

Strong Even/Odd Pattern in the Computed Gas-Phase Stability of Dicarboxylic Acid Dimers: Implications for Condensation Thermodynamics

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Abstract

The physical properties of small straight chain dicarboxylic acids are well-known to exhibit even/odd alternations with respect to the carbon chain length. For example, odd numbered diacids have lower melting points and higher saturation vapour pressures than adjacent even numbered diacids. This alternation has previously been explained in terms of solid state properties, such as higher torsional strain of odd number diacids. Using quantum chemical methods we demonstrate an additional contribution to this alternation in properties resulting from gas phase dimer formation. Due to a combination of hydrogen bond strength and torsional strain, dimer formation in the gas phase occurs efficiently for glutaric acid (C5) and pimelic acid (C7), but is unfavourable for succinic acid (C4) and adipic acid (C6). Our results indicate that a significant fraction of the total atmospheric gas phase concentration of glutaric and pimelic acid may consist of dimers.

1 - Introduction

Carboxylic acids are among the most important compounds in environmental sciences. For example, most organic carbon emitted to the atmosphere is ultimately oxidised to CO_2 , and carboxylic acids are central intermediates of this oxidation chain. Because of their acidity, water solubility and general ability to act as hydrogen bond donors and acceptors, carboxylic acids also interact strongly with other atmospheric constituents, including other organics, water, NH_3 , amines and inorganic acids such as H_2SO_4 .¹ For instance, a recent combined experimental and theoretical study has shown that formic acid and trimethylamine form a strong ion-pair at the surface of aqueous particles.² Due to these interactions, carboxylic acids are important constituents of atmospheric aerosols, and account for up to 28% of the aerosol mass in the northern hemisphere.³ Di- and polycarboxylic acids have been observed in aerosol samples around the world⁴⁻⁶ and have recently been suggested as important partners in atmospheric new particle formation.⁷ Carboxylic acids can be formed in situ in the atmosphere by photooxidation of hydrocarbons.⁸ Both mono- and dicarboxylic acids are also emitted directly by a large variety of biogenic and anthropogenic sources, with anthropogenic sources typically associated with shorter and biogenic sources with longer chain lengths.⁹ Because of a combination of their atmospheric importance, and commercial availability, straight-chain dicarboxylic acids have emerged as the standard set of polyfunctional molecules in atmospheric chemistry and physics for comparison and evaluation of methods for predicting and/or measuring molecular or aerosol particle properties such as saturation vapor pressures, hygroscopicity and CCN activity. An intriguing feature of these compounds is the alternation of many of their physical properties between even and odd carbon numbers. For example the melting points and solid saturation vapor pressures of the dicarboxylic acids with less than about ten carbon atoms have been reported to display a characteristic sawtooth pattern, imposed on an overall increasing or decreasing trend, respectively.¹⁰ These alternations have been explained in terms of stacking patterns in the solid state structures, leading to higher torsional strain for diacids with an odd number of carbon atoms.¹¹ In this

study, we investigate the formation energetics of dicarboxylic acid hydrogen bonded dimers in the gas phase, in order to determine whether or not these even-odd alternations are unique to the properties of the solid state phase. The presence of two strongly H-bonding functional groups on each dicarboxylic acid in principle permits the formation of very strongly bound dimer clusters, containing a total of four intermolecular hydrogen bonds. Such structures have been proposed in the literature for several individual dicarboxylic acids, including both straight-chain structures^{11,12} and more complex biogenic compounds.^{13,14} However, to our knowledge, the energetics of dimer formation as a function of chain length has not been systematically investigated for straight-chain dicarboxylic acids using modern computational tools. The free energy of dimer formation ($\Delta G_{\text{dimer}} = G_{\text{dimer}} - 2 \times G_{\text{monomer}}$) is often considered to be an indicator of a general ability to form clusters, and thus for example participate in atmospheric new-particle formation. We note that in this context, straight-chain dicarboxylic acids are a special case: as both their hydrogen bond donors and acceptors are saturated (see e.g. Figure 1), the dimers are unlikely to cluster efficiently with further molecules. This behaviour contrasts with that of strong inorganic acids such as H_2SO_4 , where the dimer cluster has multiple H-bond donors and acceptors accessible for further clustering. Straight-chain dicarboxylic acids dimer formation is thus a dead end in terms of clustering,¹⁵ and strong gas-phase dimer formation may actually be linked to increased/decreased vapor pressures. While the most strongly bonded dimers of straight-chain dicarboxylic acids could in principle further interact with each other via van der waals interactions, and go on to form larger clusters, these interactions will be very weak due to the lack of further functional groups. The equilibrium constants for e.g. tetramer formation from two dimers will thus be many orders of magnitude lower than those for the dimer formation studied here.

