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**SUBLIMATION ENTHALPIES OF ORGANIC COMPOUNDS: A VERY LARGE
DATABASE WITH A MATCH TO CRYSTAL STRUCTURE DETERMINATIONS
AND A COMPARISON WITH LATTICE ENERGIES**

James S. Chickos^{1*} and Angelo Gavezzotti^{2*}

¹Department of Chemistry, University of Missouri-St. Louis, Saint Louis, Missouri 63121
e-mail: jsc@umsl.edu

²Dipartimento di Chimica, Università di Milano, via Venezian 21, 20133 Milano, Italy
e-mail: angelo.gavezzotti@unimi.it

ABSTRACT

A database of 1655 critically evaluated sublimation enthalpies of organic compounds is presented. Experimental techniques are briefly reviewed. The consistency of experimental measurements is critically analyzed also as a function of temperature. Isomer effects and chain-length trends in linear substituted alkanes are described. For 737 entries a match is found with the X-ray structure determination of the corresponding crystalline material as reported in the Cambridge Structural Database. Out of these, lattice energies are calculated for 679 crystals by atom-atom potentials and for 500 crystals by the Pixel method. The procedure for the comparison between sublimation enthalpy and lattice energy is analyzed with its importance for many issues in crystal and theoretical chemistry. With Pixel, 87% of the sublimation enthalpy-lattice energy comparisons show a discrepancy below 15% with a rmsd of 8.7 kJ mol⁻¹; with atom-atom potentials the corresponding figures are 74% and 8.3 kJ mol⁻¹, but while by Pixel no deviation is larger than 30%; atom-atom energies for some compounds show very large, unexplained deviations. The intrinsic accuracies of calculated lattice energies and experimental sublimation enthalpies are similar, and are found to be in the 5-10 kJ mol⁻¹ range. Success and failures of theoretical methods are related to the fundamentals of intermolecular interactions.

1. INTRODUCTION

Advanced methods for the study of structure and properties of organic crystalline materials rely chiefly on X-ray and neutron diffraction, along with several kinds of spectroscopies, to provide a highly detailed picture of bonding geometries. However, no chemical inference on trends in intermolecular bonding can proceed accurately without quantitative energetic information. In this respect, among experimental thermodynamic data, sublimation enthalpy (SE) obviously plays a key role. As a measure of the difference between the crystalline and isolated state of the molecule, SE is directly related to the strength of intermolecular cohesion in the solid state. Current theoretical chemistry can also provide quantitative support using a wide range of computational methods of variable cost and accuracy. Calculations can provide reliable data regarding the magnitude of intermolecular interactions and lattice energies (LE), and this data can be compared to experimentally derived sublimation enthalpies when evaluated under a number of specified conditions.

The SE-LE interplay has had a long history. Predictions of SE in terms of molecular descriptors has been actively pursued by expert-system methods. A wide range of parameters have been used in these formulations: polarizability plus number of H-bond donors and acceptors¹, molecular surface and volume plus molecular hydrophilicity,² atomic and ring contributions,^{3,4} and (or) even 1644 (!) molecular descriptors that collapsed into just 5 combined variables.⁵ Methods for predicting SE based on the properties of the molecular electrostatic potential have been reported for a variety of substances,^{6,7} including energetic materials (explosives).⁸ Empirical equations employing a modified group additivity approach for estimating SE values of *o*-, *m*- and *p*-substituted benzenes has also been recently reported.⁹ In such approaches the rms of the fit on small to large datasets (~100 to 1500 substances) ranges from about 5 to 15%.

More informative are methods that compare calculated LEs with the corresponding experimental SEs, in a synergy that has been and still is a staple of the optimization of potential energy schemes, thus providing a link between crystal structure and thermodynamics. LEs can be calculated from the crystal structure when cell dimensions, space group and atomic coordinates for at least the non-hydrogen atoms are known. LE can be evaluated *ab initio* (e.g. in the CRYSTAL environment)¹⁰, at various levels of theory. A very fashionable method presently, is dispersion-corrected Density Functional Theory (DFT-D)¹¹ in which the total energy is given by a quantum chemical term accounting for coulomb-polarization and for repulsion, plus a parametric dispersion-energy term in the inverse sixth power of intermolecular distance; notably,

the quantum chemical contribution is usually around 20-30% so that most of the burden is taken by the empirical part. A highly performing approach involves Stone's DMA (Distributed Multipole Analysis)¹² as a part of a hybrid method¹³ in which localized multipoles are calculated by quantum chemistry and the Coulombic interaction is evaluated as multipole-multipole interactions as in classical physics. Dispersion and repulsion are included by atom-atom terms in the Buckingham 6-exp form. A completely parametric method coming from early developments¹⁴⁻¹⁵ but still alive for cutting-edge molecular dynamics applications¹⁶ is the atom-atom mechanics in which intermolecular energy is evaluated by sums over pairs of atomic interaction centers. This approach still ranks high in terms of the cost-to-performance ratio.

The calculation of LEs is nowadays applied to a broad range of theoretical and experimental issues, the most ambitious one being the *ab initio* prediction of crystal structure from molecular structure.¹⁷ LE-SE comparisons are less frequent and often rely on random choices of SE without an appreciation of its variability range. The LEs of some pharmaceutical compounds were computed with empirical potentials,^{18,19} but the comparison with SEs was somewhat less than satisfactory. The LEs of a few test crystals of small and mostly rigid molecules have been computed using Coulombic energies over atomic point charges or in the delocalized DMA approach.²⁰ The DMA diffuse-charge model performs much better than localized point-atom descriptions, especially for highly polar molecules. Studies based on atom-atom methods typically yield oscillating SE-LE results among different force fields.²¹ DFT-D was applied to 23 molecular crystals¹¹ with excellent results when compared to experimental SEs. The same approach was applied to aspirin and other active pharmaceutical ingredients.²² The difference between uncorrected DFT and DFT-D is well illustrated in a SE-LE comparison of 14 organic crystals²³; uncorrected DFT results are way off the mark. More complex quantum chemical methods gave somewhat contradictory results for crystals of small organic molecules.²⁴ Symmetry-adapted perturbation theory (SAPT) within the DFT framework was applied²⁵ to a few organic crystals: the SE-LE comparison oscillated between precise agreement and deviations up to 40%. One of the best quantum chemical approaches, CCSD(T), was applied to 25 organic crystals; results were characterized with a rms deviation of no better than 13%.²⁶ Benchmark sets of data are now available for the systematic comparison of computational methods for non-covalent interactions,^{27,28} also used in a critical assessment of the performance of several quantum chemical schemes.²⁹ In what seems the ultimate effort, the LE of the benzene crystal was calculated³⁰ by extreme quantum chemistry to an accuracy of less than 1 kJ mol⁻¹. Aside from its limited applicability to organic molecules of practical interest, this elegant exercise adds little to our ability to control crystal chemistry and stability, where a host of concomitant factors, last but not least entropy, introduce much larger uncertainties.

