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Prediction of Enthalpy of Formation in the Solid State (at 298.15 K) using Second-Order Group Contributions. Part 1. Carbon-Hydrogen and Carbon-Hydrogen-Oxygen Compounds

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A predictive method, based on Benson's group additivity technique, is developed for calculating the enthalpy of formation in the solid phase, at 298.15 K, of carbon-hydrogen compounds and carbon-hydrogen-oxygen compounds. A complete database compiles 398 experimental enthalpies of formation. The whole group contribution values, ring strain corrections, and nonnearest neighbor interactions evaluated are listed. Finally a comparison with Cohen's method indicates that this new estimation method leads to higher precision and reliability. © *2006 American Institute of Physics*.

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Key words: enthalpy of formation; group additivity; organic compounds; prediction; thermochemical properties.

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1. Introduction

In the study of chemical, biochemical, or environmental systems, knowledge of reliable physical and chemical properties of pure compounds, such as enthalpies of formation, heat capacities, and entropies, is required. However, it is of-

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[a)] Author to whom corresponding should be addressed. Electronic mail: Didier.Dalmazzone@ensta.fr ten difficult to find in the literature trustworthy experimental values of these thermochemical figures for molecules of interest. Indeed, it is clearly hopeless to expect to have tabulated experimental thermochemical data on all polyatomic species or even on restricted subclasses of these.

Therefore, it would be worth obtaining these data from alternative sources. In recent years there has been a considerable effort in developing methods which can result in the most precise estimation. Even though several techniques have emerged, both scientists and engineers agree that one of the best methods is that of group additivity, especially as imagined by Benson and co-workers[1] (a method which was originally developed for the gas phase). Not only is it an approach easy to apply, but it can usually predict thermochemical data with an uncertainty similar to that obtained by experiments as well.

In the group contribution approach molecules are assumed to be formed by segments chosen from a previously established set. In 1958, Benson and Buss[2] set up a hierarchical system of additivity laws. The simplest or "zeroth-"order law is the additivity of atom properties; its use is limited. The next higher, or first-order, approximation is based on the additivity of bonds, or undifferentiated groups of atoms. Such groups are assumed to share the same contribution, whatever the atom to which they are bonded (i.e., all -CH_3 groups are equivalent). First-order methods are subject to large errors in heavily branched molecules, and cannot distinguish differences of properties of isomers. In the second-order approximation, the groups are differentiated so that the nature of each next nearest ligand may be taken into account. Benson's groups are thus defined as "a polyvalent atom (ligancy≥ 2) together with all of its ligands".[1] The additivity schemes are based on the assumption that the local property of a group remains unchanged in a series of homologous compounds. This is true as long as no structural features are introduced into a molecule. In order to take into account such spatial interactions some corrections are required. Benson *et al.*[1] introduced many corrections such as the *gauche* interaction, ring strains in nonplanar cyclic molecules, or electronic interactions between substituents through a benzene ring.

The present work is part of a broader program, the aim of which is to predict the enthalpy of formation in the solid state of energetic materials, especially nitrogen-containing compounds. Domalski and Hearing[3] demonstrated the possibility of extending the Benson's technique to the condensed phase at 298.15 K and 101 325 Pa. For that purpose, they introduced changes in the definition of many contributions to nonnearest neighbor interactions. Unfortunately, the Domalski and Hearing technique is not advanced enough to obtain satisfactory predictions. The number of compounds that had been studied seems to be too short to derive enough group additivity values. Indeed this method missed some relevant group contributions, especially for nitrogen-containing groups. Cohen[4] worked on an updated database to revise the second-order group additivity values for predicting the enthalpy of formation in the three phases of molecules containing only carbon, hydrogen, and oxygen. Even though the method of Cohen appears more efficient and more precise, it was never extended to nitrogen-containing compounds. Moreover, some new values of experimental solid phase enthalpies of formation were published since 1996 and it appears that a great majority of them do not fit with the Domalski and Hearing predictions or with the Cohen predictions.

The aim of our work is to develop new sets of contributions of Benson's groups based on updated experimental data, to predict the solid phase enthalpy of formation at 298.15 K and 101 325 Pa, for C-H, C-H-O, C-H-N, and C-H-O-N compounds. This article presents the first part devoted to C-H and C-H-O compounds; the second part, for nitrogen-containing compounds, will be published in another article. A comparison between the results calculated thanks to the present work and the Cohen group additivity values is discussed. The Cohen approach is preferred compared to Domalski and Hearing since the former employed a more thorough and updated database than the latter.

2. Procedure

First, a database was established in order to compile all of the most reliable values of enthalpy of formation in the solid state of pure organic compounds. The most useful and consistent source of interesting data was published by Pedley *et al.*[5] Indeed, values stored in this database are derived from experimental thermochemical data. The two other sources used were the NIST Chemistry WebBook[6] and the ICT Database of Thermochemical Values.[7] Both of them were consulted in order to confirm whether a more recent or a more precise value of enthalpy of formation was stored in them in comparison to the Pedley's compilation.

Once the database was set up, each molecule was decomposed into groups. As all of the group contribution values remain unknown, an arbitrary value was assigned to each group. The calculation of group values was computer-assisted thanks to the solving capability of a modern spreadsheet. An enthalpy of formation was then computed by means of the group contributions calculated in order to minimize the residual value (defined as the experimental value minus the calculated one) for each compound considered. Molecules for which a large residual resulted were particularly studied. A ring strain correction or a nonnearest neighbor interaction was sought. If none could have been unearthed, group contributions were recalculated after the exclusion of the compounds for which no solution could have been ascertained.

In order to handle this task as rationally as possible, the process explained earlier was applied to C-H compounds first and then to C-H-O compounds. The main difference between the current approach and the previous ones (see Sec. 3.2.1) is that group contributions were not derived for the alkanes first and then for the alkenes, alkynes, aromatics, and polycyclics, but the whole group additivity values were evaluated at the same time, regarding C_xH_y molecules. As for C-H-O compounds, group contributions were initially derived for alcohols and afterward for a whole list of acids, esters, and polyfunctional oxygenated compounds. Moreover if a group is generated using less than three C-H compounds, and if this group can be determined with a greater number of C-H-O molecules, the group contribution of interest is then evaluated a second time due to the new set of compounds.

So as to minimize the number of ring strain corrections, one is tempted to replace the ring structure of interest by the sum of its different parts. Unfortunately such estimations entail large errors and Cohen^4 evaluated them to 10–15 kJ mol^{-1}. This can be explained by the fact that, in general, the bond angles and lengths in complex structures are dissimilar from those of the individual ring elements. Therefore each ring strain correction is considered in this work, when it is possible.

3. Results and Discussion

3.1. Results

Tables 1–5 list the group contribution values determined as well as the ring strain corrections and the nonnearest neighbor interactions. Groups containing only carbon and hydrogen atoms are presented first and groups for the C-H-O compounds are second. The first column of each table presents all the defined groups. The second and third columns list the group additivity values for each group in kilocalories per mole and in kilojoules per mole, respectively. The joule is related to the thermochemical calorie through the definition: one thermochemical calorie equals 4.184 00 joules. Finally the fourth column lists the number of compounds studied that were used to evaluate each group contribution. Notice that if group additivity values were generated owing to less than three molecules, they would certainly be more inaccurate than the other group contributions determined. The entries in Tables 1–5 are identified by footnotes at the end of the table of interest.

Tables 6 and 7 compile data obtained for the compounds of the whole list, i.e., even the molecules that were not exploited to determine the group additivity values listed in Tables 1–5. Indeed some of the compounds studied were not used to evaluate the group contributions owing to large errors which seemed to come from an experimental inconsistency. The whole C$_x$H$_y$ molecule database is stored in Table 6, whereas in Table 7 all the C$_x$H$_y$O$_z$ compounds compiled are presented. The first column of both tables lists the molecule names. Their corresponding empirical formulas and their CAS Registry Numbers, if one was found, are presented, respectively, in the second and the third column. The following column lists the enthalpy of formation in the solid phase measured experimentally. The fifth column shows the enthalpy of formation in the solid state (calculated thanks to the group contributions determined and compiled in Tables 1–5). After all, the sixth column is devoted to the residual, which means the difference between the experimental and the computed values of enthalpy of formation. The last two columns are the same but are devoted to Cohen's work in order to compare his results with those of the present study.

TABLE 1. C-H group additivity values for enthalpy of formation in the solid phase, at 298.15 K

	$\Delta_f H°$ (solid)		
Group^a	kcal mol^{-1}	kJ mol^{-1}	Number of compounds
C-(C)(H)$_3$	−9.0	−37.6	23
C-(C)$_2$(H)$_2$	−7.1	−29.8	47
C-(C)$_3$(H)	−2.3	−9.5	26
C-(C)$_4$	−3.5	−14.7	12
C-(C$_d$)(H)$_3$	−2.8	−11.7	1
C-(C$_d$)(C)(H)$_2$	−3.6	−15.0	2
C-(C$_d$)(C)$_2$(H)	9.5	39.8	4
C-(C$_d$)(C)$_3$	−0.8	−3.5	1
C-(C$_d$)2(H)$_2$	−3.6	−15.3	1
C-(C$_t$)(H)$_3$	−9.6	−40.2	1
C-(C$_t$)(C)(H)$_2$	5.6	23.4	1
C-(C$_t$)(C)$_3$	5.9	24.8	1
C-(C$_B$)(H)$_3$	−26.0	−108.7	32
C-(C$_B$)(C)(H)$_2$	−17.1	−71.6	15
C-(C$_B$)(C)$_2$(H)	−12.1	−50.8	2
C-(C$_B$)(C)$_3$	−16.8	−70.5	4
C-(C$_B$)$_2$(H)$_2$	−30.0	−125.6	6
C-(C$_B$)$_2$(C)(H)	−18.2	−76.1	3
C-(C$_B$)$_2$(C)$_2$	−19.7	−82.5	1
C-(C$_B$)$_3$(H)	−24.3	−101.8	2
C-(C$_B$)$_3$(C)	−17.6	−73.4	4
C-(C$_B$)$_4$	−28.4	−118.8	1
C$_d$-(H)$_2$	−0.4	−1.8	3
C$_d$-(C)(H)	4.9	20.6	4
C$_d$-(C)$_2$	−0.8	−3.5	1
C$_d$-(C$_d$)(H)	4.4	18.3	6
C$_d$-(C$_d$)(C)	−11.4	−47.6	1
C$_d$-(C$_d$)$_2$	10.7	44.8	2
C$_d$-(C$_B$)(H)	−0.4	−1.5	12
C$_d$-(C$_B$)(C)	−4.9	−20.5	1
C$_d$-(C$_B$)(C$_d$)	8.0	33.6	2
C$_d$-(C$_B$)$_2$	1.2	4.9	8
C$_t$-(H)	16.3	68.4	1
C$_t$-(C)	13.9	58.1	2
C$_t$-(C$_t$)	25.8	107.9	2
C$_t$-(C$_B$)	16.2	67.8	4
C$_B$-(H)	0.7	3.1	83
C$_B$-(C)	18.5	77.3	58
C$_B$-(C$_d$)	14.4	60.2	18
C$_B$-(C$_t$)	16.2	67.8	4
C$_B$-(C$_B$)	8.8	36.9	7
C$_{BF}$-(C$_{BF}$)(C$_B$)$_2$	5.8	24.4	29
C$_{BF}$-(C$_{BF}$)$_2$(C$_B$)	4.2	17.4	13
C$_{BF}$-(C$_{BF}$)$_3$	0.7	3.0	4

[a] A group is written as X-(A)$_i$(B)$_j$(C)$_k$(D)$_l$, where X is the central atom and $0 \leq i,j,k,l \leq 4$ represent the number of atoms or groups of atoms linked with the central atom. It is notable that different carbon atoms exist: C$_d$, C$_t$, C$_B$, C$_{BF}$, and C$_a$. It represents, respectively, a double-bonded carbon atom, a triple-bonded carbon atom, a carbon atom in a benzene ring, a carbon atom in a fused ring system, and an allenic carbon atom.

