0.6
1,6	-558.3 [j]	-556.2	-2.1	90.7	90.5	0.2	-467.7	-466.2	-1.7
1,7	(-582.7) [k]	-582.0	-0.7	94.8	94.8	0.0	-487.9	-487.9	1.1
1,8	-608.9 [j]	-607.8	1.1	98.7	99.0	-0.3	-509.9	-509.6	1.7
1,9	(-633.8) [k]	-633.7	-0.1	102.7	103.3	-0.6	-531.0)	-531.3	0.9
1,10	-658.7 [j]	-659.5	0.8	106.7	107.5	-0.8	-551.8	-553.0	0.8

[a] Experimental values from Tables 8 and S21.
[b] Estimated using group-additivity contributions from Table S23.
[c] Difference between columns 2 and 3 in this table.
[d] Experimental values from Table 3.
[e] Estimated using group-additivity contributions from Table S23.
[f] Difference between columns 5 and 6 in this table.
[g] Experimental values from Table 10.
[h] Estimated using group-additivity contributions from Table S23.
[i] Difference between columns 8 and 9 in this table.
[j] From Table S21.
[k] Calculated from the chain length dependence in Table S22.

The results shown in Table 9 for the vaporization enthalpies, the enthalpies of formation in the liquid and gaseous phases generally correspond to expectations. The calculated and experimental properties agree within the experimental uncertainties for the long-chain members with C ≥ 5 and are slightly outside their limits for 1,4-butanediol. The properties of 1,2-ethanediol and 1,3-propanediol are obviously affected by intramolecular hydrogen bonding, whereas its influence in 1,4-butanediol is much less. Since the strength of intramolecular hydrogen bonding is individual for all three species, their thermochemical properties do not obey the rules of additivity. So, the GA method used in this work generally supports the selection of reliable values for the thermochemical properties of α,ω-alkanediols.

7.6 Bottom-Up strategy: Where is the advantage?

Section 6 of this paper has clearly shown that modern advances in quantum chemistry are now an indispensable tool, not to compete, but to help synergistically in the challenging task of evaluating, validating, and critically revising experimental data. In combination with the evaluated phase

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transition enthalpies, the guiding values $\Delta_f H^o_m$(liq or cr, 298.15 K) were derived, and these values were helpful in clarifying the conflicting experimental data.

Sections 7.1 to 7.5 have conclusively demonstrated that the critically evaluated experimental data for $\Delta_f H^o_m$(liq or cr, 298.15 K) of *α,ω*-alkanediols are ultimately consistent and can be recommended for thermochemical calculations. The summary of the evaluated thermochemical properties for *α,ω*-alkanediols is given in Table 10.

Table 10.
Compilation of the evaluated and recommended thermochemical properties for α,ω-alkanediols (at T = 298.15 K and $p°$ = 0.1 MPa, in kJ·mol^{-1})[a].

Diol	$\Delta_f H^o_m$(liq or cr)$_{exp}$ [b]	$\Delta^g_{l,cr} H^o_m$ [c]	$\Delta_f H^o_m$(g)$_{exp}$ [d]	$\Delta_f H^o_m$(g)$_{QC}$ [e]	Δ [f]
1,2-ethanediol (liq)	-455.9±0.6	65.7±0.2	-390.2±0.6	-390.0±2.3	-0.2
1,3-propanediol (liq)	-482.8±1.6	71.5±0.3	-411.3±1.6	-412.4±2.3	1.1
1,4-butanediol (liq)	-504.7±1.7	79.0±0.7	-425.7±1.8	-426.4±2.6	0.7
1,5-pentanediol (liq)	-530.2±2.5	86.6±0.6	-443.6±2.6	-446.6±2.4	3.0
1,6-hexanediol (cr)	-579.8±2.5	112.1±0.4	-467.7±2.5	-466.7±2.1	-1.0
1,7-heptanediol (liq)	-582.7±1.5	94.8±0.4	-487.9±1.6	-487.9±2.4	0.0
1,8-octanenediol (cr)	-642.0±1.4	132.1±0.9	-509.9±1.7	-508.5±2.4	-1.4
1,9-nonanediol (cr)	-668.3±1.7	137.3±0.8	-531.0±1.8	-528.7±2.3	-2.3
1,10-decanenediol (cr)	-698.8±1.8	147.0±0.9	-551.8±2.0	-549.5±2.4	-2.3

[a] Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence).
[b] From Table 8.
[c] From Tables 3 and 5
[d] Sum of column 2 and 3 in this table.
[e] From Table 7, column 2.
[f] Difference between column 4 and 5 in this table.