In this paper we report a 1655-entry database of critically assessed experimental SEs from a comprehensive source,³¹ with a brief survey of methods for their determination. We then report a match to 737 crystal structure determinations for the corresponding materials, as present in the Cambridge Structural Database³² (CSD). We have used the atom-atom approach, in an efficient scheme called AA-CLP,³³ to calculate the lattice energy of a subset of 679 materials for which complete crystallographic information is available. A more refined approach is then taken, called Pixel-CLP,³⁴ to obtain the lattice energy for a further subset of 500 crystal structures of smaller sized compounds. The sublimation enthalpy-structure match, and the large-scale comparison between experiment and AA or Pixel calculations offer a wide and deep view of the energy landscapes of the organic solid state. The outcome provides suggestions and caveats to experimentalists in the interpretation of results, and to theoretical chemists in the calibration of computational methods as well as in applications to analysis and prediction.

2. EXPERIMENTAL TECHNIQUES FOR SUBLIMATION ENTHALPY MEASUREMENTS

Both direct and indirect methods have been used to measure or evaluate sublimation enthalpies. To a large extent, the method of choice is frequently dictated by the properties of the target material. This topic has recently been reviewed.³⁵ Most methods fall in two general categories, direct or indirect. Direct methods generally involve the use of some form of microcalorimeter which operates either isothermally or adiabatically. The sublimation enthalpy is measured by the magnitude of heat flow necessary to account for the mass loss. For materials with vapor pressures of the order of $p = 100$ Pa, flow calorimeters using an inert carrier gas have been designed.³⁶ Microcalorimeters operating at reduced pressures have been designed for less volatile substances exhibiting vapor pressures ranging from roughly $p = (0.1 \text{ to } 20000)$ Pa.³⁷ For materials with vapor pressure much lower than 1 Pa at ambient temperatures, Calvet calorimeters have been developed utilizing two different approaches. The vacuum drop calorimeter proposed by Skinner³⁸ employs two matched Calvet microcalorimeter cells. Two matched capillaries, one containing the sample are dropped simultaneously into heated cells. Following equilibration, both microcalorimeter cells are evacuated. The composite signal obtained, contains the heat necessary to raise the temperature of the sample from ambient to the temperature of the calorimeter, followed by the energy necessary to sublime the sample at the temperature of the calorimeter. The second energy term, though strictly not an enthalpy,³⁷ must also be adjusted to the reference temperature. The temperature adjustment, which can be

significant,³⁹ either needs to be estimated or the gas phase heat capacity needs to be calculated theoretically.^{40,41} A twin cell Calvet microcalorimeter run isothermally has also been used to determine sublimation enthalpies using Knudsen cells.⁴² However results reported from this instrument seems to indicate a systematic error of approximately 4 kJmol⁻¹ when compared to measurements obtained by other methods.³¹ Use of a similar calorimeter by others has not been as problematic.^{43,31}

Indirect methods of evaluating sublimation enthalpies generally include measurement of the vapor pressure of the solid as a function of temperature. Knudsen effusion, and transpiration are among the most common methods used. In Knudsen effusion, mass loss through a small orifice is measured in an enclosed cylindrical vessel over a convenient period of time and as a function of temperature. The assumption that the condensed and vapor phases are in thermal equilibrium is tested by demonstrating that the results are independent of the size of the orifice when measured under identical conditions of temperature and reduced pressure.³⁵ Analysis of the amount of mass loss with time is the most common method of analysis. The vapor pressure is evaluated using the kinetic theory of gases. More recently, Knudsen effusion has been combined with a quartz crystal microbalance to measure vapor pressures of small samples using short effusion times over a wide temperature range.⁴⁴

Transpiration methods are equally popular and if performed properly, provide comparable sublimation enthalpies to mass effusion.⁴⁵ Transpiration studies rely on mass transfer based on a flow system under conditions that equilibrium between the solid or liquid and its vapor has been achieved; this method also assumes that the vapor obeys the ideal gas law. The mass of transferred material collected in a cold trap is frequently quantified by gas chromatography.

Other techniques used somewhat less frequently to evaluate sublimation enthalpy include measuring mass loss as a function of temperature using thermogravimetric analysis equipment.^{46,47} A new and exciting development in thermochemical analysis is the use of fast scanning chip calorimetry.⁴⁸ This technique has the potential of providing both sublimation and vaporization enthalpies of low volatile and/or thermally unstable materials that can't be measured by other means by rapidly heating nanogram sample sizes on a chip sensor.⁴⁹ The ability to heat /cool with scanning rates of up to 10⁶ K/s offer the potential to either heat or cool a sample and measure its thermal properties prior to thermal decomposition, or in the case of fusion, the fusion enthalpy at a reference temperature. Developments in these areas continue.

3. METHODS

3.1. Sublimation enthalpy (SE) database. The data were sorted out of the cited compilation.³¹

Only values for unary substances (*i.e.* with only one chemical species, no complexes, hydrates, solvates, etc.) were considered, in view of the general lack of available data and the difficulty of properly defining and measuring SE's for multicomponent crystals. When only one SE value appears, it was taken as such along with its determination temperature (when given). When multiple values were reported, first of all patent outliers were rejected; if remaining values were within a small range (5-10 kJ mol⁻¹), a weighted average was adopted and the number of acceptable determinations stored, adding to the reliability of the determination; the temperature was assigned as an average of the given temperatures. When the range of reported values was large, an average was adopted but the highest and lowest values were also stored. The final SE data set had 1655 SE values for molecules with carbon atoms ranging from C₁ to C₃₄ (see Supporting Information, Tables S1 and S2). The sample included, among others, 192 hydrocarbons, 104 carboxylic acids, 68 alcohols, 74 DNA bases and uracils, 129 nitro compounds, a mix of a total of 365 amines, amides, and aromatic azo compounds, and over 120 ketones, plus a wide variety of halogen and sulfur containing compounds. The panel adequately represents the typical functionality found in organic chemical compounds encountered in theoretical and experimental investigations and in industrial practice.

3.2 Intermolecular energies. In the AA-CLP scheme,³³ LE is calculated by atom-atom sums over empirical Coulomb point-charge, polarization, dispersion and repulsion terms. The Pixel approach³⁴ is so called because the electron density is calculated⁵⁰ *ab initio*/MP2/6-31G** on a grid of "e-pixels", typically some 10,000-30,000 for an ordinary organic molecule. Coulombic energies are calculated by a parameter-free sum of pixel-pixel interactions, polarization and dispersion terms are estimated by empirical London-type formulas, and repulsion is approximated by a modulated "Pauli" proportionality with electron density overlap. Computing times are virtually zero in the AA approach and scale as the square of the number of e-pixels in Pixel, where they are of the order of minutes for one crystal, plus the time needed to evaluate the electron density. The inherent software, widely distributed and tested, can be downloaded from www.angelogavezzotti.it