Examining Tables 8–13 permits the evaluation of the quality of the group values determined in Tables 1–5. Indeed the magnitude of the difference observed between the literature and calculated enthalpies of formation in the solid phase

TABLE 2. Values of ring strain corrections for enthalpy of formation in the solid phase, at 298.15 K (C-H groups)

Ring strain correction	$\Delta_f H^\circ$ (solid) kcal mol^{-1}	$\Delta_f H^\circ$ (solid) kJ mol^{-1}	Number of compounds
Cyclobutane	24.6	102.7	2
Cyclopentane	8.1	33.8	7
Cyclopentene	1.9	7.7	2
Cyclopentadiene	−9.0	−37.7	3
Cyclohexane	1.4	5.7	19
Cyclohexene	−4.3	−17.8	3
1,4-Cyclohexadiene	−6.4	−26.7	3
Cycloheptane	8.4	35.1	2
1,3,5-Cycloheptatriene	3.4	14.1	3
Cyclooctane	3.7	15.3	2
Cyclododecane	12.1	50.5	1
Cyclotetradecane	10.2	42.6	1
Cyclopentadecane	16.8	70.2	1
Cyclohexadecane	17.4	72.7	1
Cycloheptadecane	18.0	75.4	1
1,5,9-Cyclododecatriene	−1.7	−7.0	1
1,8-Cyclotetradecadiyne	0.1	0.4	1
Biphenyl	−3.2	−13.5	5
Biphenylene	38.6	161.4	1
Bicyclo[2.2.1]heptane	17.3	72.4	5
Bicyclo[2.2.1]hept-2-ene	5.1	21.5	1
Bicyclo[2.2.2]octane	12.1	50.6	1
Bicyclo[2.2.2]octene	−6.0	−25.0	1
Bicyclo[3.3.1]nonane	11.7	49.0	1
Bicyclo[3.3.3]undecane	32.1	134.2	1
Tricyclo[8.2.2.$2^{4,7}$]hexadecane	36.1	150.8	1
Acenaphthene	−2.1	−8.7	1
Acenaphthylene	0.4	1.6	1
[2.2]Metacyclophane	7.3	30.6	1
[2.2]Metaparacyclophane	19.8	83.0	1
Benzo[c]phenanthrene	5.6	23.4	1
[16]Annulene	60.9	254.7	1
[18]Annulene	−39.7	−166.0	1
Identical substitution in para position of 2 aromatics[a]	8.2	34.5	2
1 carbon atom between 2 aromatics[b]	−0.7	−3.0	11

[a] Correction applied to [2.2]paracyclophane, [3.3]paracyclophane, [1.8]paracyclophane, and [6.6]paracyclophane.

[b] Correction applied, for instance, to diphenylmethane or to triphenylmethane.

gives information on the reliability of the method applied. Residuals within ±5 kJ mol^{-1} are considered to be in excellent or good agreement. Those that are between ±5 and ±10 kJ mol^{-1} are judged to be quite satisfactory whereas residuals lying between ±10 and ±20 kJ mol^{-1} seem to be at the limit of acceptability. Regarding differences larger than ±20 kJ mol^{-1}, they are certainly due to either poor quality literature data or a neglected interaction. Those six tables lead to a comparison between the group contribution method established in this article and the one established by Cohen.[4]

Tables 8, 10, and 12 compile the number of compounds, and the corresponding percentage, for the residual that is

TABLE 3. C-H-O group additivity values for enthalpy of formation in the solid phase, at 298.15 K

Group	$\Delta_f H^\circ$ (solid) kcal mol^{-1}	$\Delta_f H^\circ$ (solid) kJ mol^{-1}	Number of compounds
C-(CO)$(H)_3$[a]	−20.5	−85.8	6
C-(CO)(C)$(H)_2$	−16.9	−70.9	14
C-(CO)$(C_d)(H)_2$	−7.0	−29.1	1
C-(CO)$(C_t)(H)_2$	6.5	27.2	2
C-(CO)$(C_B)(H)_2$	−28.8	−120.6	3
C-(CO)(C_B)(C)(H)	−16.1	−67.3	3
C-(CO)$(C)_2$(H)	−11.8	−49.4	9
C-(CO)$(C)_3$	−9.1	−37.9	6
C-$(CO)_2(H)_2$	−23.9	−100.0	1
C-(O)$(H)_3$	−9.9	−41.4	7
C-(O)(C)$(H)_2$	−6.3	−26.4	44
C-(O)$(C)_2$(H)	−4.6	−19.4	44
C-(O)$(C)_3$	−7.7	−32.4	8
C-(O)(C_d)(C)(H)	−1.4	−5.8	2
C-(O)$(C_t)(C)_2$	7.6	31.7	2
C-(O)$(C_B)(H)_2$	−20.3	−85.1	2
C-(O)(C_B)(C)(H)	−16.5	−69.2	3
C-(O)$(C_B)(C)_2$	−18.5	−77.3	1
C-(O)$(C_B)_2$(C)	−5.7	−23.7	1
C-(O)(CO)$(H)_2$	−17.8	−74.5	2
C-(O)(CO)(C)(H)	−11.0	−46.0	9
C-(O)(CO)$(C)_2$	−3.3	−14.0	2
C-(O)(CO)(C_B)(H)	22.5	94.2	1
C-$(O)_2(H)_2$	−15.6	−65.3	1
C-$(O)_2$(C)(H)	−16.0	−66.8	11
C-$(O)_2(C_d)$(H)	8.4	35.3	1
C_d-(CO)(H)	−7.3	−30.4	1
C_d-(CO)(C)	−16.7	−69.7	1
C_d-(CO)(O)	−25.0	−104.4	4
C_d-(O)(H)	−8.0	−33.4	3
C_d-(O)(C)	8.4	35.3	1
C_d-(O)(C_d)	−12.1	−50.7	1
C_t-(CO)	−9.1	−38.2	1
C_B-(CO)	−26.4	−110.5	13
C_B-(O)	−16.2	−67.9	29
CO-(C)(H)	−31.0	−129.6	2
CO-$(C)_2$	−17.8	−74.5	2
CO-$(C_d)_2$	−4.1	−17.2	2
CO-(C_B)(H)	−7.0	−29.2	1
CO-(C_B)(C)	1.8	7.6	7
CO-(CO)(C)	−15.7	−65.8	1
CO-(CO)(C_d)	−4.1	−17.0	1
CO-(O)(C)	−43.8	−183.1	19
CO-(O)(C_d)	−28.2	−118.1	3
CO-(O)(C_t)	−9.1	−38.2	1
CO-(O)(C_B)	−20.7	−86.7	5
CO-(O)(CO)	−50.4	−210.8	3
CO-$(O)_2$	−59.4	−248.5	3
O-$(H)_2$	−70.8	−296.0	4
O-(C)(H)	−48.4	−202.4	78
O-(C_d)(H)	−41.5	−173.7	4
O−$(C)_2$	−30.8	−128.7	14
O−$(C_d)_2$	−8.0	−33.4	3
O-(C_B)(H)	−30.1	−125.9	28
O-(C_B)(C)	−12.2	−51.0	3

TABLE 3. C-H-O group additivity values for enthalpy of formation in the solid phase, at 298.15 K—Continued

	$\Delta_f H°$ (solid)		
Group	kcal mol^{-1}	kJ mol^{-1}	Number of compounds
O-(C_B)(CO)	−7.6	−31.7	6
O-(CO)(H)	−50.8	−212.4	11
O-(CO)(C)	−28.9	−120.9	15
O-(CO)(O)	20.8	86.8	6
O-(O)(H)	−50.3	−210.6	4
O-(O)(C)	−18.5	−77.3	1

[a] The polyatomic pseudoelement CO corresponds to the carbonyl function >C=O.

lying in each stage cited just before. A comparison between the two group contribution methods, i.e., this work and Cohen, is therefore enabled.

Tables 9, 11, and 13 show the mean residual corresponding to each stage of difference between the literature and the calculated values of enthalpy of formation in the solid phase. The averages are computed for the two group contribution methods referred to earlier.

Finally, Table 14 compiles the best results obtained with both techniques, i.e., values for which residuals were larger than ±20 kJ mol^{-1} were excluded.

3.2. Discussion

3.2.1. Existing Methods

In 1993 Domalski and Hearing[3] published group additivity values for compounds containing the elements: carbon, hydrogen, oxygen, nitrogen, sulfur, and halogens in the gas, liquid, and solid phases. Thermodynamic properties, including enthalpy of formation in the solid state, are shown for 1512 compounds. Fifty-seven hydrocarbon substances and 140 organic oxygen molecules, in the solid state, appear in the study. This is not exhaustive but the authors consider that this database suffices to demonstrate the applicability of the Benson's technique to the condensed phase.

TABLE 4. Values of ring strain corrections for enthalpy of formation in the solid phase, at 298.15 K (C-H-O groups)

	$\Delta_f H°$ (solid)		
Ring strain correction	kcal mol^{-1}	kJ mol^{-1}	Number of compounds
Ethylene oxide	40.5	169.4	1
Tetrahydrofuran	22.5	94.1	1
Tetrahydropyran	17.8	74.5	12
Furan	−8.0	−33.4	3
3-Cyclobuten-1,2-dione	−1.9	−8.0	1
Phenyl ester benzoic acid	5.9	24.8	2
Cyclic (poly)saccharide[a]	−9.9	−41.5	11
Hydrated cyclic polysaccharide[b]	9.9	41.5	11

[a] Correction applied, for instance, to α-D-xylose or to D-sucrose.

[b] Correction applied to β-maltose monohydrate and to α-lactose monohydrate.

TABLE 5. Values of nonnearest neighbor interactions for enthalpy of formation in the solid phase, at 298.15 K (C-H and C-H-O groups)

	$\Delta_f H°$ (solid)		
Nonnearest neighbor interaction	kcal mol^{-1}	kJ mol^{-1}	Number of compounds
Gauche interaction	0.2	0.7	34
But-2-ene structure	−0.5	−2.2	12
Ortho correction (non polar/non polar)	0.4	1.7	13
Ortho correction (non polar/polar)	0.0	0.1	6
Ortho correction (polar/polar)	−0.3	−1.2	9
1,8-Alkylnaphthalene correction	5.4	22.7	2
2,6-Dimethylnaphthalene correction	−2.5	−10.4	1
2,7-Dimethylnaphthalene correction	−2.4	−10.1	1
2,7-Naphthalenediol correction	−10.0	−41.9	1
2,6-Dimethyl benzoic acid correction	5.1	21.5	6
Symmetrical phenyl	1.4	6.0	8
Alkanedioic acid except C_3 and C_5[a]	3.5	14.6	18
Alkanedioic acid C_n and C_{n+1} from C_9[a]	3.1	13.0	5
Intramolecular hydrogen bond	4.7	19.8	9

[a] This correction has to be applied to every alkanedioic acid except to malonic acid and to pentanedioic acid. Besides butanedioic acid requires the opposite of this correction and hexanedioic acid requires one third of the opposite of this correction.

[b] Correction applied to nonanedioic acid and to decanedioic acid. Undecanedioic acid and dodecanedioic acid require twice this correction, and so on.