Our main aim has therefore been achieved. It may appear now that the "bottom-up" strategy is unnecessary - at least for the purposes of this paper. But this is incorrect as will be shown in the following discussion:

Let us compare the experimental (Table 10, column 4) and QC calculated (Table 10, column 5) $\Delta_f H^o_m$(g) values. Except for 1,5-pentanediol, the difference between their values does not exceed 3 kJ mol^{-1}, which is significantly better than "chemical accuracy". This perfect correspondence confirmed that our assumption that the most stable conformer of α,ω-alkanediol adequately represents the gas phase mixture of the conformers is correct.

At the same time, as noted above (Section 3), the QC calculations do not provide an unambiguous conclusion about the most stable conformer of 1,4-butanediol (see Table 2). Although an approximate accounting of vibrational anharmonicity (Table 2) suggests that F-lin may be the main conformer of this diol, a comparison of the Gibbs free energies indicates that the most stable conformer should be HB. The experimental data obtained in this work, in our opinion, make it possible to solve this problem, which has long been discussed in the literature. Fig. 8 shows that for

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the C_4-C_{10} diols, the QC calculations agree within their uncertainties with the experiment when F-lin is considered as the main conformer, whereas for HB conformers the discrepancies go far beyond the calculation errors.

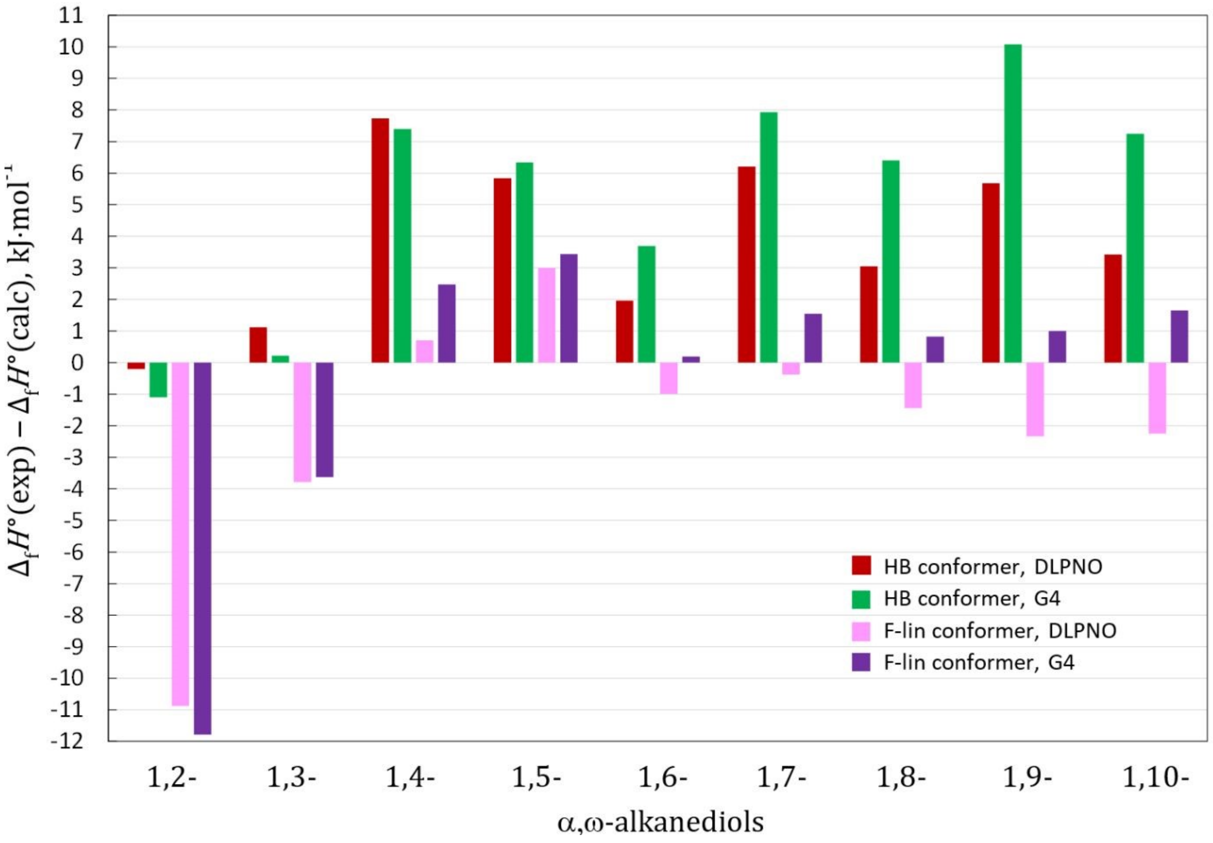

Fig. 8. Difference between the experimental enthalpies of formation α,ω-alkanediols (1,2-ethanediol, 1,3-propanediol etc.) and those calculated for most stable HB and F-lin conformers using DLPNO-CCSD(T_1)/CBS and G4 methods.

The opposite result is evident for 1,2-ethanediol and 1,3-propanediol, where only the HB conformers match the experimental enthalpies of formation. This example shows that carefully evaluated experimental values are still indispensable and that the "bottom-up" strategy should not be neglected, even as QC methods continue to advance.

8. Hybrid strategy: Bridging the two approaches

The previous section made clear that only a judicious combination of top-down and bottom-up strategies paves the way for a successful experimental and thermochemical work. This combination, known as a hybrid strategy, offers the following advantages:

- Improvement of the reliability of predicted enthalpies.
- Cross-validation of computational and experimental methods.
- Time savings by providing guidance for experiments (*e.g.*, avoiding redundant runs).

- Provision of databases with highly reliable thermodynamic values for new organic compounds.

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This hybrid strategy is particularly important for the workflow in modern experimental thermodynamics. In the last century, experiments took precedence over theoretical and empirical methods. Experimental thermochemical results were usually published without any validation. The mandatory discussion of the data was generally limited to a comparison with results already available in the literature (if available). Interestingly, the data measured later were considered more reliable. As a consequence, compilations of experimental data available in the literature (*e.g*. the most popular NIST Webbook [83]) only contain a list of a given thermochemical property as published in the original work. This means that users of the data are free to choose any value from this list or to calculate the average of the values, regardless of how large the spread of values within the list is.