3.3 SE-crystal structure match and LE calculations. For each SE in the 1655-entry database the Cambridge Structural Database was scanned using its ConQuest software, searching for the crystal structure (identified by the CSD refcode) of the corresponding material. When many structure determinations are available for the same compound, the one with the lowest R-factor and/or closest to room temperature was selected. Cell dimensions, space group and atomic coordinates for non-

hydrogen atoms were passed through a set of in-house sieving programs, sorting out a number of disordered, incomplete or otherwise erroneous items. In the process, the positions of hydrogen atoms attached to carbon were routinely reset or determined when absent, by obvious geometrical criteria. The position of H-atoms in COOH groups was sometimes uncertain due to disorder;⁵¹ these hydrogens were reset by geometrical considerations. The position of alcohol or amino H-atoms, when not determined, cannot be evaluated because of free rotation around the C-O(H) bond and of unknown pyramidalization at the NH₂ groups. Such cases had to be excluded from the final data set. Out of the 1655 SE data set, 737 pairs with corresponding entry in the CSD were identified. After sieving only 679 had complete crystallographic information as needed to proceed to lattice energies, as calculated by the AA-CLP scheme. Then 500 structures with $N_{\text{atoms}} < 35$ were extracted for the calculation of Pixel-LEs. From previous experience, Pixel LEs for chlorinated compounds were corrected by subtracting 3 kJ mol⁻¹ per chlorine atom due to overestimated dispersion contributions, and those for nitro compounds were upgraded by 5 kJ mol⁻¹ per nitro group.⁵² SE data were rescaled to 298 K as $SE(298) = SE(T) + \Delta C_p (298-T)$, with $\Delta C_p = -0.04 \text{ J mol}^{-1} \text{ K}^{-1}$; LE data were also corrected by the empirical rescaling law $LE(298) = LE(T) + \Delta E (298-T)$, with $\Delta E = -0.01 \text{ J mol}^{-1} \text{ K}^{-1}$.

3.4 Handling the SE-LE comparison. The lattice energy for a one-component crystal is the difference in calculated internal energy between one mole of constituent molecules at infinite separation and one mole of the same constituents in the crystal. If infinite separation in the gas phase with zero interaction energy is taken as a reference, LE is stabilizing (i.e. < 0). The physicochemical interpretation of SE as a measure of purely intermolecular cohesion energy in the crystal is straightforward whenever a) the crystal is an ordered (long-range periodic) phase without disorder, faults, twinning, or inclusions, solvation or impurities; b) molecules in the gas phase allow no aggregation (a semi-ideal gas); c) there are no rotatable bonds or other soft intramolecular degrees of freedom in the crystal that may cause large conformational differences between crystal and gas; d) there are no bonding rearrangements, as for example keto-enol tautomerism, neutral to zwitterion transition in aminoacids, or in extreme cases, molecular fragmentation. Otherwise, the measured SE includes a contribution from the enthalpy of any concomitant process, that may be lumped into a "configurational" difference $\Delta H'$ (gas-cryst). Usually, flexible molecules are conformationally more stable in the gas phase because upon entering the crystal lattice they quite often adapt to intermolecular requirements with expenditure of some conformational energy. In principle $\Delta H'$ could be estimated by evaluating the intramolecular energy of the crystalline molecule and optimizing the molecular structure of the gas-phase molecule by quantum chemical methods, but in practice this can seldom be done with

the required accuracy. Besides, the gas phase could be a mixture of conformers. $\Delta H'$ is more likely to be non-zero with increasing molecular size and complexity. No systematic attempt was made to calculate $\Delta H'$; specific cases and outliers may be discussed using chemical intuition.

A very approximate consideration of global equipartition energies in the crystal and in the gas leads to the following relationships: for vaporization enthalpy, $\Delta H(\text{gas-liq}) = -U(\text{liq}) + RT$, for sublimation enthalpy, $\Delta H(\text{gas-cry}) = -U(\text{cry}) - 2RT$ or $\text{SE} = -\text{LE} - 2RT$.⁵³ These corrections however depend on a number of heavy approximations, almost none of which apply to real organic molecules (as detailed in Supporting Information, Correction-RT part). At room temperature the correction is not negligible for a medium-size molecule, and it may introduce more inaccuracy than adhesion to physical principles. In the following, the comparison will be made directly between SE and LE, without any RT terms, which is anyway how theoretical methods have been calibrated - no correction is better than a bad correction.

4. RESULTS

4.1 The sublimation enthalpy database. The bulk of the data are for $10 < N_{\text{at}} < 40$, and $70 < M_{\text{w}} < 300$ (Figure 1). The distribution shows a sharp peak at $N_{\text{c}} = 6$, due to substituted benzenes, and a rapidly decreasing frequency for $N_{\text{c}} > 15$. It also shows larger numbers for even than for odd N_{c} , an alternation that appears in other kinds of statistics in organic compounds, for example for those present in the Cambridge Structural Database.

Figure 2 shows the landscape of sublimation enthalpies as a function of the number of atoms in the molecule. Hydrocarbons are generally at the lowest edge of the distribution; those with very high SE for a relatively small atom number are PAH's (condensed polycyclic aromatic hydrocarbons). The very low SE for some t-butyl derivatives relative to other isomers may be explained by the difficulty of adjusting such a bulky and non-polar group to crystal-lattice close-packing requirements, thus affecting the fusion enthalpy; reduction of the accessible surface area by a t-butyl group also reduces the vaporization enthalpy. As expected acids, alcohols, amides, and in general hydrogen-bonding compounds are at the upper end of the distribution. The reason for the comparatively high SE of nitro derivatives is open to discussion; a reasonable guess is that it depends on stabilizing Coulombic interactions between polar nitro groups. A similar effect may be active for compounds containing S=O groups (sulfones and sulfoxides) but the presence of such species in our database is currently too limited to draw a clear conclusion.