The method employed by Domalski and Hearing[3] was a systematic procedure which consisted of deriving group additivity values for the *n*-alkanes first. These contributions were then fixed in order to compute group values present in branched alkanes, alkenes, alkynes, aromatic compounds, and so on. A new treatment (in comparison to Benson's approach) was developed for dealing with the repulsive interaction of hydrogen atoms on methyl groups attached to tertiary or quaternary carbon atoms. This different approach is described in detail by Domalski and Hearing.[8]

In 1996 Cohen[4] published the group additivity values for the prediction of enthalpy of formation of C-H and C-H-O molecules, in the three phases. He worked on 143 hydrocarbon compounds and 438 oxygen compounds for the solid phase. The approach used by the author is much the same as the method of Domalski and Hearing. The main difference is that the database is updated. As the evaluation method is applied step by step, if group additivity values derived from alkanes are substituted, almost all other group contributions therefore have to be reevaluated. Notice that Cohen did not use the new treatment recommended by Domalski and Hearing regarding the *gauche* isomers. The study appears to be really complete, and the group contribution values published are consequently reliable. That is the reason why a comparison between the present work and Cohen's study is shown hereafter.

3.2.2. Hydrocarbon Compounds

A total of 145 hydrocarbon compounds have been examined. Table 6 compiles them and shows the residuals ob-

TABLE 6. Enthalpy of formation in the solid phase of carbon-hydrogen compounds—comparison of results observed between this work and the method of Cohen[4]

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
2-norbornene	C_7H_{10}	498-66-8	52.9	52.9	0.0	53.0	−0.1
Norbornane	C_7H_{12}	279-23-2	−95.1	−95.3	0.2	−96.2	1.1
Cubane	C_8H_8	277-10-1	541.8	540.6	1.2	−133.6	675.4
Bicyclo[2.2.2]oct-2-ene	C_8H_{12}	931-64-6	−23.3	−23.3	0.0	−23.2	−0.1
Bicyclo[2.2.2]octane	C_8H_{14}	280-33-1	−146.9	−146.9	0.0	−209.2	62.3
2,2,3,3-tetramethylbutane	C_8H_{18}	594-82-1	−268.9	−250.8	−18.1	−256.2	−12.7
7,7-dimethyl-bicyclo[2.2.1]heptane	C_9H_{16}	2034-53-9	−148.2	−150.1	1.9	−144.2	−4.0
Bicyclo[3.3.1]nonane	C_9H_{16}	280-65-9	−178.2	−178.2	0.0	−177.8	−0.4
Azulene	$C_{10}H_8$	275-51-4	212.3	212.3	0.0	212.1	−0.2
Naphthalene	$C_{10}H_8$	91-20-3	77.9	73.8	4.1	85.6	−7.7
1,2,4,5-tetramethylbenzene	$C_{10}H_{14}$	95-93-2	−119.9	−110.0	−9.9	−108.2	−11.7
3a,4,5,6,7,7a-hexahydro-4,7-methanoindene	$C_{10}H_{14}$	4488-57-7	−23.9	−20.8	−3.1	−7.4	−16.5
Octahydro-4,7-methano-1H-indene	$C_{10}H_{16}$	6004-38-2	−112.9	−110.3	−2.6	−129.6	16.7
Adamantane	$C_{10}H_{16}$	281-23-2	−194.1	−193.6	−0.5	−193.6	−0.5
Protoadamantane	$C_{10}H_{16}$	53130-19-1	−150.8	−136.2	−14.6	−242.6	91.8
Camphene	$C_{10}H_{16}$	79-92-5	−75.4	−65.3	−10.1		
Bicyclo[3.3.2]decane	$C_{10}H_{18}$	283-50-1	−164.2	−171.5	7.3	−164.0	−0.2
2-methylnaphthalene	$C_{11}H_{10}$	91-57-6	44.9	39.3	5.6	49.1	−4.2
Pentamethylbenzene	$C_{11}H_{16}$	700-12-9	−133.6	−147.2	13.6	−134.7	1.1
1-methyladamantane	$C_{11}H_{18}$	768-91-2	−239.3	−236.4	−2.9	−215.3	−24.0
2-methyladamantane	$C_{11}H_{18}$	700-56-1	−219.6	−210.9	−8.7	−214.8	−4.8
Bicyclo[3.3.3]undecane	$C_{11}H_{20}$	29415-95-0	−152.5	−152.5	0.0	−152.3	−0.2
Biphenylene	$C_{12}H_8$	259-79-0	334.0	334.0	0.0	334.5	−0.5
Acenaphthylene	$C_{12}H_8$	208-96-8	186.7	186.7	0.0	151.0	35.7
Biphenyl	$C_{12}H_{10}$	92-52-4	99.4	91.6	7.8	99.8	−0.4
Acenaphthene	$C_{12}H_{10}$	83-32-9	70.3	70.3	0.0	70.8	−0.5
1,8-dimethylnaphthalene	$C_{12}H_{12}$	569-41-5	25.9	27.4	−1.5	33.5	−7.6
2,3-dimethylnaphthalene	$C_{12}H_{12}$	581-40-8	−2.3	6.4	−8.7	15.1	−17.4
2,6-dimethylnaphthalene	$C_{12}H_{12}$	581-42-0	−5.7	−5.7	0.0	12.6	−18.3
2,7-dimethylnaphthalene	$C_{12}H_{12}$	582-16-1	−5.4	−5.4	0.0	12.6	−18.0
Hexacyclo[$6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}$]decane	$C_{12}H_{14}$	704-02-9	51.1	58.4	−7.3	−250.8	301.9
Hexamethylbenzene	$C_{12}H_{18}$	87-85-4	−161.5	−178.4	16.9	−166.2	4.7
(E,E,E)-1,5,9-cyclododecatriene	$C_{12}H_{18}$	676-22-2	26.6	26.6	0.0	27.6	−1.0
2,2,7,7-tetramethylocta-3,5-diyne	$C_{12}H_{18}$	6130-98-9	156.1	156.1	0.0	157.0	−0.9
2,2-dimethyladamantane	$C_{12}H_{20}$	19740-34-2	−256.3	−253.7	−2.6	−241.6	−14.7
1,3-dimethyladamantane	$C_{12}H_{20}$	702-79-4	−286.4	−279.1	−7.3	−240.4	−46.0
Cyclododecane	$C_{12}H_{24}$	294-62-2	−306.6	−306.6	0.0	−305.6	−1.0
4-methyl-1,1′-biphenyl	$C_{13}H_{12}$	644-08-6	55.4	57.0	−1.6	63.3	−7.9
Diphenylmethane	$C_{13}H_{12}$	101-81-5	71.5	57.3	14.2	62.1	9.4
1,3,5-trimethyladamantane	$C_{13}H_{22}$	707-35-7	−332.3	−321.9	−10.4	−258.7	−73.6
Diphenylethyne	$C_{14}H_{10}$	501-65-5	312.4	302.6	9.8	305.6	6.8
Anthracene	$C_{14}H_{10}$	120-12-7	129.2	128.8	0.4	133.4	−4.2
Phenanthrene	$C_{14}H_{10}$	85-01-8	116.2	114.9	1.3	122.4	−6.2
9,10-dihydro-anthracene	$C_{14}H_{12}$	613-31-0	66.4	56.3	10.1	63.2	3.2
(E)-stilbene	$C_{14}H_{12}$	103-30-0	136.9	146.6	−9.7	136.8	0.1
4,4′-dimethylbiphenyl	$C_{14}H_{14}$	613-33-2	14.1	22.5	−8.4	26.8	−12.7
Bibenzyl	$C_{14}H_{14}$	103-29-7	51.5	42.7	8.8	32.8	18.7
1,4,5,8-tetramethylnaphthalene	$C_{14}H_{16}$	2717-39-7	−18.2	−19.0	0.8	−18.6	0.4
1,2,3,4,5,6,7,8-octahydro-anthracene	$C_{14}H_{18}$	1079-71-6	−119.5	−125.5	6.0	−119.8	0.3
1,8-cyclotetradecadiyne	$C_{14}H_{20}$	1540-80-3	147.8	147.8	0.0	147.2	0.6
Diadamantane	$C_{14}H_{20}$	2292-79-7	−241.8	−220.1	−21.7	−229.9	−11.9
1,1,4,6,7-pentamethylindan	$C_{14}H_{20}$	6682-67-3	−175.1	−174.0	−1.1	−171.8	−3.3
Trans-anti-*trans*-tetra-decahydroanthracene	$C_{14}H_{24}$	28071-99-0	−293.3	−318.3	25.0	−330.0	36.7
1,3,5,7-tetramethyladamantane	$C_{14}H_{24}$	1687-36-1	−365.8	−364.7	−1.1	−300.8	−65.0

Table 6. Enthalpy of formation in the solid phase of carbon-hydrogen compounds—comparison of results observed between this work and the method of Cohen[4]—Continued