In this study we compute the structure and energetics of a range of dicarboxylic acid monomers ($\text{HOOC}(\text{CH}_2)_{n-2}\text{COOH}$); with n between 2 (oxalic) and 8 (suberic) as well as their corresponding hydrogen bonded homodimers. For comparison we also compute the corresponding data for the monocarboxylic acids from formic acid to hexanoic acid. In real-

istic atmospheric conditions heterodimer formation can also occur but we limit our study to the homodimers as these are relevant for the pure substance properties measured in laboratory experiments and which are subsequently used in atmospheric and climate models.¹⁶

2 - Computational Details

Carboxylic and dicarboxylic acid monomers were generated using the systematic conformer sampling routine in Spartan 14¹⁷ using MMFF. Based on benchmarking calculations (see section S1) the 500 lowest conformers were optimized and frequencies calculated at the ω B97X-D/6-31++G(d,p) level in Gaussian 09.¹⁸ Sensitivity tests (see section S4) indicates that the results are only weakly dependent on the choice of density functional. Previous benchmarks have shown that the 6-31++G(d,p) basis set is a cost efficient choice.^{19?} The dimer structures of the carboxylic acids were obtained from pairing the three lowest free energy monomers in all combinations and ensuring the maximum number of hydrogen bonded interactions between the carboxylic acid groups when possible.

For the lowest free energy DFT structures, single point energies were calculated with ORCA 4.0.0,²⁰ using the domain based local pair natural orbital coupled cluster (DLPNO-CCSD(T)^{21,22}) method with the aug-cc-pVTZ basis set. This approach has been shown to perform well for atmospheric molecular clusters.²³ The calculated binding energies have not been corrected for basis set superposition errors, as we have extensively demonstrated that the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory is in good agreement with the complete basis set limit. For instance, we have previously shown that the formic acid - sulfuric acid dimer calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory has an error of 0.09 kcal/mol compared to CCSD(T)/CBS estimates.²⁴ Such a low error can be deemed negligible as it is significantly lower than the inherent error of the method.²⁴⁻²⁸

Errors resulting from low vibrational frequencies were mitigated via the quasi-harmonic approximation, where vibrations below 100 cm^{-1} were treated as rotations. The "Good-

vibes.py” script by Funes-Ardois and Paton²⁹ was used. The effect of anharmonicity was tested by using vibrational frequency scaling factors of 0.95, 0.90 and 0.85. We find that for every increment of 0.05 decrease in the scale factor the Gibbs free energy of dimer formation is found to be lowered by consistently ~ 0.20 kcal/mol for all the studied systems. This implies that including anharmonicity in the form of a scale factor in our calculations will have no effect on the trend in the computed free energies. All presented thermochemical parameters correspond to 298.15 K and 1 atm. All the cluster structures and the corresponding thermochemical properties have been added to the Atmospheric Cluster Database.³⁰

3 - Results and Discussion

Figure 1 presents the molecular structures of the lowest free energy homodimers, calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory, in the quasi-harmonic approximation. See the supporting information for the corresponding structures of all the monomer structures (section S1) and the monocarboxylic acid dimers (section S2).