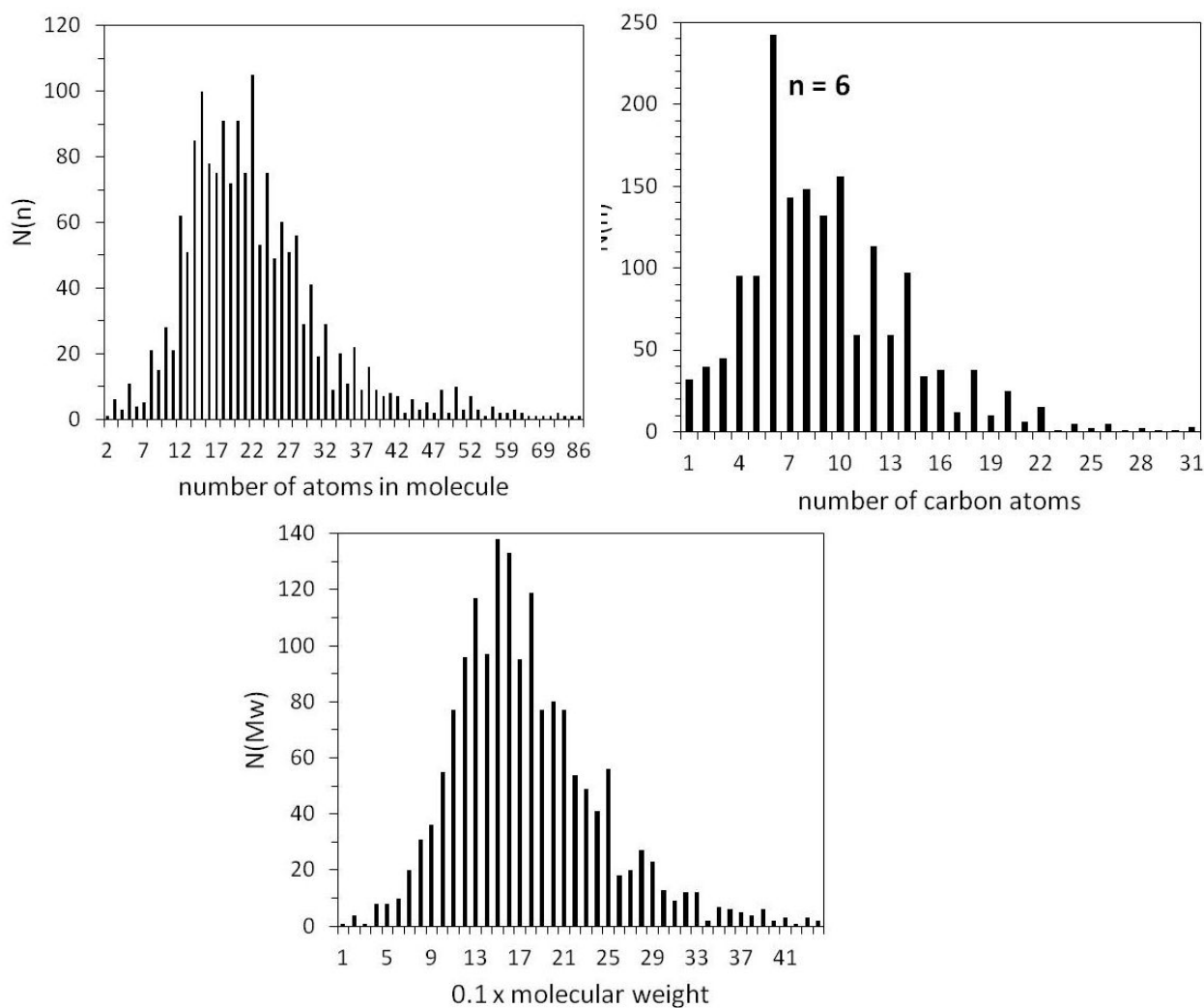


Figure 1. Histograms for the distribution of sublimation enthalpy data among number of atoms, number of carbon atoms and molecular weight.

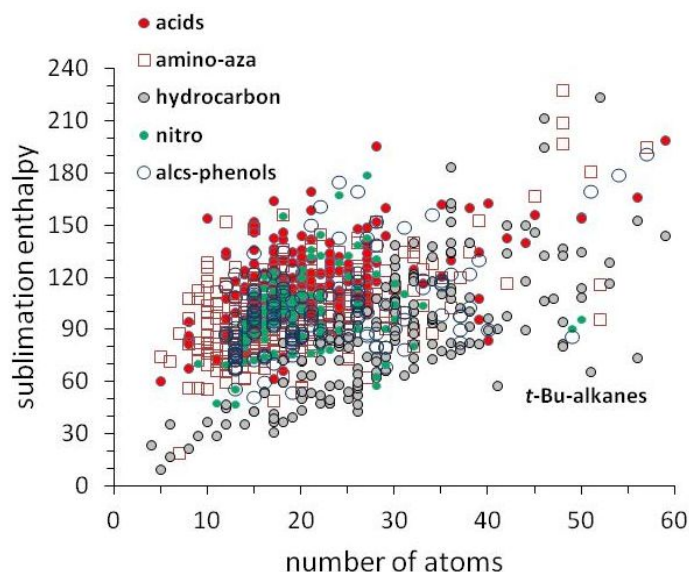


Figure 2. Scatterplot of sublimation enthalpy (kJ mol^{-1}) against number of atoms in the molecule for some chemical classes. The data on extreme lower right are for *tert*-butyl derivatives.

Table 1. Compounds for which many sublimation enthalpy (SE) measurements are available

a)

compound	n.data ^a	n.out ^b	T range/K	SE range/ kJ mol ⁻¹	consistency ^c
benzoic acid	45	0	300-400	84-95	good <i>T</i> -fit ^d
anthracene	43	0	300-450	92-103	poor, <i>T</i> -scatter ^d
phenanthrene	20	2	300-380	84-96	poor, <i>T</i> -scatter
naphthalene	37 37	4 13	245-320 245-360	66-78 70-74	poor fair ^d
benzophenone	16	5	298-308	91-95	good ^d
biphenyl	15	3	290-319	75-83	poor ^d
benzene	12	1	230-300	42-47	fair
pyrene	10	1	298-410	99-103	fair
acridine	9	1	298-333	90-95	good
uracil	8	1	425-523	121-134	poor
2-hydroxybenzoic acid	7	2	298-330	93-96	very good
2-naphthol	7	1	298-323	79-95	bad
dibenzofuran	7	0	298-323	77-86	poor
diphenylmethane	7	1	290	72-89	bad
phenazine	7	2	285-300	90-92	very good
benz(a)anthracene	6	0	345-405	104-121	bad
norbornane	5	1	298	40	perfect
tetracene	6	1	383-473	125-133	poor
perylene	6	0	370-415	120-140	bad
dibenzo-1,4-dioxin	5	0	300	90-94	fair
butyramide	5	1	298-363	85-87	very good
trans-azobenzene	5	0	298-323	92-95	good
acetamide	4	0	284-323	77-80	good
perylene	5	0	370-418	121-139	bad
triphenylene	4	0	360-425	107-118	bad
hexamethylbenzene	5	0	298-320	81-86	fair
1,3,5,-triphenylbenzene	4	0	376-425	141-146	good

Number of available data. b) Number of patent outliers excluded. c) Subjective judgment

d) Recommended SE at $T = 298.15$ K as a primary (P), secondary (S), tertiary (T) SE reference standard: benzoic acid (P): 89.7 ± 1.0 ; naphthalene (P): 72.6 ± 0.6 ; anthracene (P): 103.4 ± 2.7 ; benzophenone(T): 93.77 ± 3.500 ; biphenyl: 82.12 ± 2.13 kJ·mol⁻¹.⁵⁴

An obvious help in assessing the reliability of SE measurements is the consistency of multiple data for the same compound. For 73% of the entries in our database only one measurement is considered acceptable, and for just another 17% two data are retrieved. Table 1 lists some compounds for which SE has been measured many times; some of them, like naphthalene, benzophenone, and benzoic acid, are actually used as experimental benchmarks.⁵⁴

Consistency goes from perfect (in the unique case of norbornane) to good or fair or even poor, with uncertainties in the 3-10% range.

When extended SE- T sets of values were found, a linear fit was attempted. Figure 3 has two typical examples. Table S3 (Supporting Information) has some examples in which both a linear fit and an average are given, by different choices of outliers: generally speaking, the temperature fit is rather poor. Tentative ΔC_p 's range from -0.01 to -0.04 J K⁻¹ mol⁻¹. While there is no standard method recommended for temperature adjustments of either vaporization, sublimation or fusion enthalpies, several methods have been employed. As a consequence, some of the observed scatter reported in the literature for a given substance at $T = 298.15$ K is a direct consequence of the nature of the temperature adjustment employed by the author. Several of these methods for adjusting SEs are described briefly below.