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
Cyclotetradecane	$C_{14}H_{28}$	295-17-0	−374.0	−374.0	0.0	−374.2	0.2
Cis-1,4-Di-*tert*-butyl-cyclohexane	$C_{14}H_{28}$	4789-34-8	−374.1	−387.0	12.9	−399.8	25.7
Trans-1,4-Di-*tert*-butyl-cyclohexane	$C_{14}H_{28}$	4789-35-9	−401.8	−387.0	−14.8	−417.0	15.2
1,4-dimethyl-7-(1-methylethyl)-azulene	$C_{15}H_{18}$	489-84-9	−61.1	−44.2	−16.9	61.5	−122.6
4-methyldiadamantane	$C_{15}H_{22}$	30545-28-9	−261.5	−262.8	1.3	−255.0	−6.5
3-methyldiadamantane	$C_{15}H_{22}$	28375-86-2	−260.4	−262.8	2.4	−255.0	−5.4
1-methyldiadamantane	$C_{15}H_{22}$	26460-76-4	−247.4	−262.8	15.4	−244.8	−2.6
Cyclopentadecane	$C_{15}H_{30}$	295-48-7	−376.1	−376.1	0.0	−376.7	0.6
1,1′-(1,3-butadiyne-1,4-diyl)bis-benzene	$C_{16}H_{10}$	886-66-8	518.4	518.4	0.0	512.2	6.2
Fluoranthene	$C_{16}H_{10}$	206-44-0	189.9	189.9	0.0	190.6	−0.7
Pyrene	$C_{16}H_{10}$	129-00-0	125.5	134.9	−9.4	171.8	−46.3
Bis-(2-methylphenyl)-acetylene	$C_{16}H_{14}$	5294-03-1	234.8	236.9	−2.1	237.6	−2.8
Di-p-tolylacetylene	$C_{16}H_{14}$	2789-88-0	225.8	233.5	−7.7	232.6	−6.8
Cis,cis-1,4-diphenylbutadiene	$C_{16}H_{14}$	5807-76-1	198.8	185.4	13.4	188.8	10.0
(E,E)-1,4-diphenyl-1,3-butadiene	$C_{16}H_{14}$	538-81-8	178.8	181.0	−2.2	180.4	−1.6
2,7-dimethylphenanthrene	$C_{16}H_{14}$	1576-69-8	36.4	45.8	−9.4	49.4	−13.0
4,5-dimethylphenanthrene	$C_{16}H_{14}$	3674-69-9	89.0	45.8	43.2	91.2	−2.2
9,10-dimethylphenanthrene	$C_{16}H_{14}$	604-83-1	47.6	47.5	0.1	51.9	−4.3
1,1-Di-o-tolylethylene	$C_{16}H_{16}$	2919-19-9	89.0	89.1	−0.1	108.9	−19.9
1,1′-(1,2-ethenediyl)bis[2-methylbenzene]	$C_{16}H_{16}$	10311-74-7	85.9	80.9	5.0	73.0	12.9
Trans 1,2-Di-o-tolylethene	$C_{16}H_{16}$	36888-18-3	74.9	80.9	−6.0	68.8	6.1
1,1′-ethenylidenebis[4-methylbenzene]	$C_{16}H_{16}$	2919-20-2	85.9	85.8	0.1	103.9	−18.0
(Z)-1,2-bis(4-methylphenyl)ethene	$C_{16}H_{16}$	2510-76-1	97.9	77.5	20.4	68.0	29.9
(E)-1,2-bis(4-methylphenyl)ethene	$C_{16}H_{16}$	18869-29-9	57.9	77.5	−19.6	63.8	−5.9
[2.2]metacyclophane	$C_{16}H_{16}$	2319-97-3	78.5	78.5	0.0	−10.0	88.5
[2.2]paracyclophane	$C_{16}H_{16}$	1633-22-3	145.1	82.4	62.7	−10.0	155.1
[2.2]metaparacyclophane	$C_{16}H_{16}$	5385-36-4	130.9	130.9	0.0	−10.0	140.9
[16]annulene	$C_{16}H_{16}$	3332-38-5	547.5	547.5	0.0	549.6	−2.1
1,1′-(1,2-ethanediyl)bis[2-methylbenzene]	$C_{16}H_{18}$	952-80-7	−40.0	−23.0	−17.0	−35.2	−4.8
1,1′-(1,2-ethanediyl)bis[4-methylbenzene]	$C_{16}H_{18}$	538-39-6	−42.1	−26.3	−15.8	−40.2	−1.9
1,1′-(1,4-butanediyl)bis-benzene	$C_{16}H_{18}$	1083-56-3	−9.9	−16.8	6.9	−25.8	15.9
Tricyclo[8.2.2.$2^{4,7}$]hexadecane	$C_{16}H_{28}$	283-68-1	−244.1	−244.1	0.0	−418.4	174.3
Cyclohexadecane	$C_{16}H_{32}$	295-65-8	−403.4	−403.4	0.0	−403.5	0.1
Cycloheptadecane	$C_{17}H_{34}$	295-97-6	−430.4	−430.4	0.0	−431.2	0.8
Triphenylene	$C_{18}H_{12}$	217-59-4	151.8	142.0	9.8	−148.2	3.6
Chrysene	$C_{18}H_{12}$	218-01-9	145.3	155.9	−10.6	159.2	−13.9
Benzo[c]phenanthrene	$C_{18}H_{12}$	195-19-7	184.9	172.0	12.9	156.4	28.5
Benzo[a]anthracene	$C_{18}H_{12}$	56-55-3	170.8	169.9	0.9	170.2	0.6
Naphthacene	$C_{18}H_{12}$	92-24-0	158.8	183.9	−25.1	181.2	−22.4
5,12-dihydro-naphthacene	$C_{18}H_{14}$	959-02-4	106.4	111.3	−4.9	111.0	−4.6
[18]annulene	$C_{18}H_{18}$	2040-73-5	163.4	163.4	0.0	402.4	−239.0
3,4,5,6-tetramethylphenanthrene	$C_{18}H_{18}$	7343-06-8	23.4	−20.0	43.4	23.2	−0.2
2,4,5,7-tetramethylphenanthrene	$C_{18}H_{18}$	7396-38-5	12.2	−23.3	35.5	18.2	−6.0
[3.3]paracyclophane	$C_{18}H_{20}$	2913-24-8	26.3	22.9	3.4	−68.6	94.9
1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-triphenylene	$C_{18}H_{24}$	1610-39-5	−193.9	−197.6	3.7	−194.0	0.1
1,2,4-tri-tert-butylbenzene	$C_{18}H_{30}$	1459-11-6	−251.6	−236.2	−15.4	−131.9	−119.7
1,3,5-tri-tert-butylbenzene	$C_{18}H_{30}$	1460-02-2	−321.9	−308.2	−13.7	−320.4	−1.5
Octadecane	$C_{18}H_{38}$	593-45-3	−567.4	−551.2	−16.2	−553.4	−14.0
Triphenylmethane	$C_{19}H_{16}$	519-73-3	171.2	168.2	3.0	171.8	−0.6
2,2′,4,4′,5,5′-hexamethyldiphenylmethane	$C_{19}H_{24}$	4957-16-8	−154.4	−139.9	−14.5	−141.9	−12.5
Perylene	$C_{20}H_{12}$	198-55-0	182.8	162.0	20.8	166.8	16.0
9,10-dihydro-9,10[1′,2′]benzenoanthracene	$C_{20}H_{14}$	477-75-8	217.1	217.6	−0.5	217.2	−0.1
1,1′,1″-(1-ethenyl-2-ylidene)tris-benzene	$C_{20}H_{16}$	58-72-0	233.4	226.6	6.8	224.4	9.0
5,8-dimethylbenzo[c]phenanthrene	$C_{20}H_{16}$	54986-63-9	108.2	79.4	28.8	83.4	24.8

TABLE 6. Enthalpy of formation in the solid phase of carbon-hydrogen compounds—comparison of results observed between this work and the method of Cohen[4]—Continued

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
1,12-dimethylbenzo[c]phenanthrene	$C_{20}H_{16}$	4076-43-1	154.5	79.4	75.1	104.3	50.2
3,9-dimethylbenz[a]anthracene	$C_{20}H_{16}$	316-51-8	76.2	100.8	−24.6	97.2	−21.0
1,12-dimethylbenz[a]anthracene	$C_{20}H_{16}$	313-74-6	139.0	100.8	38.2	139.0	0.0
9,10-dimethyl-1,2-benzanthracene	$C_{20}H_{16}$	56-56-4	143.8	106.8	37.0	118.1	25.7
5,6-dimethylchrysene	$C_{20}H_{16}$	3697-27-6	132.5	88.5	44.0	109.6	22.9
1,1,1-triphenylethane	$C_{20}H_{18}$	5271-39-6	157.2	159.0	−1.8	214.0	−56.8
1,1,2-triphenylethane	$C_{20}H_{18}$	1520-42-9	130.2	128.2	2.0	127.0	3.2
1-(2-naphthalenylmethyl)naphthalene	$C_{21}H_{16}$	611-48-3	162.0	167.4	−5.4	157.7	4.3
1′,2′,3′,4′-tetrahydro-1,2-dinaphthylmethane	$C_{21}H_{20}$	56818-06-5	44.1	43.3	0.8	4.8	39.3
[1.8]paracyclophane	$C_{21}H_{26}$	6169-94-4	−81.9	−78.5	−3.4	−156.5	74.6
1,2,4,5-tetra-*tert*-butylbenzene	$C_{22}H_{38}$	796-97-4	−297.9	−413.8	115.9	−296.8	−1.1
Tris(2-methylphenyl)-ethylene	$C_{23}H_{22}$	62155-47-9	125.2	128.0	−2.8	122.4	2.8
Tris(4-methylphenyl)-ethylene	$C_{23}H_{22}$	6629-83-0	121.2	123.0	−1.8	114.9	6.3
1,1,2-tri-o-tolylethane	$C_{23}H_{24}$		24.4	29.6	−5.2	25.0	−0.6
1,1,2-tri-p-tolylethane	$C_{23}H_{24}$	27497-47-8	16.4	24.6	−8.2	17.5	−1.1
1,3,5-triphenylbenzene	$C_{24}H_{18}$	612-71-5	224.6	237.2	−12.6	223.8	0.8
[6.6]paracyclophane	$C_{24}H_{32}$	4384-23-0	−192.7	−155.6	−37.1	−244.4	51.7
Tetraphenylmethane	$C_{25}H_{20}$	630-76-2	247.1	241.2	5.9	247.6	−0.5
1,3,6-triphenylcycloheptatriene	$C_{25}H_{20}$	17760-68-8	273.9	273.9	0.0	274.2	−0.3
9,10-diphenylanthracene	$C_{26}H_{18}$	1499-10-1	308.7	280.5	28.2	257.4	51.3
Tetraphenylethylene	$C_{26}H_{20}$	632-51-9	311.5	304.4	7.1	312.0	−0.5
1,1,1,2-tetraphenylethane	$C_{26}H_{22}$	2294-94-2	223.0	217.9	5.1	272.7	−49.7
1,1,2,2-tetraphenylethane	$C_{26}H_{22}$	632-50-8	216.0	213.7	2.3	221.2	−5.2
3-phenyleicosane	$C_{26}H_{46}$	2400-02-4	−548.8	−537.5	−11.3	−539.9	−8.9
9,9′-bianthracene	$C_{28}H_{18}$	1055-23-8	326.2	325.2	1.0	291.0	35.2
9,9′-biphenanthryl	$C_{28}H_{18}$	20532-03-0	212.8	297.2	−84.4	269.0	−56.2
1,1,4,4-tetraphenyl-1,3-butadiene	$C_{28}H_{22}$	1450-63-1	329.9	341.0	−11.1	355.6	−25.7
1,2,3,4-tetraphenyl-1,3-butadiene	$C_{28}H_{22}$	806-71-3	358.9	358.9	0.0	367.2	−8.3
1,1,4,4-tetraphenylbutane	$C_{28}H_{26}$	1483-64-3	163.3	159.5	3.8	366.8	−203.5
Tetra-p-tolylethene	$C_{30}H_{28}$	5831-43-6	171.5	166.3	5.2	166.0	5.5
1,1,2,2-tetra-p-tolylethane	$C_{30}H_{30}$	40673-57-2	73.6	80.9	−7.3	279.4	−205.8
Cyclotriacontane	$C_{30}H_{60}$	297-35-8	−895.7	−892.6	−3.1	−879.0	−16.7
13-phenylpentacosane	$C_{31}H_{56}$	6006-90-2	−687.0	−686.3	−0.7	−686.4	−0.6
Pentaphenylethane	$C_{32}H_{26}$	19112-42-6	381.2	303.4	77.8	366.9	14.3
Dotriacontane	$C_{32}H_{66}$	544-85-4	−968.3	−967.8	−0.5	−963.6	−4.7
Hexaphenylethane	$C_{38}H_{30}$	17854-07-8	511.8	393.1	118.7	512.6	−0.8
5,6,11,12-tetraphenylnaphthacene	$C_{42}H_{28}$	517-51-1	620.3	574.4	45.9	471.0	149.3

served. The comparisons reveal that 48% of the residuals are less than ±5 kJ mol^{-1}, 20% are $>\pm 5$ kJ mol^{-1} but $\leq \pm 10$ kJ mol^{-1}, and 17% are lying between ±10 and ±20 kJ mol^{-1}. Finally 15% are symptomatic of a problem.

Table 8 shows that this work leads to better results than Cohen's. Indeed the more significant figures are 42% of the residuals being $\leq \pm 5$ kJ mol^{-1} (against 48% in this work), and 28% of the compounds for which the enthalpy of formation in the solid state is nearly unpredictable (versus 15% in the present study).

Notice that only 144 enthalpies of formation in the solid state were predicted by the method of Cohen due to a lack of group contribution value.

What is more, Table 9 reveals that in every case the mean residuals observed are smaller or equivalent to those obtained with the method of Cohen.

Finally, it should be emphasized that results could be improved whether more experimental data existed on molecules containing groups that are generated by less than three compounds, such as the group C-$(C_B)_2(C)_2$.