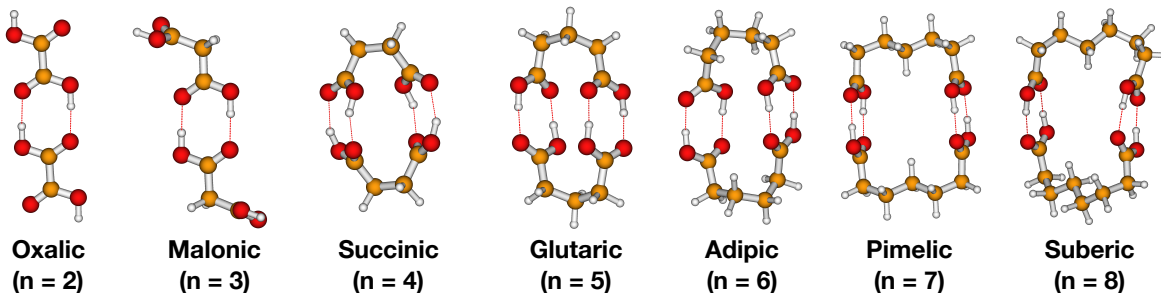


Figure 1: Molecular structure of the identified carboxylic acid homodimers obtained at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory, in the quasi-harmonic approximation. Color coding: brown = carbon, red = oxygen and white = hydrogen.

Oxalic acid ($n = 2$) and malonic acid ($n = 3$) form only a single set of hydrogen bonds (i.e one direct acid-acid interaction) and thus resemble the monocarboxylic acid structures rather than the dicarboxylic acids. For malonic acid ($n = 3$) a dimer conformer with four

hydrogen bonds also exist, but it is found to be 6.9 kcal/mol higher in free energy. The lowest free energy homodimers of all the larger dicarboxylic acids ($n = 4-8$) contain two direct acid-acid interactions.

Figure 2 shows the Gibbs free energy change ΔG_{dimer} for the gas phase formation for the mono and dicarboxylic acid homodimers at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory, in the quasi-harmonic approximation. Results obtained using other density functionals show identical trends (see supporting information S3).

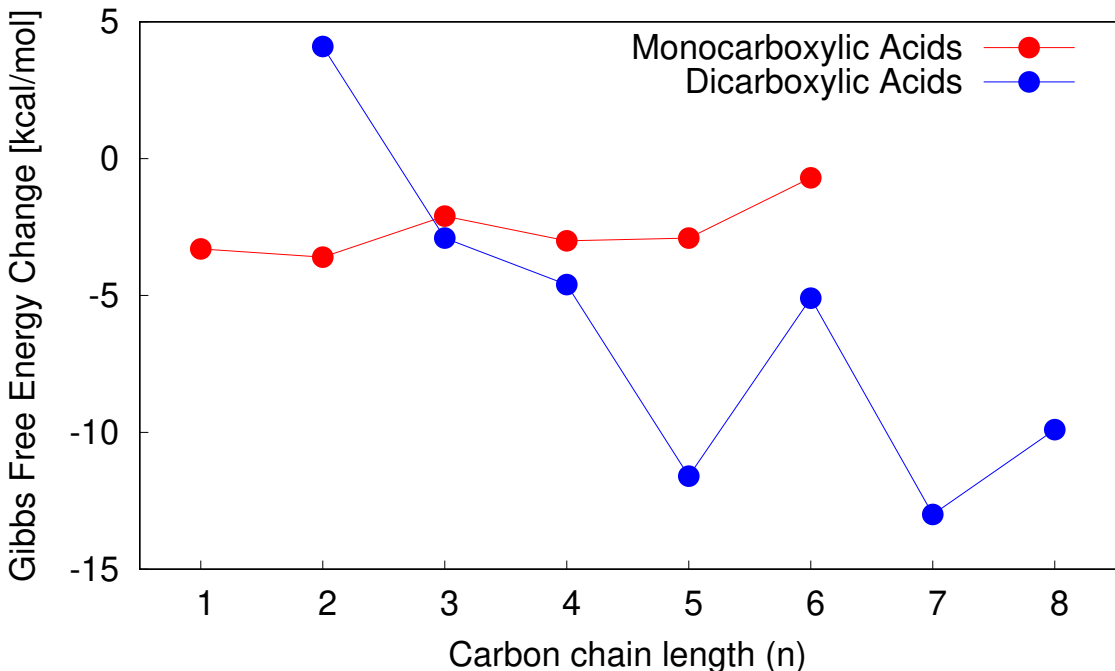


Figure 2: Gibbs free energy change (in kcal/mol) for the dimer formation of monocarboxylic acids (—●—) and dicarboxylic acids (—●—). The free energies have been calculated using the quasi-harmonic approximation with a 100 cm^{-1} cutoff. All values are calculated at 298.15 K and 1 atm.