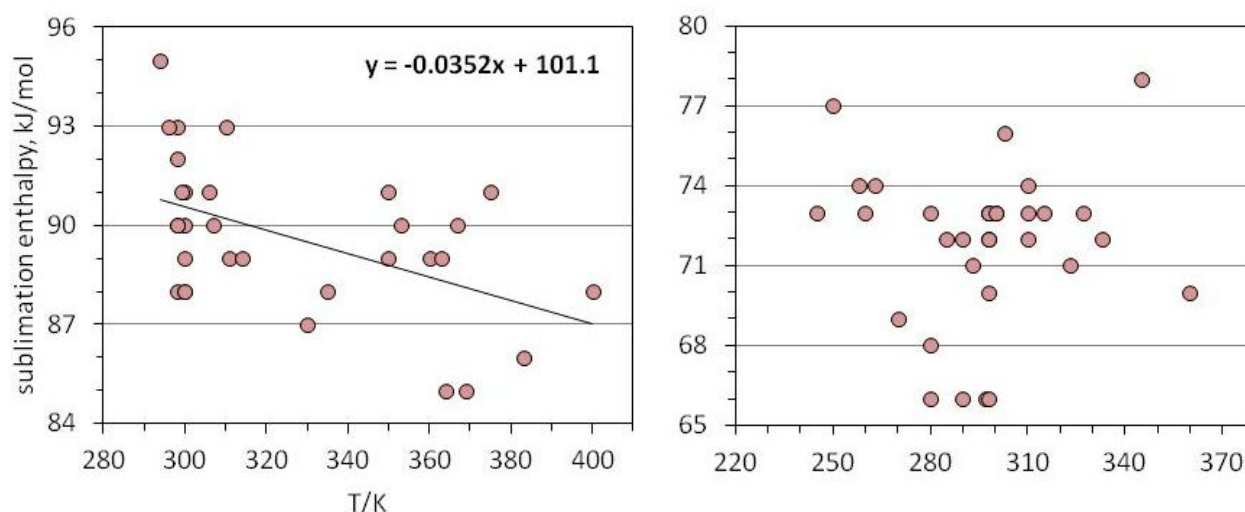


Figure 3. Some examples of sublimation enthalpy data as a function of temperature. Left: benzoic acid, tentative T -fit. Right: naphthalene, oscillation without apparent T -dependence.

4.2 Temperature adjustments of phase change enthalpies

Several simple relationships have been proposed to adjust phase change enthalpies to a common reference temperature, usually $T = 298.15$ K. Equation (1) with $n = 2$ has been derived for sublimation enthalpies for substances without any additional phase transitions occurring between the mean temperature of measurement and the reference temperature. Assumptions in the derivation include ideal gas behavior and that the Dulong -Petit value holds for the solid.^{55,56} Depending on the nature of the substance investigated, additional coefficients of R as indicated in Eq (1), have been recommended.⁵⁷⁻⁵⁹

$$\Delta H_s(T_{\text{ref}}) = \Delta H_s(T_m) + n R(T_m - 298 \text{ K}) \text{ where } n = 2, 4.8, 6, 7.2 \quad (1)$$

Heat capacities of organic substances are known to vary depending on the presence and nature of the functionality present and on molecular size. Group additivity methods have been reasonably successful in estimating their magnitude for both solids and liquids at 298 K.^{31,60} Lack of group values for some functionality, however, remains a current limitation. Taking advantage of the success of available group methods, relationships have been established that have been successful in modelling the effects of temperature on heat capacity differences between the condensed and gas phase. Equation (2), for example, has been derived to adjust sublimation enthalpies while equation (3) has been useful for similar temperature adjustment of vaporization enthalpies. Application of these equations have been detailed previously.³¹

$$\Delta_{\text{cr}}^{\text{g}}Cp = 0.75 + 0.15 Cp_{\text{cr}}(298 \text{ K}) \quad (2)$$

$$\Delta_{\text{l}}^{\text{g}}Cp = 10.58 + 0.26 Cp_{\text{l}}(298 \text{ K}) \quad (3)$$

$$\Delta_{\text{cr}}^{\text{g}}Cp = -0.9 + 0.176 Cp_{\text{g}}(298 \text{ K}) \quad (4)$$

$$Cp_{\text{g}}(298 \text{ K}) = 0.85Cp_{\text{cr}}(298 \text{ K}) - 0.75 \quad (5)$$

$$\Delta_{\text{cr}}^{\text{l}}Cp = [0.15 Cp_{\text{cr}}(298 \text{ K}) - 0.26 Cp_{\text{l}}(298 \text{ K}) - 9.83] \quad (6)$$

The terms $Cp_{\text{cr}}(298 \text{ K})$, $Cp_{\text{l}}(298 \text{ K})$ and $Cp_{\text{g}}(298 \text{ K})$ refer to the heat capacity of the solid, liquid and gas, respectively. The heat capacities of the condensed phase used in Eqs. (2) and (3) have either been estimated by group additivity or measured experimentally.³¹ The gas phase heat capacity in Eq. (4) has either been calculated by statistical thermodynamics⁶¹ or evaluated using Eq (5) obtained by rearranging Eq. (2).⁶² These equations have been used successfully to adjust appropriate phase change enthalpies from approximately 400 K to 298.15 K. Fusion enthalpies have also been adjusted to the standard state using Eq. (6). Eq (6) was derived by solving for the $Cp_{\text{g}}(298 \text{ K})$ term in both Eqs (2) and (3), setting them equal to each other, and rearranging to solve for $(Cp_{\text{l}} - Cp_{\text{cr}})(298 \text{ K})$.⁶³ An additional application of these equations is that together, they can be used to complete the following thermodynamic cycle in cases where all three phase change enthalpies are available.

$$\Delta H_{\text{s}}(T_{\text{ref}}) = \Delta H_{\text{v}}(T_{\text{ref}}) + \Delta H_{\text{fus}}(T_{\text{ref}}) \quad (7)$$

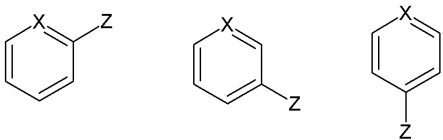
Equation (7) has been useful in validating sublimation enthalpies measured directly.⁶⁴

4.3 Isomer effects. Melting points⁶⁵ are always higher for 1,4- than for 1,2- or 1,3-benzene derivatives. In parallel, the crystal lattice energies of 1,4-disubstituted benzenes are more stabilizing than those of their 1,3- or 1,2-isomers. Moreover, with appropriate substituents, in

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1,2-isomers an intramolecular hydrogen bond is often formed, subtracting intermolecular valence and lowering the SE by an amount roughly equivalent to the energy of the missing intermolecular hydrogen bond(s). The drive to intramolecular hydrogen bond formation is so strong that in some cases (see Figure 4) the conformation at the COOH group becomes *trans* in order to approach the acceptor terminus. Examples of the isomer effects are shown in Table 2: the difference can be 10-20 kJ kmol⁻¹, or just about the energy of an alcohol hydrogen bond, or 34 kJ kmol⁻¹ for the pair 2,6- and 2-4-dihydroxybenzoic acid, almost exactly the energy of a carboxylic acid single hydrogen bond. These results on the one hand confirm the reliability of the SE measurements, and strongly suggest that 1,2-disubstituted compounds sublime with the intramolecular hydrogen bond intact.