3.2.3. Oxygen Compounds

The examination of 253 C-H-O compounds resulted in the values presented in Tables 10 and 11. It appears that 44% of the substances studied have an enthalpy of formation in the solid phase which can be predicted with a very good precision; whereas only 33% of the compounds of interest can

TABLE 7. Enthalpy of formation in the solid phase of carbon-hydrogen-oxygen compounds—comparison of results observed between this work and the method of Cohen[4]

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
Phenol	C_6H_6O	108-95-2	−165.1	−178.2	13.1	−168.1	3.0
2-methylphenol	C_7H_8O	95-48-7	−204.6	−212.7	8.1	−198.3	−6.3
4-methylphenol	C_7H_8O	106-44-5	−199.3	−212.7	13.4	−204.6	5.3
4-ethylphenol	$C_8H_{10}O$	123-07-9	−224.4	−213.2	−11.2	−231.8	7.4
2,3-dimethylphenol	$C_8H_{10}O$	526-75-0	−241.2	−245.6	4.4	−232.3	−8.9
2,5-dimethylphenol	$C_8H_{10}O$	95-87-4	−246.6	−247.2	0.6	−234.8	−11.8
2,6-dimethylphenol	$C_8H_{10}O$	576-26-1	−237.4	−247.2	9.8	−228.5	−8.9
3,4-dimethylphenol	$C_8H_{10}O$	95-65-8	−242.3	−245.6	3.3	−238.6	−3.7
3,5-dimethylphenol	$C_8H_{10}O$	108-68-9	−244.4	−247.3	2.9	−241.1	−3.3
2-isopropylphenol	$C_9H_{12}O$	88-69-7	−246.6	−229.9	−16.7	−244.8	−1.8
3-isopropylphenol	$C_9H_{12}O$	618-45-1	−263.0	−230.0	−33.0	−251.1	−11.9
4-isopropylphenol	$C_9H_{12}O$	99-89-8	−279.7	−230.0	−49.7	−251.1	−28.6
1-naphthol	$C_{10}H_8O$	90-15-3	−121.0	−123.2	2.2	−120.3	−0.7
2-naphthol	$C_{10}H_8O$	135-19-3	−124.2	−123.2	−1.0	−120.3	−3.9
1,2,3,4-tetrahydro-1-naphthol	$C_{10}H_{12}O$	529-33-9	−241.4	−253.3	11.9	−253.6	12.2
5,6,7,8-tetrahydro-1-naphthol	$C_{10}H_{12}O$	529-35-1	−285.3	−250.3	−35.0	−271.6	−13.7
2-isopropyl-5-methylphenol	$C_{10}H_{14}O$	89-83-8	−280.3	−264.4	−15.9	−281.3	1.0
1-adamantanol	$C_{10}H_{16}O$	768-95-6	−397.6	−418.9	21.3	−399.3	1.7
2-adamantanol	$C_{10}H_{16}O$	700-57-2	−388.0	−385.5	−2.5	−369.2	−18.8
Exo-4-hydro-exo-exo-tetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodecane	$C_{12}H_{18}O$	74007-11-7	−284.9	−282.6	−2.3	−284.2	−0.7
Exo-4-hydro-exo-endo-tetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodecane	$C_{12}H_{18}O$	107133-43-7	−294.3	−282.6	−11.7	−285.9	−8.4
Exo-4-hydro-endo-endo-tetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodecane	$C_{12}H_{18}O$	7273-98-5	−264.2	−282.6	18.4	−285.9	21.7
(1,1′-biphenyl)methanol	$C_{13}H_{12}O$	41376-19-6	−104.8	−121.7	16.9	−116.2	11.4
1-tridecanol	$C_{13}H_{28}O$	112-70-9	−599.4	−593.6	−5.8	−594.7	−4.7
1-diamantanol	$C_{14}H_{20}O$	30545-19-8	−428.8	−415.6	−13.2	−399.5	−29.3
3-diamantanol	$C_{14}H_{20}O$	30545-24-5	−413.8	−402.5	−11.3	−390.5	−23.3
4-diamantanol	$C_{14}H_{20}O$	30651-03-7	−434.9	−415.6	−19.3	−409.7	−25.2
1-tetradecanol	$C_{14}H_{30}O$	112-72-1	−629.6	−623.4	−6.2	−624.0	−5.6
1-pentadecanol	$C_{15}H_{32}O$	629-76-5	−658.2	−653.1	−5.1	−653.3	−4.9
1-hexadecanol	$C_{16}H_{34}O$	36653-82-4	−686.5	−682.9	−3.6	−682.6	−3.9
3′,5′-diisopropyl-4,4-dimethyl-3-phenyl-1,2-benzocyclobuten-3-ol	$C_{22}H_{28}O$	33574-16-2	−218.8	−214.6	−4.2		
3-butynoic acid	$C_4H_4O_2$	2345-51-9	−241.8	−241.8	0.0		
3-pentynoic acid	$C_5H_6O_2$	36781-65-4	−292.3	−292.3	0.0	−184.1	−108.2
Cis-1,2-cyclopentanediol	$C_5H_{10}O_2$	5057-98-7	−485.1	−498.9	13.8	−510.5	25.4
Trans-1,2-cyclopentanediol	$C_5H_{10}O_2$	5057-99-8	−490.1	−498.9	8.8	−514.7	24.6
2,2-dimethyl-1,3-propanediol	$C_5H_{12}O_2$	126-30-7	−551.2	−544.7	−6.5	−544.3	−6.9
Hydroquinone	$C_6H_6O_2$	123-31-9	−364.5	−369.2	4.7	−374.0	9.5
Resorcinol	$C_6H_6O_2$	108-46-3	−368.0	−375.2	7.2	−374.0	6.0
1,6-hexanediol	$C_6H_{14}O_2$	629-11-8	−569.9	−576.5	6.6	−577.4	7.5
Benzoic acid	$C_7H_6O_2$	65-85-0	−385.2	−394.0	8.8	−377.3	−7.9
2-hydroxy-2,4,6-cycloheptatrien-1-one	$C_7H_6O_2$	533-75-5	−239.3	−252.5	13.2	−246.2	6.9
1-(2-hydroxyphenyl)ethanone	$C_8H_8O_2$	118-93-4	−357.6	−351.3	−6.3	−360.7	3.1
1-(3-hydroxyphenyl)ethanone	$C_8H_8O_2$	121-71-1	−370.6	−370.0	−0.6	−363.2	−7.4
1-(4-hydroxyphenyl)ethanone	$C_8H_8O_2$	99-93-4	−364.3	−370.0	5.7	−363.2	−1.1
2-methylbenzoic acid	$C_8H_8O_2$	118-90-1	−416.5	−428.4	11.9	−409.6	−6.9
3-methylbenzoic acid	$C_8H_8O_2$	99-04-7	−426.1	−428.5	2.4	−413.8	−12.3
4-methylbenzoic acid	$C_8H_8O_2$	99-94-5	−429.2	−428.5	−0.7	−413.8	−15.4
1,4-benzenedimethanol	$C_8H_{10}O_2$	589-29-7	−393.9	−401.7	7.8	−394.2	0.3
2,5-dimethyl-3-hexyne-2,5-diol	$C_8H_{14}O_2$	142-30-3	−385.7	−375.4	−10.3	−375.0	−10.7
2,5-dimethyl-2,5-hexanediol	$C_8H_{18}O_2$	110-03-2	−681.7	−676.6	−5.1	−686.2	4.5
(Z)-3-phenyl-2-propenoic acid	$C_9H_8O_2$	102-94-3	−312.1	−288.6	−23.5	−322.4	10.3
(E)-3-phenyl-2-propenoic acid	$C_9H_8O_2$	140-10-3	−336.9	−288.6	−48.3	−326.6	−10.3
2,3-dimethylbenzoic acid	$C_9H_{10}O_2$	603-79-2	−450.4	−461.3	10.9	−443.6	−6.8
2,4-dimethylbenzoic acid	$C_9H_{10}O_2$	611-01-8	−458.5	−463.0	4.5	−446.1	−12.4

TABLE 7. Enthalpy of formation in the solid phase of carbon-hydrogen-oxygen compounds—comparison of results observed between this work and the method of Cohen[4]—Continued