In this century, the "hybrid strategy" should dominate, and the "top-down" strategy must be applied before the experiments are planned in order to understand the quality of the existing thermochemical properties. This strategy provides important information on whether new experiments are really necessary or whether the available data correspond to the "theoretical" expectations. In addition, every new thermochemical result should be validated using the "top-down" strategy before publication.

In our experience, the new experimental results were in many cases far from the theoretical "expectations". Such a discrepancy was seen as a good opportunity to further purify the sample and repeat the experiment or to use a different thermochemical method to verify the questionable result. Only if these efforts were unsuccessful and the result remained unchanged using different techniques, the "bottom-up" strategy was applied to uncover possible shortcomings, inconsistencies or simplifications in the theoretical, quantum chemical or empirical methods used for the "top-down" assessments. Consequently, any new result can only be recommended after applying the "hybrid strategy" for thermochemical calculations.

9. Conclusions

Literature data describing the vaporization thermodynamics of different α,ω-alkanediols have been evaluated and significant inconsistencies between standard enthalpies of formation and vaporization have been show. In this work, an hybrid strategy was applied that combines experimental results with quantum chemical calculations. This way the actual properties are accessed in a two-fold way: starting from the gas phase data with modelling data (top-down) and starting with experimental data for the condensed phase (bottom-up). Based on these results, it could be demonstrated that the available thermodynamic property data for α,ω-alkanediols deviate from the regular trend that could be expected for homologous series. Due to the significant contribution of intramolecularly hydrogen-

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bonded conformers in smaller molecules with the OH-groups close to each other, the properties of 1,2-ethanediol, 1,3-propanediol, and 1,4-butanediol differ considerably from those of their longer-chain counterparts. Starting from 1,5-pentanediol, the enthalpies of vaporization and the standard enthalpies of formation in the gas phase follow a regular linear trend. It can be assumed that this is due to the predominance of conformers without intramolecular hydrogen bonding.

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Data Availability Statement: All data are available in the text and in the electronic supporting information.

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