Table 2. Sublimation enthalpies of substituted benzene and pyridine isomers, with CSD refcodes of the corresponding X-ray crystal structures.



X	Z	1,2	1,3	1,4	name
(C)NO ₂	NH ₂	89 ONITAN	94 MNIANL	101 NANILI	nitroaniline
(C)OH	OH	85 CATCOL	93 RESORA	100 HYQUIN	dihydroxybenzene
(C)OH	NH ₂	101 AMPHOM	104 MAMPOL	108 AMPHOL	aminophenol
(C)COOH	OH	97 SALIAC 109 LEZJAB	123 BIDLOP 143 WUYPOW	115 JOZZIH -	hydroxybenzoic acid 2,6 and 3,5-dihydroxy benzoic acid
(C)OH	NO ₂	73 ONITPH	97 -	95 NITPOL	nitrophenol
(C)COOH	NH ₂	110 AMBACO	128 AMBNZA	116 AMBNAC	aminobenzoic acid
N	OH	87 -	88 -	115 -	hydroxypyridine
N→O	COOH	94 PICANO	152 VATNUA	-	pyridine N-oxide carboxylic acid

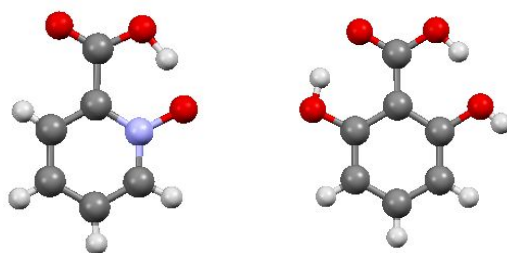


Figure 4. The *trans* conformation adopted by carboxyl groups. Left: pyridine-N-oxide carboxylic acid (CSD refcode PICANO); right, 2,6-dihydroxybenzoic acid (CSD refcode LEZJAB).

4.4 Chain length effects. Figure 5 shows SE as a function of the number of carbon atoms in *n*-alkanes and analogous terminal-substituted carboxylic monoacids and terminal-disubstituted diacids. The alternation shown in the SE measured directly for alkanes for $C > 12$ is presumably due to differences in packing⁶⁶ and largely disappear when SE is estimated by sums of enthalpies of fusion and of transition between polymorphs,³¹ and their enthalpies of vaporization at $T = 298.15$ K.⁶⁷ The least-squares lines have very similar slopes, while the difference of intercepts between hydrocarbons and acids or between acids and diacids is 39–43 kJ mol⁻¹. Since all the acids form cyclic intermolecular hydrogen bonds in the solid state, these differences provide a direct experimental measure of the energy of a pair of cyclic, O–H...O hydrogen bonds.

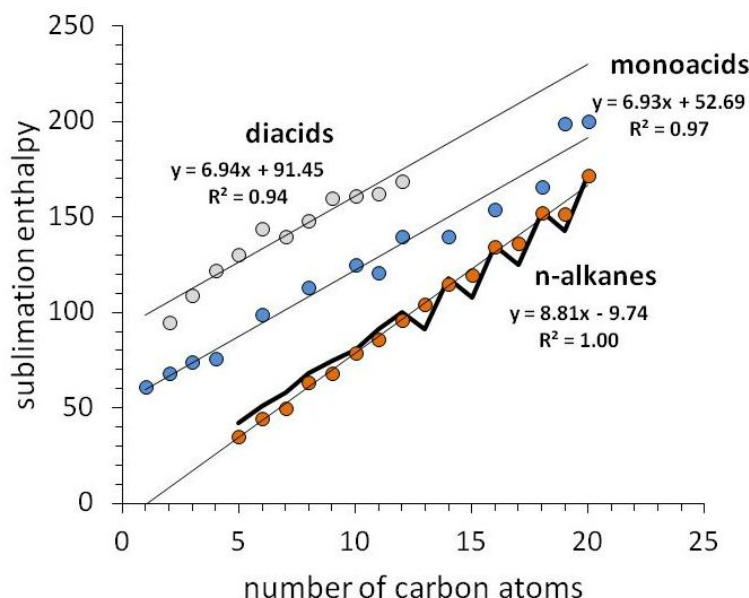


Figure 5. Sublimation enthalpy as a function of chain length. For *n*-alkanes: black line, measured directly, red circles: sum of heats of fusion, vaporization and polymorph transition(s). Other lines: experimental values for terminal monoacids and diacids.

4.5 Large-scale comparisons between sublimation enthalpies and lattice energies.

A detailed list of all calculated LEs by both methods with corresponding deviations from SE is given in Supporting Information, Table S4.

The comparison shows some items for which SE is much lower than LEs calculated by both methods. The subsequent analysis reveals some reasons for which these SEs must be wrong (Table 3). These cases were therefore excluded from the subsequent discussion leaving 490 Pixel LEs and 669 AA-CLP LEs. The analysis by comparison with similar compounds can often provide a guideline to judge the reliability of a newly produced value of SE. This is one of the many proficient uses of a well established database.

Table 3. Sublimation enthalpy much lower than lattice energy, with possible explanation. All quoted numbers are in kJ mol⁻¹.

refcode	reported SE	LE, Pixel	name	possible explanation
CUKCIU02	34	54	1,4-dioxane	evaporation, not sublimation; sum of evaporation and fusion enthalpies 55.6 ⁶⁸
IJUMEG05	79	145	3,4,5-trihydroxy-benzoic (gallic) acid	new measurement ⁶⁹ gives 149.3
OVANIL01	54	81	o-vanillin, 2-hydroxy-3-methoxy benzaldehyde	evaporation? 4-hydroxy-3-methoxybenzaldehyde, vanillin, is 99.6 ⁷⁰
TRPHAM03	63	160	terephthalamide	benzamide is 100
TCLHQU11	90	137	tetrachloro-benzoquinone	most likely evaporation (93.8) (tetrachlorobenzene is 83)
TAZPEN01	74	100	dibenzo-1,3a,4,6a-tetraazapentalene	naphthalene (2 rings less) is 72.6± 0.6
KUBMAX01	62	80	1,2,4-trichloro-benzene	sum of evaporation and fusion enthalpies is 74.4; other trichloro isomers are 74
TBRETH10	41	58	tetrabromoethylene	dibromomethane is 52
AFAZEM01	67	419	sulfanilic acid	zwitterionic crystal, must have a very large Coulombic energy
HEVRUV	48	70	trinitromethane	trinitroethane is 72

The discrepancy between experiment and calculation can be appreciated from the absolute value, $D_{abs} = SE - LE$, or can be measured by $\%D = 100 (SE-LE)/SE$, the former expression being more suitable for small values of SE where a small D_{abs} turns into a large $\%D$. Figure 6 shows the graphic view of the SE-LE comparison for the Pixel calculations, while Table 4 shows some

numerical data for a quantitative appreciation of the performance of the computational methods. With Pixel, two thirds of the SEs are simulated with D lower than 10%, and for only 13% of the cases the discrepancy exceeds 15% or what can be considered a tolerable deviation. Also relevant is the fact that Pixel gives no "wild" outliers with $\%D > 25$.