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
2,5-dimethylbenzoic acid	$C_9H_{10}O_2$	610-72-0	−456.1	−463.0	6.9	−446.1	−10.0
2,6-dimethylbenzoic acid	$C_9H_{10}O_2$	632-46-2	−440.7	−441.4	0.7	−441.9	1.2
3,4-dimethylbenzoic acid	$C_9H_{10}O_2$	619-04-5	−468.8	−461.4	−7.4	−447.8	−21.0
3,5-dimethylbenzoic acid	$C_9H_{10}O_2$	499-06-9	−466.4	−463.0	−3.4	−450.3	−16.1
2-ethylbenzoic acid	$C_9H_{10}O_2$	612-19-1	−441.3	−428.9	−12.4	−436.8	−4.5
3-ethylbenzoic acid	$C_9H_{10}O_2$	619-20-5	−445.8	−428.9	−16.9	−441.0	−4.8
4-ethylbenzoic acid	$C_9H_{10}O_2$	619-64-7	−460.7	−428.9	−31.8	−441.0	−19.7
2,6-dimethyl-2,6-heptanediol	$C_9H_{20}O_2$	6257-51-8	−761.1	−706.4	−54.7	−715.5	−45.6
2,7-naphthalenediol	$C_{10}H_8O_2$	582-17-2	−362.1	−362.1	0.0	−326.2	−35.9
2,3-naphthalenediol	$C_{10}H_8O_2$	92-44-4	−316.4	−281.7	−34.7	−319.9	3.5
2,4-dimethylbenzeneacetic acid	$C_{10}H_{12}O_2$	6331-04-0	−495.8	−490.6	−5.2	−444.9	−50.9
2,3,4-trimethylbenzoic acid	$C_{10}H_{12}O_2$	1076-47-7	−486.6	−494.2	7.6	−477.6	−9.0
2,3,5-trimethylbenzoic acid	$C_{10}H_{12}O_2$	2437-66-3	−488.7	−495.8	7.1	−480.1	−8.6
2,3,6-trimethylbenzoic acid	$C_{10}H_{12}O_2$	2529-36-4	−475.7	−474.3	−1.4	−475.9	0.2
2,4,5-trimethylbenzoic acid	$C_{10}H_{12}O_2$	528-90-5	−495.7	−495.8	0.1	−480.1	−15.6
2,4,6-trimethylbenzoic acid	$C_{10}H_{12}O_2$	480-63-7	−477.9	−475.9	−2.0	−478.4	0.5
3,4,5-trimethylbenzoic acid	$C_{10}H_{12}O_2$	1076-88-6	−500.9	−494.2	−6.7	−477.6	−23.3
2-hydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one	$C_{10}H_{12}O_2$	499-44-5	−340.6	−353.8	13.2	−333.0	−7.6
Decanoic acid	$C_{10}H_{20}O_2$	334-48-5	−713.7	−712.2	−1.5	−713.9	0.2
1,10-decanediol	$C_{10}H_{22}O_2$	112-47-0	−693.5	−695.5	2.0	−694.6	1.1
2,7-dimethyl-2,7-octanediol	$C_{10}H_{22}O_2$	19781-07-8	−730.0	−736.1	6.1	−744.8	14.8
1-naphthalenecarboxylic acid	$C_{11}H_8O_2$	86-55-5	−333.5	−338.9	5.4	−329.5	−4.0
2-naphthalenecarboxylic acid	$C_{11}H_8O_2$	93-09-4	−346.1	−338.9	−7.2	−329.5	−16.6
2,3,4,5-tetramethylbenzoic acid	$C_{11}H_{14}O_2$	2529-39-7	−514.4	−527.0	12.6	−511.6	−2.8
2,3,4,6-tetramethylbenzoic acid	$C_{11}H_{14}O_2$	2408-38-0	−507.7	−507.1	−0.6	−509.9	2.2
2,3,5,6-tetramethylbenzoic acid	$C_{11}H_{14}O_2$	2604-45-7	−506.1	−507.1	1.0	−509.9	3.8
3,5-diethylbenzoic acid	$C_{11}H_{14}O_2$	3854-90-8	−511.9	−463.9	−48.0	−504.7	−7.2
2-*tert*-butylbenzoic acid	$C_{11}H_{14}O_2$	1077-58-3	−476.2	−502.9	26.7	−475.4	−0.8
3-*tert*-butylbenzoic acid	$C_{11}H_{14}O_2$	7498-54-6	−504.3	−502.9	−1.4	−496.7	−7.6
4-*tert*-butylbenzoic acid	$C_{11}H_{14}O_2$	98-73-7	−502.9	−502.9	0.0	−496.7	−6.2
Adamantane-1-carboxylic acid	$C_{11}H_{16}O_2$	828-51-3	−643.1	−617.5	−25.6	−593.9	−49.2
Adamantane-2-carboxylic acid	$C_{11}H_{16}O_2$	15897-81-1	−627.2	−617.5	−9.7	−593.9	−33.3
Undecanoic acid	$C_{11}H_{22}O_2$	112-37-8	−735.9	−742.0	6.1	−743.2	7.3
1-naphthylacetate	$C_{12}H_{10}O_2$	830-81-9	−305.0	−297.8	−7.2	−262.1	−42.9
2-naphthylacetate	$C_{12}H_{10}O_2$	1523-11-1	−309.6	−297.8	−11.8	−262.1	−47.5
1-naphthaleneacetic acid	$C_{12}H_{10}O_2$	86-87-3	−359.2	−368.2	9.0	−326.6	−32.6
2-naphthaleneacetic acid	$C_{12}H_{10}O_2$	581-96-4	−371.9	−368.2	−3.7	−326.6	−45.3
Pentamethylbenzoic acid	$C_{12}H_{16}O_2$	2243-32-5	−536.1	−538.3	2.2	−541.4	5.3
3,6-diethyloct-4-yne-3,6-diol	$C_{12}H_{22}O_2$	2044-37-3	−481.5	−491.8	10.3	−485.4	3.9
Dodecanoic acid	$C_{12}H_{24}O_2$	143-07-7	−774.6	−771.7	−2.9	−772.5	−2.1
2,9-dimethyl-2,9-decanediol	$C_{12}H_{26}O_2$	22092-57-5	−789.6	−795.6	6.0	−803.4	13.8
Phenyl ester benzoic acid	$C_{13}H_{10}O_2$	93-99-2	−241.6	−240.7	−0.9	−239.5	−2.1
2-biphenylcarboxylic acid	$C_{13}H_{10}O_2$	947-84-2	−349.1	−321.1	−28.0	−311.1	−38.0
Tridecanoic acid	$C_{13}H_{26}O_2$	638-53-9	−806.6	−801.5	−5.1	−801.8	−4.8
2,10-dimethyl-2,10-undecanediol	$C_{13}H_{28}O_2$	22092-58-6	−835.8	−825.4	−10.4	−832.7	−3.1
2-hydroxy-1,2-diphenylethanone	$C_{14}H_{12}O_2$	119-53-9	−247.7	−247.7	0.0	−263.8	16.1
Tetradecanoic acid	$C_{14}H_{28}O_2$	544-63-8	−833.5	−831.2	−2.3	−831.1	−2.4
2,11-dimethyl-2,11-dodecanediol	$C_{14}H_{30}O_2$	22092-59-7	−846.2	−855.2	9.0	−862.0	15.8
2,2′-bis(4-hydroxyphenyl)propane	$C_{15}H_{16}O_2$	80-05-7	−368.6	−368.6	0.0	−368.2	−0.4
3,5-Di-*tert*-butylbenzoic acid	$C_{15}H_{22}O_2$	16225-26-6	−624.6	−611.9	−12.7	−616.1	−8.5
Pentadecanoic acid	$C_{15}H_{30}O_2$	1002-84-2	−861.7	−861.0	−0.7	−860.4	−1.3
Hexadecanoic acid	$C_{16}H_{32}O_2$	57-10-3	−891.5	−890.8	−0.7	−889.7	−1.8
2-naphthyl ester benzoic acid	$C_{17}H_{12}O_2$	93-44-7	−184.8	−185.7	0.9	−191.7	6.9
Heptadecanoicacid	$C_{17}H_{34}O_2$	506-12-7	−924.4	−920.5	−3.9	−919.0	−5.4

TABLE 7. Enthalpy of formation in the solid phase of carbon-hydrogen-oxygen compounds—comparison of results observed between this work and the method of Cohen[4]—Continued

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
Octadecanoic acid	$C_{18}H_{36}O_2$	57-11-4	−947.7	−950.3	2.6	−948.3	0.6
Nonadecanoic acid	$C_{19}H_{38}O_2$	646-30-0	−984.0	−980.0	−4.0	−977.6	−6.4
Eicosanoic acid	$C_{20}H_{40}O_2$	506-30-9	−1011.9	−1009.8	−2.1	−1006.9	−5.0
(E)-13-docosenoic acid	$C_{22}H_{42}O_2$	506-33-2	−960.7	−939.1	−21.6	−939.1	−21.6
(S)-2-hydroxypropanoic acid	$C_3H_6O_3$	79-33-4	−694.0	−681.4	−12.6	−685.8	−8.2
Furancarboxylic acid	$C_5H_4O_3$	26447-28-9	−498.4	−498.4	0.0	−506.2	7.8
2-(hydroxymethyl)-2-methyl-1,3-propanediol	$C_5H_{12}O_3$	77-85-0	−744.6	−734.5	−10.1	−728.7	−15.9
2-ethyl-2-(hydroxymethyl)-1,3-propanediol	$C_6H_{14}O_3$	77-99-6	−750.9	−764.3	13.4	−758.0	7.1
Perbenzoic acid	$C_7H_6O_3$	93-59-4	−367.0	−305.3	−61.7	−285.0	−82.0
2-hydroxy-benzoic acid	$C_7H_6O_3$	69-72-7	−589.9	−552.5	−37.4	−579.0	−10.9
3-(2-furanyl)-2-propenoic acid	$C_7H_6O_3$	539-47-9	−459.0	−459.0	0.0	−455.1	−3.9
3-hydroxy-4-methoxy-benzaldehyde	$C_8H_8O_3$	621-59-0	−453.4	−465.9	12.5	−461.5	8.1
2,4-dihydroxyacetophenone	$C_8H_8O_3$	89-84-9	−573.5	−548.3	−25.2	−562.8	−10.7
(R,S)-α-hydroxybenzeneacetic acid	$C_8H_8O_3$	611-72-3	−579.4	−574.1	−5.3	−570.6	−8.8
(S)-α-hydroxybenzeneacetic acid	$C_8H_8O_3$	17199-29-0	−580.6	−574.1	−6.5	−570.6	−10.0
2-methoxybenzoic acid	$C_8H_8O_3$	579-75-9	−538.5	−538.8	0.3	−560.6	22.1
3-methoxybenzoic acid	$C_8H_8O_3$	586-38-9	−553.5	−557.5	4.0	−564.8	11.3
4-methoxybenzoic acid	$C_8H_8O_3$	100-09-4	−561.7	−557.5	−4.2	−564.8	3.1
3-hydroxy-2-naphthoic acid	$C_{11}H_8O_3$	92-70-6	−547.8	−497.4	−50.4	−531.2	−16.6
Dodecaneperoxoic acid	$C_{12}H_{24}O_3$	2388-12-7	−680.3	−683.1	2.8	−680.2	−0.1
Phenyl 2-hydroxybenzoate	$C_{13}H_{10}O_3$	118-55-8	−436.6	−419.0	−17.6	−441.2	4.6
Carbonic acid diphenyl ester	$C_{13}H_{10}O_3$	102-09-0	−401.2	−416.3	15.1	−376.3	−24.9
Carbonic acid dicyclohexyl ester	$C_{13}H_{22}O_3$	4427-97-8	−830.2	−815.1	−15.1	−807.7	−22.5
Tetradecaneperoxoic acid	$C_{14}H_{28}O_3$	19816-73-0	−749.9	−742.6	−7.3	−738.8	−11.1
Benzenecarboperoxoic acid 1-methyl-1-phenylethyl ester	$C_{16}H_{16}O_3$	7074-00-2	−231.5	−231.5	0.0	−196.9	−34.6
Hexadecaneperoxoic acid	$C_{16}H_{32}O_3$	7311-29-7	−801.9	−802.1	0.2	−797.4	−4.5
Octadecaneperoxoic acid	$C_{18}H_{36}O_3$	5796-86-1	−857.3	−861.6	4.3	−856.0	−1.3
Oxalic acid	$C_2H_2O_4$	144-62-7	−821.7	−831.8	10.1	−815.0	−6.7
Dioxybismethanol	$C_2H_6O_4$	17088-73-2	−665.8	−689.8	24.0	−665.2	−0.6
Malonic acid	$C_3H_4O_4$	141-82-2	−891.0	−891.0	0.0	−844.3	−46.7
2-butynedioic acid	$C_4H_2O_4$	142-45-0	−577.4	−577.4	0.0	−585.0	7.6
3,4-dihydroxy-3-cyclobutene-1,2-dione	$C_4H_2O_4$	2892-51-5	−598.2	−598.2	0.0	−598.3	0.1
(Z)-2-butenedioic acid	$C_4H_4O_4$	110-16-7	−587.3	−723.9	136.6	−785.8	198.5
(E)-2-butenedioic acid	$C_4H_4O_4$	110-17-8	−811.7	−723.9	−87.8	−790.0	−21.7
Butanedioic acid	$C_4H_6O_4$	110-15-6	−940.5	−947.3	6.8	−933.0	−7.5
Ethanedioic acid dimethyl ester	$C_4H_6O_4$	553-90-2	−756.3	−746.2	−10.1	−754.0	−2.3
2(R),3(S)-1,2,3,4-butanetetrol	$C_4H_{10}O_4$	149-32-6	−910.4	−898.3	−12.1	−880.2	−30.2
(E)-2-methyl-2-butenedioic acid	$C_5H_6O_4$	498-24-8	−824.4	−777.1	−47.3	−820.6	−3.8
Methylenebutanedioic acid	$C_5H_6O_4$	97-65-4	−841.1	−841.1	0.0	−830.6	−10.5
Methylbutanedioic acid	$C_5H_8O_4$	498-21-5	−958.2	−962.7	4.5	−950.2	−8.0
Pentanedioic acid	$C_5H_8O_4$	110-94-1	−960.0	−962.5	2.5	−962.3	2.3
2,2-bis(hydroxymethyl)-1,3-propanediol	$C_5H_{12}O_4$	115-77-5	−920.6	−924.4	3.8	−913.1	−7.5
2,2-dimethylbutanedioic acid	$C_6H_{10}O_4$	597-43-3	−987.8	−988.2	0.4	−974.9	−12.9
Meso-2,3-dimethylbutanedioic acid	$C_6H_{10}O_4$	608-39-9	−977.5	−978.1	0.6	−967.4	−10.1
Racemic-2,3-dimethylbutanedioic acid	$C_6H_{10}O_4$	608-40-2	−983.8	−978.1	−5.7	−967.4	−16.4
(−)-2,3-dimethylbutanedioic acid	$C_6H_{10}O_4$	57694-62-9	−982.5	−978.1	−4.4	−967.4	−15.1
2-ethylbutanedioic acid	$C_6H_{10}O_4$	636-48-6	−989.2	−992.5	3.3	−979.5	−9.7
Hexanedioic acid	$C_6H_{10}O_4$	124-04-9	−994.3	−997.1	2.8	−991.6	−2.7
5-(1α,2β,3β,4α)-1,2,3,4-cyclohexenetetrol	$C_6H_{10}O_4$	526-87-4	−836.3	−836.3	0.0	−836.0	−0.3
Trimethylbutanedioic acid	$C_7H_{12}O_4$	2103-16-4	−1000.8	−1002.9	2.1	−990.4	−10.4
Heptanedioic acid	$C_7H_{12}O_4$	111-16-0	−1009.4	−1007.5	−1.9	−1020.9	11.5
1,2-benzenedicarboxylic acid	$C_8H_6O_4$	88-99-3	−782.0	−768.2	−13.8	−766.9	−15.1
1,3-benzenedicarboxylic acid	$C_8H_6O_4$	121-91-5	−803.0	−806.7	3.7	−792.4	−10.6
1,4-benzenedicarboxylic acid	$C_8H_6O_4$	100-21-0	−816.1	−800.7	−15.4	−792.4	−23.7