The ΔG_{dimer} -values for the monocarboxylic acids are all around -3 kcal/mol. The length of the carbon chain backbone does not influence the ΔG_{dimer} -values, likely due to the lack of interactions between the hydrocarbon tails. This is consistent with our recent study of the interaction between carboxylic acids and sulfuric acid.³¹ ΔG_{dimer} for malonic acid is similar in magnitude to that of the monocarboxylic acids, as only one of the carboxylic acid groups

on each acid participates in the hydrogen bonding. Oxalic acid ($n = 2$) dimer formation is substantially less favourable as it is capable of forming intramolecular hydrogen bonds in the monomer (see Supporting Information Figure S2), which hinders dimer formation as the intramolecular hydrogen bonds have to be broken before the dimer can be formed.³² For the larger dicarboxylic acids, ΔG_{dimer} displays the even/odd alternation characteristic to several of their other physical properties. Specifically, the odd number glutaric ($n = 5$) and pimelic acids ($n = 7$) form dimers much more strongly compared to the even numbered succinic ($n = 4$), adipic ($n = 6$) and to a lesser extent suberic acid ($n = 8$). To understand the origin of this pattern we assess two different energy contributions to ΔG_{dimer} : (1) The torsional strain in the carbon backbone that is required to form the four hydrogen bonds present in all structures for $n \geq 4$ and (2) the isolated hydrogen bonding energy contribution (See Figure 3). Figure 3 also shows the dimer formation entropies ΔS_{dimer} , defined analogously to ΔG_{dimer} .