Table 4. Number of SE-LE pairs below a given discrepancy $\%D = 100 \text{ abs(SE-LE)/SE}$

$\%D$ less than	Pixel, out of 490		AA-CLP, out of 669	
	%	rmsd, kJ mol ⁻¹	%	rmsd, kJ mol ⁻¹
5	34	2.7	31	3.2
10	68	5.5	59	6.2
15	87	7.8	74	8.3
20	98	8.8	82	9.6
25	99	9.9	90	11.6
30	100	10.4	93	16.7

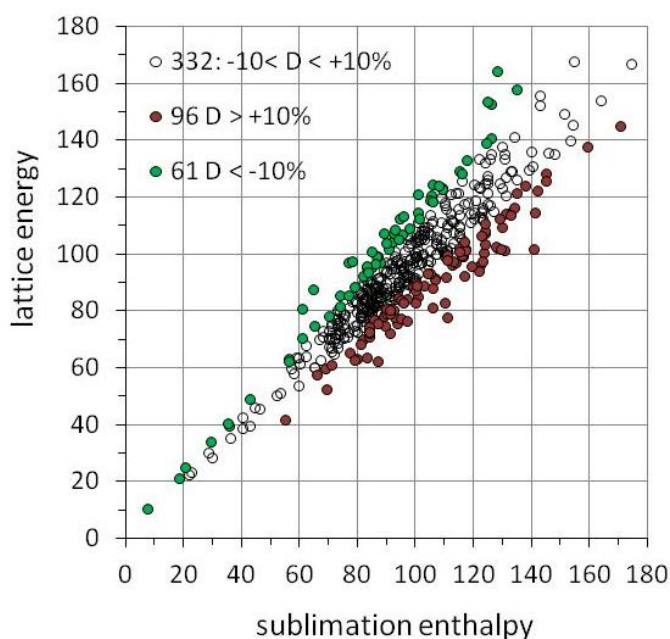


Figure 6. Pixel lattice energy vs. experimental sublimation enthalpy (kJ mol⁻¹) for 490 crystals. The least-squares line for 332 data with $-10 < D < +10\%$ is $LE = 0.989 SE$ with $R^2 = 0.945$. The corresponding plot with AA-CLP lattice energies is in Supporting Information, Figure S1.

4.6 Results by classes of compounds. In Figure 7, for hydrocarbons the agreement is almost too good to be true, especially for the parametric AA method. Pixel performs much better than AA for carboxylic acids. These are two instances in which SE and LE reinforce each other's reliability. On the other hand, the picture for alcohols and phenols shows that AA overestimates the SEs while Pixel performs somewhat better, but both approaches produce a more substantial scatter. This result

could be due to shortcomings of the computational methods, but the suspicion arises that experimental data may also have more uncertainty: the crystal packing of alcohols is problematic with many molecules in the asymmetric unit or disorder often undetected or misrepresented in the X ray work. Also, the crystal-gas transition in these materials may not be a 'clean' one, either by conformational flexibility or even by gas-phase aggregation ($\Delta H' \neq 0$). Pixel performs much better than AA for amides.

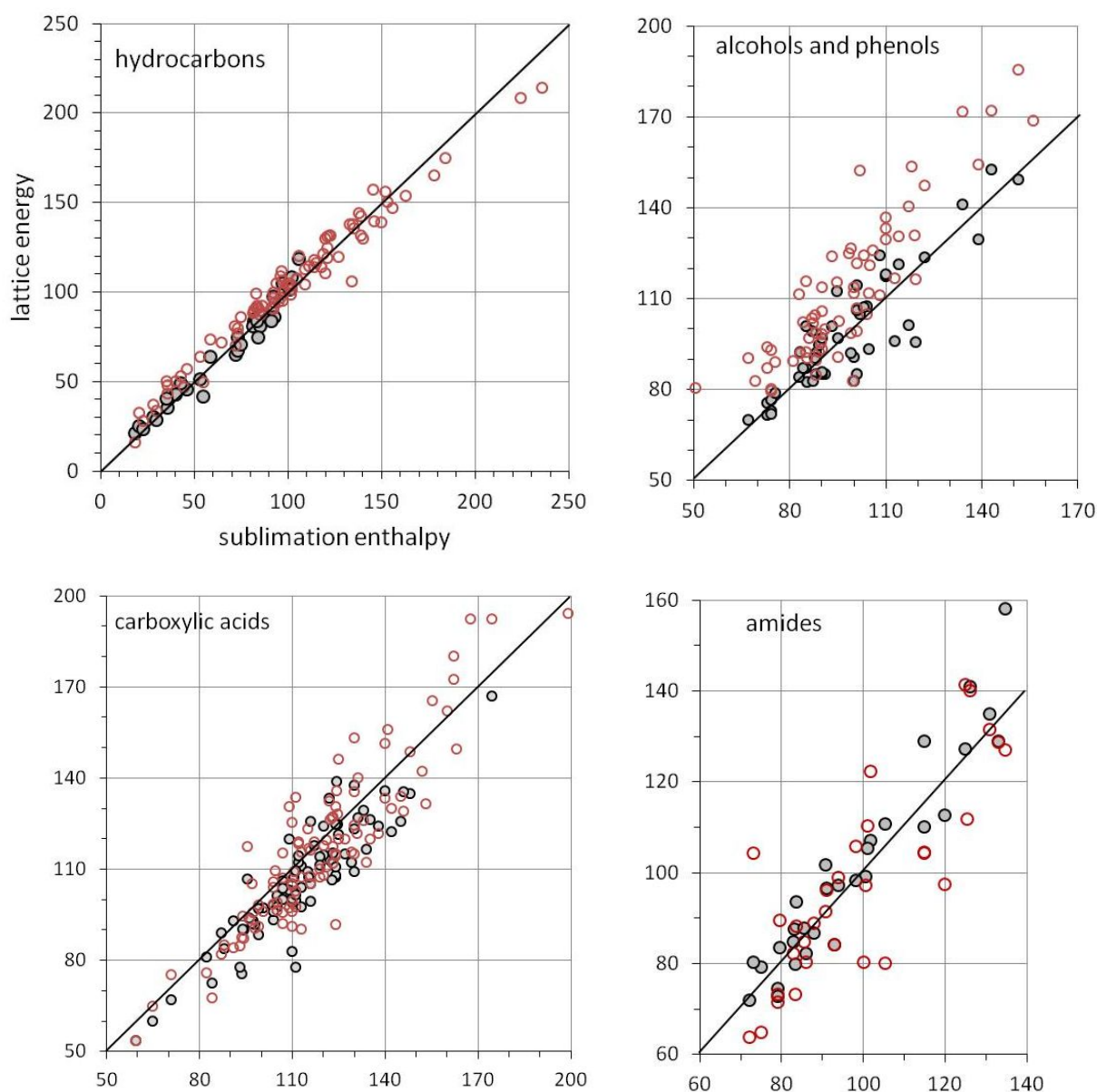


Figure 7. Comparisons between sublimation enthalpy (horizontal axis) and lattice energy (vertical axis; Pixel, black circles, or atom-atom, red) for some chemical classes: hydrocarbons, excellent agreement with both methods; for alcohols and phenols the AA match is problematic; carboxylic acids, reasonable agreement; amides, fair agreement with Pixel, scatter with AA.