TABLE 7. Enthalpy of formation in the solid phase of carbon-hydrogen-oxygen compounds—comparison of results observed between this work and the method of Cohen[4]—Continued

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
Cis-cyclohexane-1,2-dicarboxylic acid	$C_8H_{12}O_4$	610-09-3	−961.1	−1003.0	41.9	−1003.4	42.3
Trans-cyclohexane-1,2-dicarboxylic acid	$C_8H_{12}O_4$	2305-32-0	−970.7	−1003.0	32.3	−1003.4	32.7
Tetramethylbutanedioic acid	$C_8H_{14}O_4$	630-51-3	−1012.4	−1013.1	0.7	−1013.4	1.0
2,2-diethylbutanedioic acid	$C_8H_{14}O_4$	5692-97-7	−1032.7	−1030.5	−2.2	−1026.7	−6.0
Meso-2,3-diethylbutanedioic acid	$C_8H_{14}O_4$	35392-80-4	−1019.2	−1023.0	3.8	−1026.0	6.8
Racemic-2,3-diethylbutanedioic acid	$C_8H_{14}O_4$	35392-77-9	−1026.3	−1023.0	−3.3	−1026.0	−0.3
Octanedioic acid	$C_8H_{14}O_4$	505-48-6	−1038.0	−1037.2	−0.8	−1050.2	12.2
2-acetoxy benzoic acid	$C_9H_8O_4$	50-78-2	−758.1	−746.9	−11.3	−720.8	−37.3
Nonanedioic acid	$C_9H_{16}O_4$	123-99-9	−1054.3	−1054.0	−0.3	−1079.5	25.2
Phenylbutanedioic acid	$C_{10}H_{10}O_4$	635-51-8	−841.0	−834.9	−6.1	−820.7	−20.3
2,4-diacetyl-1,3-benzenediol	$C_{10}H_{10}O_4$	2163-12-4	−753.5	−722.6	−30.9	−745.3	−8.2
4,6-diacetyl-1,3-benzenediol	$C_{10}H_{10}O_4$	2161-85-5	−776.5	−721.4	−55.1	−751.6	−24.9
1,3-benzenedicarboxylic acid dimethyl ester	$C_{10}H_{10}O_4$	1459-93-4	−730.9	−706.6	−24.3	−731.4	0.5
1,4-benzenedicarboxylic acid dimethyl ester	$C_{10}H_{10}O_4$	120-61-6	−732.6	−700.5	−32.1	−731.4	−1.2
1-monobenzoylglycerol	$C_{10}H_{12}O_4$	3376-59-8	−777.3	−779.3	2.0	−768.9	−8.4
1,2,3-propanetriol 2-benzoate	$C_{10}H_{12}O_4$		−772.8	−779.3	6.5	−768.9	−3.9
Triethylbutanedioic acid	$C_{10}H_{18}O_4$	2103-18-6	−1066.3	−1074.3	8.0	−1069.8	3.5
Decanedioic acid	$C_{10}H_{18}O_4$	111-20-6	−1082.6	−1083.8	1.2	−1108.8	26.2
Undecanedioic acid	$C_{11}H_{20}O_4$	1852-04-6	−1099.4	−1100.5	1.1	−1138.1	38.7
Tetraethylsuccinic acid	$C_{12}H_{22}O_4$	4111-60-8	−1096.5	−1132.2	35.7	−1130.6	34.1
Dodecanedioic acid	$C_{12}H_{22}O_4$	693-23-2	−1130.0	−1130.3	0.3	−1167.4	37.4
Tridecanedioic acid	$C_{13}H_{24}O_4$	505-52-2	−1148.3	−1147.1	−1.2	−1196.7	48.4
1,2,3-propanetriol 1-decanoate	$C_{13}H_{26}O_4$	2277-23-8	−1109.0	−1096.3	−12.7	−1102.1	−6.9
1,2,3-propanetriol 2-decanoate	$C_{13}H_{26}O_4$	3376-48-5	−1095.7	−1096.3	0.6	−1102.1	6.4
Oxalic acid diphenyl ester	$C_{14}H_{10}O_4$	3155-16-6	−539.7	−534.1	−5.6	−535.2	−4.5
1,2,3-propanetriol 1-dodecanoate	$C_{15}H_{30}O_4$	142-18-7	−1160.9	−1155.8	−5.1	−1160.7	−0.2
1,2,3-propanetriol 2-dodecanoate	$C_{15}H_{30}O_4$	1678-45-1	−1152.6	−1155.8	3.2	−1160.7	8.1
Meso-2,3-diphenylbutanedioic acid	$C_{16}H_{14}O_4$	1225-13-4	−733.5	−738.3	4.8	−711.8	−21.7
Racemic-2,3-diphenylbutanedioic acid	$C_{16}H_{14}O_4$	7584-72-7	−740.1	−738.3	−1.8	−711.8	−28.3
(−)α-desmotroposantonin acetate	$C_{17}H_{20}O_4$	14794-71-9	−870.6	−951.4	80.8	−891.9	21.3
(+)β-desmotroposantonin acetate	$C_{17}H_{20}O_4$	14794-69-5	−879.2	−951.4	72.2	−891.9	12.7
1,2,3-propanetriol1-tetradecanoate	$C_{17}H_{34}O_4$	589-68-4	−1222.6	−1215.3	−7.3	−1219.3	−3.3
1,2,3-propanetriol 2-tetradecanoate	$C_{17}H_{34}O_4$	3443-83-2	−1212.9	−1215.3	2.4	−1219.3	6.4
1,2,3-propanetriol 1-hexadecanoyl ester	$C_{19}H_{38}O_4$	542-44-9	−1281.5	−1274.8	−6.7	−1277.9	−3.6
1,2,3-propanetriol 2-hexadecanoyl ester	$C_{19}H_{38}O_4$	23470-00-0	−1268.7	−1274.8	6.1	−1277.9	9.2
1,2-benzenedicarboxylic acid diphenyl ester	$C_{20}H_{14}O_4$	84-62-8	−489.2	−501.4	12.2	−491.3	2.1
1,2-benzenedicarboxylic acid dicyclohexyl ester	$C_{20}H_{26}O_4$	84-61-7	−931.4	−949.7	18.3	−922.7	−8.7
1,2,3-propanetriol 1-octadecanoyl ester	$C_{21}H_{42}O_4$	123-94-4	−1337.4	−1334.3	−3.1	−1336.5	−0.9
1,2,3-propanetriol 2-octadecanoyl ester	$C_{21}H_{42}O_4$	621-61-4	−1321.3	−1334.3	13.0	−1336.5	15.2
(R)-hydroxybutanedioic acid	$C_4H_6O_5$	636-61-3	−1105.7	−1109.6	3.9	−1108.3	2.6
(S)-hydroxybutanedioic acid	$C_4H_6O_5$	97-67-6	−1103.6	−1109.6	6.0	−1108.3	4.7
2-oxopentanedioic acid	$C_5H_6O_5$	328-50-7	−1026.2	−1026.2	0.0	−1026.3	0.1
α-D-xylose	$C_5H_{10}O_5$	31178-70-8	−1057.8	−1056.4	−1.4	−1060.7	2.9
D-ribose	$C_5H_{10}O_5$	50-69-1	−1051.1	−1046.9	−4.2		
D-arabinose	$C_5H_{10}O_5$	10323-20-3	−1057.9	−1056.4	−1.5	−1060.7	2.8
Xylitol	$C_5H_{12}O_5$	87-99-0	−1118.5	−1118.7	0.2	−1090.2	−28.3
1,2-anhydro-3,4,5,6-alloinositol	$C_6H_{10}O_5$	23559-36-6	−879.2	−879.2	0.0	−906.4	27.2
2-(diacetoxymethyl)furan	$C_9H_{10}O_5$	613-75-2	−772.5	−772.5	0.0	−882.0	109.5
Benzoylcarboxyperoxide phenyl ester	$C_{14}H_{10}O_5$	962-16-3	−484.9	−340.3	−144.6	−506.4	21.5
Benzoyl(cyclohexyloxy)carbonylperoxide	$C_{14}H_{16}O_5$	20666-86-8	−539.7	−539.7	0.0	−722.1	182.4
(E)-1-propene-1,2,3-tricarboxylic acid	$C_6H_6O_6$	4023-65-8	−1160.9	−1187.8	26.9	−1246.5	85.6
(Z)-1-propene-1,2,3-tricarboxylic acid	$C_6H_6O_6$	585-84-2	−1224.4	−1187.8	−36.6	−1246.5	22.1
L-ascorbic acid	$C_6H_8O_6$	50-81-7	−1164.6	−1111.1	−53.5	−1164.3	−0.3
α-D-glucose	$C_6H_{12}O_6$	26655-34-5	−1273.3	−1278.1	4.8	−1274.1	0.8

TABLE 7. Enthalpy of formation in the solid phase of carbon-hydrogen-oxygen compounds—comparison of results observed between this work and the method of Cohen[4]—Continued