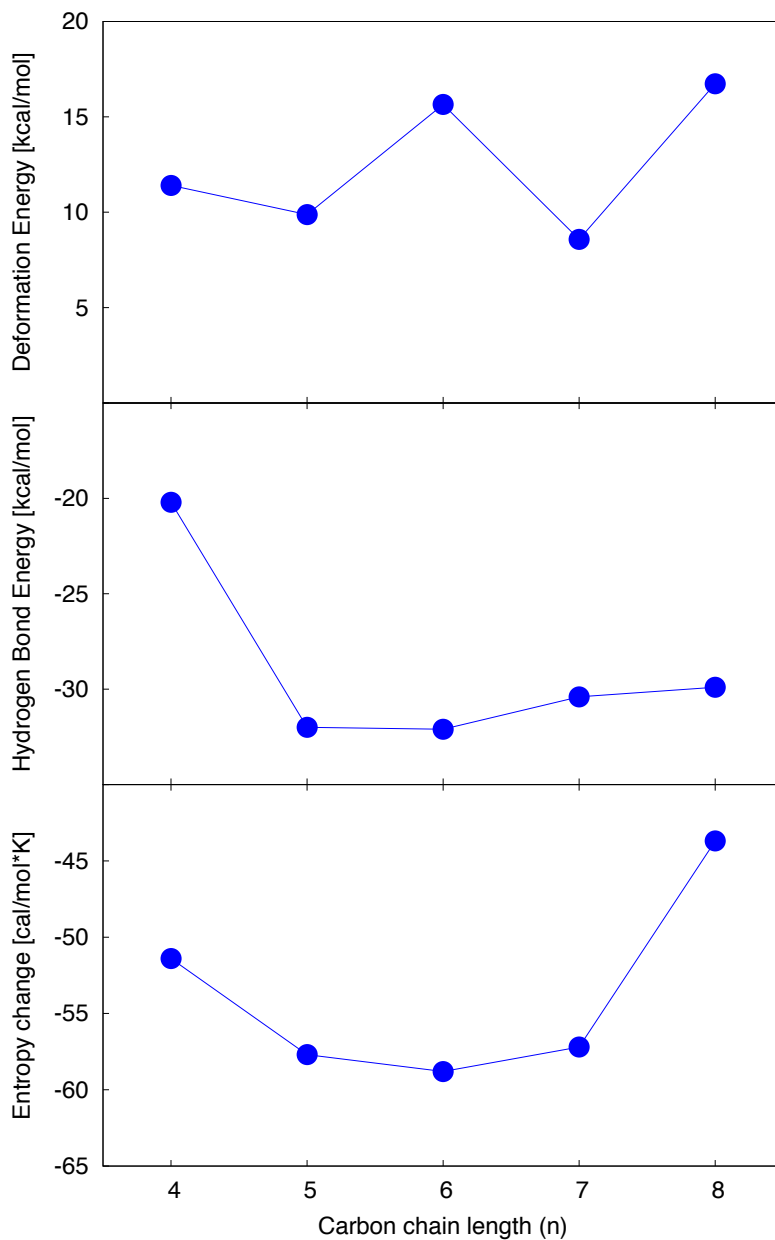


Figure 3: Deformation energy (*top*), hydrogen bond energy (*middle*) and the dimer formation entropy (*bottom*) as a function of carbon chain length. The energies are calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory on top of the dimers optimized at the ω B97X-D/6-31++G(d,p) level and the entropy is obtained at the ω B97X-D/6-31++G(d,p) level in the quasi-harmonic approximation. The energy values are presented in kcal/mol and the entropy in cal/mol·K.

The deformation energy (ΔE_{deform}) was estimated by computing the energies of the two isolated monomers, frozen at their structures in the lowest free energy dimer struc-

tures ($E_{m_1(d)}$, $E_{m_2(d)}$) and subtracting twice the energy of the optimized lowest free energy monomer (E_m):

$$\Delta E_{\text{deform}} = E_{m_1(d)} + E_{m_2(d)} - 2 \times E_m \quad (1)$$

The hydrogen bond energy ($\Delta E_{\text{H-bond}}$) was calculated by replacing the carbon chain of each of the dicarboxylic acids by two hydrogen atoms. This leaves two formic acid dimers frozen in the interaction pattern of the original dimer, with a total energy of $E_{d(\text{truncated})}$. The C-H bond length was constrained to 1.10 Å, corresponding to the C-H bond length in the isolated formic acid dimer. The hydrogen bond contribution is given by:

$$\Delta E_{\text{H-bond}} = E_{d(\text{truncated})} - 4 \times E_{\text{formic}} \quad (2)$$

As seen in Figure 3, the deformation energies display an even/odd alternation for carbon chains of length $n = 4$ to 8. Succinic acid ($n = 4$) has a high (unfavorable) deformation energy, as the carbon backbone has to be compressed in order to form the lowest free energy dimer structure with two direct acid-acid interactions. The torsional strain in the glutaric acid ($n = 5$) dimer is much lower, as the five carbon chain linker yields an ideal symmetric geometry for almost linear intermolecular hydrogen bonds. Similarly, pimelic acid ($n = 7$) can form an extra kink in the carbon chain, permitting the formation of near linear hydrogen bonds without significant strain. In contrast, the carbon chain in adipic acid ($n = 6$) is too long to adopt the symmetric dimer structure of glutaric acid ($n = 5$), yet too short to accommodate the additional carbon atoms analogous to pimelic acid ($n = 7$).

The hydrogen bond energy contribution is similar for all acids with at least five carbon, but significantly less favourable for succinic acid ($n = 4$). Despite the substantial torsional strain, succinic acid is thus still not able to adopt favourable near linear hydrogen bonding observed in the larger dimers. This contributes to the very low stability of the succinic acid dimer (see Figure 2).

The difference in ΔG_{dimer} between pimelic acid ($n = 5$) and suberic acid ($n = 8$) is less pronounced and cannot be explained solely by the energy factors shown in Figure 3. Suberic acid has the highest deformation energy, which originates from the fact that not only the dimer but also the monomer forms an intramolecular hydrogen bond. However, this does also lead to a significantly lower entropy penalty for dimer formation compared to the other dicarboxylic acids, as the entropy of the monomer is also lowered by the constraints imposed by the intramolecular H-bonding. It should be noted that the ω B97X-D and M06-2X functionals both identify that the lowest free energy monomer have an intramolecular hydrogen bond, while the PW91 functional predict the straight chain monomer to be more stable. Furthermore, it should be noted that the existence of a large number of low energy conformers of suberic acid and larger acids will lead to larger error sources in their computed thermodynamics.³³ Nevertheless, we tentatively suggest that straight chain dicarboxylic acids with seven or more carbon atoms and hence flexible backbones will likely display less pronounced even/odd alternations in their physical properties.