4.7 A note on polymorphism. In our 679-entry crystal structure database there are 169 crystals labeled as polymorphic, although others may be present but not labeled, and some polymorphs may be named but not fully characterized by X-ray analysis. Our unique choice for LE calculations has been made in terms of *R*-factor and completeness of characterization, but regardless of polymorphism. On the other hand, the original SE repertory³¹ has just a handful of entries denoted as polymorphs, witness of the difficulty of performing such a critical discriminating experiment. One example with clear denominations is for oxalic acid, polymorphic with an orthorhombic (α) and a monoclinic (β) phase. Experimental SEs are 93.4, 93.7, 97.9 and 98.5 kJ mol⁻¹ for the α -phase and 92.5, 93.3 and 93.3 for the β -phase. The uncertainty range within each phase is of the same order of magnitude as the difference between phases, and both quantities are of the order of the overall uncertainty in both calculation and experiment. Making clear distinctions among crystal polymorphs needs extreme care and justification by theory, and is a hard task by experiment.

5. SUMMARY AND CONCLUSIONS

The sublimation energy table presented in this paper with 1655 entries is probably the most exhaustive compilation of its kind and could well be considered a definitive benchmark. A primary use of the experimental database is to provide a strong guideline to judge the reliability of any proposed value for SE, by comparison with similar compounds. The match of 737 entries to the corresponding crystal structure is an unprecedented bonus for both experimentalists and theoreticians, coupling structural and thermodynamic information.

The results for compounds whose SE has been measured a number of times show quite a few patent outliers; even when these are eliminated, it appears that an overall uncertainty range of 5-10% among different experimental determinations is more the rule than the exception. This result, which presumably also depends on differences in the quality and quantity of the sample used, leaves room for the suspicion that this same uncertainty range is inherent to any experimental SE measurement, unless a specific justification is presented. Different theoretical approaches, even based on sophisticated quantum chemical methods, may well have the same range of variability. For an average crystal energy of 100 kJ mol⁻¹ for a typical medium-size organic compound this means that one is dealing with an uncertainty pool of 5-10 kJ mol⁻¹ in both theory and experiment. The origin of this uncertainty in the experimental number comes from two sources. The first is associated with the precision of the method. A second source of uncertainty is associated with any temperature adjustment included in converting their results to the standard state. It has not been uncommon for authors in the past to cite the uncertainty of their measurement at $T = 298.15$ K simply as the precision of their measurements measured at

other temperatures.⁷¹ The convention and importance of adjusting results to a standard state for comparisons frequently requires properties that cannot be accessed experimentally. A realistic assessment of the uncertainty of the property evaluated by other means is extremely important in such cases. This should be kept in mind in all work that uses SEs as calibration data for computational schemes and potential energy parameterization, as well as in crystal structure prediction efforts.

Both Pixel and AA have some overall tuning parameters that can be adjusted to particular classes of compounds. Anyway, according to Table 4 a casual Pixel operator using the default values stands a 68% chance of matching the selected SE with a rmsd of 5.5 kJ mol⁻¹, or an 87% chance of fitting the SE with a rmsd of 7.8 kJ mol⁻¹. The corresponding numbers for the AA method are 59% (6.2) and 74% (8.3), not so bad in terms of cost/performance ratio if one thinks that an AA calculation takes just fractions of a second and yields its result in a few minutes of preliminaries after submission of the corresponding crystal data (even directly from a CSD cif file). However, Pixel has only 30 values above the 20% threshold of large disagreement, and the rmsd can never exceed 10.4 kJ mol⁻¹, while AA has some 10% of wild outliers that cannot be reconciled with experiment.

In general, the prediction of SE by LE calculations is quite reliable for hydrocarbons, a class of compounds for which it may be said that calculation is as effective, and probably much less expensive, than experiment. Things are different for hydrogen-bonding compounds, where the SE-LE match seems less reliable. On the one hand, it is well known that the computational simulation of the hydrogen bond is a challenge to theory; on the other hand, it may well be that hydrogen-bonding compounds suffer from some molecular rearrangement on going from crystal to gas, making the SE-LE match less straightforward. Systematic disagreement on crystal classes throws light at the same time on the shortcomings of the theory and on the structural and physicochemical factors that cause this poor reproduction of intermolecular bonding; this is an example of how the match between experimental sublimation energies and calculated lattice energies can be mined in many ways for chemical and structural trends.

ASSOCIATED CONTENT

Supporting information.

The supporting information is available free of charge on the ACS Publication website at DOI... Criticism of *nRT* corrections to the sublimation enthalpy-lattice energy comparison; Table of 1655 heats of sublimation with 737 matches to crystal structure, and attempted temperature fitting for some compounds; Table with calculated lattice energies; plot of comparison between sublimation enthalpies and atom-atom lattice energies (PDF).

AUTHOR INFORMATION

Corresponding authors

James S. Chickos Email jsc@umsl.edu

Angelo Gavezzotti Email angelo.gavezzotti@unimi.it

ORCID

James S. Chickos 0000-0002-8385-1665

Angelo Gavezzotti 0000-0002-8837-3789

Notes.

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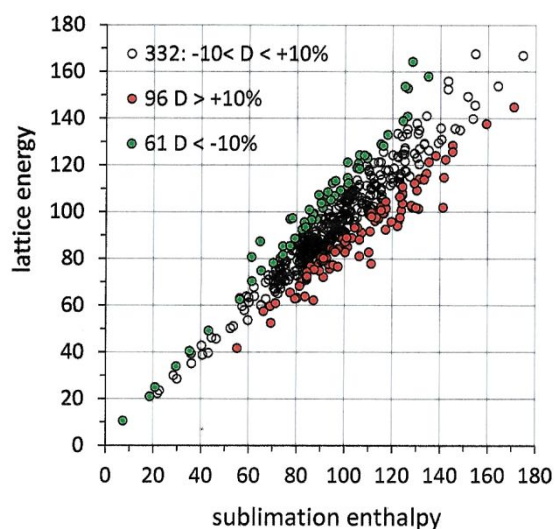
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SUBLIMATION ENTHALPIES OF ORGANIC COMPOUNDS: A VERY LARGE DATABASE WITH A MATCH TO CRYSTAL STRUCTURE DETERMINATIONS AND A COMPARISON WITH LATTICE ENERGIES

James S. Chickos^{1*} and Angelo Gavezzotti^{2*}

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1655 sublimation enthalpies of organic compounds, 737 matched to the X-ray crystal structure; lattice energies for 679 crystals by atom-atom potentials and for 500 crystals by the Pixel method; 87% of sublimation enthalpies-lattice energies match by less than 15% with a rmsd of 8.7 kJ mol⁻¹. The intrinsic accuracies of calculated lattice energies and experimental sublimation enthalpies are in the 5-10 kJ mol⁻¹ range.