				This work		Cohen[4]	
Compound	Formula	CAS	$\Delta_f H_s^\circ$ (expt.)	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})	$\Delta_f H_s^\circ$ (calc.) (kJ mol^{-1})	Residual (kJ mol^{-1})
L-sorbose	$C_6H_{12}O_6$	87-79-6	−1271.5	−1268.6	−2.9	−1263.0	−8.5
β-D-fructose	$C_6H_{12}O_6$	57-48-7	−1265.6	−1268.6	3.0	−1263.0	−2.6
D-mannose	$C_6H_{12}O_6$	3458-28-4	−1263.0	−1267.2	4.2		
α-D-galactose	$C_6H_{12}O_6$	3646-73-9	−1286.3	−1278.1	−8.2	−1274.1	−12.2
D-mannitol	$C_6H_{14}O_6$	87-78-5	−1337.1	−1339.0	1.9	−1300.2	−36.9
Galactitol	$C_6H_{14}O_6$	608-66-2	−1346.7	−1339.0	−7.7	−1300.2	−46.5
α-D-methylglucopyranoside	$C_7H_{14}O_6$	97-30-3	−1233.3	−1245.8	12.5	−1211.8	−21.5
β-D-methylglucopyranoside	$C_7H_{14}O_6$	709-50-2	−1237.5	−1245.8	8.3	−1211.8	−25.7
1,2,3-benzenetricarboxylic acid	$C_9H_6O_6$	569-51-7	−1160.3	−1162.3	2.0	−1156.5	−3.8
1,2,4-benzenetricarboxylic acid	$C_9H_6O_6$	528-44-9	−1179.1	−1181.0	1.9	−1182.0	2.9
1,3,5-benzenetricarboxylic acid	$C_9H_6O_6$	554-95-0	−1190.1	−1219.4	29.3	−1207.5	17.4
4-hydroxy-2H-pyran-3,3,5,5,(4H,6H)-tetramethanol	$C_9H_{18}O_6$	4744-47-2	−1267.7	−1273.0	5.3	−1294.9	27.2
1,3,5-benzenetricarboxylic acid trimethyl ester	$C_{12}H_{12}O_6$	2672-58-4	−1101.1	−1069.2	−31.9	−1116.0	14.9
Peroxydicarbonic acid dicyclohexyl ester	$C_{14}H_{22}O_6$	1561-49-5	−1102.5	−889.9	−212.6	−1074.6	−27.9
2-hydroxy-1,2,3-propane-tricarboxylic acid	$C_6H_8O_7$	77-92-9	−1543.8	−1543.3	−0.5	−1487.7	−56.1
D-glucaric acid 1,4-lactone	$C_6H_8O_7$	389-36-6	−1435.8	−1437.3	1.5	−1431.8	−4.0
D-glucaric acid 3,6-lactone	$C_6H_8O_7$	2782-04-9	−1437.5	−1437.3	−0.2	−1431.8	−5.7
α-D-glucose hydrate	$C_6H_{14}O_7$	16824-90-1	−1572.2	−1574.1	1.9	−1565.9	−6.3
2, 2′-(oxybis(methylene))bis(hydroxymethyl)-1,3-Propanediol	$C_{10}H_{22}O_7$	126-58-9	−1572.3	−1572.7	0.4	−1512.4	−59.9
Citric acid monohydrate	$C_6H_{10}O_8$	5949-29-1	−1837.5	−1838.0	0.5	−1776.1	−61.4
1,2,3,4-benzenetetracarboxylic acid	$C_{10}H_6O_8$	476-73-3	−1548.6	−1550.3	1.7	−1546.1	−2.5
1,2,3,5-benzenetetracarboxylic acid	$C_{10}H_6O_8$	479-47-0	−1562.3	−1569.0	6.7	−1571.6	9.3
1,2,4,5-benzenetetracarboxylic acid	$C_{10}H_6O_8$	89-05-4	−1570.8	−1549.2	−21.6	−1571.6	0.8
1,2,4,5-benzenetetracarboxylic acid dimethyl ester	$C_{12}H_{10}O_8$	39900-53-3	−1475.5	−1488.7	13.2	−1510.6	35.1
1,2,4,5-benzenetetracarboxylic acid tetramethyl ester	$C_{14}H_{14}O_8$	635-10-9	−1432.5	−1428.2	−4.3	−1449.6	17.1
1,2,4,5-benzenetetracarboxylic acid diethyl ester	$C_{14}H_{14}O_8$	50853-29-7	−1589.8	−1533.8	−56.0	−1552.4	−37.4
1,2,4,5-benzenetetracarboxylic acid dipropyl ester	$C_{16}H_{18}O_8$	56941-72-1	−1644.2	−1593.3	−50.9	−1611.0	−33.2
1,2,4,5-benzenetetracarboxylic acid tetraethyl ester	$C_{18}H_{22}O_8$	6634-01-1	−1579.6	−1518.3	−61.3	−1533.2	−46.4
Benzenepentacarboxylic acid	$C_{11}H_6O_{10}$	1585-40-6	−1929.7	−1944.4	14.7	−1935.7	6.0
Benzenepentacarboxylic acid pentamethyl ester	$C_{16}H_{16}O_{10}$	3327-06-8	−1788.1	−1793.1	5.0	−1783.2	−4.9
D-sucrose	$C_{12}H_{22}O_{11}$	57-50-1	−2226.1	−2226.1	0.0	−2226.8	0.7
β-lactose	$C_{12}H_{22}O_{11}$	5965-66-2	−2236.7	−2238.7	2.0	−2234.4	−2.3
α-D-glucose 2,3,4,5,6-pentaacetate	$C_{16}H_{22}O_{11}$	3891-59-6	−2249.4	−2215.2	−34.2		
Benzenehexacarboxylic acid	$C_{12}H_6O_{12}$	517-60-2	−2298.7	−2339.6	40.9	−2299.8	1.1
β-maltose monohydrate	$C_{12}H_{24}O_{12}$	6363-53-7	−2459.6	−2451.8	−7.8	−2526.2	66.6
α-lactose monohydrate	$C_{12}H_{24}O_{12}$	10639-26-6	−2484.1	−2489.4	5.3	−2618.2	134.1
Benzenehexacarboxylic acid hexamethyl ester	$C_{18}H_{18}O_{12}$	6237-59-8	−2110.8	−2158.1	47.3	−2116.8	6.0

have the same good results concerning the evaluation of their enthalpy of formation by means of Cohen's method. Approximately the same number of compounds is classified in the two following residual intervals, that is to say 5–10 and 10–20 kJ mol^{-1}. Indeed 20% have a residual between 5 and 10 kJ mol^{-1} (against 23% for Cohen), and 18% of the residuals are >10 kJ mol^{-1} but ≤ 20 kJ mol^{-1} (versus 17% for Cohen). Finally better results are obtained in this work concerning molecules for which the enthalpy of formation in the crystalline state cannot be predicted satisfactorily (18% vs 27%).

TABLE 8. Comparison of the residuals observed for C-H compounds between this work and the method of Cohen[4]

Method	0–5 kJ mol^{-1}	5–10 kJ mol^{-1}	10–20 kJ mol^{-1}	More than 20 kJ mol^{-1}
This work	70/145 (48%)	28/145 (20%)	25/145 (17%)	22/145 (15%)
Cohen[4]	61/144 (42%)	20/144 (14%)	23/144 (16%)	40/144 (28%)

TABLE 9. Comparison of the mean residuals obtained for C-H compounds between this work and the method of Cohen[4]

Method	0–5 kJ mol^{-1}	5–10 kJ mol^{-1}	10–20 kJ mol^{-1}	More than 20 kJ mol^{-1}
This work	1.2	7.5	14.1	47.9
Cohen[4]	1.6	7.1	15.3	96.1

TABLE 10. Comparison of the residuals observed for C-H-O compounds between this work and the method of Cohen[4]

Method	0–5 kJ mol^{-1}	5–10 kJ mol^{-1}	10–20 kJ mol^{-1}	More than 20 kJ mol^{-1}
This work	112/253 (44%)	51/253 (20%)	45/253 (18%)	45/253 (18%)
Cohen[4]	82/248 (33%)	57/248 (23%)	42/248 (17%)	67/248 (27%)

In all cases the mean residual obtained in this work is less than that obtained in the method of Cohen, except regarding the residuals superior to 20 kJ mol^{-1}. Notice that as residuals larger than 20 kJ mol^{-1} are symptomatic of a problem, it makes no real difference whether the mean residual equals to 44 or 49 kJ mol^{-1}.

Finally the same observation as for the C-H compounds could be made regarding group contributions that are determined thanks to less than three molecules. Some supplementary experimental data would be very helpful so that group additivity values could be improved.

3.2.4. Uncertain Points

A part of the uncertainty of predictive methods may be attributed to the lack of reliable experimental data. Examining Tables 1–5 permits the observation that some group contributions have been determined owing to less than three molecules, especially the C-H ring strain corrections (see Table 2). These groups would obviously need more experimental data in order to confirm the group additivity values computed. Besides, some compounds have large discrepancies among the reported experimental values of enthalpy of formation. These molecules would therefore need to be restudied so as to validate either one source or the other. The naphthacene compound can be cited as an example. Indeed Cox and Pilcher[9] published a value of enthalpy of formation in the solid phase equal to 158.8 kJ mol^{-1} whereas Nagano[10] reported the value of 206.9 kJ mol^{-1}. Moreover, a great deal of compounds studied has their enthalpy of formation in the solid state which has been published only once. It should be very interesting to reanalyze these molecules in order to double check whether the data used are exact or not.

TABLE 11. Comparison of the mean residuals obtained for C-H-O compounds between this work and the method of Cohen[4]

Method	0–5 kJ mol^{-1}	5–10 kJ mol^{-1}	10–20 kJ mol^{-1}	More than 20 kJ mol^{-1}
This work	1.8	6.8	13.3	49.0
Cohen[4]	2.4	7.5	13.6	43.5

TABLE 12. Comparison of the residuals observed for C-H and C-H-O compounds between this work and the method of Cohen[4]

Method	0–5 kJ mol^{-1}	5–10 kJ mol^{-1}	10–20 kJ mol^{-1}	More than 20 kJ mol^{-1}
This work	182/398 (46%)	79/398 (20%)	70/398 (17%)	67/398 (17%)
Cohen[4]	143/392 (36%)	77/392 (20%)	65/392 (17%)	107/392 (27%)

TABLE 13. Comparison of the mean residuals obtained for C-H and C-H -O compounds between this work and the method of Cohen[4]

Method	0–5 kJ mol^{-1}	5–10 kJ mol^{-1}	10–20 kJ mol^{-1}	More than 20 kJ mol^{-1}
This work	1.6	7.1	13.6	48.6
Cohen[4]	2.0	7.4	14.2	63.1

TABLE 14. Summary of the best results obtained with this work and with the method of Cohen[4]

Method	Number of compounds	Mean residual (kJ mol^{-1})
This work	331/398 (83%)	5.5
Cohen[4]	285/392 (73%)	6.2

For some compounds, the prediction error obtained using both Cohen's method and our method are very close. If new experimental determinations were considered, it would be interesting to set the focus on these particular compounds. Several examples can be cited: 5,8-dimethylbenzo[c]phenanthrene, 3,9-dimethylbenz[a]anthracene, (E)-13-docosenoic acid, *cis*-cyclohexane-1,2-dicarboxylic acid, *trans*-cyclohexane-1,2-dicarboxylic acid, and tetraethylsuccinic acid (cf. Tables 6 and 7).

It should also be noticed that enthalpies of formation in the solid phase are not well predicted for a lot of polycyclic aromatic hydrocarbons, either with the method developed in this paper or with Cohen's one. Typical examples are: 1,12-dimethylbenzo[c]phenanthrene, 9,10-dimethyl-1,2-benzanthracene, and 5,6-dimethylchrysene (cf. Table 6). Some additional corrections should be considered to take into account such particular structures. Prior to any modification, it would be necessary to restudy these molecules to make sure experimental data are right.

Notice finally that molecules for which the highest prediction errors were observed were pointed up and eliminated from the database which served to determine the group contribution values.

4. Summary and Conclusions

Table 12 confirms that this study provides better results than the method developed by Cohen. Indeed the percentage of residuals lying between 0 and 5 kJ mol^{-1} and between 5 and 10 kJ mol^{-1} are superior in this work or are equal to those obtained thanks to Cohen's study (46% vs 36%, and 20% vs 20%). Additionally, less compounds have a residual between 10 and 20 kJ mol^{-1} or superior to 20 kJ mol^{-1} in applying the present method than with Cohen's. Moreover a lack of group additivity values in the technique developed by Cohen entails the comparison of the efficiency of the two methods for only 392 molecules (vs 398 molecules listed). Indeed two C-H group contributions and two C-H-O group contributions are missing: C_d-$(C)_2$, C_t-(H), C-(O)$(C_B)_2$(C), and CO-(C)(H).

Finally, in each case the mean residuals obtained in this work are smaller than those found with the method of Cohen, as showed in Table 13.

To conclude, Table 14 summarizes the best results obtained with both techniques. Compounds for which the residual is superior to 20 kJ mol^{-1} are excluded in this outline.

Table 14 reveals the superiority of the method developed in this work compared to the method of Cohen. Indeed, the mean residual found for 83% of the compounds listed is smaller than that obtained with Cohen's method.

The group contributions evaluated in this article then result in a more precise and more reliable technique predicting the enthalpy of formation in the solid phase, at 298.15 K, of C-H and C-H-O molecules than any previous method.

This compilation allows the extension of the determination of group additivity values to compounds containing more elements, especially organic nitrogen substances. This work is in progress and will be reported in another article.

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