To evaluate the atmospheric implications of gas phase dicarboxylic acid dimer formation we plotted the [dimer]/[monomer] ratio as a function of carbon chain length at different vapour pressures (See Figure 4). It was tested whether the calculations changed if the saturation vapour pressure is assumed to include also the dimers in Figure 4. By including the dimers, the [Dimer]/[Monomer] ratio is shifted slightly down, but the results are qualitatively similar (See supporting information Section S4).

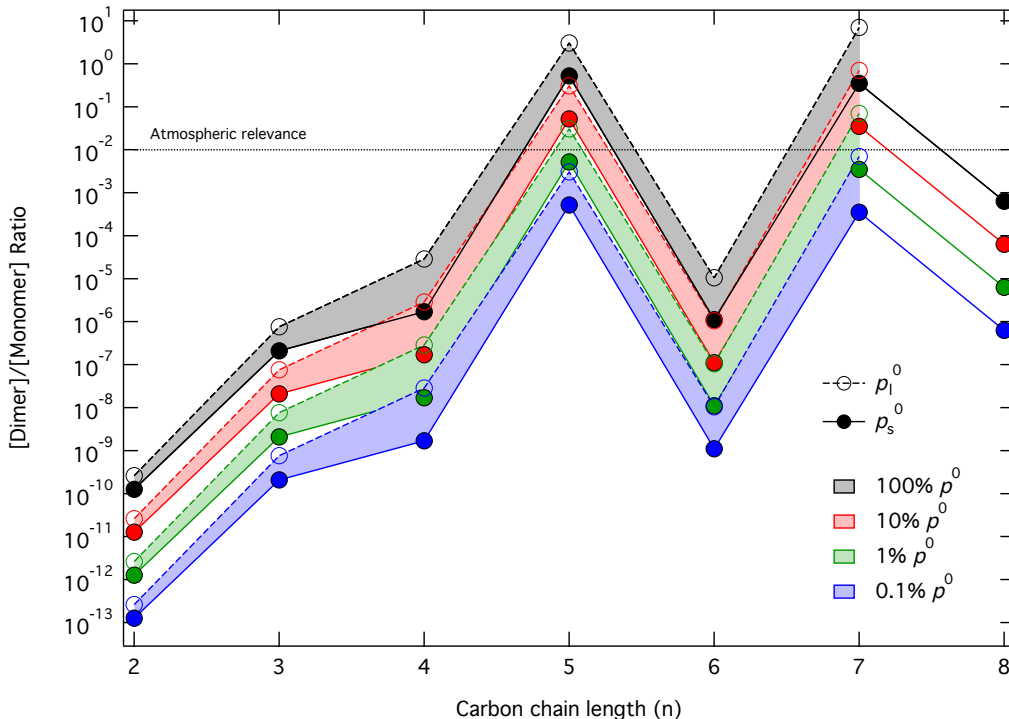


Figure 4: Equilibrium dimer to monomer partial pressures ratio of dicarboxylic acids as a function of carbon chain length. The lower limits correspond to the lower limits of the solid state p_s^0 and the upper limits correspond to the upper limits of the subcooled liquid p_l^0 . For $n = 8$ only a single p_s^0 value is available in the literature.

The range of saturation vapour pressures (p^0) were taken from Bilde et al¹⁶ with the lower limits corresponding to the lower limits of the solid state p_s^0 and the upper limits corresponding to the upper limits of the subcooled liquid p_l^0 . The dimer partial pressure ($[A_2]$) was computed from the monomer partial pressure as $K_{\text{eq}} \times [A]^2$, with $K_{\text{eq}} = (p_{\text{ref}})^{-1} \exp(-\Delta G_{\text{dimer}}/RT)$, where $p_{\text{ref}} = 1$ atm is the reference pressure at which the ΔG_{dimer} is computed and monomer partial pressure $[A]$ is set to the supersaturation ratio times p^0 . Figure 4 corresponds to 298.15 K, but the qualitative results are relatively insensitive to temperature as temperature dependence on the saturation vapor pressures and equilibrium constants largely cancel out. This is reflected from the fact that the vaporization enthalpies of the dicarboxylic acids and the enthalpies of dimer formation lie mostly in a similar range, but with opposite sign. For instance the vaporization enthalpies for the dicarboxylic acids lie in the range 23.9 to 33.7 kcal/mol,¹⁶ while our calculated corresponding ΔH_{dimer} -values lie in the range -15.9

kcal/mol to -30.kcal/mol. The vaporization enthalpies tend to be a bit larger in magnitude than the dimerization enthalpies, which suggest that the temperature dependence of p_{sat} will be a bit stronger than that of K_{dimer} , however, in opposite directions. With decreasing temperature p_{sat} will decrease slightly faster than K_{dimer} increases. At constant supersaturation, carboxylic acid dimer formation can thus be expected to be somewhat less important at lower temperatures, and somewhat more important at higher temperatures.

Figure 4 shows that at equilibrium, dimers can constitute a significant fraction of the total gas phase acid concentration only for glutaric ($n = 5$) and pimelic acids ($n = 7$). For all other studied cases the [dimer]/[monomer] ratio is less than 10^{-3} , even at saturation ratios of one. For the smaller acids, this is due to low equilibrium constants for dimer formation, while for suberic acid ($n = 8$) the main reason is the low p^0 . Hence, gas phase dimer formation will only contribute to the atmospheric phase state equilibria, for instance affecting the saturation vapor pressure, in case of glutaric ($n = 5$) and pimelic acid ($n = 7$). Our results explain why the observed even/odd alternation is stronger for solid state vapour pressure compared to subcooled liquid state vapor pressure. In the solid case, the odd members are destabilised by torsional strain in the condensed phase¹¹ and stabilized by dimer formation in the gas phase, leading to a significant elevation of vapor pressures. In the liquid phase only the latter of these two effects is present, leading to less pronounced even/odd alternation in the vapor pressures.

To illustrate the effect of dimer formation for a more complex dicarboxylic acid, we also compute the structures and free energies for pinic acid (See Figure S8). Pinic acid is a product from α -pinene oxidation that is routinely identified in secondary organic aerosol both in chamber experiments^{34,35} and in the field.³⁶ Despite having $n = 5$ carbon atoms in the backbone connecting the two carboxylic acid groups the constraint added by the cyclobutyl ring prevents the dimer from adopting the favourable geometry seen for glutaric acid, resulting in a ΔG_{dimer} -value of -1.7 kcal/mol. Gas phase dicarboxylic acid dimer formation is thus likely to remain an exception. The participating monomers need to simultaneously have a

high flexibility while remaining volatile enough for their saturation vapour pressure not to be too low.

4 - Conclusions

We have shown that part of the well-known even/odd alternation of dicarboxylic acids with between 4 and 8 carbon atoms is likely to at least partly result from differences in gas phase dimer formation. Specifically, glutaric ($n = 5$) and pimelic ($n = 7$) acids form much more stable dimers than succinic ($n = 4$) and adipic ($n = 6$) acids due to a combination of hydrogen bond strength and torsional strain. At saturation ratios approaching one, dimers constitute a large fraction of the total gas phase of glutaric and pimelic acid. This likely acts to increase the saturation vapour pressures of these compounds, further enhancing the pattern resulting from lower stability of the odd dicarboxylic acids in the solid state.¹¹ This strong even/odd pattern is likely unique to the straight chain $n = 4$ to $n = 7$ dicarboxylic acids. Larger acids with $n = 8$ or above will have too low volatilities for significant dimer formation to occur in the gas phase, while more complex multifunctional compounds will likely contain additional torsional constraints which make the dimer formation less favourable.

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Supporting Information Available

The following is available as supporting information:

Depiction of the molecular structures of all the monomers and dimers. The performance of different DFT functionals in calculating the free energy and entropy changes for dimer formation of the mono and dicarboxylic acids (PDF).

All the obtained lowest free energy molecular structures of the mono- and dicarboxylic acids (both monomers and dimers), using the ω B97X-D, PW91 and M06-2X functionals with a 6-31++G(d,p) basis set. Both the lowest structure in the harmonic and quasi-harmonic description is available (XYZ).

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Graphical TOC Entry

